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PROCEEDINGS OF
ALTA 2016 GOLD-PM SESSIONS

26-27 May 2016

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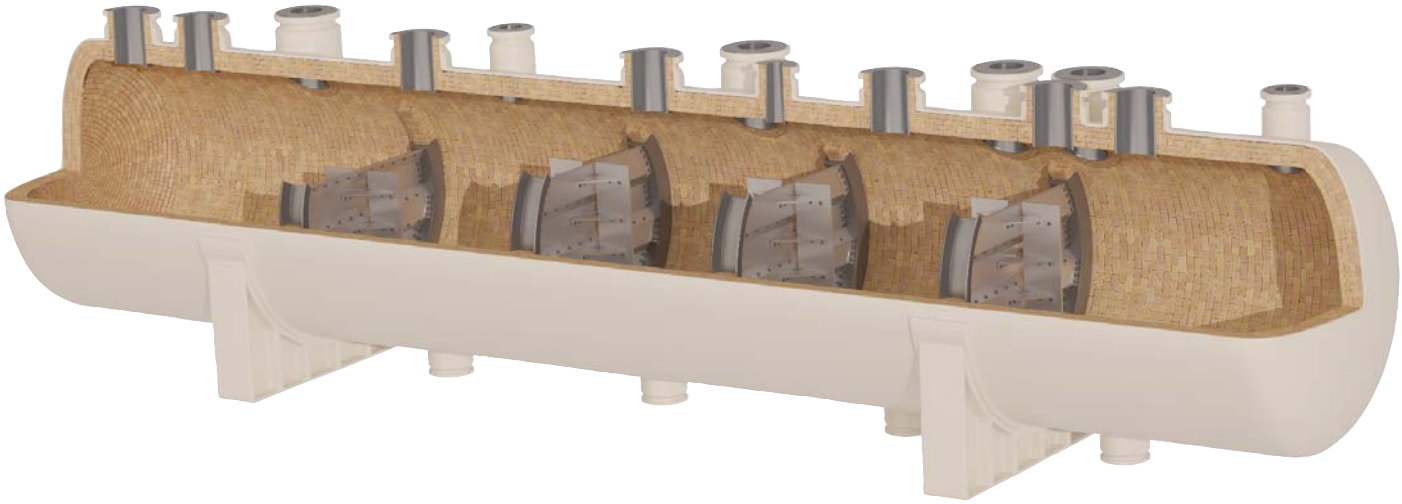
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Alan has over 40 years' experience in the metallurgical, mineral and chemical processing industries in Australasia, New Zealand, North and South America, Africa, Asia and Europe. He has worked in metallurgical consulting, project development, engineering/construction, plant operations, plant start-up and technology development. Projects and studies have involved copper, gold/silver, nickel/cobalt, uranium and base metals.

Since 1985, as an independent metallurgical consultant, Alan has as undertaken feasibility studies, project assessment, project development, supervision of testwork, flowsheet development, basic engineering, supervision of detailed engineering, plant commissioning and peer reviews and audits. Clients have included a variety of major and junior mining, exploration and engineering companies throughout Australia and overseas.

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SELECTING THE BEST PROCESS FOR THE TREATMENT OF A REFRACTORY GOLD ORE - BARRICK'S EXPERIENCE

By

Dr Yeonuk Choi
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ABSTRACT

More ore bodies have been found where the gold is not amenable to simple cyanidation alone. In the simplest of terms, these are refractory ores. The best choice of a processing route to treat a refractory ore will in most cases be site specific, due mainly to the metallurgical and mineralogical characteristics of the ore. The successful application of these processing techniques can result in mining operations that would otherwise have been impossible. However for an increasing number of low grade refractory ores, the estimated capital and operating costs mean that very careful project evaluation will be necessary, particularly at current gold prices. This paper will review some of the existing technologies and operations that are being used for the treatment of refractory gold ores, with particular emphasis on the technologies developed and practiced in Barrick's operations. Pressure oxidation, roasting and thiosulfate technologies will be reviewed.



Barrick Operations

- Focus on high potential assets in core regions
- Leverage competitive advantages
- Strong base of existing high quality mines
- Ongoing asset optimization
- Gold production of 6.12 Moz @ $831/oz all-in sustaining costs in 2015



Barrick Operation - Cornerstone Mines



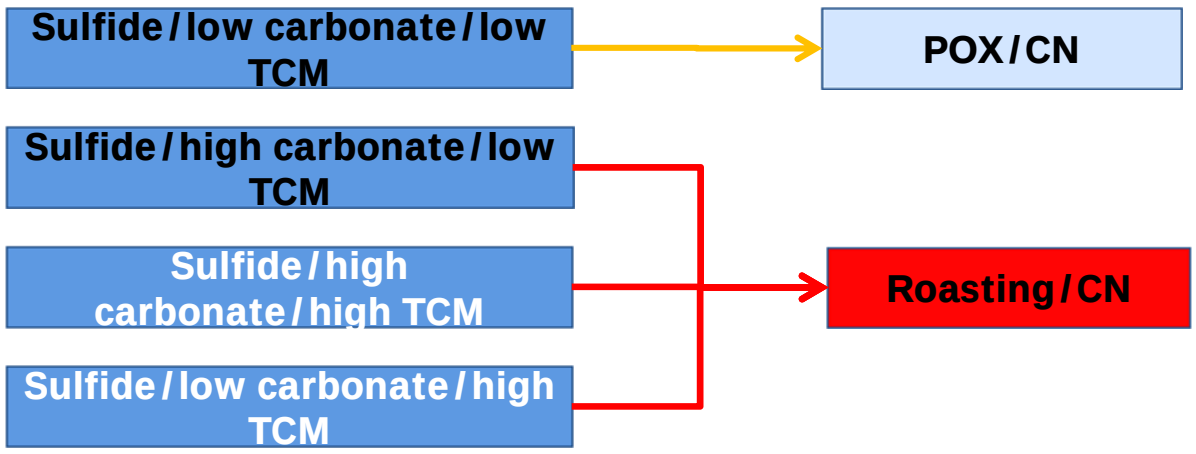
Goldstrike – Carlin Trend, Nevada



Goldstrike

- The Goldstrike property is located in Elko and Eureka counties in north-central Nevada, USA on the Carlin geological trend.
- The property was discovered in 1960's and purchased by Barrick in 1987.
- Autoclave facilities were built in 1989 to process sulfide refractory ores.
- Roasting facilities were built in 1999 to process high TCM double refractory ores.

Goldstrike



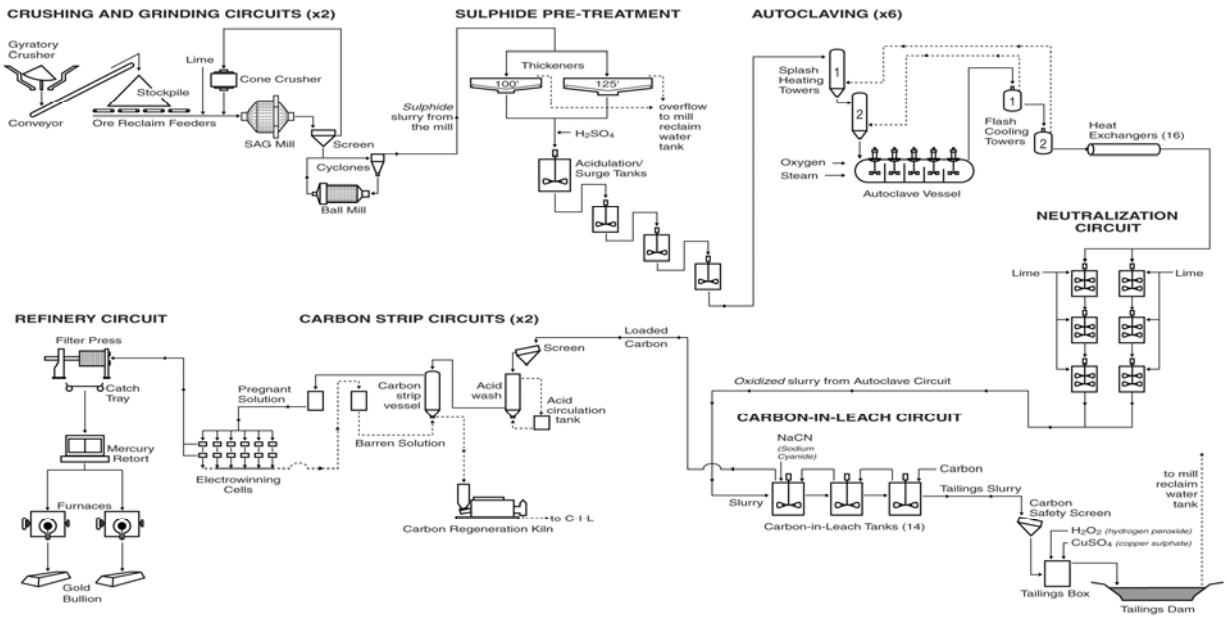
Autoclave Circuit – Goldstrike



Autoclave Circuit Design Criteria

- Throughput:
  - Mill 1: 6,500 TPD (80% passing 200 mesh)
  - Mill 2: 12,500 TPD (60% passing 200 mesh)
- 6 autoclaves :
  - 1 small autoclave: 92.6 STPH, 435 ^{o}F
  - 5 large autoclaves: 129.6 STPH, 437 ^{o}F,
- CIL: 19 hrs RT

Autoclave Circuit Flowsheet



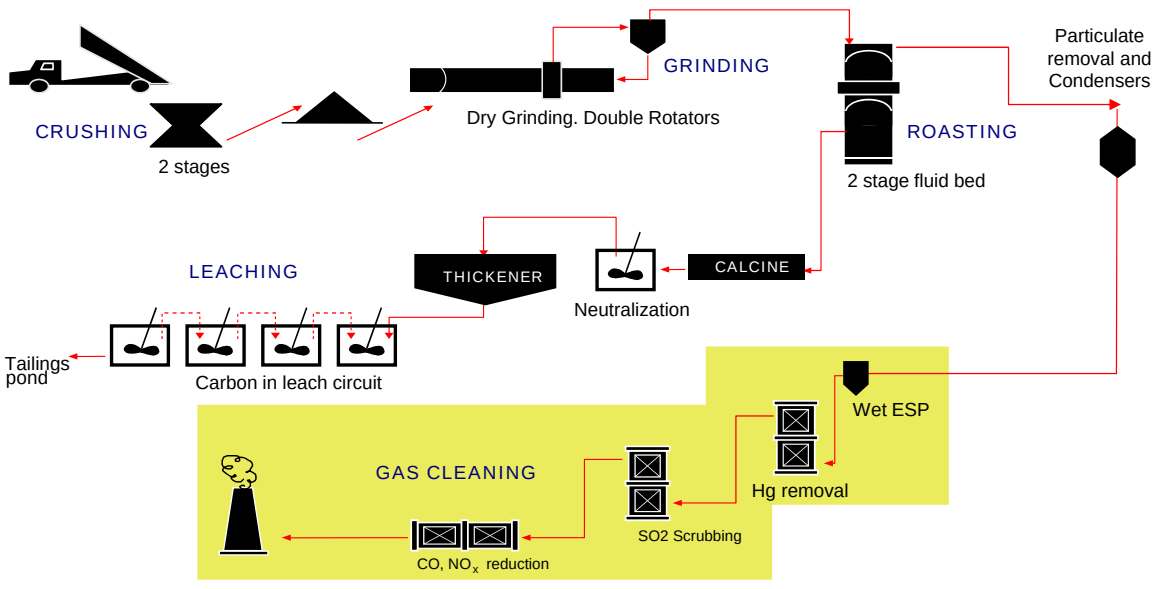
Roaster Circuit - Goldstrike



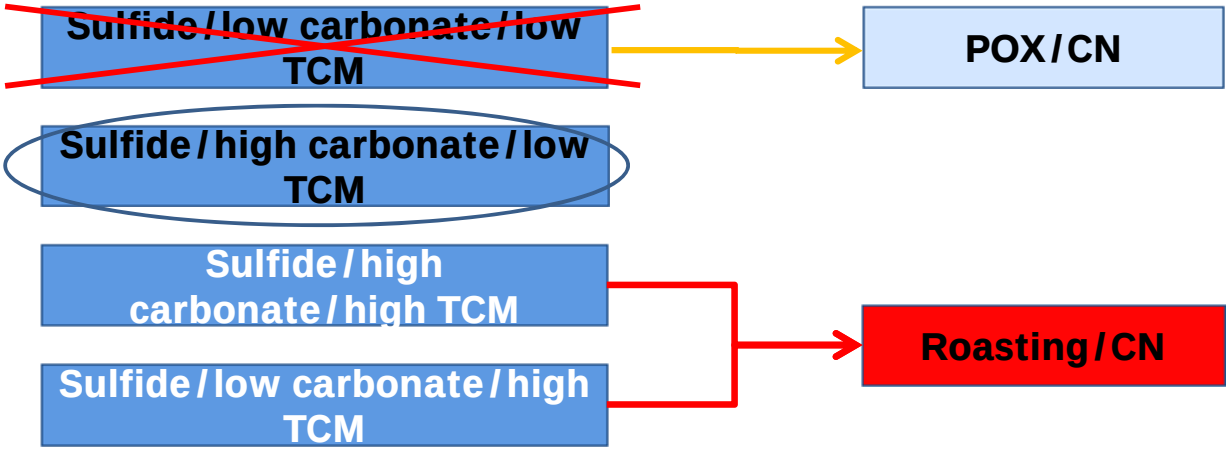
Goldstrike Roaster Circuit Design Criteria

- Throughput: 12,000 TPD
- Sulfide sulfur: 1.9%
- Total carbon matter: 1.4%
- Carbonate: 4%
- Mill Product, P_{80}: 74 µm
- First stage bed temperature: 1025 ^{o}F
- Second stage bed temperature: 1050 ^{o}F
- Retention time: 44min
- Gold recovery: 90%

Roaster Circuit Flowsheet



Goldstrike – Process Conversion



1st Conversion of the Circuit

- Evolving and changing ore body composition
- Running out of traditional acid ore
- High grade, high carbonate ore available (CO_3>4%)
- Maintain total ounce production
- Possible to process alkaline ore in existing autoclaves
- Challenge was to use existing facilities to process both acid and alkaline ores

Process Options Considered

- Copper concentrate POX/SXEW/CIL
- Flotation
  - Flotation/APOX/CIL
  - Flotation/AlkPOX/CIL
- AlkPOX/ATS/RIL
- Alkaline POX (whole ore)/ CIL

Copper Conc. Process

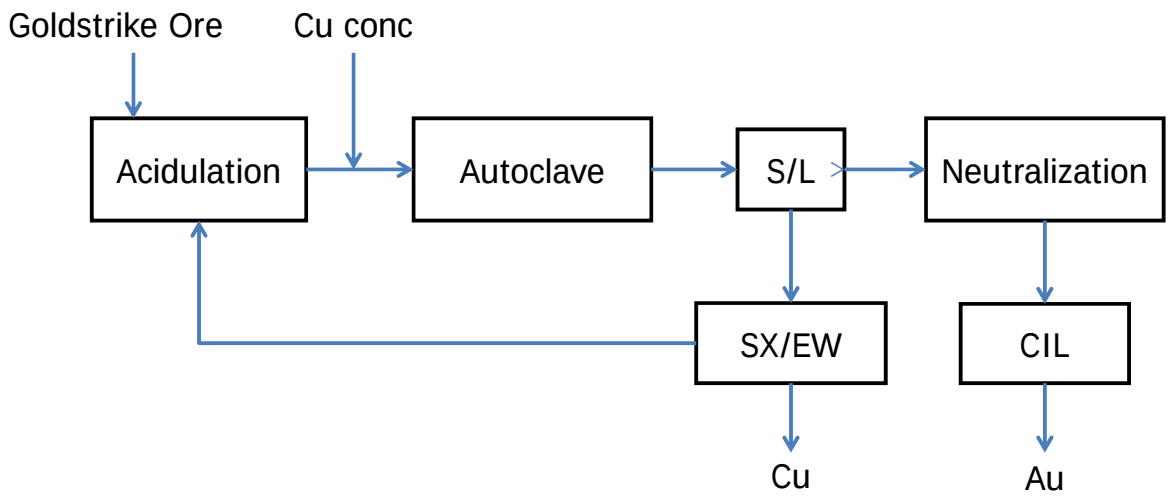




Copper Conc. Concept

- Add chalcopyrite conc. to POX to supply enough sulfide to form acid which could be used to neutralize carbonate in the gold ore.
  - Recover copper by conventional Cu SX/EW
  - Reduce acid requirement ahead of APOX
  - Improved Au recovery: APOX > AlkPOX

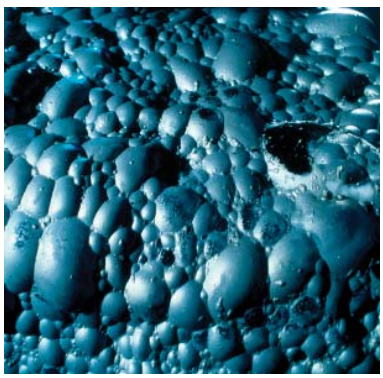
Copper Conc./SX-EW/CIL



Results from Copper Conc. Process

- Batch tests indicate good Copper and Gold recovery
- CAPEX estimate indicates a significant investment required
- Possible sources of concentrate are known but are not owner (Barrick) operated
- Long leads on equipment and design, not easily implemented within current time frame
- Need to compete with conventional smelting markets
  - Difficult to predict cycles
  - May offer economical advantage for dirty conc's

Flotation





Flotation Concepts

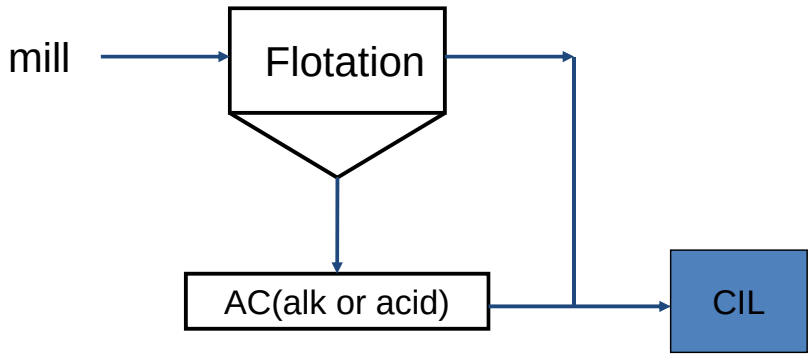
The Classic Flotation

- Selectively float mineralization (pyrite) into a high recovery concentrate that would be amenable to APOX and subsequent CIL gold recovery

The Reverse Flotation

- Selectively float gangue material (carbonate and or TCM) effectively forming as tailing a suitable product for either APOX or AlkPOX followed by CIL

Flotation/POX/CIL



Test Work Results - Flotation

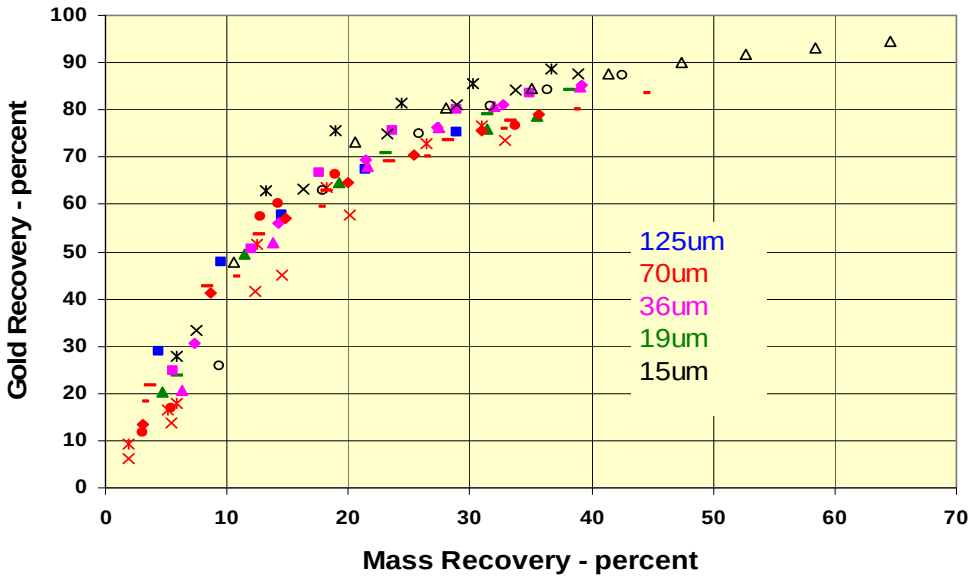
The Classic Flotation

- Selectivity was poor for most ore types
- Liberation dependent – fine grind required for increased recovery

The Reverse Flotation

- Selectivity again poor for either component (TCM or CO_3)
- Various reagent schemes tried with the search continuing

Effect of primary grind size on Au recovery



Results from Flotation Option

- Mineral liberation is the key for effective flotation of pyrite
  - Au recovery into con of ~85% at 35-40% mass pull with a primary grind of 75 micron
  - Poor selectivity of TCM against pyrite varied with ore type
  - Little selectivity was observed for carbonate flotation
- Poor selectivity in TCM and carbonate flotation was attributed to poor mineral liberation. Need ~15 micron for good liberation.

Alkaline POX

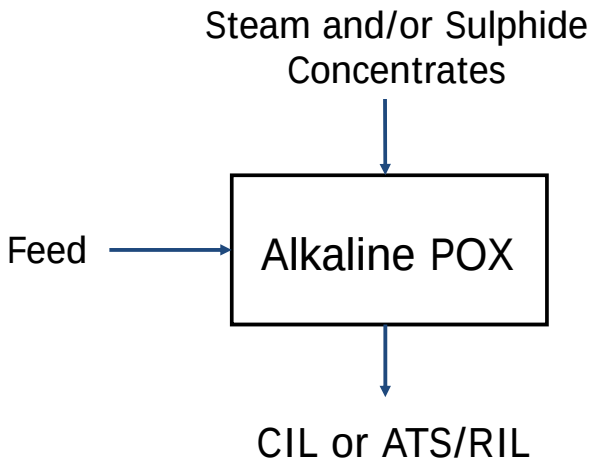




Alkaline POX Concepts

- AlkPOX/CIL
  - Injection of steam and oxygen at a rate great enough to maintain oxidation of pyrite followed by standard CIL extraction and recovery
- AlkPOX/ATS/RIL
  - Same AlkPOX conditions as before followed by ammonium thiosulfate lixiviant leaching, resin absorption and recovery

Alkaline POX/CIL or ATS/RIL



Alkaline POX Results

- AlkPOX/CIL
  - Bench top tests, pilot plant runs and two plant trials have been completed
  - Results have confirmed reagent consumption and gold recovery models
- AlkPOX/ATS/RIL
  - Numerous bench top and pilot plant tests have been completed
  - High reagent consumption, more complicated and environmental issue

Summary of Results

- Gold Recovery
  - Cu > AlkPOX > Float
- CAPEX
  - Cu > Float > AlkPOX
- OpEX
  - Cu > AlkPOX > Float
- Ease of Implementation
  - AlkPOX > Float > Cu

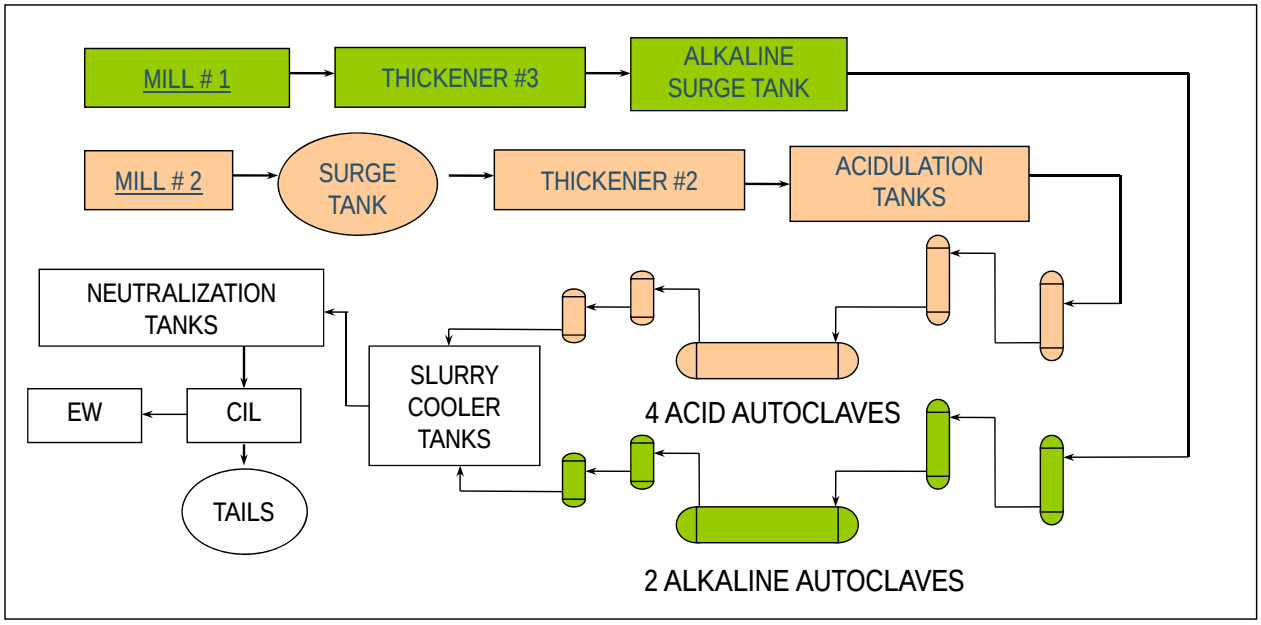
Alkaline Autoclave

- Oxidizing high CO_3 ore without the addition of sulfuric acid
- All sulfuric acid generated in the autoclave reacts with CO_3, buffering the autoclave discharge pH
- Higher temperatures and pressures required (437°F, 480 PSIG)
- Loss of temperature in autoclave results in loss reaction
- Alkaline autoclaving is less effective than acid autoclaving
- Sulfide oxidation 60% TO 70%
- Gold recovery ranges in 78% TO 83%

Alkaline Autoclave - Challenges

- Convert one circuit into two separate and independent circuits with minimum cost
- Two mills, two thickeners, one acidulation/surge tank circuit, six autoclaves
- Remain flexible

Autoclave acid/alkaline POX Flowsheet

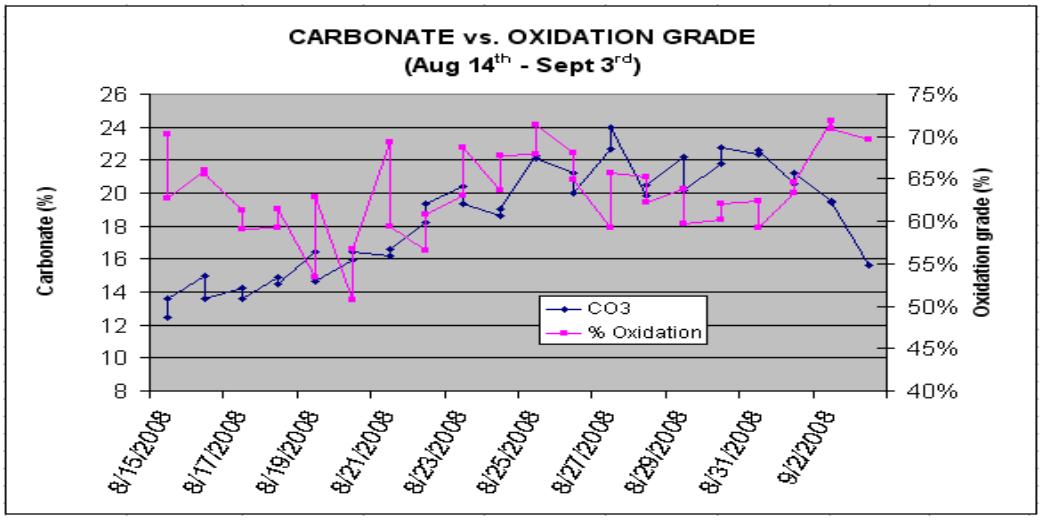


Alkaline Autoclave- 21 days Plant Trial

- 178,504 tons processed
- Sulfide: 1.32%
- Carbonate: 17.94%

Autoclave	Ore (tons)	S2- % discharge	O2 ton/ S2- ton	Steam (Klbs/ton)	Oxidation percent	Avg. Pressure (psig)
1	45,616	0.45	4.17	0.45	65.84%	430.0
2	48,109	0.51	3.85	0.51	62.04%	429.6
3	51,038	0.49	3.94	0.48	63.27%	429.6
4	33,742	0.46	3.99	0.43	64.08%	428.7

Alkaline POX - Oxidation Behavior

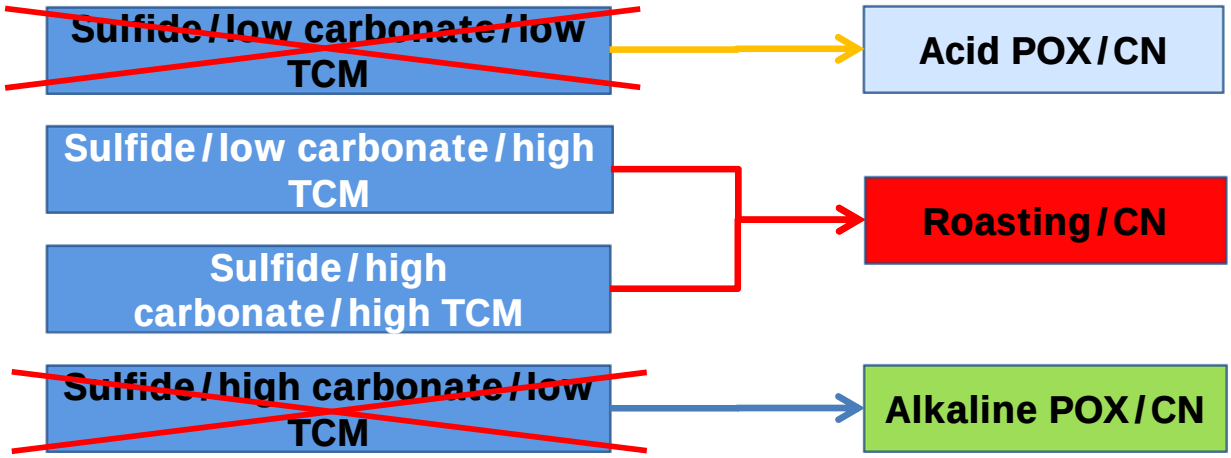


- Extent of oxidation is independent of the carbonate contents in the ore

Alkaline POX - Highlights

- Able to increase ounce production by utilizing high grade alkaline ores
- Oxidation of sulfides directly proportional to oxygen addition, but limited by pressure design of vessels
- Four tones of oxygen required for each ton of sulfide in the feed
- Carbonate content doesn't affect the oxidation
- Savings in acid and lime usage, but increase in propane usage

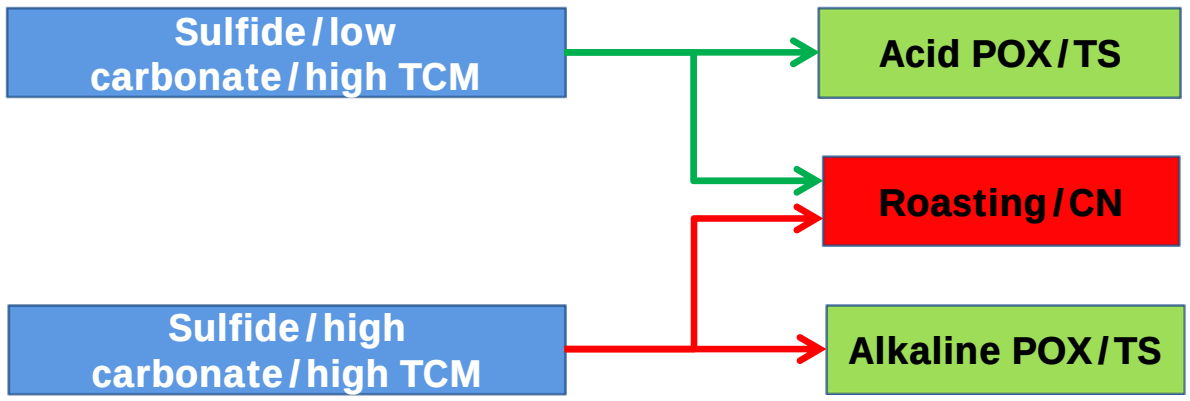
Goldstrike – Process Conversion



2nd Conversion of the Circuit

- Ores amenable to Acid Pressure Oxidation were exhausted by the end of 2008
- Alkaline POX technology has been adopted to extend the life of autoclaves for a few more years
  - Roaster operates until 2025
- The remaining orebody typically consists of:
  - Higher CO_3 content than historically processed, coupled with
  - High preg robbing levels/TCM's

Goldstrike – Process Conversion



TCM Leach Testing History

- Research Efforts Ongoing Past ~ 15 Years
  - Bench-scale thiosulfate testing since 2005
  - Bench scale testing of CaTS in 2009
  - Continuous pilot testing of CaTS in 2009
- Testing was used to identify key process variables and test the process variables on various ore types.



ATS RIL Test on Various Ore Samples

User Sample ID	Test No.	Sample head assays								Results	
		Au	S tot	S^{2-}	S_{SO4}	S^{o}	C tot	TCM	CO3	POX sulfide oxidation	4 hr-ATS Au recovery
		(g/t)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
NORTH MILL FEED Mar 24, 2009 BGMI	POX/ATS - 22	5.48	2.26	1.96	0.30	≤0.02	3.71	0.62	15.5	54.1	84.3
SOUTH MILL FEED Mar 24, 2009 BGMI	POX/ATS - 24	6.75	3.05	2.73	0.32	≤0.02	3.65	0.79	14.3	49.8	81.7
BR24-A, Mar 24, 2009 BGMI	POX/ATS - 26	6.72	1.18	1.11	0.07	≤0.02	5.92	1.54	21.9	70.3	82.2
BR24-B, Mar 24, 2009 BGMI	POX/ATS - 28	6.85	1.20	1.12	0.08	≤0.02	5.67	1.48	21.0	67.0	81.3
MP3, Mar 24, 2009 BGMI	POX/ATS - 30	8.47	2.38	2.13	0.25	≤0.02	2.58	0.77	9.1	53.1	77.4
BR20-A, Mar 24, 2009 BGMI	POX/ATS - 32	3.43	1.47	1.31	0.16	≤0.02	4.47	1.79	13.4	60.3	74.6
BR20-B, Mar 24, 2009 BGMI	POX/ATS - 34	4.63	1.54	1.39	0.15	≤0.02	4.50	1.78	13.6	61.2	81.0
BR25-A, Mar 24, 2009 BGMI	POX/ATS - 36	8.27	2.56	2.35	0.21	≤0.02	2.23	0.71	7.6	80.0	83.4
BR25-B, Mar 24, 2009 BGMI	POX/ATS - 38	9.15	2.71	2.51	0.20	≤0.02	2.46	0.67	9.0	80.9	83.5
MP4-A, Mar 24, 2009 BGMI	POX/ATS - 40	15.13	1.62	1.46	0.16	≤0.02	3.97	1.23	13.7	56.8	73.8
MP4-B, Mar 24, 2009 BGMI	POX/ATS - 42	18.42	1.78	1.61	0.17	≤0.02	4.02	1.24	13.9	64.0	72.3

Alkaline POX conditions: P80 particle size = 75 µm, 225°C, O_2 pressure=100 psi, retention time=1 hour, trona addition to POX feed=10 kg/t ore

CaTS RIL Pilot Campaign – Summary

- CaTS RIL achieved higher gold extraction for Acid POX treated ores than for Alkaline POX treated ores due to improved exposure of gold, similar to CIL for non-preg-robbing ores
- The trade-offs between Acid POX and Alkaline POX for CaTS RIL are expected to be similar to the trade-offs in CIL for non-preg-robbing ores

TCM LEACH ~ Project History

- Demo plant testing of CaTS for 16 months
  - Full simulation of leach/adsorption/elution/EW process, including full recycle of all streams
  - The demo plant processed oxidized slurry from the Goldstrike autoclave facility



Demo Plant-Objectives

- Demonstrate RIL Technology & ancillary equipment
- Determine achievable gold recovery and resin loading with different ore types
- Determine reagent consumption
- Determine effect of Au, Hg and As on process performance
- Demonstrate R/O, regeneration, and effect of recycling
- Collect pertinent data for permitting
- Train employees and develop operational expertise

Demo Operation - Limitation

1) Various operating conditions, reagents, and reagent strengths were tested as part of the Demo Plant operation
2) Feed availability issue: Shortly before the Demo Plant started up it was learned that the Goldstrike Autoclaves could emit mercury when running in the Alkaline autoclave mode. As a result a tank full of Alkaline autoclave discharge slurry was saved and ran through the Demo plant in July 2010, August 1 through 6, 2010, and again on September 29 through October 6, 2010. All other Demo Plant feed was Acid autoclaved ore as the plant autoclaves were not able to run in the Alkaline autoclave mode until after the Autoclave Mercury Controls Project was permitted, built, and operational.

Demo Operation – Feed Processed

Dates	Ore Processed	Ore Characteristics
8/1 – 8/6	Alkaline	Alkaline
8/6 – 8/17	BR31	Med Preg-robbing
8/17 – 8/20	BR10, BRSO AP	Med Preg-robbing
8/21 – 8/24	Storm	High grade
8/25 – 8/29	BR6, BRSO AP	Med Preg-robbing
8/29 – 9/23	BR31	Med Preg-robbing
9/23 – 9/26	Storm	High grade
9/26 – 9/27	BR3	High Preg-robbing
9/28 – 9/29	BR31	Med Preg-robbing
9/29 – 10/6	Alkaline	Alkaline
10/6 -	PR2	High Preg-robbing

Demo Plant: Gold Recovery Summary

- No significant gold in tails solution even with higher head grades
- Best recoveries at low grade (2.5 -3 ppm) with BR31;
  - Consistent and constant recoveries at 80 to 82%
- Typical Goldstrike BRSO/BR33 blend was good
  - Gold recovery 78.9% (actual) vs 79.3% (pred)
- Lowest recoveries at low grade with ALK (70% in July and August at 3.2 ppm) and 60% in October at 2.9 ppm feed with recycle streams and different leaching conditions
- PR2 showing low recovery (60 to 70% with average of 65%) in October (to the 17th) due to storage issue and leach conditions

Demo Plant: Gold Recovery Summary

- STORM high grade ore has a good initial response (over 90% recovery), which is decreased when gold inventory in the circuit becomes high: less pronounced at high resin flow rate
- Proposed operational strategy to blend high grade in full scale plant
- Note: The Demo Plant ran many different types of ores and grades in the 16 months of operation. The Demo Plant results were limited to one type of Alkaline autoclave oxidized ore. The Demo Plant also did not run a lot of extremely high TCM or extremely strong preg robbing ores as doing so meant running the ores through the entire Autoclave facility which would experience extremely poor gold recovery as it was utilizing cyanide and activated carbon.

Demo Plant Product

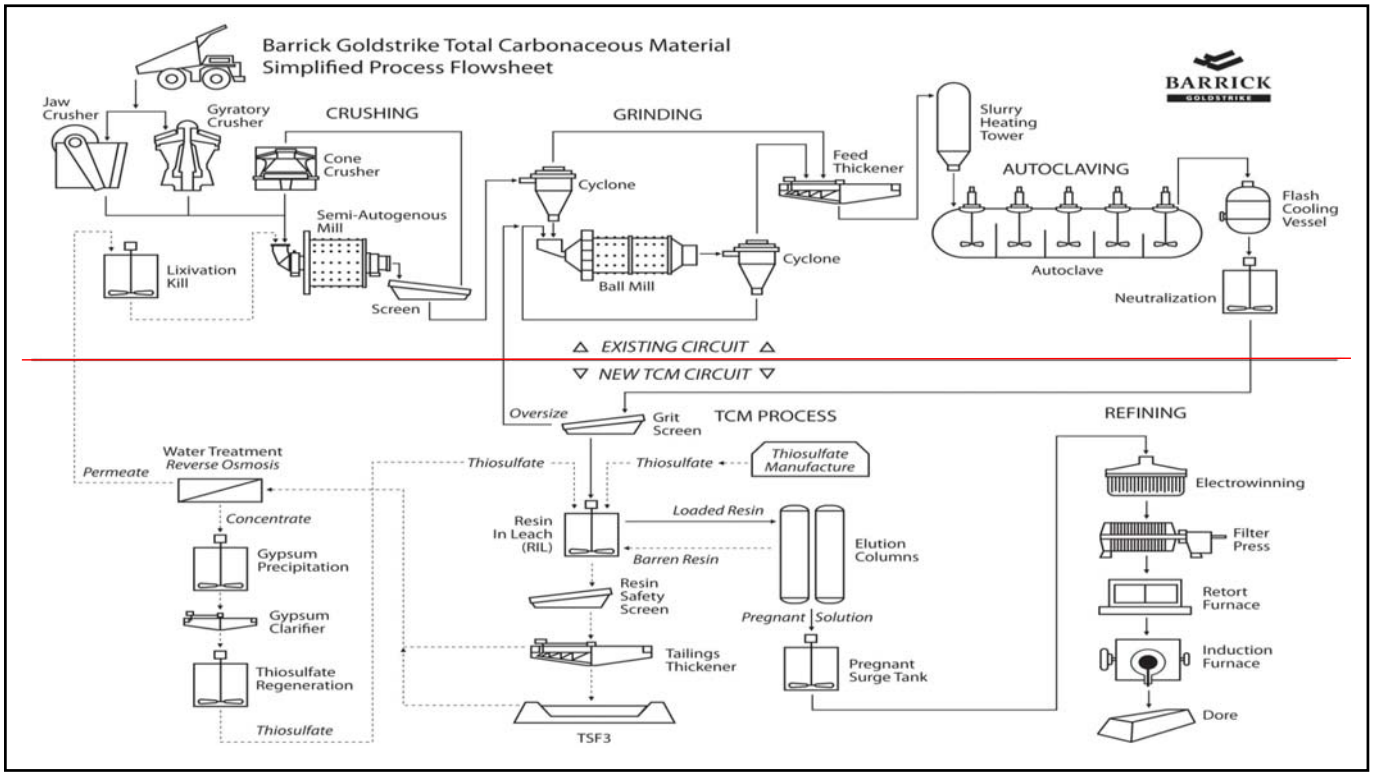
The Demo Plant was utilized to test all of the TCM Leach Processing circuits up to and including the pouring of one small bar of gold.



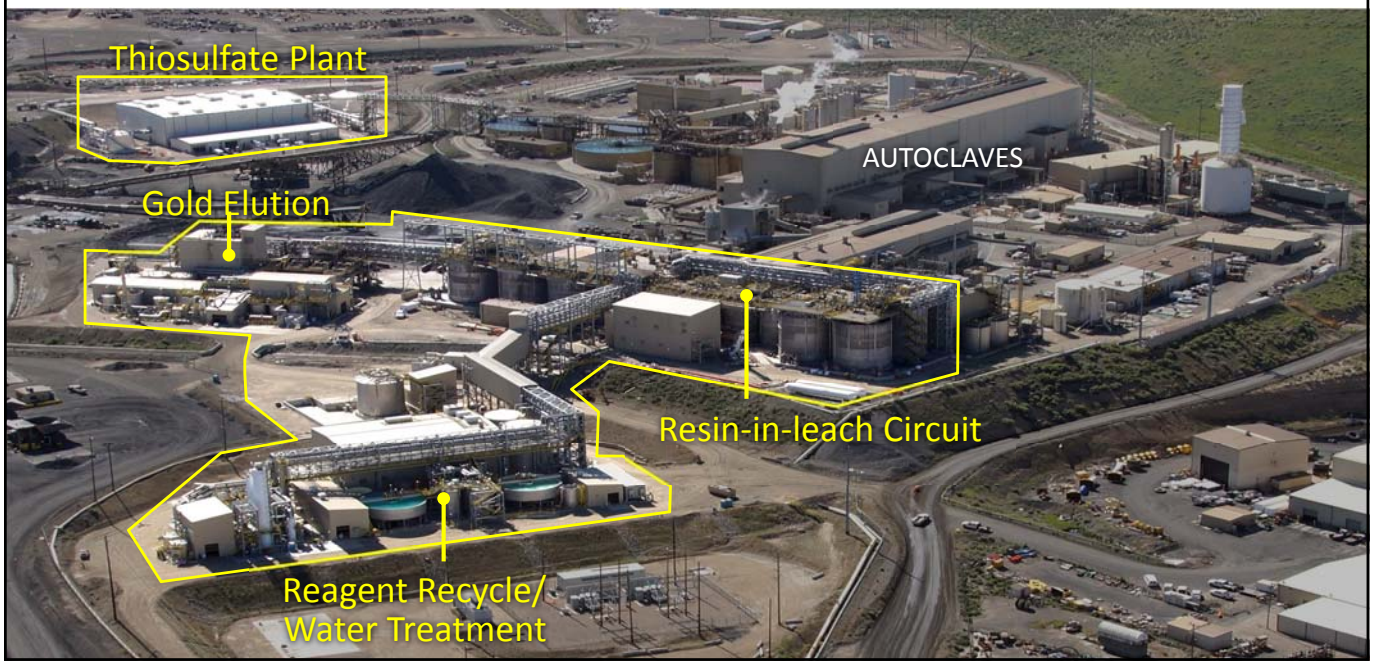


TCM Leach – Design Criteria

- Ore throughput 600 st/h
- Target feed P80 200 mesh (75 µm)
- Mill 1 Alkaline (270 TPOH)
- Mill 2 Acid (330 TPOH)
- Interstage screen: 500 µm
- Safety screen: 300 µm
- RIL condition: 50 ^{o}C, 0.1 M CaTS, with Cu and air
- Elution: Trithionate with sulfite



TCM Circuit – Thiosulfate Leaching



Innovation: Goldstrike TCM Process



Commissioning and Start up

Brownfield/Greenfield Project

- Operate A Train in CIL mode during construction of B Train
- Shut down process operations January, 2014
- Start up B Train in CIL mode (new tanks) May 1, 2014
- Shut down BCIL operation October 8, 2014
- Start new RIL operation on B Train November 10, 2014

Commissioning and Start up

- TCM BRIL first gold poured November 28, 2014
  - Startup of roughly half of the TCM facility
  - In December identified water treatment bottleneck with UF membranes fouling. Only able to maintain 25% of design feed flow rate.
- TCM ARIL commissioned January 22, 2015
- TCM ARIL first gold poured January 31, 2015

Commissioning and Start up

Ausenco Utilized for Commissioning

- Commissioning system well developed/understood
- Strong commissioning leadership & system knowledge

Barrick TCM Team

- Worked with Ausenco through water testing phase
- Assumed responsibility with ore processing phase

Goldstrike Operational Team

- Participated in energization and water testing phases
- Required for ore processing phase

Water Treatment plant was a turn key facility and was commissioned by Auburn

Commissioning and Start up



Operational Highlights in 12 Months

- Processed: ~ 3M tonnes feed
- Produced: over 220,000 oz

Current Status - Challenges

The TCM Leach process is a new process with complex chemistry and with unit operations that are extremely dependent on the product quality and quantity from the preceding unit operations.

A few of the challenges seen are:

Grinding

- Hard ores are challenging fine grind and throughput
  - Fine grind is important for recovery
  - Grits from grinding contributes to challenges in RIL screening, tank over flows, and RIL screen cleaning

Current Status - Challenges

RIL

- Lowering resin loadings (gold and polys) to design target will improve gold in solution losses and recovery.
  - Need to move more resin (elution challenges)
- RIL tanks over flowing
  - Clean inter-tank screens thoroughly and regularly
  - Tank over flows upset resin profile and lowers recovery
    - Grits from grinding contributes to RIL challenge
    - If testing of larger resin proves out it could be a big help
  - By-passing of a few RIL tanks to prevent overflowing could have more impact on recovery at higher throughput rates.

Current Status – Challenges

Water Treatment

- Permanent solution to MF/UF fouling is needed
  - MF trailers need to be ready for cold weather conditions
- Water Treatment automation has gaps and is being assessed

Elution

- More elutions per day are needed to move more resin through RIL and bring down gold in solution losses.
  - Engineering design warranty was for 8 elutions per day as maximum (for high grade ores).
  - More automation may be needed

Conclusions

- Goldstrike has been a flagship operation for Barrick.
- The processes have been evolved to meet the feed constraints and the process has been selected based on the economics.
- Various option options allow to treat various feeds from the area.

Innovation: Goldstrike TCM Process



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Gold-PM Proceedings

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SYAMA EXPANSION PROJECT – CREATING VALUE AND SHARING WITH OUR STAKEHOLDERS

By

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ABSTRACT

The Syama Gold Mine is located in southern Mali, West Africa. This paper describes the development of the USD 186M Syama Expansion Project (SEP), from a positive Definitive Feasibility Study (DFS) and the project's approval by the Board of Directors in June 2012, to the successful completion of the project in December 2014. During this period, the owners, Resolute Mining Limited, (RML) overcame a number of significant, external issues, which included a military coup d'état, a major regional military conflict in the North of Mali and the West African ebola virus epidemic. At the same time, RML trained and improved local engineering companies and thus aided the development of a resilient local engineering capability for the benefit of the company and the region.

RML also implemented a project methodology which included engagement of *independent* cost control professionals, to continuously monitor and report on whole-of-project costs, thereby providing real time, up-to-date cost control information to facilitate rapid and informed decision making. This was a key contributor to managing project costs.

Following a successful commissioning period of the oxide circuit, the SEP was closed out three months ahead of schedule and USD 17M under budget.

Keywords: Oxide Gold Project, West Africa, Process Development

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PROJECT BACKGROUND

In 2011, RML appointed GR Engineering Services to conduct a DFS for the design and construction of an oxide processing circuit at the Syama Gold Mine, to treat ore delivered from nearby oxide deposits along the Syama mineralised corridor.

The project received formal approval from the RML board in June 2012. During the construction period, the project was exposed to several external political, security and health and safety risks that had the potential to seriously affect the final cost and to delay the construction schedule. The most challenging external factors were:

- a military coup in Mali; and
- an ebola crisis in West Africa.

An independent risk assessment conducted during the project design phase correctly identified many of the internal and external risks that were eventually encountered during the project, with the notable exception of the regional ebola virus epidemic. While Mali experienced only a limited number of ebola cases, RML implemented its own risk mitigation steps in conjunction with its medical advisors, International SOS and other international medical organisations working in the region.

The delineation of near-surface, oxide ore reserves in excess of 550,000 ounces provided the support for a decision to construct a new 1 mtpa, dedicated processing circuit in 2012. In addition to the parallel oxide circuit, significant infrastructure to be utilised by both circuits was approved and included: a 28km water pipeline from the Bagoe River, new control room and plant offices, new reagent storage facility and a modern engineering workshop.

RML's history in other parts of Africa highlighted the importance of supporting local businesses wherever possible. Hence, RML utilised and trained local labour and equipment suppliers, with the goal of enhancing the pool of local contractors for future construction and ongoing maintenance projects. An unforeseen benefit of this plan was the continued support and operation of local suppliers during the military coup and the ebola crisis, whereas non-local companies were avoiding the region.

RML had direct experience with major capital expansion projects in West Africa and were able to leverage from this previous experience, by focusing on several key components of the approach to project implementation. One such component was RML's choice to employ a modified Engineering Procure Construct and Manage (EPCM) model, which included removing the planning and cost control functions from the EPCM Contractor.

These decisions and approach all contributed to a successful project, which was completed under budget and delivered ahead of time, with zero lost time injuries (LTI) despite the pronounced effect of a regional ebola crisis and the political unrest in West Africa.

LOCATION, OWNERSHIP AND GEOLOGY

The Syama Gold Mine is located approximately 30 km from the Cote d'Ivoire border and 300 km southeast of the Mali capital, Bamako. RML has an 80% interest in the project, through its equity in Societe des Mines de Syama SA (SOMISY). The Malian Government hold a 20% interest in SOMISY.

In the 1980s, Broken Hill Propriety Limited (BHP Utah) commenced mining operations on the available oxide resources in the area and commenced mining operations at the Syama Gold Mine in the 1990s. BHP-Utah Minerals International entered into a joint venture with the Mali Government in 1987 and in 1990, commenced treating of the delineated oxide ore. In 1994, a decision was made to build a sulphide ore processing facility, to treat fresh refractory ore, based on 'whole of ore' roasting.

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RML acquired the Syama project in 2004 and following a positive feasibility study, RML upgraded and reconfigured the plant in 2008, to enable primary sulphide ore to be processed via a flotation, roast and CIL (Carbon-In Leach)[1] flow sheet. This became the Syama Expansion Project.

Figure 1 *shows* the location of the Syama Gold Mine in southern Mali.

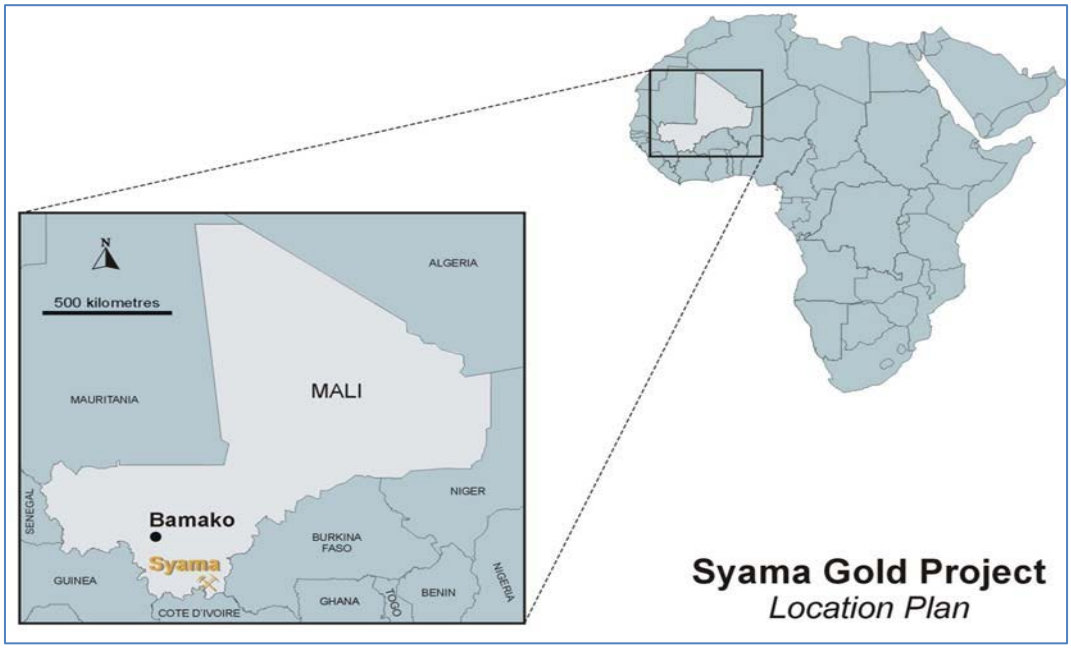


Figure 1: Project Location

In 1994, the process plant was expanded to include a primary ore processing facility to treat fresh refractory sulphide ore, based on 'whole-of-ore' roast circuit. It was operated by BHP until 1996 and subsequently by Randgold Resources until 2001, when the low gold price forced cessation of operations and the mine was placed into care and maintenance mode, following five years of falling gold prices and metallurgical issues. The nature of the ore, being refractory, extremely hard and abrasive, with high levels of organic carbon, was the primary source of metallurgical problems encountered.

RML acquired its 80% interest in the project in April 2004 and a definitive feasibility study for the redevelopment of Syama was completed in April 2005. Redevelopment didn't commence until July 2006, following a significant lift in the gold price and RML Board approval. Mining operations commenced on a cutback to the existing sulphide open pit, while ore feed for the process plant derived from fresh ore stockpiles and processing of material from in situ and stockpile sources recommenced in the second half of 2008.

PROCESSING METHODOLOGY

RML adopted a modified flow sheet, which incorporated flotation of a sulphide-rich concentrate prior to roasting, to oxidise both sulphide and organic carbon. The roasted product passes to a conventional CIL circuit for gold recovery to bullion. The modified plant was designed to treat 2.4 million tonne per annum (mtpa).

Currently, the plant can treat 2.0 mtpa, producing approximately 192,000 tpa of flotation concentrate as roaster and subsequent CIL feed. The existing treatment facility is a refurbished form of the original BHP facility constructed in the mid 1990s and subsequently modified and operated by Randgold in the early 2000s.

Mali is a landlocked country, with poor roads and infrastructure, which presented a logistical challenge to the construction project. All equipment and supplies were required to be transported 1,357 km, from the port of Dakar in Senegal, to the mine site. Sea freight from Australia required 14

[1] A gold extraction process called cyanidation, where carbon is added to leach tanks or (or reaction vessels) so that leaching and adsorption take place in the same tanks.

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weeks and 10-12 weeks from Europe, whilst air freight required only 2 - 3 weeks but came at a significant cost premium.

It was intended to mine ore feed for the oxide circuit, from a number of satellite pits close to the processing plant and within the Syama mineralised corridor. Some of these deposits had been previously exploited by BHP during the 1990s and exposed small pits and workings remained. Much of the geology within the satellite deposits is similar to that exposed in the sulphide open pit at Syama. The trend of the satellite deposits follows the regionally-extensive 200- to 500-metre thick package of Syama Formation rocks, which includes interlayered mafics and sediment units. Exposures in the deeper Syama pit confirm that intrusive lamprophyre units also play an important role in the mineralising event. The Syama Formation is bounded to the east by Syama Bananso Fault Zone, which forms a sharp contact against a matrix-supported conglomerate unit that grades eastward into greywackes and argillites. Weathering extends to a depth of typically 30 to 80 metres below surface, resulting in an overlaying oxidised ore zone, which exhibits free milling characteristics.

Surface mapping, combined with logging and drill section interpretation, was used to construct a mineralisation interpretation for each of the deposits and helped define domains for metallurgical investigation. Field mapping shows the geology is probably folded about large-scale isoclinal folds.

The gold mineralisation is structurally hosted within the deformed and altered Syama Formation rocks. Rheological contrasts between the different lithology units was considered critical to enabling the development of structural conduits and to maximise the fluid-wall rock interaction during the introduction of sulphides and the deposition of gold. Zones of improved gold mineralisation are typically developed within and adjacent to contact zones between basalt and sediment units.

Supergene processes create an additional, horizontal geometric control in the weathering zone.

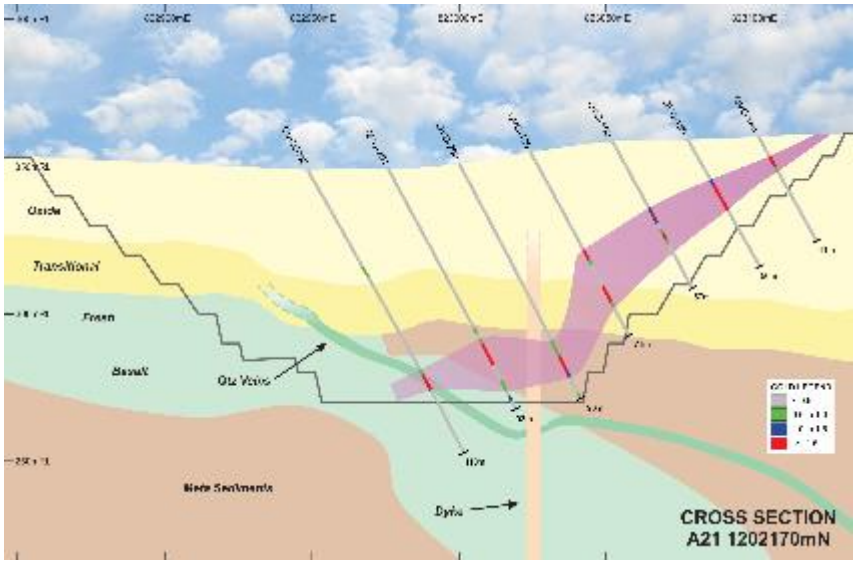


Figure 2: Typical Cross Section, Showing Mineralisation in The Satellite A21 Deposit

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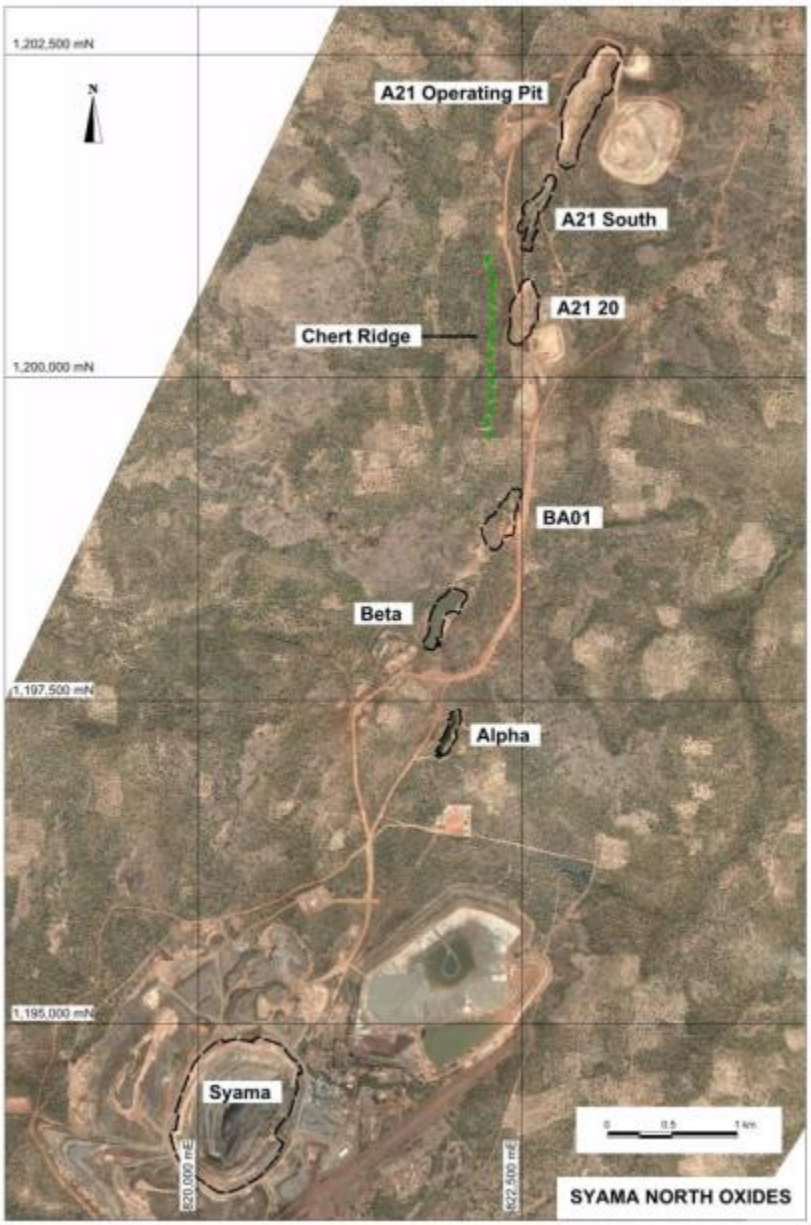


Figure 3: Aerial Photograph Showing the Location of the Syama Operation and Assorted, Satellite Deposits

METALLURGICAL TEST WORK

Test work programs were completed at various times as material became available from deposit-evaluation drilling programs. As the work was in a region with refractory sulphide behaviour, it was important to maintain a well-designed test work program that was grounded in the geological interpretation.

RML conducted test work in 2008, 2009 and 2011 on samples from A21 and Tabakoroni deposits (Tabakoroni is a pit 33kms south of the plant). The three test work programs produced a mixture of pulverised RC chip samples, ½ HQ core samples and whole HQ core samples, which were considered to be a reasonable representation of the spatial, depth and material type variance of the resource. The aims for the three test work programs were to understand the:

- Chemical composition of the various ores;
- Comminution characteristics;
- Gravity concentration and gravity tail cyanide leach response;
- Cyanide leach response;

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- Leach and leach tail viscosity;
- Leach tail thickening response; and
- Acid mine drainage characteristics of the ores and waste.

Resolute's plan to mine seven, separate, open pits (the six pits shown in figure 3 plus Tabakoroni) over a seven-year period will result in significant variances in the feed material to the processing plant and as a result, the test work cannot be definitive. Sample material from the two largest pits dominated the metallurgical test work program and comprised A21 to the north of Syama and the Tabakaroni deposit, which had some challenging metallurgical characteristics. By its very nature, the oxide ore varies with depth and its exact intersection with the transitional weathering profile can be, at times, subjective.

The metallurgical data selected for the process design criteria was necessarily a mix of the various ore sources, whilst for the crushing and grinding circuits, selected criteria tended more towards the transitional competent rock. The one design figure that was proved to be incorrect was the slurry viscosity. Whilst the test work indicated a large range of data, the viscosity figure selected for the process design criteria, pumping calculations and CIL design underestimated how viscous the actual oxide material was, particularly closer to the surface of the pits. As a consequence, the pump motors were upgraded and the CIL intertank screens changed out to larger pumping screens.

The amount of metallurgical drilling and test work required for a plant design varies with each deposit and each company's appetite for risk. However, for the SEP, a conscientious decision was made to limit the drilling and test work to what was absolutely necessary to develop the process plant design. In the case of an oxide deposit, this reduced amount of data as input to design does not have a significant effect on the plant performance and overall gold recovery. This is because an oxide ore processing plant is designed to handle typical changes in ore characteristics as the pit gets deeper and the ore becomes more competent.

FLOW SHEET DEVELOPMENT

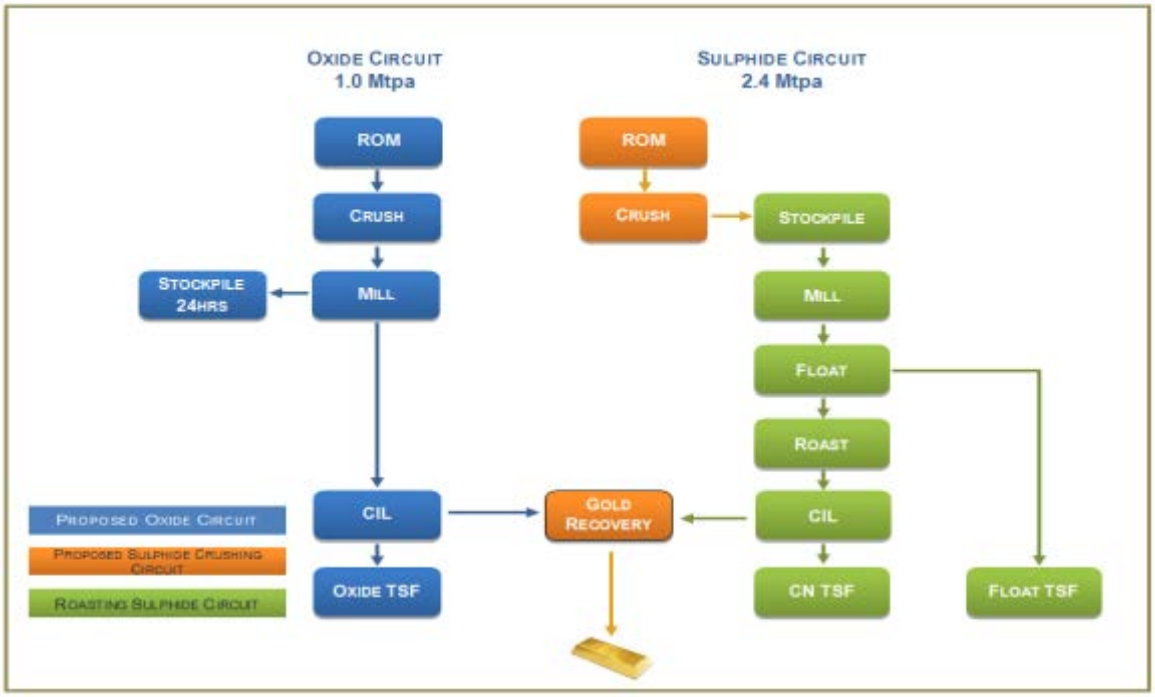


Figure 4: Flow Sheet Development

The test work determined that a conventional, free milling ore flow sheet be installed for the SEP. The treatment of ore would operate in parallel to the existing sulphide treatment facility, with separate tailings facilities.

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The oxide circuit consists of a single-stage Metso 140 crusher, followed by a single-stage, 20 foot (6.1 m) diameter SAG mill, the slurry being feed to a conventional CIL circuit, followed by a thickener and a new oxide tailings storage facility (OTSF). Comminution simulations during the design phase of the project sized the SAG mill at 18.5 foot. However, there was a 20-foot diameter SAG mill that had been recently designed and was (and is) operating at an Australian gold mine and so the choice to purchase the 20-foot mill resulted in a schedule reduction of 6 weeks, given that there were preexisting design drawings . *Figure 5: Mill Enroute Dakar to Syama,* below, shows a photograph of the SAG mill on its 1,357 km trip from Dakar in Senegal to Syama.



Figure 5: Mill Enroute Dakar to Syama

MANUFACTURING COSTS

There are pricing variances amongst the larger multinational companies, in that some companies offer different pricing structures to different geographic locations. Purchasing in today's global market requires the purchaser to be more diligent. Recently, more of the major manufacturers have relocated their manufacturing facilities to countries where the labour and power is cheaper. However, the potential financial benefits of these relocations are not necessarily shared with the purchaser, despite the purchaser taking the possible risks of product failure due to the different quality control standards and procedures in the lower cost countries. Our experience during this specific project showed that in some specific instances lower cost countries produced lower quality output despite being manufactured under the same corporate standards, however for other companies the quality control was identical no matter the country of manufacture.

PIPING

The plant design incorporated several interesting technologies, which added great value to the final project, namely:

- Double-walled HDPE cyanide pipe; and
- Abrasion-resistant, lined HDPE pipe.

Following a risk assessment of the cyanide distribution system, RML identified a potential safety and environmental risk of piping cyanide solution and slurries in pipe racks through the plant, particularly around other reagents. A solution to this problem was identified using technology developed for piping systems in fuel reticulation and this has subsequently revolutionised the piping system for transport of cyanide internationally. The coaxial pipe system uses the principle of a pipe within a pipe but is designed to be a close fit and has stand-off legs, allowing for easy fluid movement within the interstitial space, in case of a leak between the pipes. The double-wall system is a close fit, therefore smaller diameter pipe diameters can be used, allowing more space on pipe racks. The piping system has the ability to go around bends (45° and 90°) without losing the secondary containment and significant loss of flow. The system also allows branch offs ('tees')

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within the secondary pipe – which is not possible with a butt-welded system. Electrofusion joints are used to securely join pipe lengths and bends together. Unlike butt welding, electrofusion does not negatively impact the pipe pressure rating.

The piping system consists of a primary carrier line, rated to the required pressure rating (e.g., PN10 or PN16) inside a secondary 'retainer pipe', with a working pressure of typically 4 Bar. The close fit of pipes reduces space usage on racks and allows for jointing that is water tight. Coaxial fittings allow change of direction, whilst maintaining the secondary containment of the primary carrier pipe. Electrofusion is fast, safe and an easy way to weld HDPE pipe together, particularly in confined spaces such as pipe racks. Welding can be done in situ, with no need to remove pipe from racks to weld. Welding equipment is light, small and easy to handle, whilst being intrinsically safe, even in explosive-rich atmospheres. Welding speed is faster and joining method is superior to that of butt welding for smaller lines. Once welded, all heating element wires are encapsulated in the polymer wall of the fittings, thus there is no possibility of corrosion caused by carrier fluid. Unlike butt-welded systems, electrofusion systems ensure a continuously-smooth internal bore, allowing for greater flow, with less turbulence, than with butt-welded systems.

Another significant advancement for slurry piping within gold plants was the introduction of HDPE pipelines lined with GXCG-1101. Lined, HDPE pipework replaces what would otherwise have been expensive, rubber-lined, steel pipe, such as the mill discharge line to the cyclone cluster and the cyclone underflow line. *Figure 6* and *Figure 6*: Comparison of Abrasion Resistance for Piping Materials shows the abrasion resistance of this GXCG-1101composite pipe, compared to other conventional pipework. This data has been anecdotally confirmed in an onsite trial, which is continuing.

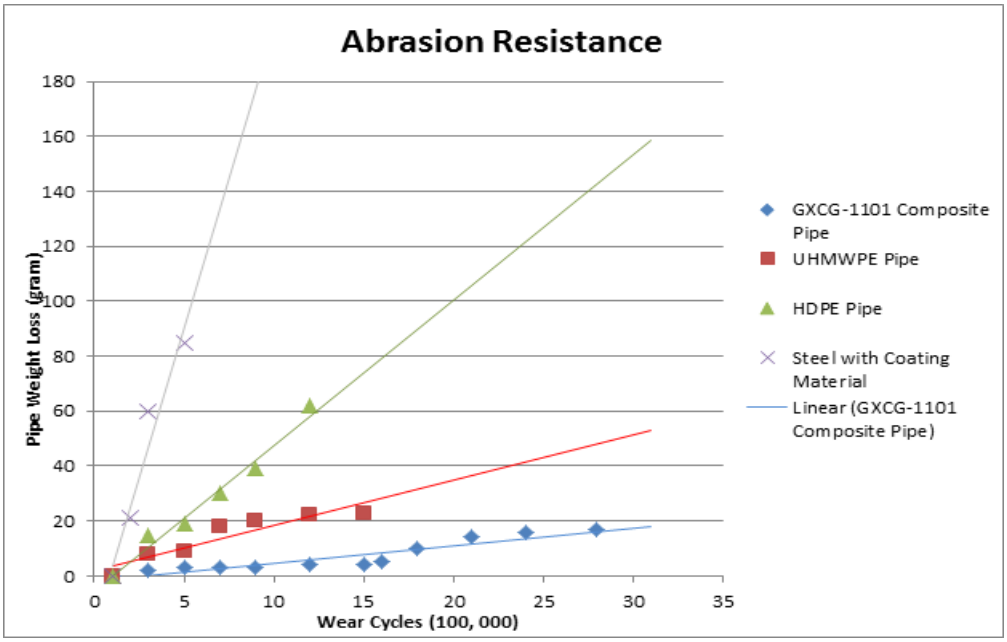


Figure 6: Comparison of Abrasion Resistance for Piping Materials

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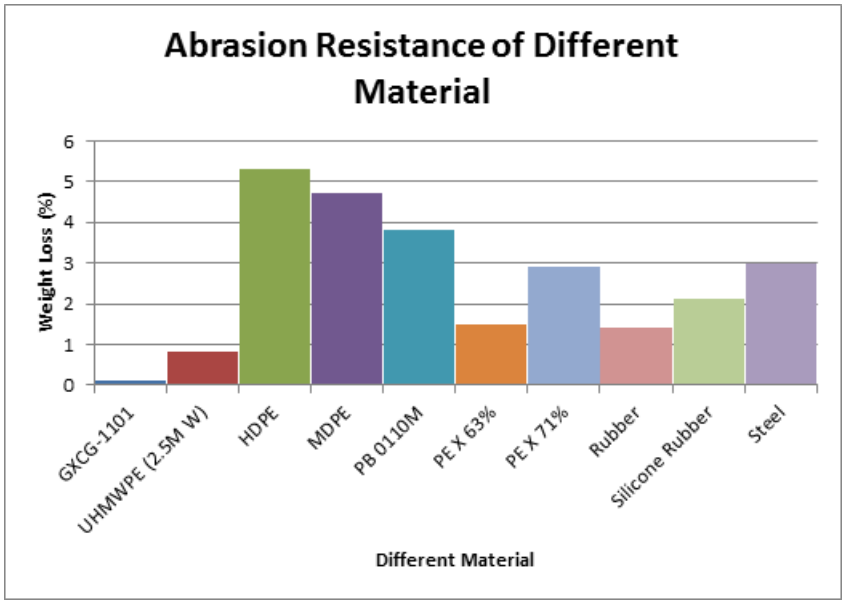


Figure 7: Comparison of Abrasion Resistance by Percentage

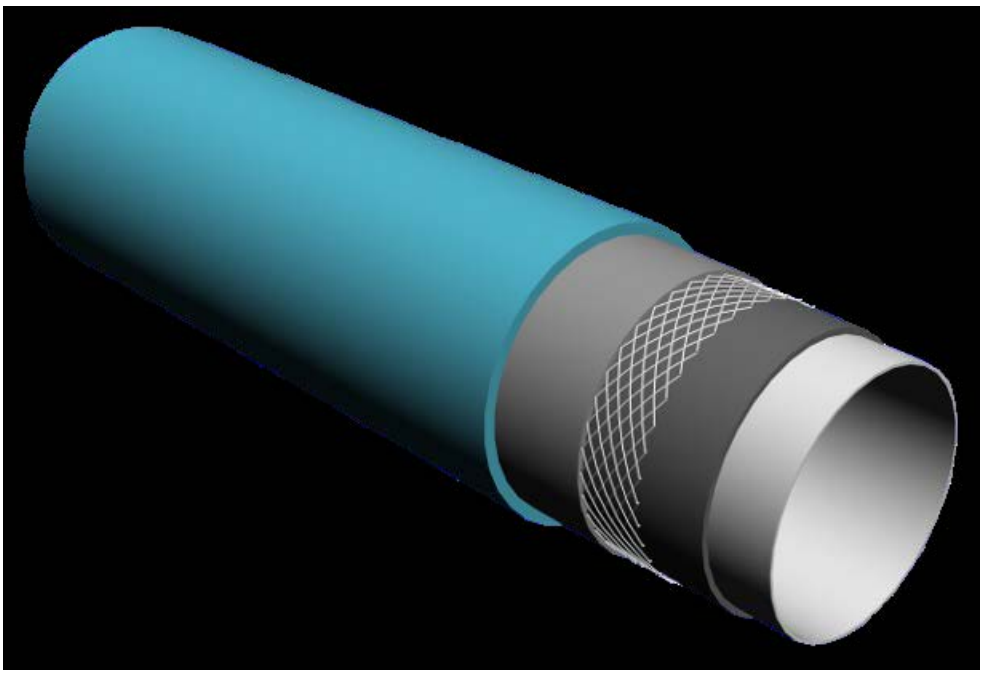


Figure 8: HDPE Line Components

The components of the abrasion-resistant HDPE pipe are shown in *Figure 8: HDPE Line Components.*

PROJECT MANAGEMENT METHODOLOGY

The right project delivery method for a project will not guarantee success but does contribute towards avoiding disputes and time or cost blow outs. Globally, in the resources sector, the most common project delivery methods are:

- engineering procurement and construction (EPC), also known as a turnkey; and
- engineering, procurement and construction management (EPCM).

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EPCM is the typical approach for Australian junior and mid-tier mining companies. This was the method chosen by RML for construction of the oxide processing plant which constituted the highest value and most complex part for the SEP. The remaining components of the SEP used the construct only method, supported by internal and external engineering resource inputs.

While RML implemented the traditional EPCM delivery method for the process plant, they modified the consultant's functions (described below), which, in hindsight, was a valuable decision.

Traditionally, the EPCM consultant's scope of services includes project control functions. However, for the delivery of the process plant, RML removed these from the EPCM consultant's scope of services and instead appointed a specialist consultant, Professional Cost Consultants ('PCC'), to perform the planning and cost control functions.

Although this variation to the traditional EPCM delivery method may seem unusual to the Australian resource sector, the approach is commonplace in the commercial sector, as well as in the resource sector in other countries.

The rationale behind RML's project delivery strategy was four fold-:

i. Typically, the EPCM Consultant's responsibility is to use reasonable skill and care in monitoring and reporting of costs and their relationship to the budget, however, the EPCM consultant usually has no contractual obligations with regards to the budget and schedule performance of the project.

ii. The EPCM consultant can only report on its own scope of work relative to engineering and procurement. To avoid production of a range of potentially conflicting reports produced by the various project stakeholders, PCC was tasked with reporting on the overall budget and schedule performance of the entire project.

iii. The EPCM consultant will not be influenced in their design and procurement decisions as a result of cost and time implications, thus directing their entire focus to superior design and constructability during the execution phase.

iv. RML had a strict set of corporate reporting criteria, particularly financial and the most effective way to meet these criteria was for an independent party to gather information from the various project stakeholders to produce one, 'all-embracing' report to reflect the true budget and schedule performance of the project.

'Project controls' encompass the people, processes and tools used to plan, manage and mitigate cost and schedule issues and any risk events that may impact a project. Application and implementation of effective project controls is an integral component to the success of a project. It provides timely information to management, which in turn empowers management to make decisions that ensure a project is completed on schedule and within budget.

An International Building Code® 2000 Project Control Best Practice Study carried out by Independent Project Analysis identified that good project control practices reduce execution schedule slip by 15%. Project controls cost between 0.5% to 3% of total project budget (including cost accounting). Consequently, to break even, project control needs to improve cost effectiveness by around 2%. A sample study carried out by the International Building Code® Cost Engineering Committee in 1999, showed cost improvements for the projects in the study was more than 10%. Success factors are based on good project control practices, which result in good cost and schedule outcomes.

Figure 9 below, broadly outlines the functions that the project controls group provided in establishing project baselines and the subsequent provision of project controls services to the SEP.

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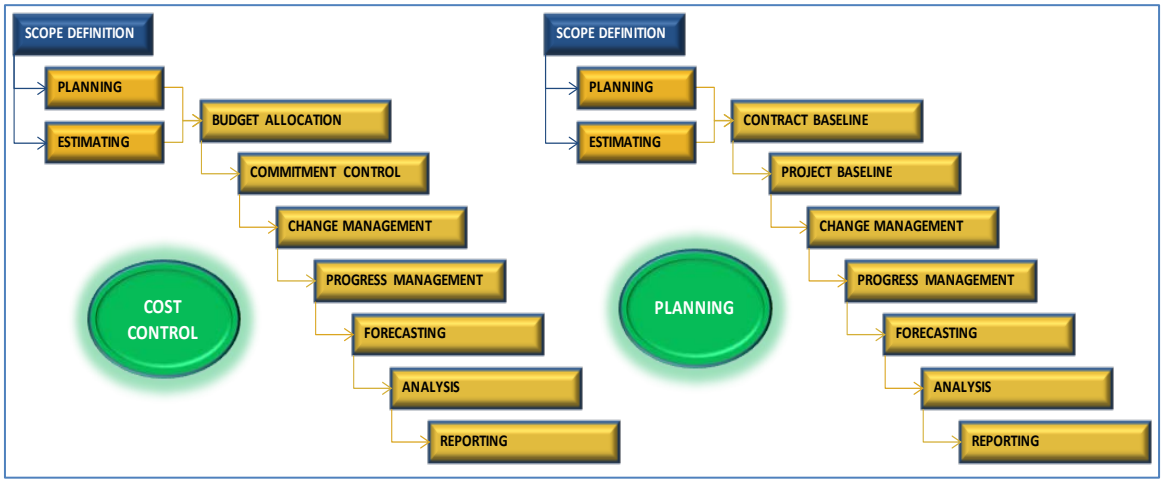


Figure 9: Project Cost and Time Controls

Not dissimilar to most resource projects, the SEP faced its fair share of risks that materialised as design and construction progressed. To name a few:

i. the project was executed during the commodity market downturn that commenced late in 2012;

ii. gold was particularly hard hit, losing approximately 30% of its value during the course of the project, which influenced the project business case;

iii. the project was located in a region which became politically unstable;

iv. the ruling Malian government was overturned in 2012 by a military coup d'état;

v. a major regional military conflict broke out in the north of Mali;

vi. the West African ebola virus epidemic broke out in December 2013, leading to various, key vendors refusing to mobilise to site during the critical pre-commissioning and commissioning phases of the project; and

vii. due to the brownfields nature of the project, continuous growth of scope had to be managed very closely.

Despite facing these major risks, of which any could have had catastrophic consequences, the SEP was completed three months ahead of schedule and 9% below budget. This noteworthy success is attributed to the entire project team and particularly RML management, who were able to repeatedly make informed decisions to put risk-mitigating measures in place. Hindsight has proven that RML could not have been able to make such informed decisions without the accurate reports produced by the independent project controls group.

CONCLUSIONS

Major construction projects benefit significantly from engagement of independent cost controllers, who are assigned only cost control and reporting activities and therefore not influenced by the need to undertake construction responsibilities. Combined with technological advancements and development of mutually-beneficial relationships with suppliers, the use of this project management approach assisted the SEP project to be completed 3 months ahead of schedule and 9% below budget.

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SMALL-SCALE GOLD MINING IN TANZANIA: PAST, PRESENT AND FUTURE

By

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ABSTRACT

Gold production has dominated Tanzanian industry for more than a century and stands at roughly 40 tonnes a year. Artisanal and small-scale mining (ASGM) is a feature of gold mining regions in Tanzania and plays a significant role as a direct source of employment in mining and in generating additional jobs in rural areas. Since the 1990s the Government has developed a legal and policy framework for integrating ASGM into a national mineral development strategy for economic growth and improvement of social well-being of the population. By now ASGM accounts for approximately 10% of Tanzanian gold production. However, the processing of gold ores can be highly problematic for ASGM, due to implication of low grade and more complex ores containing copper, arsenic and antimony minerals. It can cause lower gold recovery, increased reagent consumption and higher toxicity of the effluent.

This paper identifies the main problems for ASGM, causes of failure and presents oriented keys to overcome mistakes, optimize the process, develop successful operations and manage the risks. Large companies engagement strategies for ASGM (e.g., Anglo Gold Ashanti, Acacia Mining, Shanta Gold, etc.) are critically reviewed and compared with particular focus on the advantages and limitations in large-scale/small-scale partnerships.

Keywords: Refractory Gold Ores, Small-Scale Mining, Process Development, Large-Scale/Small-Scale Partnerships

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INTRODUCTION

The Geological Survey of Tanzania shows that the country has 103 million tonnes of iron ore, 2.222 million tonnes of gold, 13.65 million tonnes of copper, 209 million tonnes of nickel, 50.9 million carats of diamonds, tanzanite (12.60 million carats) and 911 million tonnes of coal. Tanzania`s mineral potential can be harnessed to make a significant contribution to the national economy and the benefits may reach a wide spectrum of the population[(1)]. Gold production has dominated Tanzanian industry for more than a century and stands at roughly 40 tonnes a year. Artisanal and small-scale gold mining (ASGM) is a feature of gold mining regions in Tanzania and plays a significant role as a direct source of employment in mining and in generating additional jobs in rural areas. ASGM activities involve gold production from hard rocks and alluvial deposits located in multiple regions of the country, especially in the area near Lake Victoria in North Tanzania[(2)]. Figure 1 shows the location of ASGM activities in Tanzania.

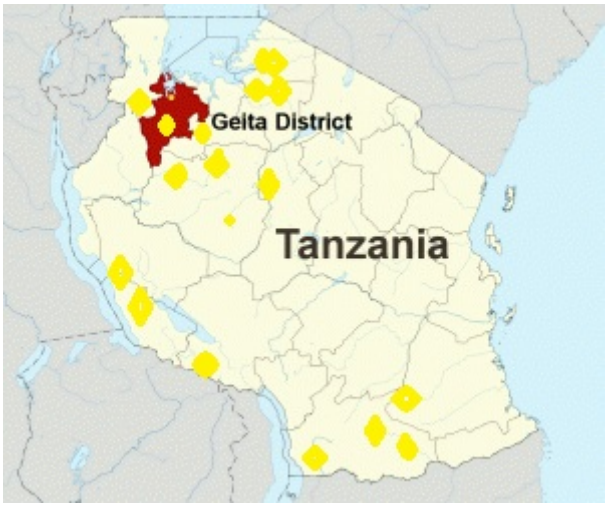


Figure 1: Map of ASGM mining in Tanzania

Generally speaking ASGM is characterized as the sector exploiting marginal or small deposits, lacks capital, is labour intensive, has poor access to markets and support services, and has low standards of health and safety[(3)]. In regards to the number of ASGM there are 20 million small-scale miners over the world. In view of the occurrence of ASGM it is evident that they can be found in the most distanced regions and areas in the world and involve the poorest people[(4)].

Opinion in recent years, influenced partly by some governments simply neglecting small-scale miners, has tended forwards making the ASGM the potential for environmental damage and conflicts because it falls outside the regular frameworks. On the other hand there is a tendency over the past 15 years to recognize ASGM as a legitimate route out of poverty.

Tanzania's ASGM sector began to grow in the 1980s. The global increase in gold price has become a significant factor to attract people into small-scale mining. The downturn in the performance of other productive industries, poor markets for agriculture and other factors have been associated with the increase in the number of people working in ASGM in the 1980s and 1990s. By now the population of artisanal and small-scale miners in Tanzania is estimated to be 500,000 -1,500,000[(5)].

Since 1990s the Government of Tanzania has developed a legal and policy framework for integrating ASGM into a national mineral development strategy for economic growth and improvement of social well-being of the population. According to statistical data by now ASGM accounts for approximately 10 % of Tanzanian gold production[(6)]. However, the processing of gold ores can be highly problematic for ASGM, due to implication of low grade and more complex ores containing copper, arsenic and antimony minerals. It can cause lower gold recovery, increased reagent consumption and higher toxicity of the effluent.

This paper shows the key problems affecting the ASGM sector and exploits the existing experience for improvement and development. Problem framing, engagement of legal activity, important contribution from the Government and large-scale companies are also under investigation**.** Large

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companies' engagement strategies for ASGM are critically reviewed and compared with particular focus on the advantages and limitations of large-scale/small-scale partnerships. The study used interviews and questionnaires conducted to involve Mineral Processing Engineering students of the University of Dodoma (Tanzania) in assistance to evaluate the problems in the ASGM sector. The knowledge generated in these studies is extremely helpful in further understanding the perspective of the co-existence of small-scale and large-scale mining as well as in the designing of new legal frameworks for ASGM.

PROBLEMS DESCRIPTION

We assume that ASG miners lack the most significant technical, social, economic and other infrastructures not allowing them to take advantages of technical progress and get out of poverty. The main problems and causes of failure should be indicated to avoid mistakes in near future. Table 1 shows the various causes and effects on the situation in ASGM sector.

Table 1: Cause and effect

Cause	Effect
Poor geological prospecting	Low efficiency of excavating
Exploiting the same mining sites	Competition leading to increase in poverty
Depletion of mineral resources	Low efficiency
Low education	Unskilled labour
Lack of appropriate technologies	Low recovery
Lack of appropriate equipment and tools	Low productivity and high level of accidents
Lack of legal framework	Low economic development
Lack of financial assistance	Low investments
Poor safety and working conditions	Health degradation and high level of diseases
Application of cheap but harmful chemicals	Environmental damage

According to Table 1 the reported information indicates strong correlation between cause and effect of low productivity in the ASGM sector. Consequently, the information generated from interviews in Table 1 revealed that the majority of respondents agreed with the factors that were provided.

Poor Geological Prospecting

Gold from alluvial deposits can be assessed easily and does not need the complicated preparation stage for ASGM. They totally neglect the prospecting stage and have no reserve estimation. Very often they are poorly organized and lacking in work preparation before production. As a result ASG miners are working in tiny mining sites with low efficiency.

Exploiting the Same Mining Sites

According to poor organization the ASG miners exploit the same mining sites which create great competition between them. This competition leads to an even greater level of poverty. As a consequence they have to shift from one site to another, working on both registered and unregistered land.

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Depletion of Mineral Resources

Nowadays this is the tendency to which leads to the exploitation of refractory gold ores. The majority of these ores are complex and many of them contain significant amounts of arsenic, bismuth, antimony and copper minerals. The presence of copper, arsenic and antimony cause a number of problems, including lower gold recoveries, increased cyanide consumption and increased toxicity of the effluent. The selection of options to treat a specific ore is significantly impacted by factors such as mineralogy, precious metal grades and deportment, gold to sulfur ratios and hazardous impurities.

Over the years, a variety of processes has been developed or proposed to recover valuable metals including acidification based technologies such as AVR and SART, direct electrowinning, activated carbon, ion exchange resins, solvent extraction, polychelating polymers, and membrane technologies. Unfortunately, most of these technologies can only be applied by large-scale mining companies, leaving ASGM out of progress. It appears that ASG miners need to move to far distances searching for large and rich ore bodies or accept the situation and treat the existing resources. As a result the efficiency of mining and mineral processing operations to extract gold from refractory ores without appropriate modern technology is very low.

Low Education

The majority of small scale miners possesses minor technical knowledge of mining and mineral processing, which results in unskilled labour with low efficiency.

Lack of Appropriate Technologies

Operations range from semi-mechanized and mechanized mining to the extraction of minerals using simple technologies and no mechanization. In fact the lack of appropriate and innovative technologies leads to wastage of minerals due to poor gold recovery. Another problem is gold extraction by amalgamation, the ancient method of gold recovery, which releases large amounts of mercury into the environment as metallic mercury, which is later transformed to metholated mercury, a powerful neurotoxin that is readily absorbed by biological tissue and is toxic to humans and wildlife alike [(7)(8)].The high health risk of mercury is well known over the world but in the remote and rural areas in Tanzania small-scale miners lack this information. It was established that by now more than 500,000 ASG miners in Tanzania still extract gold using mercury.

Lack of Appropriate Equipment and Tools

Equipment used for mineral extraction by ASGM can be differentiated between those whose operations are purely manual and those that have introduced some mechanical equipment. In most manual operations, the equipment, most of which is fabricated at the mining site, are very rudimentary[(9)]. For excavation and mineral processing operations they are using picks, shovels, pans and hand hammers.

Lack of Legal Framework

We must take into consideration the informal mining operations involving ASGM. A legal framework has significant value for ASGM. Unlicensed miners are vulnerable to losing official support which can lead to lack the protection and opportunities provided by the Government. It appears that small-scale miners have a fear of being recognized officially due to various reasons. Firstly, there is the small scale of the operations. Then they are not familiar with the market fluctuation showing the instability of it. Small-scale miners do not expect to continue their activity for many years. The law of “gut feeling" goes into play giving rise to the reaction of minimizing the legal activity. Most of them do not expect assistance but rather increase in the load of regulations restricting the activity.

Lack of Financial Assistance

It has been recognized that 80% of small-scale mining activity in the region is informal[(9)]. This sector is flexible and difficult to control. ASG miners often rely on informal financiers, who often control the sale of this gold in an organized and sophisticated way. It is an activity that has been done in many communities for centuries. However, given the low levels of formal employment

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where large-scale operations exist, it has taken on an increasing level of risk where communities encroach on mining lease areas and illegally enter company mining areas.

Poor Safety and Working Conditions

ASG miners are self-employed people working in the smallest underground mines in unsupported tunnels. Most probably they are drilling and removing rock with hand tools and carrying the ore to the surface in sacks. It is known that application of masks and gloves is very rare. Poor ventilation causes high level of heat and humidity, and lack of oxygen leading to a negative effect on health. In addition, working in unsafe conditions with a high level of noise and vibration small-scale miners can be hit by machinery moving parts or falling rocks. As a result many accidents occur.

Application of Cheap but Harmful Chemicals

In environmental aspects ASGM shows poor handling of chemicals during mineral processing operations. Very often small-scale mining operations cause erosion, deforestation, water pollution and finally, degradation of the environment. It is known that traditionally gold is recovered through crushing, grinding, gravity separation and amalgamation. Because of its simplicity and cheapness, it is not surprising that mercury amalgamation should be an ideal method to extract gold for ASGM. However, ASGM also poses significant environmental and health risks arising from mercury application. During this process, mercury is introduced into the environment through disposal of process water and tailings, while open-air firing of the gold/mercury amalgam releases mercury vapour to the atmosphere. It has been established that annually more than 1000 tons of mercury are released into soil, water and air. Mercury emissions from informal gold-mining operations represent a serious environmental problem in Tanzania[10].

ORIENTED KEYS TO OVERCOME THE PAST MISTAKES

Legalization

Often the process of legalization is complicated and bureaucratic, creating obstacles for miners. It is obvious that the way to attract the small-scale miner to this process is improvement in the legalization procedure to make it simple and clear for people. There is every indication that the Tanzanian Government continues to manage this sector to create suitable conditions to turn to the formal and legal sector to use country resources efficiently.

Training Programs

Mining, Material and Metallurgical Education in Tanzania has experienced constant and considerable change over the last ten years. Dar-es-Salaam Institute of Technology and the University of Dodoma became leading providers of Engineering education within Tanzania. To create a place where knowledge and skills in Mining, Material and Metallurgical Education will be transferred from one generation to another and produce sustainable economic development of the country, the university becomes a center of training innovative talents, scientific research and consultancy services in the areas of Earth Sciences and Engineering[11]. It has been established that ASG miners lack of appropriate technical knowledge and best practice approach for mining operations. Therefore the Institute of Technology came with the initiative to conduct and promote short-term courses for ASGM[12]. Also the project will serve as a platform of dialogue for enhanced collaboration between small-scale and large-scale mining. The authors believe that it will be the strengthening effect on ASG miners' capacity to become more productive. In addition the authors consider that creative dialogue between ASGM and the Government is the universal approach to formulate new meaning and help miners to adhere to the new knowledge. In 2006, the Tanzanian Government partnered with the United Nations Industrial Development Organization (UNIDO) to develop a "Manual for Training Artisanal Miners" and create training programs in ASGM communities in Geita District[13]. By using relevant teaching methods, the professional competent supervisors and consultants can stimulate small-scale miners for self-improvement.

Innovative Technologies

Some ASGM communities continue to practice the same method of gold extraction developed by their forefathers, whereas other groups are creative and try to improve working techniques to increase gold recovery rates. The innovative method was suggested by group of researchers to

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replace harmful amalgamation for gold recovery[14]. According to the reported results the borax method is cheaper than amalgamation and gives a higher recovery of gold. This method is successfully implicated in the ASGM sector in the Philippines. Some studies have been done in Tanzania. It gives the hope of convincing millions of miners around the world to use borax for gold extraction, significantly reducing global mercury pollution. Unfortunately, it should be noted that the borax method is not appropriate for all types of gold ores. Ores which are rich in sulfur or contain fine gold grains, can show some difficulties in successful extraction. It is evident that appropriate mineralogical testing should be done.

Financial Support

The Government emphasizes the improvement of small-scale miners' access to credit and small-scale mining loans by formal financial institutions. It has been proposed to formulate affordable credit schemes to the miners as well as establishment of mobile banking systems, to use third-party guarantees to enable other institutions to assist miners to get loans, to create mineral property markets to enable discoverers to sell their properties to developers at competitive prices. It is obvious that this strategy can improve small-scale miners' access to finance.

SMALL-SCALE AND LARGE-SCALE MINING: CONFLICT OF INTERESTS OR PARTNERSHIP

History of Relationships

Tanzania is one of the main countries for small-scale mining activity. However, compared with Tanzania's large-scale mining, the ASGM sector is smaller in its output but larger by labour absorption. It is a safe assumption that more people are involved in the small-scale rather than in the large-scale mining industry. Moreover, it also has had exceptional increase within ten years, outperforming the large-scale mining by at least 30% in this respect. Although the Tanzanian Government recognizes small-scale mining as an important contributor to national economy, very often the ASGM sector is taken into account as a serious and potential strategic means to pressure foreign companies to accept more stringent conditions for mineral exploitation[15]. It is likely that in some specific areas a growing ASGM can provide the establishment and development of local mining as well as play the role as a temporally limited alternative to large-scale mining operations.

Since the last century, the relationship between small-scale and large -scale mining remains a troublesome question for the researchers, showing conflicts as well as a chance for cooperation. From the German colonial period, gold discoveries had been made in Geita, Kahama and Sekenke in the Lake Victoria region in the 1890s. At this time, small-scale gold mining was carried out on alluvial rich deposits. The ASGM sector was negligible due to lack of native artisanal activities. Although the first small-scale gold mine was opened at Sekenke in 1909, the activities of large companies was started with development of gold mines in Musoma and Geita. Establishment of the Geological Survey Department and enactment of mining laws in 1920s by the British administration led to an increase in prospecting involvement of medium and large scale companies. Before the Second World War gold production was in progress in Tanganyika with record levels attained in 1940 to the value of £1.2 Million. As a consequence artisanal and ASGM had often adhered to virgin exploration sites and larger-scale mines in the Lake Victoria region and Southern Lupa Goldfields, to take advantage of better access to deposits[9].

Present Co-existence

By now in many cases the relationship between small scale and large mining companies has been troubled by mutual distrust and indignation from both sides giving strong negative feelings. There is a number of reasons which cause these difficulties in understanding. The most important reason is the competition for the same mineral resources. Many deposits now extracted by large-scale mining companies were initially discovered by artisanal miners. These difficulties arise in gold-rich areas when the large scale mining companies have got the license for mining and processing. In addition ASGM are usually allocated tiny mining sites that make it difficult to operate without interfering with each other. Nevertheless there are some important factors indicating the prospective successful cooperation between small-scale/ large scale mining sectors in Tanzania. As a country Tanzania is politically stable and safe. The government focuses on legal and regular frameworks. Finally, the geology of the country assures peaceful co-existence of both small- and large-scale mining companies for further mineral resource discoveries.

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Future Partnership

Large-scale mining companies in Tanzania recognize positive contributions of the ASGM sector to the national economy such as employment of people from the rural areas, discovery of minerals and economical mineral production located in remote areas, and profit generation. During recent years large companies have started to establish engagement strategies for ASGM. They understood that construction of trust and strengthening of relationships is the key to avoid conflicts between small-scale/large-scale mining. In 2014 a pilot project initiated by World Bank group started in Geita region. It is the collaborate efforts of the Government of Tanzania, the World Bank group, large-scale mining companies Anglo Gold Ashanti and African Barrick Gold and ASGM[16]. The project aims to improve conditions and livelihoods for small-scale miners, decrease environmental degradation and facilitate the peaceful co-existence between LSM and ASM. Acacia Mining company has made a comprehensive effort to improve community relations and security at North Mara Gold Mine in order to prevent violent confrontation. The company provided for investment across health, water, education and alternative livelihoods within the seven villages surrounding the mine and has significantly improved the relationship with the community[17]. Acacia Mining became a signatory to a multi-stakeholder partnership to improve the relationship between ASGM and large -scale mining. The Multi-Stakeholder Partnership seeks to improve ASM-LSM coexistence in Tanzania by fostering the legal, regulated, safe, sustainable development of an ASM sector that operates within the rule of law and with respect for human rights. North Mara is participating in one of two pilot projects. It is obvious that now large-scale mining companies recognize that the future is a dialogue, a collaboration between ASGM and large business. However, there are some steps which should be done for further successful co-existence of these two sectors.

- Providing the general information about exploration and closure of the mine to minimize negative effect of LSM activities on ASGM
- Training of ASGM to improve their skills in mining methods, geology, mine pegging, environmental management, health and safety, business planning and management
- Promoting change in the mining and refining methods to reduce environmental impacts and improve gold recovery
- Strategic planning for contribution to the development of the ASGM communities
- Providing financial assistance for technical improvement
- Involving local people in construction and maintenance activities
- Managing the security in accordance with the COP provision on Security which references the Voluntary Principles on Security and Human Rights.

CONCLUSIONS

Artisanal and small-scale mining (ASGM) is a feature of gold mining regions in Tanzania and plays a significant role as a direct source of employment in mining and in generating additional jobs in rural areas. However, the processing of gold ores can be highly problematic for ASGM, due to implication of low grade and more complex ores containing copper, arsenic and antimony minerals. Which can cause lower gold recovery, increased reagent consumption and higher toxicity of the effluent. The main problems and causes of failure such as low education, poor geological prospecting, exploiting the same mining sites, depletion of mineral resources, lack of appropriate equipment, technologies, legal framework and financial assistance, poor safely and working conditions have been indicated. It has been established that the oriented keys to overcome mistakes, optimize the process, develop successful operations and manage the risks are legalization, training programs, innovative technologies, collaboration and financial support from large-scale mining companies and the government. While it is early to draw conclusions regarding the impact of large companies engagement strategies for ASGM to future success of co-existence and collaboration between small-scale and large-scale mining, it appears that recent efforts have been the important steps in developing partnerships.

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PROCESSING HIGH CLAY GOLD ORES

By

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ABSTRACT

Clay minerals can cause nightmares with Mineral Processing because of the inherent difficulties of processing high clay gold ores.

These clay minerals typically form in near surface geological environments due to weathering, particularly above the natural water table, sedimentation and digenesis and are common in hydrothermally altered rocks.

Understanding the geology, mineralogy and correctly selecting representative samples of the ore to be processed is critical in getting the mineral processing right. Clays have the potential if not recognised to destroy project economics. Testing at an early stage of representative ore samples is critical.
The presence of clays in hard rock comes as a surprise if not fully understood. Similarly waste dilution from country rock containing clay can adversely affect the process. There are some solutions which assist in processing ores but do not negate all of the difficulties.

The presence of clays has a major influence on the process selection and equipment used in the final flowsheet.

The industry has paid a heavy price on a number of projects where the clay was not recognised or the process plant was based on a hard rock design which later proved to be totally unsuitable. Trying to mitigate the impact of clay on the process if the percentage of clay in the feed cannot be controlled is a mineral processing challenge.

Reference is made to two specific gold projects where wet sticky clay ores caused processing difficulties.

Keywords: Materials handling, clays, kaolinite, montmorillite, smectite, oxide ore, viscosity, scrubbing, Tunra, belt scrapers, screen blinding, mass flow bins, rat holing, filtering, tailings, pumping, dirty overflow.

Introduction

- Clays cause inherent materials handling issues in mineral processing because of their wet sticky nature
- Clays are typically < 2 microns
- They have high surface areas and reactivity (swelling and adsorbing power)
- There are many clay mineral groups-identification
- Mostly weathering products are above the water table and have high moisture levels
- The Mineral Processing issues are problematic- more particularly crushing, thickening & filtering issues

Introduction

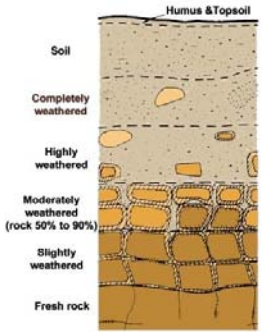
- Clays and problems they cause. These issues are exacerbated in wet tropical climates
- Scrubbing and its purpose and application in removing clays
- Scrubbing testwork required before design
- Materials Handling issues- conveyors, chutes, stockpiles
- Stockpiles & Bins
- TUNRA Testing
- Processing Wet Sticky Clay Ores- tricks and traps
- Conclusions and take aways

The Problem with High Clay Ores

- Materials handling-bins & stockpiles
- Crushing & screening
- Milling & classification
- Thickening
- Leaching
- Pumping
- Thickening & filtering
- Tailings drainage

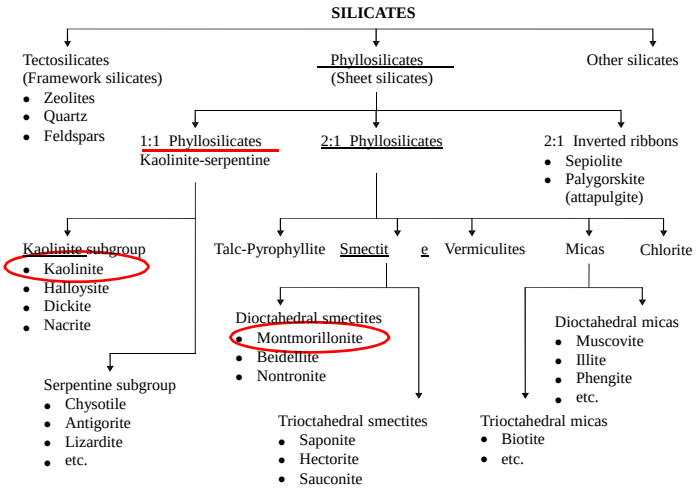
The Weathering Profile & Significance

- **Clay minerals exist in the areas above the water table** but can in some instances exist below it.
- The reaction of feldspars and water to form kaolinite involves the exchange of cations and produces a clay mineral.
- **No clear zoning**. This makes it difficult to clearly define the zone of oxidation and therefore selectively mine these zones. Even mining fresh ore there are occasional patches of weathered clay ore within the sulphide zone.
- Must recognise and test zones at the development stage. Metallurgical mapping-Geomet.



Source: METS library

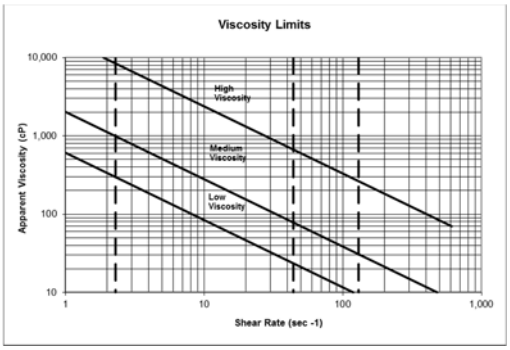
Clay Classification



Source: METS table

Clay Impact on Metallurgical Testwork

- **Warning**
  - Don't dry clay ores or you will change the characteristics-Murrin Murrin example
- **Keep some samples undried**



Source: METS library

Mineralogical Techniques

Techniques	Applications
Scanning electron microscopy (SEM) (qualitative versus quantitative image analysis)	Mineral identification, liberation, surface morphological study and modal analysis
QEMSCAN with Mineral Liberation Analysis (MLA)	
Secondary ion mass spectrometry (SIMS)	Quantification and mapping of elements
Particle-induced x-ray emission (PIXE)	
Laser ablation microprobe inductively coupled plasma mass spectroscopy (LAM-ICP-MS)	
Time-of-flight laser ion mass spectroscopy (TOF-LIMS)	Quantification of adsorbed metal on the surface of carbonaceous matters and other minerals determination of inorganic surface composition

What Does Clay Look Like?



Source: METS photo

Soft friable sticky material

- Usually near surface ore
- Soft
- Wet - high moisture
- Sticky
- Difficult to handle
- Common problem

Sampling For Testwork



Source: METS photos



- Representivity of samples is an issue
- Drying samples changes clay properties- reduced viscosity
- Thickening characteristics will change- may improve settling rates- not realistic
- Filter characteristics will change- may improve filtration rates- not realistic

Why Scrubbing? – Can it Apply to Gold?

- Beneficiation of low grade ores
- Remove clays prior to processing
- Reduce size of downstream processing
- Improve separation downstream units
- Improve materials handling characteristics
- Simberi, PNG- scrubber ahead of the ball mill- scrubber undersize direct to mill discharge sump



Source: METS photo



Source: METS Library

Laboratory Scrubbing Tests



Source: ALS photo

- 1.0m by 0.5m
- Variable speed
- 2 by 50 mm lifters
- Vary scrub time
- Calculate power kWh/t

Screening & Washing



Source: ALS photo

- Mass split after screening
- Screen at 31.5, 6.0, 3.35, 1.0mm or desired sizes
- Assess efficiency

Potential Problems



Source: ALS photo

- Clay balls form
- Clays not efficiently removed
- Power overloading
- Transport through the scrubber - lifters/breakers
- Quantity of Water required to wash

Crushing WSO

- Blend feed- 50/50 hard/soft- can operate crusher
- 100 % clay ore. Remove top & bottom deck- screening very difficult. Bypass screen and secondary crusher
- Secondary crushing can very difficult with high clay- bridging
- 100 % clay ore -bypass secondary crusher
- 100% clay ore. Operate longer to achieve production
- Ensure conveyors are covered. Don't add water



Source: METS Library



Gold CIP & Clay Ores

- Stepped tanks - tanks overflow - insufficient head-minimum 200mm/tank
- Extremely high viscosity slurries wont agitate and solids separate from water on the surface. Tanks overflow.
- Slurry like porridge - limit % of clay feed as a constraint in feed to plant
- Viscosity modifiers –Freevis-cost involved -Boddington
- Use of caustic not lime



Source: METS Library

Thickening

- Thickening of clays is very difficult due to the fine particles(<2 microns) which are highly charged surfaces.
- This requires flocculant screening and optimisation of the pH to achieve acceptable settling rates.
  - The overflows can be dirty which may cause problems with downstream processing & water circuits
  - In addition the presence of clays affects the ultimate underflow density and the choice of underflow pumps (positive displacement not centrifugal pumps).



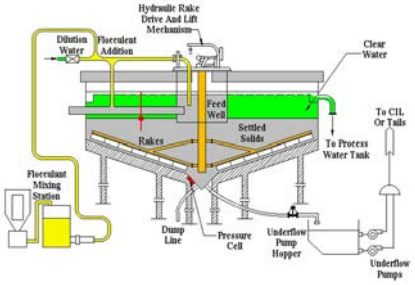
Source: METS Library



Source: METS testwork

Thickening Issues

- Hi-Rate was a great innovation- suitable for clay?
- Conventional or high rate? Pre Leach or tailings thickener
- Limited underflow density achievable may be as low as 40% w/w
- Over flocculation results in potential pumping problems- blockages
- Evaporation and water chemistry changes can result in the laboratory flocculant screening being incorrect
- Other problems with mixes of clay and sand



Source: Vendor diagram

Thickening Issues – Confidence Testwork

- Normal procedures don't apply- the risks are magnified with clay
- Predictability not as good- potential to get it wrong- thickener too small
- Variable clay in feed samples makes this more complex
- Settling columns-conventional
- 90mm continuous thickening



Source: Outotec photo

Thickening Issues – Confidence Testwork

- 190mm continuous thickening
- Pilot 1m scale thickener- de risk scale up
- 50/50 hard rock and clay is manageable
- 100% clay thickener overflows dirty after 12 hours operation
- Paste thickening may not be possible



Source: Outotec photo



Source: METS photo libary

Filtering of Clay Ores

- Pressure filters will always provide higher performance than vacuum filters.
- The nature of the clay and the volume percentage in the feed impacts adversely on filtration rates, clarity of filtrate, spillage and maintenance issues.
- Filter aids will increase filtration rates including, high pH, Coagulants, Guar and combinations of which all result in lower water recovery and have to be tested in the laboratory.
- The presence of clays causes excess spillage with clays sticking to cloths requiring washing and excess maintenance issues. Provide for clean up
- Solution-guar, coagulants, diatomaceous earth



Source: METS Library

Filtering of Clay Ores - Issues

- Pressure filters are superior to belt filters
- Vertical stack Tower Press pressure filters (Larox) are better for wet sticky cakes
- Air blowing can reduce moisture level and improve materials handling significantly
- Critical moisture level of say 15%. Above this wet and sticky whilst below this it is friable and can be conveyed without difficulty
- Dry stacking residues is a significant industry trend occurring around the globe



Source: Vendor photos

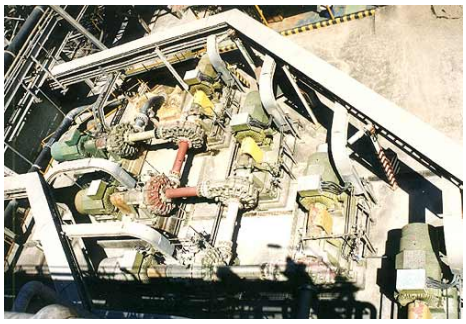


Filtering of Clay Ores – Issues Testwork

- Risks are high- don't skimp on testwork- design basis 500 kg/m2/h; actual 100 kg/m2/h - disaster zone
- Guar- Can give very large improvements to filtration rates
- Flocculants- negative and positive or no benefit
- Coagulants- can be good, costly and high moisture in the cake
- Diatomaceous earth- improved filterability and release
- Cloths- based on permeability, have to test, testwork will not predict scale issues
- Scale up- Difficult to predict with clay ores
- Piloting recommended

Slurry Pumping

- Derates the capacity of slurry pumps
- Oversize pumps are another option to allow for the difficulties encountered when pumping highly viscous clay ores.
- Viscosity measurements are critical to plot yield stress against shear rate and benchmark this against other problematic ores.
- Pump selection is also an issue because highly viscous clay ores can de rate the calculated pump capacity by up to 50%.
- For pumps under thickeners centrifugal pumps may be totally unsuitable and either peristaltic or mono pumps will be required.



Source: METS Library

Tailings Dams

- High clay ores require larger tailings dam footprints and have lower water recovery and are geotechnically less stable.
- The tailings don't beach and drying of a thin layer with a high insitu density is slow and difficult.
- The economic and potential environmental issues are serious when treating high clay ores.
- Water recovery is low



Source: METS Library

Process Water Contamination



Source: METS Library

- Clays don't settle and thickener overflow water or tailings return water is dirty as a result.
- This dirty water causes problems in the water distribution system pipes, etc.

Current TUNRA Test Pricing

01 - Determination of Worst Case Moisture Content	$3,700
02 - Low Consolidation Testing Under Instantaneous Conditions (single mc)	$5,700
Additional wall liner	$500
03 - Low Consolidation Testing with Undisturbed Storage Time (single mc)	$2,200
04 - Low Consolidation Testing with Vibrated Storage Time (single mc)	$2,300
05 - High Consolidation Testing Under Instantaneous Conditions (single mc)	$1,100
06 - High Consolidation Testing with Undisturbed Storage Time (single mc)	$1,400
07 - Static Angle of Repose (single mc)	$200
Material/Conveyor Interaction Test Work:	
08 - Conveyor Surcharge Angle (single mc)	$650
09 - Conveyor Inclination Angle (single mc)	$750

Source: TUNRA price table

Dozing ROM Stockpiles

- Dozing can push up stockpiles to keep ore from getting wet from heavy tropical rain
- Inside of stockpiles will be dry allowing better processing
- Dozing in crushed ore stockpiles can recover ore and keep the mill operating during crusher shutdowns
- 50/50 hard rock and clay is more manageable. Ore rills.



Source: METS Library



Source: METS site photo

Jaw Crusher

- Apron feeders only for feeding jaw crushers. Jaw crusher will work on 100% clay ores.
- Toothed rolls only applicable if there is no rock
- Larger openings for jaw crushers when crushing clay ore
- Build up of clay sticking to walls and jaw liners will occur blocking off the opening
- Use air spears to clear- very effective. Avoid using water to clear build ups
- Don't add water as it makes downstream issues worse



Source: METS site photo

Air Cannons

- Air canons are applicable in bins and chutes
- Applicable in bins, slot feeders and on chutes
- Will clear build ups



Source: Vendor photo



Source: Vendor photo



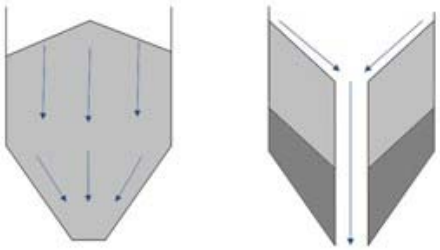
Source: Vendor photo

Bin & Hopper Design

Mass flow only- avoid bins with clay ores

Use plane flow bins with slotted opening

NOT DESIRABLE



Source: Materials handling textbook

Materials Handling Before Scrubbing

Before Transfer Chute



After Transfer Chute



Source: METS site photo

Conveyor Design Issues

Carry Back-wash stations



Source: METS site photo

Material Profile



Source: METS site photo

- Cant have stockpiles ahead of scrubbers
- Splitting feed to scrubbers is difficult-trade off studies
- Limits on scrubber sizes

Build Up of Clays

- Build up of clay on head pulley
- Slipping of belt when clay builds up
- Tracking problems
- Belt washing stations may be required



Source: METS Library

Conveyor Design Principles

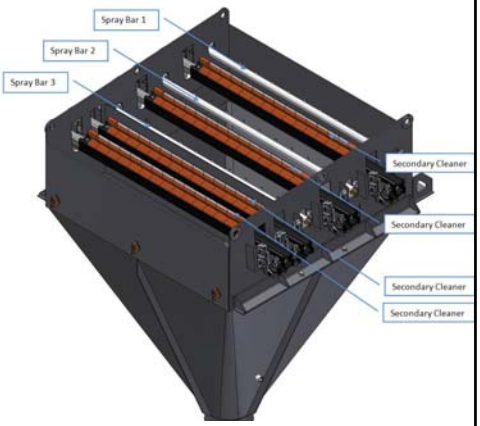
Individually tensioned centre blades



Source: Sandvik photo

Scrapers and belt wash

Source: Sandvik photo



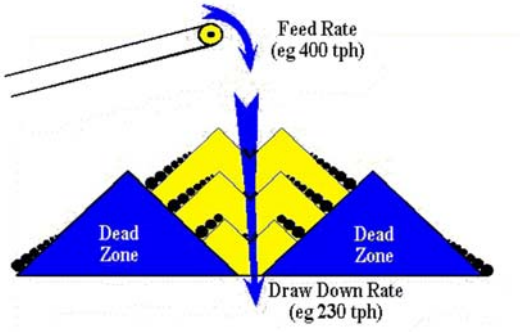
Chute Cleaner

- Air line and valve used to clear build up of WSO in chute
- Turn HP air ON/OFF several times a shift
- Can use water on final transfer chute onto mill feed belt. Water causes clay to slip and not build up



Source: METS Library

Live Stockpile / Dead Stockpile



Source: METS library

Cannot stockpile clay ores-set go hard- Covered stockpiles are workable –excavators and backhoes

Stockpiling Wet Clay Ore

- Stockpiled ore is insurance to keep the mill operating
- Covered stockpiles to keep the rain off
- Excavator can be used to stockpile wet clay ore when crushing
- Clay does dry out under cover



Source: METS Library

Unblocking Slot Feeders

- With wet sticky ore the slot under the stockpile will bridge
- Clay wont rill- in fact it compacts
- Backhoe can be used to unblock slot feeders
- Apron feeders better than belt feeders
- Don't use vibe feeders-bad



Source: METS Library

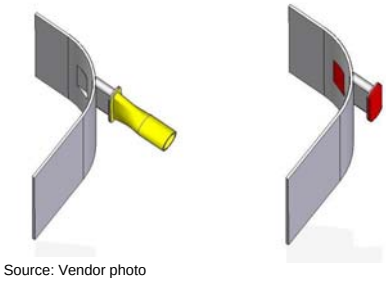
Chute Design Principles

Flow Assistance

Water Sprays
Air Cannons (fan jet)



Source: METS Site photo



Source: Vendor photo

Conclusions Processing Clay Ores

- Understanding the geology, mineralogy and correctly selecting representative samples of the ore to be processed is critical in getting the mineral, processing right.
- Clays have the potential if not recognised to destroy project economics. Testing at an early stage of representative ore samples is critical. Blending can mitigate some of the problems.
- The presence of clays in hard rock comes as a surprise if not fully understood. Similarly waste dilution from country rock containing clay can adversely affect the process. There are some solutions which assist in processing ores but don't negate all of the difficulties. Most open pit deposits contain clays above the water table.
- Scrubbing up front can significantly improve downstream ore processing. The scrubber sizing must be based on laboratory testwork.
- Trying to mitigate the impact of clay on the process if the percentage of clay in the feed cannot be controlled is a mineral processing nightmare.
- Processing WSO in tropical environments with heavy rain is the ultimate challenge.
- There are tricks and tips that can be used to help process the ore.

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NEXT GENERATION OF AGITATORS FOR PROCESSING ABRASIVE ORES

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ABSTRACT

In process plants, rotating equipment and piping components are subject to wear especially if the process media contains solids. Next to bulk solids, it is primarily suspensions that cause wear to mechanical apparatus, pumps, pipes or valves. In the following article, particular attention is paid to wear that naturally occurs to impellers with high tip speeds. Such conditions can be specifically found in hydrometallurgical leaching processes, either atmospherically or in pressure autoclaves, in large storage and conditioning tanks, for handling gypsum slurries in FGD plants or with crystallizers.

One basic design criteria to decrease abrasion is to minimize the impeller tip speed without compromising the mixing task. A new level of abrasion resistant agitators has been established over the years with the improvements in materials of construction and coating technology.

However, it is now possible to even further significantly improve the lifetime of agitator components compared to the present state-of-the-art. One achievement in this direction has been the development of hydrodynamically optimized impeller shapes by using modern numerical simulation tools and newly applied manufacturing processes. Another upcoming development is the partial construction of impeller blades in solid ceramic parts. The aim of this article is to show that an investment in such new agitator technology is highly profitable even in a shortest period of time. This technology also holds great potential for future minerals processing applications yet to be seen.

Keywords: abrasion, ceramics, impeller, agitator, coatings

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INTRODUCTION

Wear and corrosion issues are encountered in different mixing applications in the minerals processing industries. Cost-effective solutions are carbon steels, see (1), in combination with rubber lining for open tanks and typical operating temperatures ranging from 5°C to round about 80°C. Stainless or even duplex steels are not so common, but can be found in applications such as bioleaching or direct leaching operating close to the boiling point. At the end of the scale are HPAL and POX autoclaves for hydrometallurgical leaching at high temperatures and in a harsh acidic environment. For such conditions, titanium and titanium alloys are the only suitable materials of construction up to now. Operators can be confronted with high costs for repair work and downtime as high solid loads must be processed if the agitators are not designed accordingly. Apart from the optimization of the state-of-the-art technologies, impellers made of solid ceramics represent a completely new approach. An intensive abrasion test work program was conducted in the 50 litre, 1 m^3 and in the 15 m^3 scale with ceramic impellers of a diameter of up to 1,100 mm. This technology can even be scaled-up to the size of the world largest POX autoclaves based on mechanical design rules adapted to ceramics.

DESIGN CRITERIA FOR ABRASION IMPROVED AGITATOR EQUIPMENT

Enhanced wear of impellers occurs in hydrometallurgical applications processing slurries typically under the following conditions:

- Processing of slurries with high to very high concentration of solids (high volumetric fraction)
- Suspension of coarse, hard and dense particles
- High volumetric power input
- In combination with stress - corrosion mechanisms

Figure 1 shows a worn titanium blade of a flat blade disc turbine in a POX autoclave after only a few months in operation. Such a situation leads to increased operating costs, due to unproductive downtimes for the replacement of the impeller and the costs for the repair work itself. Another issue that can be found with standard flat blade disc turbines is wear directly at the carrier disc adjacent to the blade holder, see Fig. 1. Such uneven or locally concentrated wear phenomena can even lead to the loss of an individual blade, which causes imbalances that can damage the shaft, mechanical seal or even the gearbox.



Figure 1: Wear on one blade of a flat blade disc turbine after operating only a few months

However, the power requirements in POX autoclaves are high and are dictated by the process demands. The absorbed volumetric specific power must be in a range of 1.0 – 5.0 kW/m^3 as pure oxygen gas has to be dispersed efficiently. Therefore, the classic flat blade turbines must be modified in order to fulfil these power requirements at moderate impeller tip speeds.

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A satisfactory service life can be achieved if the following general aspects are considered carefully:

1. **Minimization of impeller tip speed for a given power input**
2. **Use of optimized impeller geometry avoiding uneven local wear**
3. **Material selection for optimal life time representing a cost-effective solution**

In the following, this article will discuss these aspects in more detail by exemplary case studies. It is important to note here that an optimum in abrasion reduction is obtained by applying a combination of all three basic design rules, well balanced instead of only optimizing one or two of these aspects alone.

OPTIMIZATION OF THE IMPELLER TIP SPEED

Basic Wear Mechanisms

Figure 2 illustrates the two fundamental mechanisms of slide and impact wear, also see (2).

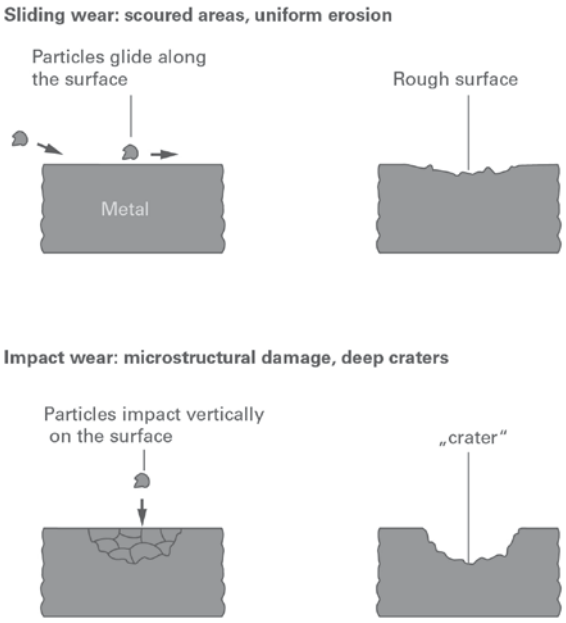


Figure 2: Wear on a plate of flat blade disc turbine

The wear rate $\dot{w}$ is a function of the incident flow velocity, which correlates with the tip speed u

$$\dot{w} \sim u^x$$

wherein x ≈ 3.0 applies for parallel flow (slide wear) and x ≈ 5.0 for incident flow perpendicular to the surface (impact wear).

For the same power number Po and same absorbed power P the wear rate of an impeller decreases inversely reciprocal to the square of the impeller diameter:

$$\text{Note that } P = Po \cdot \rho \cdot n^3 \cdot d_{imp}^5$$

$$\dot{w} \sim \frac{1}{d_{imp}^2}$$

On the other hand the pumping rate increases, as

$$q = Q \cdot n \cdot d_{imp}^3$$

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E.g. if the absorbed power P is held constant this can be expressed by

$$q \sim d_{imp}^{\frac{4}{3}}$$

From the process point of view a higher pumping rate is in most cases advantageous for solid suspension and faster mixing. However, from the mechanical point of view the shaft torque increases when larger impeller diameters are used for a given motor power.

$$M_t = \frac{P}{2 \cdot \pi \cdot n}$$

and with P = const.

$$M_t \sim d_{imp}^{\frac{5}{3}}$$

The costs for the mechanical design will depend mainly on the resulting gearbox size, the necessary shaft diameter and the mechanical design of the impeller to transfer the higher torque.

As an example, by increasing the impeller diameter by +25.0% (for the same absorbed power) the abrasion rate will decrease by approximately -36.0 % compared to a previously installed impeller of the same type. However, the shaft torque will increase by +45 % which must be considered in the mechanical design.

MATERIALS OF CONSTRUCTION

Cost Overview

The selection for the material of construction (MOC) for the product wetted part of an agitator depends on the chemical requirements of the process and on the requirements of the mechanical design.

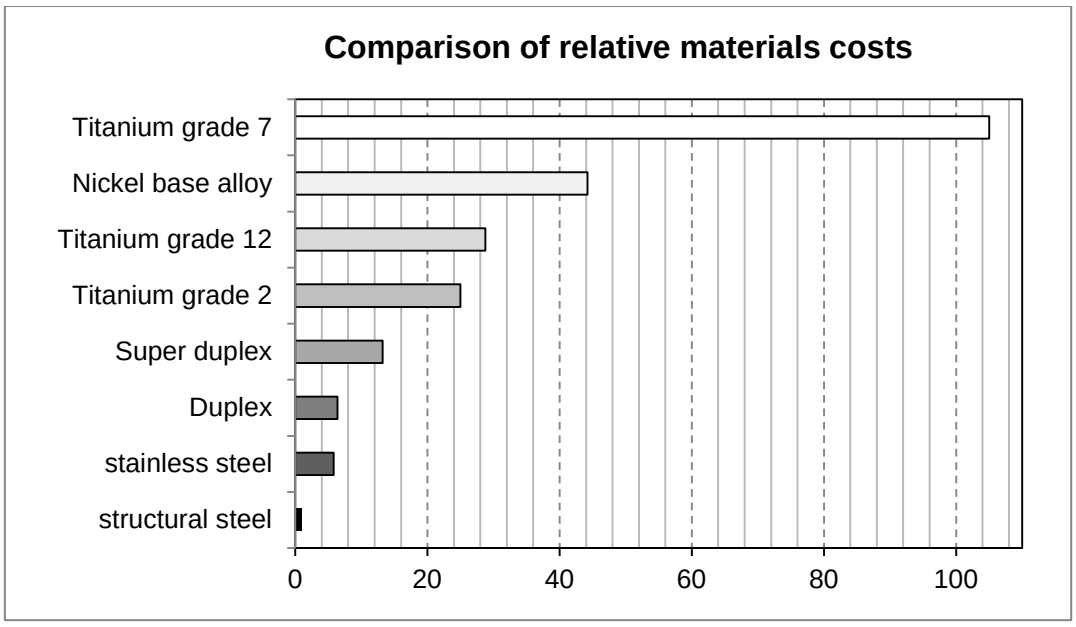


Figure 3: MOC – comparison of relative materials costs – basis is carbon steel

Figure 3 shows the wide spread of material costs beginning with carbon or structural steel (normalized to one) and ending with Titanium with a grade 7, with a kilo price approximately 100 times more expensive than carbon steel.

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ATMOSPHERICAL AGITATOR APPLICATIONS

Suspension Tanks – EKATO VISCOPROP

Carbon steel is a common material of construction for agitators in minerals processing applications, especially for the so-called open tanks. In many cases the product wetted parts made of carbon steel are rubber lined. One reason is that steel is exposed to a certain level of corrosion in acidic environments. Apart from the level of acidity, the corrosion potential also depends on other parameters such as chloride content - only to name one among many. Another reason for rubber lining is the protection against abrasion from the solids in the slurry. Figure 4 shows the EKATO VISCOPROP impeller, which is typically used for solid suspension tasks e.g. in storage and conditioning tanks and in leaching tanks with no or low specific gassing rates.

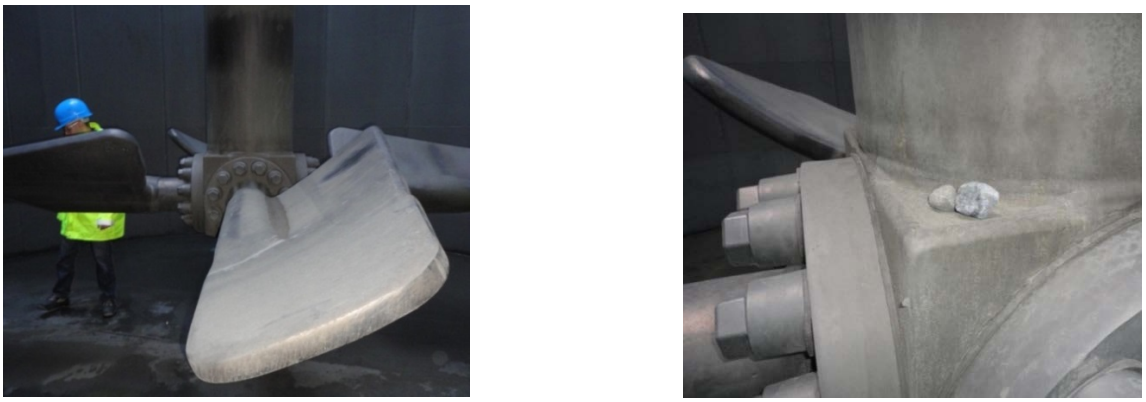


Figure 4: EKATO VISCOPROP (rubber lined) for solid suspension of very large particles

The type of rubber lining can be described by two main categories: soft and hard rubber. Hard rubber is advantageous with respect to adhesion to steel and the material is denser compared to soft rubber showing higher sealing properties. However, hard rubber is not optimal for abrasion protection. Therefore, a combination of hard and soft rubber lining provides the best results. However, depending on the application it is also possible to line the impeller blades only with soft rubber, which is a more cost-effective solution. If required for corrosion protection, agitator shafts are only hard rubber lined, as no abrasion issues will occur due to the quite low circumferential velocities.

Gassed Applications – EKATO COMBIJET

Gassed applications in atmospheric tanks are increasing for the processing of complex ores. These applications are demanding because large slurry volumes must be kept in suspension and good gas dispersion must be realized in order to achieve the process requirements. Normal hydrofoil or widefoil impellers work well under low and moderate gassing conditions, however, at high gassing rates the gas dispersion and solid suspending results are poor. For applications with high gassing rates, EKATO has developed the EKATO COMBIJET impeller which has a much higher ‘flooding limit’ compared to the aforementioned types of impellers.

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Figure 5: EKATO COMBIJET made of stainless steel in a BIOX® gold bioleaching application (left side) – EKATO COMBIJET made of duplex steel plus rubber lining for a copper ore leaching application (right side).

This allows the gassed leaching reactors to run with a lower specific motor power and reduce installed compressor power due to higher gas utilization. Figure 5 shows two examples. On the left the material of construction of the COMBIJET is stainless steel. It is used very successfully in a BIOX® bioleaching application for the pretreatment of sulfuric gold ore, also see (7). On the right the material of construction is duplex steel with an additional rubber lining for wear protection in a gassed copper ore leaching application. For both cases, the abrasion is minimal even after two years in operation and exceeds by far the expectations of the customers.

Hard Coatings

The EKATO WINGJET is a specially optimized axial pumping impeller that is mainly used for side-entry agitators in flue gas desulphurization units of fossil fuel-fired power stations; see Figure **6**, left side. The primary task of these impellers is to disperse air in very large absorber tanks to form gypsum. At the same time the agitator must keep the gypsum slurry in suspension.

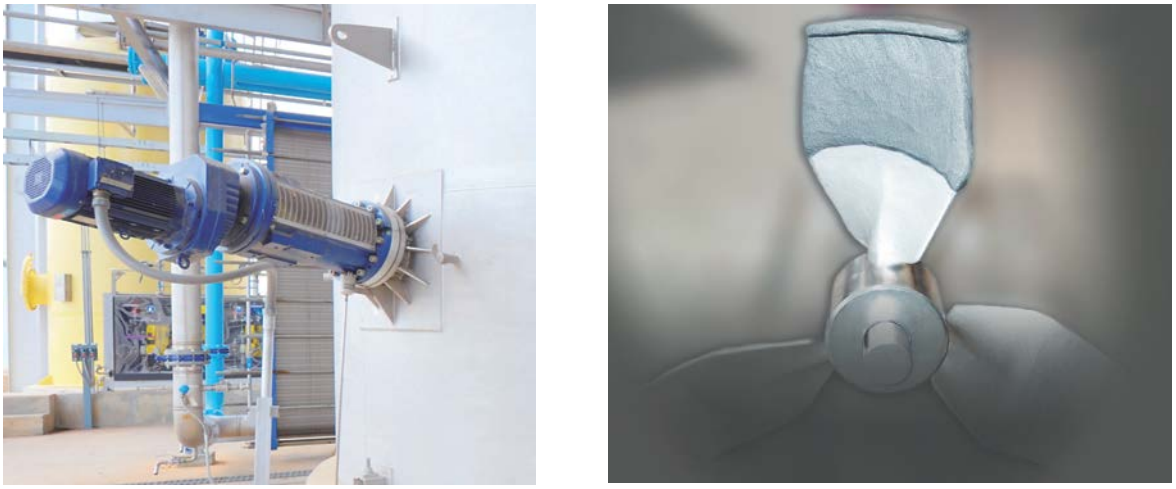


Figure 6: Side entry application (left side) with EKATO WINGJET (right side)

The impellers are made of cast steel, which is economic because standardized impeller diameters are used. The EKATO WINGJET can be rubber lined or coated with filled polymers in order to achieve a high resistance against the abrasive gypsum slurry. Filled polymer consists of a polymer matrix in which ceramic particles (filler) are embedded thus increasing the resistance against abrasion.

Figure 6, the picture on the right side shows the EKATO WINGJET with a SiC coating exemplarily. Other popular fillers are aluminium oxides such as corundum or Al_2O_3. Finally the particle size, the concentration of the ceramic particles and the polymer composition can be varied depending on the application.

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The EKATO WINGJET has a significantly higher pumping capacity compared to standard marine propellers at the same absorbed power. In return, the life-time is much higher as the abrasion is reduced because of the uniform power transmission over the blade length and the circumference due to the unique blade geometry. Additionally, the winglets suppress vortexing around the tips thus minimizing the wear rate even further.

AUTOCLAVE APPLICATIONS

Autoclaves are used for the hydrometallurgical processing of a broad range of ores such as gold, nickel, copper, aluminium, PGM's, uranium, molybdenum and zinc.

Typical operating temperatures range from ~140 up to 270°C in order to increase the chemical reaction rates. The environment is highly corrosive due to these elevated temperatures and shows highly acidic leaching conditions in most cases. All product wetted parts are typically made of titanium because titanium is characterized by a high corrosion resistance in combination with good strength properties and a low material density. Furthermore, impeller blades should undergo a surface treatment to improve the abrasion resistance. EKATO recommends reinforcing the blades with a titanium dioxide coating that is applied by flame spraying. However, good and reproducible results can only be achieved by highest manufacturing standards. EKATO has therefore a titanium welding clean room and over 15 in-house certified welders for titanium.

In general, there are gassed and ungassed autoclave applications. In POX (pressure oxidation) applications large amounts of pure oxygen are sparged from the bottom below of the impeller that has to be dispersed. A modified hydrofoil impeller, the EKATO EPAL, is used for moderate to no gassing. One such application is autoclaves for the leaching of nickel laterite ores.



Figure 7: EPOX (left side) and EPAL (right side) with titanium dioxide coating

Figure 7 shows an EKATO EPOX for POX applications (left) and the EKATO EPAL for moderate or no gassing such as high acid leach applications for nickel (right).

OPTIMIZED IMPELLER GEOMETRIES

The EKATO EPOX and the EKATO EPAL obtain superior life times compared to competitor installations because tip speeds are optimized case-specifically and material qualities exceed highest standards. In addition, even a second, improved generation of impellers have been developed - namely the EKATO EPOX-R and the EKATO EPAL-R.

EPAL-R

The life time of the standard EKATO EPAL impellers has already doubled (~ 1 year) compared to competitor installations.

Figure 8 left side, shows an EKATO EPAL impeller after one year in operation in a nickel leaching application. EKATO engineers analysed the abrasion patterns and an extensive lab test and CFD

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simulation program was carried out in order to understand the flow dynamic effects. The critical spots could be identified and were in good agreement with the field results, see Figure **8**, pictures on the right.

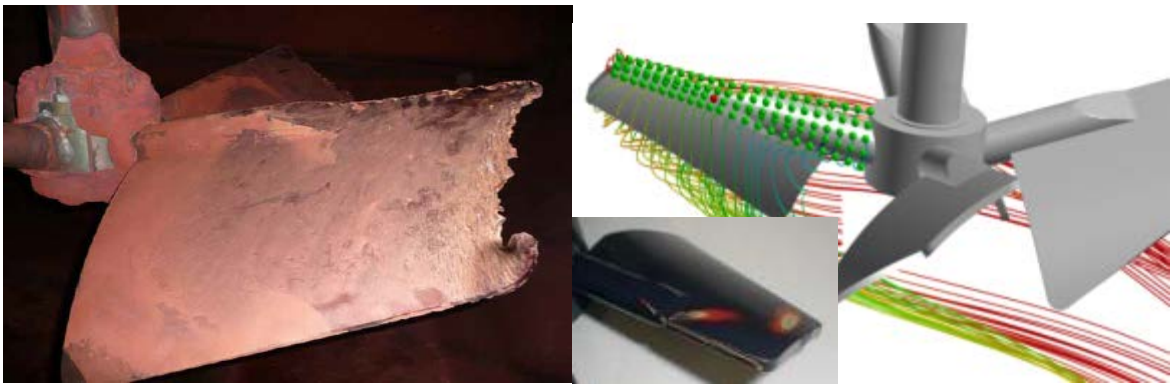


Figure 8: Example of a worn impeller in an HPAL application after one year in operation (left side), Lab test work (small picture in the middle) and analysis by means of Computational Fluid Dynamics (CFD) – picture on the right side.

The improved blade shape reduces vortexing and suppresses abrasion to a minimum. The EKATO EPAL-R has an expected life time of ~ 1.5 years in typical nickel laterite leach autoclave, based on first field test results in the large commercial production scale.



Figure 9: Improved impeller geometry EPAL-R

Figure 9 shows the improved EKATO EPAL-R. The titanium blades and the impeller spars are completely coated with titanium dioxide to avoid any transition zones.

EPOX-R

Pressure oxidation (POX) autoclaves count for the most demanding applications in minerals processing. Flat blade disc or Rushton turbines are used for the gas dispersion of pure oxygen to meet the high specific power requirements of up to 5 kW/ m^3. EKATO has successfully been using the EKATO EPOX impeller which is a modified flat blade disc turbine as the life time can already be doubled when compared to standard solutions. The next step was to improve these good results even further.

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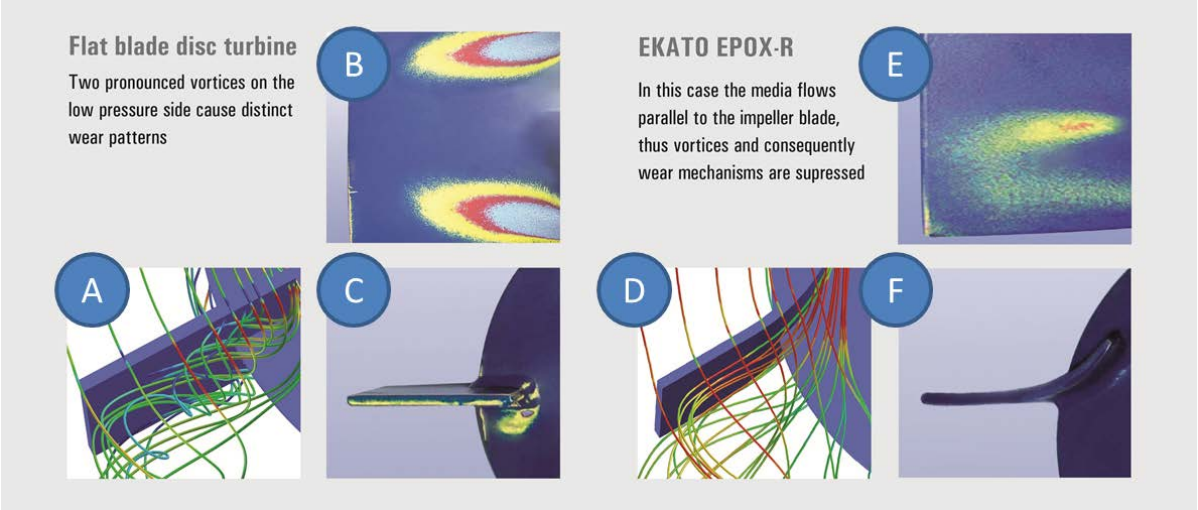


Figure 10: Standard flat blade disc turbine (left), improved impeller geometry EPOX-R (right)

Numerical simulation methods such as CFD (Computational Fluid Dynamics) can be used to investigate the flow around the impeller blades.

Figure 10, picture A shows the results of such a simulation. The flow around the standard flat blade disc turbine creates pronounced vortex shedding on the low pressure side of the impeller blade. In a media with solid particles this results in a continuous "sanding" of the blade surface by the particles which thus leads to abrasion as shown by lab test work with model sands, see
Figure 10, pictures B and C. At the same time, larger particles leave the vortex path due to their inertia and directly impact the impeller blade leading to additional wear. Wear issues at the carrier disc close to the blade holder must also be seen as critical. This was already discussed in the introduction of this article, compare with Figure 1.

The EKATO EPOX-R, as seen in
Figure 10, pictures D shows no such vortex shedding. It suppresses this wear mechanism without performance loss for the gas dispersion mixing task, as described by Keller[3]. Validation experiments using a paint layer technique in laboratory scale confirm the improved wear reduction provided by the EKATO EPOX-R, see pictures E and F. Especially the carrier disc and blade holder are no longer subject of abrasion.

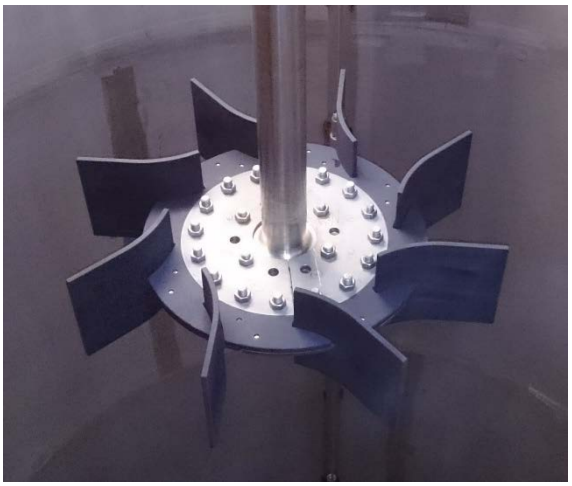


Figure 11: Commercial scale EPOX-R with titanium dioxide coating

Figure 11, shows a commercial scale EKATO EPOX-R impeller with titanium dioxide coating in the 100 m³ test pit for hydraulic testing before delivery.

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NEW MATERIALS – CERAMICS IN MIXING APPLICATIONS

Recently EKATO has launched a new product, the EKATO Ceramic Mizer Disc[4]. The innovative step of this product is that the disc itself is made of a solid ceramics piece, see Figure 12.

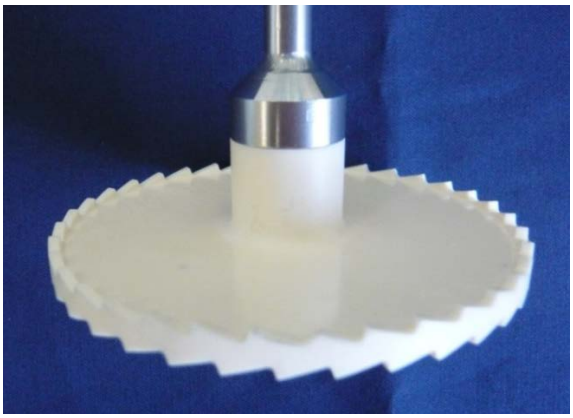


Figure 12: EKATO mizer with ceramic disc

The life time of such discs that run at very high tip speeds is increased dramatically by a factor of 10 – 15 times compared to discs made of duplex steels. A further advantage is that metallic abrasion in the product is often undesired and it can be completely avoided by using ceramics in chemical applications.

It is a common belief that solid ceramics have very poor mechanical strength and should therefore not be applicable in mechanical design of agitators. However, technical ceramics can even exceed the mechanical strength of steel. Generally speaking, ceramics are characterized by:

- Long life time due to hardness and corrosion resistance
- Constant materials properties over 500 °C for extreme operating conditions
- Manufacturing and processing know-how enable the production of complex geometries

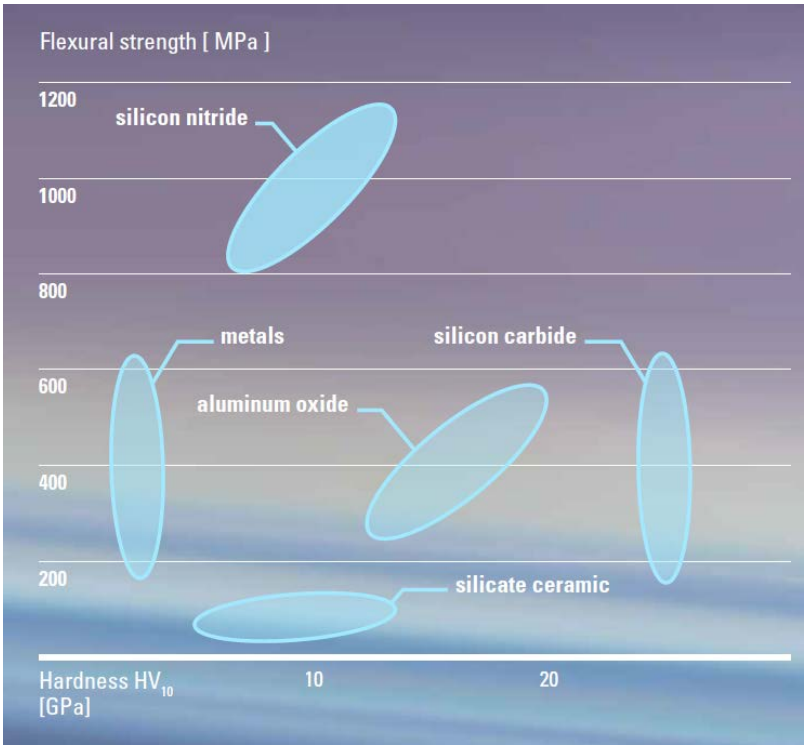


Figure 13: Comparison of mechanical properties of different ceramic materials with metals

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Figure 13 shows different types of ceramics, such as silicon nitride, silicon carbide, aluminium oxide and silicate ceramics compared to metallic materials regarding flexural strength and hardness. Silicon nitride e.g. is not only harder than metallic materials but also provides a significantly higher flexural strength. More details on ceramics can be found in (5) and (6).

However, the mechanical design rules for ceramics are different compared to metals. The following must be considered carefully:

- Generally speaking, ceramics are brittle and therefore the shape and contour of ceramic parts must meet certain ceramic-specific design standards.
- Furthermore the manufacturing process must meet high quality standards to avoid any defects such as lunkers or cracks.
- Special attention must also be paid to the mechanical connection between ceramic and metallic parts.

Test Work

Abrasion tests were carried out in a 1 m³ autoclave vessel to measure the wear rate of impeller blades of an EKATO EPOX. In Figure 14, the left picture shows the test set-up. Different materials of construction were used as blade material such as titanium, titanium with TiO_2 coating, stainless steel and ceramic material. The test work was carried out under atmospheric conditions and ambient temperature. The vessel was equipped with a water cooled jacket in order to avoid overheating during endurance trials. The volume specific power input was ~ 7.5 kW /m³ and the tip speed was > 5 m/s to obtain and even exceed the requirements in a POX autoclave. The mass loss of the impeller blades was measured over time, see Figure 14 picture on the right side. A 35 wt.-% abrasive quartz sand suspension was used for this comparative test work. Pure titanium and stainless steel show the highest and nearly similar wear rates. The titanium dioxide coating helps to reduce the wear rate by a factor of five! By far the best results showed the impeller blades made of ceramics. The wear rate is at least a factor 10 lower compared to titanium blades that are TiO_2 coated.

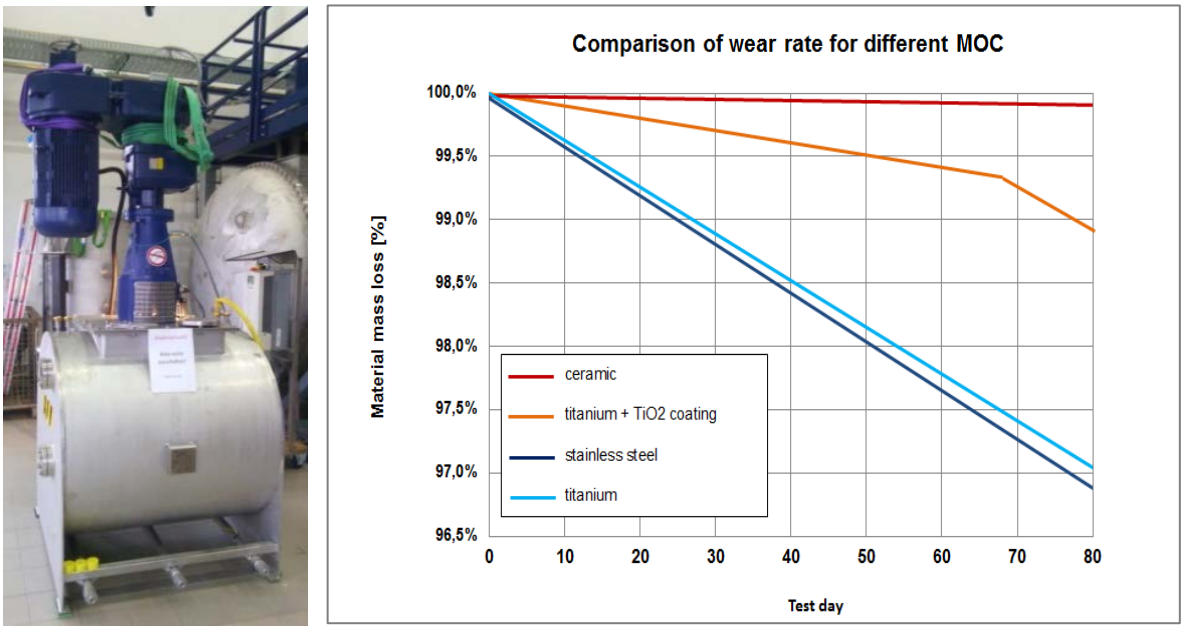


Figure 14: 1 m³ abrasion test scale (left), measured curves of material loss for different MOCs

Next hydraulic and abrasion tests were performed in a large pilot scale of 7 m³ (one compartment). The test impeller, see Figure 15, had a diameter of 1,100 mm.

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Figure 15: Pilot tests with EKATO EPOX-C impeller with a diameter of 1,100 mm (left side) – hydraulic and abrasion test work (right side)

The tests were carried out under atmospheric conditions with abrasive sands. Finally, a large quantity of gravel (particle diameters of 10 mm) was added to the autoclave compartment in order to verify if the ceramic would survive the impact of such accidental operation conditions. The micro-analytic analysis by the material supplier showed that the ceramic withstands such very extreme conditions as no micro-cracks or other material damages could be detected.

CONCLUSIONS

Abrasion and corrosion are common phenomenon in minerals processing applications. An optimized process design and the correct choice of material are of utmost importance to prevent the wear and corrosion of impeller blades. Modern blade geometries help to further decrease the wear rate and are an integral part of EKATO's development strategy.

The correct choice of material of construction is important for the CAPEX and OPEX of agitator equipment. Very common in Minerals Processing is the use of carbon steel with rubber lining as material and maintenance costs are comparably low. Duplex steels are used in more specific applications, e.g. in atmospheric leaching reactors. The EKATO COMBIJET impeller is a good example how to combine excellent gas dispersion with very low abrasion for atmospheric gassed applications.

For pressure applications, such as POX and HPAL, titanium in combination with TiO_2 coatings provide the best results compared to all other solutions on the market. Having said this, ceramics have the potential to boost the life time of impeller blades. The life time of the EKATO EPOX-C (patent pending) is up to 10 – 20 times higher compared to the state-of-the-art technology. Ceramics will definitely help increase life time and dramatically bring down maintenance costs. Ceramics could also hold the key to realize applications for which there previously was no agitator solution available.

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OPERATING EXPERIENCE AND DEVELOPMENTS OF G-REX AND AURIX100 RESIN EXCHANGE TECHNOLOGY

By

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ABSTRACT

Gekko Systems developed the Gekko Resin Exchange Column (G-REX) in order to optimise the recovery of gold in complex leach-to-electrowinning processes, as an intermediate step using a highly gold-selective resin to isolate contaminant metals. The AuRIX®100 resin produced by Purolite is licensed exclusively to Gekko, with the G-REX column designed specifically for this resin (Lewis-Gray et al, 2015). Operational experience has been gained at the CGT Ballarat Gold Plant in near continuous operation since 2008, treating unclarified concentrate leach solution. The extension of the technology to higher throughputs and more complex chemistry is discussed.

Keywords: Resin, gold, AuRIX, ILR, column, absorption, stripping, gravity, flotation, concentrate, carbon,

Gekko Resin Exchange Column (G-REX)

Development

- In late 1990's Gekko developed the Inline Leach Reactor (ILR) to leach gravity concentrates produced from the Inline Pressure Jig (IPJ) and/or Batch Centrifugal Concentrators
- Around the same time AuRIX®100 was developed which led Gekko to develop the resin exchange column suitable for lower grade or high impurity concentrates which did not respond well to direct electrowinning
- G-REX is a multi-staged counter current, pulsed, resin ion exchange contactor

Gekko Resin Exchange Column (G-REX)

First Installation at Bong Mieu – Vietnam in 2005



Gekko Resin Exchange Column (G-REX)

Development – G-REX 2700 Model

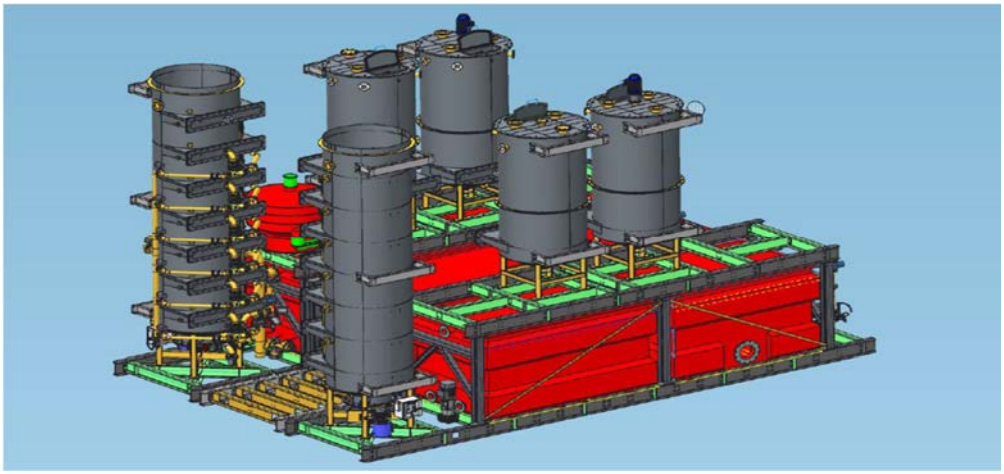
- Installed in 2008 at Ballarat Goldfields project (now Castlemaine Goldfields – Lion Gold Corp)



Gekko Resin Exchange Column (G-REX)

Development – G-REX 13000 Model

- To be installed in 2016 at Hope Bay – TMAC Resources



Gekko Resin Exchange Column (G-REX)

Model Specifications

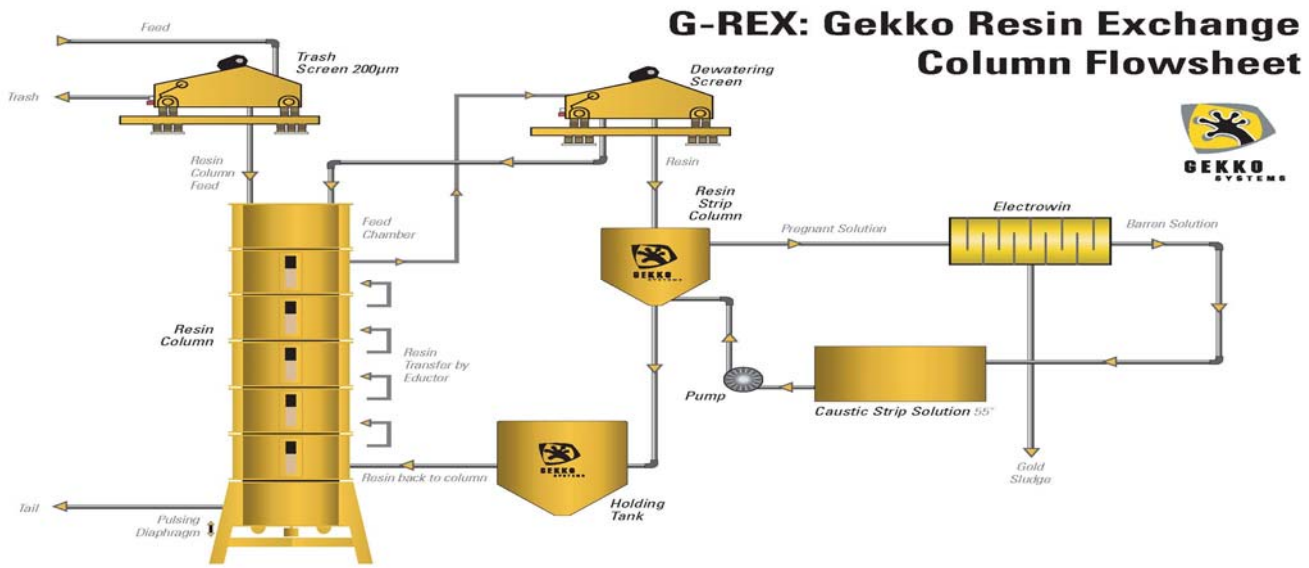
G-REX model	units	2700	13000
Column Height	m	4.2	7.2
Column Width	m	0.9	1.5
Stage Height	m	0.6	0.9
Number of Stages		5	6
Column volume	m^3	2.7	12.7
Volume of resin/stage	m^3	0.19	0.8
Total resin volume	m^3	0.95	4.8
Solution direction		**Down**	**Up**
Maximum feed flow	m^3/h	13	36
Maximum feed velocity	m/h	20.4	20.4

Gekko Resin Exchange Column (G-REX)

Operation

- Dirty solution flowing through multiple, pulsed beds of resin. Up to 2% solids at -200µm
- Resin periodically moved one stage at a time – counter current via eductors using barren solution for motive water
- Loaded resin is educted from the first contacting stage to dedicated strip vessel
- Heated caustic solution circulates from the strip vessel and an electrowinning cell.

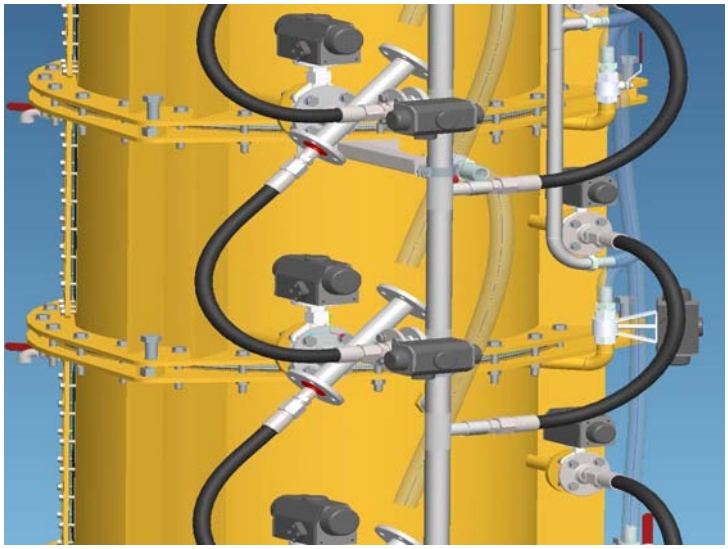
Gekko Resin Exchange Column (G-REX)



Gekko Resin Exchange Column (G-REX)

Resin Transfer

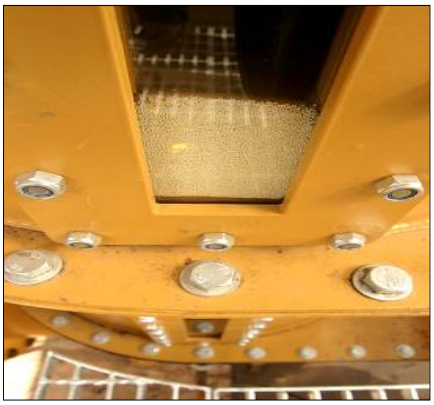
- Central pressurised barren solution pipe
- Resin eductors to move resin between stages
- Chamber mixing to assist resin transfer
- Air bleeds
- Sample points for each stage

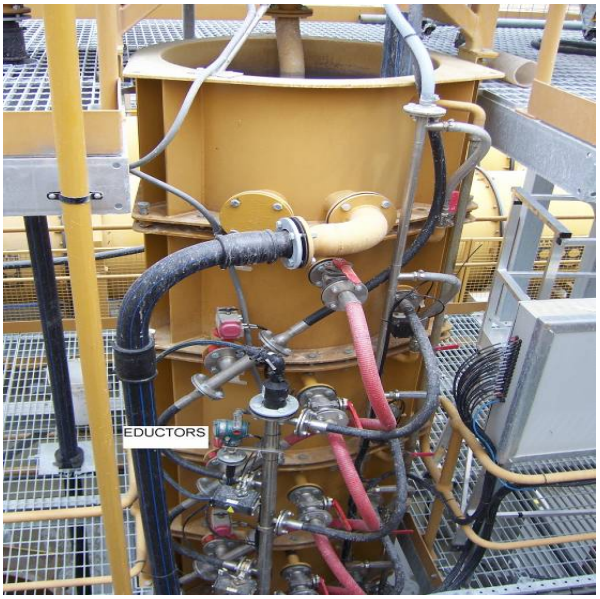


Gekko Resin Exchange Column (G-REX)

Resin Transfer

- Resin bed indicators

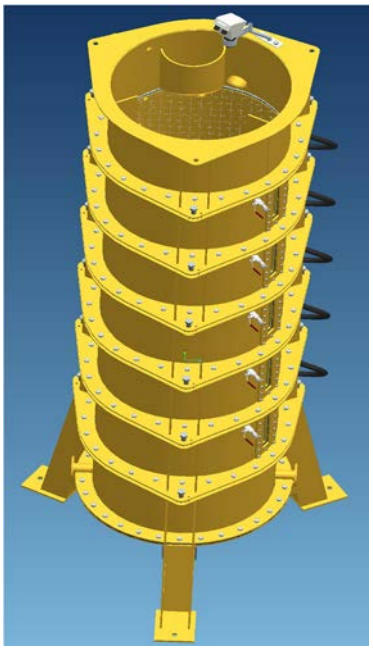




Gekko Resin Exchange Column (G-REX)

Interstage Screens

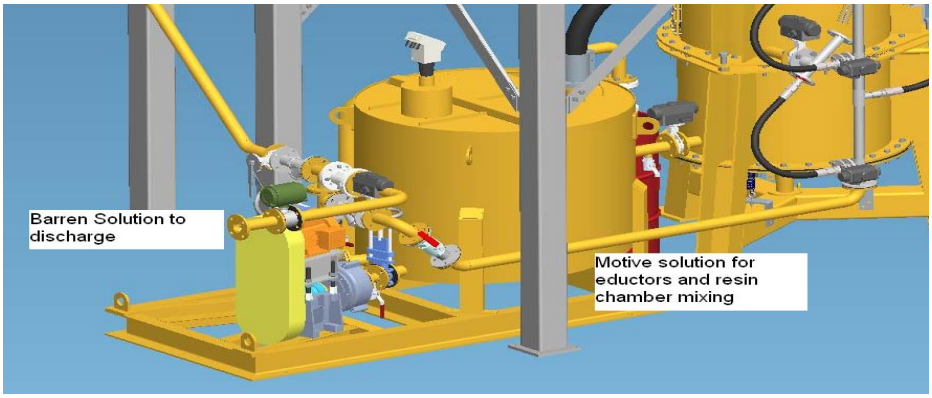
- Polyester 400 µm woven mesh
- Supported on a powder-coated 20 x 50 mm mild steel mesh
- EPDM molded seal around circumference
- Screen removal facilitated via 3 jacking bolts
- Screens can be removed from two directions



Gekko Resin Exchange Column (G-REX)

Dual function Barren Solution Pump

- Barren solution sump control and eductor motive solution pressure control
- Fixed pump speed and variable pinch valve position controls level and motive pressure at approximately 300 kPa



G-REX In Modern Process Plant Design

Adaptability

- Complex chemistries
- Gravity or Flotation concentrates
- Potential to utilize resin selectivity for concentrates with higher copper content (through pH control)
- Alternative resins based on different chemistries or lixiviants

Modularity

- Vertical aspect and relatively low footprint
- Expandable for higher solution flows

AuRIX®100 RESIN



Cross-Linked Polystyrene Alkaline Resin

Spherical beads +600µm in size

Highly selective absorption of precious metals based on pH

$$Au > Ag > Hg > Zn > Ni > Cu > Co > Fe$$

Alternative to Carbon-In-Solution (CIS)

Advantages

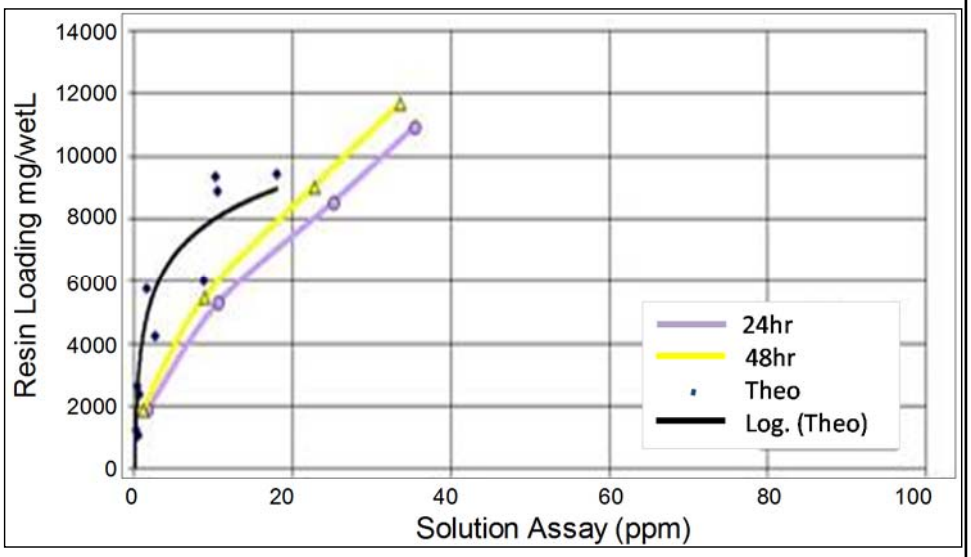
- Not susceptible to fouling
  - Inorganic salts, organics, blanking agents (kerosene)
- Simple stripping cycle
  - Minimal osmotic shock → pH remains alkali
  - Strip Solution → 35 g/L NaOH, 200ppm NaCN, 72 g/L $NaC_7H_5O_2$ @ 55-60 ˚C
  - Ambient acid wash every 6 cycles to remove calcium scale build up
- Reduced capital and operating cost
  - 4% – 12% capital cost savings
  - 27% - 40% operating cost savings

Alternative to Carbon-In-Solution (CIS)

Advantages

- High gold loading / fast kinetics at medium solution grades

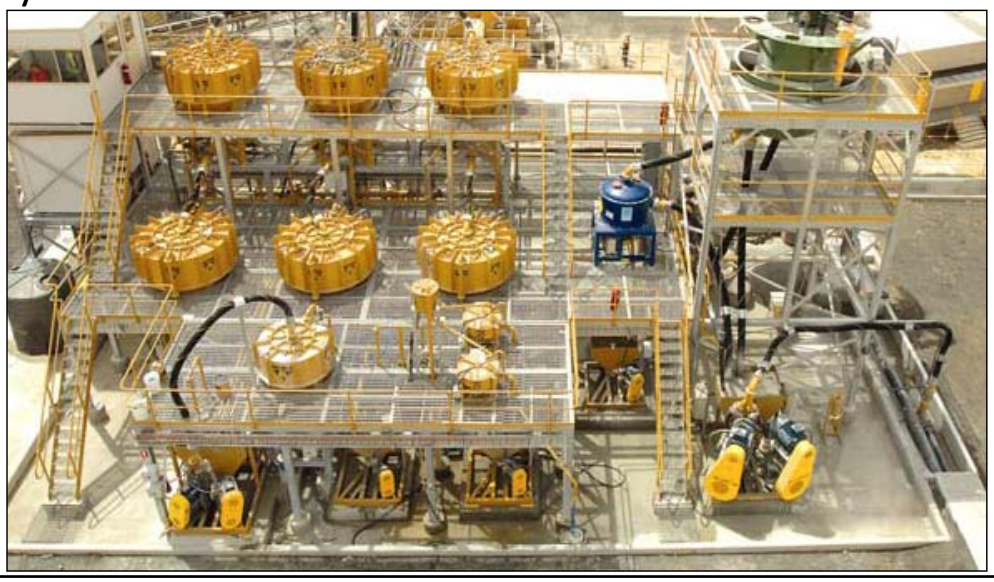
Ideal for low to medium grade gravity and/or flotation concentrates due to short cycle times and small resin inventory required



G-REX Operation at CGT

Flowsheet

- Gravity Circuit – Series of Gekko IPJs and ISPs



G-REX Operation at CGT

Flowsheet

- Two parallel continuous ILR5000s, Resin Column, Electrowinning



- Recently installed a flotation circuit on the gravity tails

G-REX Operation at CGT

G-REX Plant Detail – June 2014 to January 2015

- Feed is “dirty” thickener overflow – up to 2% solids -200µm
- 500 Strips per year – although capacity for double based on future requirements
- Top-up of resin is about 300 litres / year (due to wear)
- Worn Resin <500 µm is recovered and sent to the gold room
- Absorption efficiency ranged between 95.8% and 98.5%

G-REX Operation at CGT

G-REX Plant Detail – June 2014 to January 2015

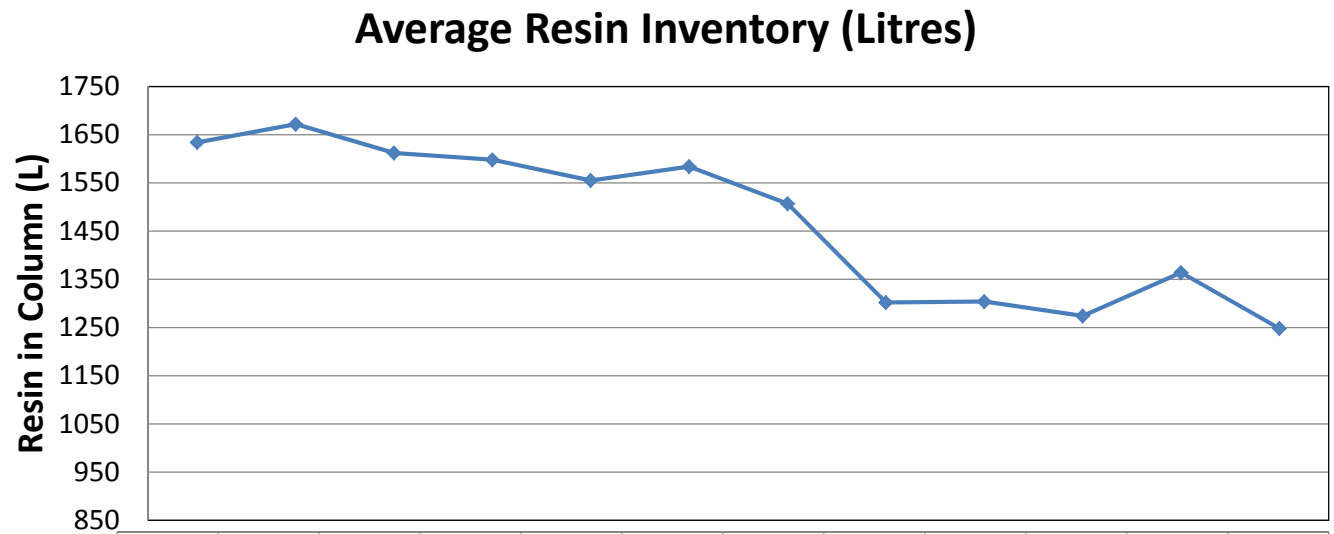
- Flowrate maintained at 9 m^3/hr to match EW operation
- Stripping solution volume is 3,500 L
- Fresh stripping solution prepared every 60 resin strips
- NaOH maintained at >35 g/L, NaCN maintained at 200 ppm
- Sodium Benzoate is added at 100kg/week

G-REX Operation at CGT

G-REX Plant Detail – June 2014 to January 2015

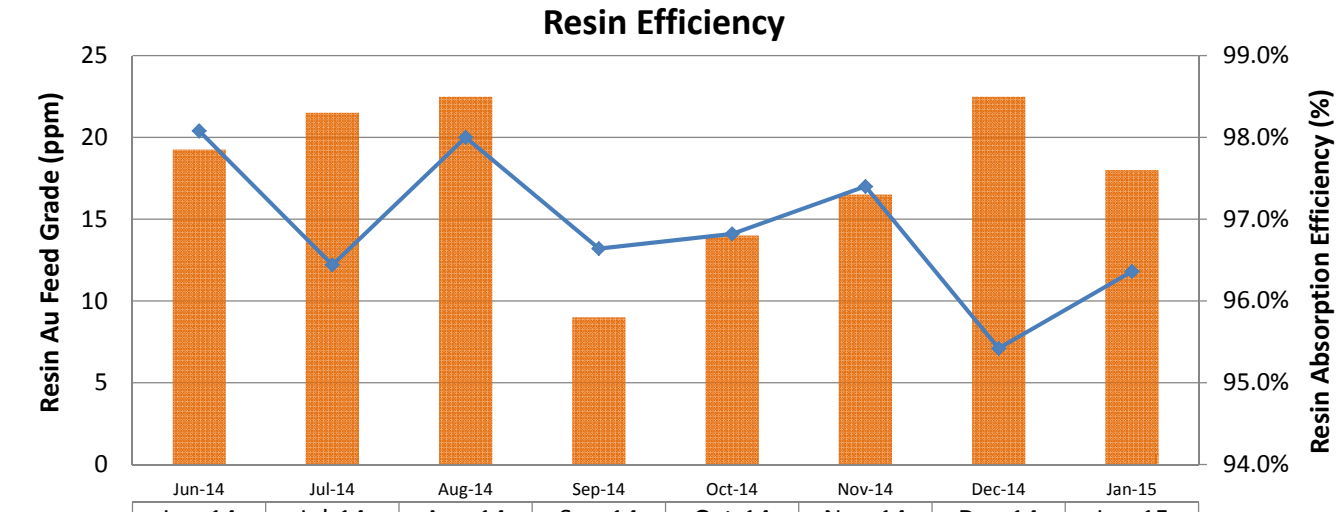
- Acid wash of resin every 6 cycles (300 hrs)
- The 6 interstage cloths are replaced once per month
- In 2015 CGT installed a flotation circuit to scavenge fine gold in gravity tails after changes in their ore.
- Flotation concentrate is mixed with gravity concentrate and has had no adverse impact on the resin circuit performance

G-REX Operation at CGT



	Feb-14	Mar-14	Apr-14	May-14	Jun-14	Jul-14	Aug-14	Sep-14	Oct-14	Nov-14	Dec-14	Jan-15
Resin	1634	1672	1612	1598	1555	1584	1507	1302	1304	1274	1364	1248

G-REX Operation at CGT

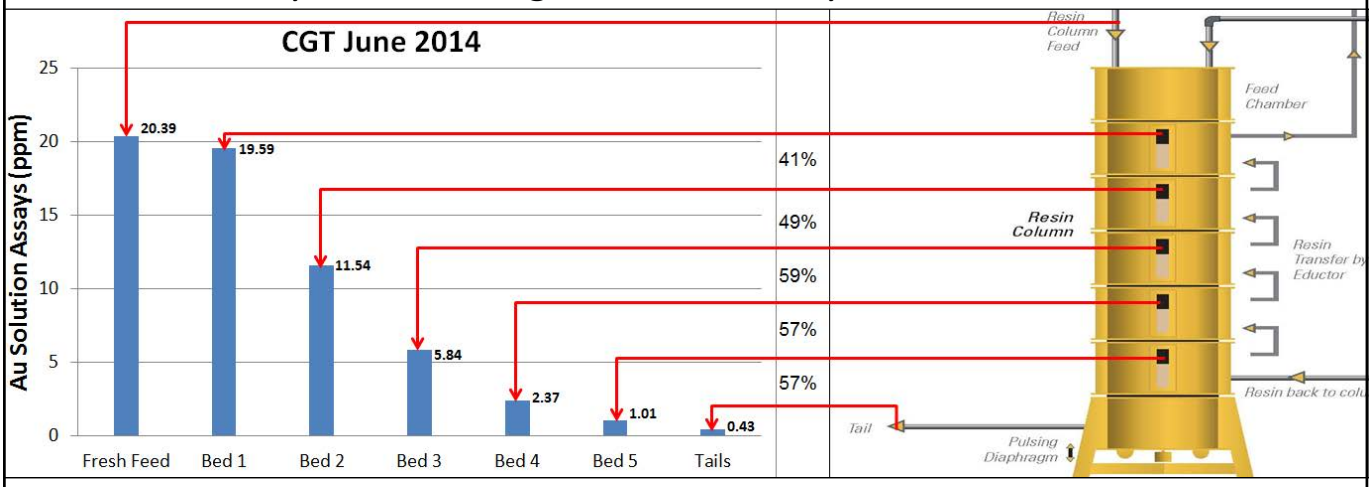


	Jun-14	Jul-14	Aug-14	Sep-14	Oct-14	Nov-14	Dec-14	Jan-15
Eff. (%)	97.8%	98.3%	98.5%	95.8%	96.8%	97.3%	98.5%	97.6%
Feed Grade	20.4	12.2	20	13.2	14.1	17	7.1	11.8

G-REX Operation at CGT

A closer look at the month of June 2014

- Bed Recovery Profile – Single Pass Efficiency



G-REX Optimization at CGT

Optimization Projects

- Strip time reduction vs. gold loading
  - Identify whether the trade-off in gold loading can be exceeded by additional strips for overall greater gold values
  - The data showed stopping the transfer to EW when solution grades dropped to 2.5 ppm Au provided an additional strip every 2 weeks
- Double bed stripping trials
  - Introduce 2 fresh beds into the column
  - Alternative was reducing feed rate to leach circuit

G-REX In Modern Process Plant Design

G-REX vs. CIS

- G-REX works at atmospheric conditions, no high temperatures or pressures, no thermal regeneration kilns
- Based on long term operating data from CGT the G-REX system operating cost is ~50% of conventional CIS plant.

Operating Cost	Activated Carbon	G-REX
AUD/month	13,200	6,800
AUD/year	158,400	81,600

Basis: 80,000oz Au/y, 600,000tpa, 5% mass to concentrate, 40g/t Carbon consumption.

Summary

- G-REX is a proven technology with reduced operating costs
- Small footprint
- G-REX has a simple stripping process
- Modularity lends itself to rapid installations, commissioning and/or expansions

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SELECTIVE REMOVAL OF MERCURY FROM GOLD MINING

By

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ABSTRACT

Selective separations of metals and ions in mineral extraction and refining are becoming more challenging as ore bodies become more complex and environmental pressures increase. Johnson Matthey is addressing a number of these separations using a set of proprietary advanced ion exchange technologies. Already a recognised leader in precious metal recovery, the acquisition of Purity Systems Inc has extended capabilities into other key separations.

This paper will discuss the implementation of the JM HgFree selective mercury removal process, which is designed to electively remove co-leached mercury from heap leached gold ores from either the heap PLS or EW preg without affecting gold or silver recovery rates. The processes utilises a highly selective adsorption-desorption step in which mercury is recovered on an adsorbent and then desorbed to form a precipitated, safe-to-handle salt. The HgFree adsorbent is recycled in situ and is reused multiple times. The process is compatible with existing gold processing conditions and practises. The process offers significant environmental and sustainability benefits including reductions the need to retort mercury, and a subsequent reduction in mercury air emissions. Pilot operation of the HgFree process at two operating mines will be discussed and analysed.

Keywords: Gold, selective mercury adsorption, mercury elution, Mining

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INTRODUCTION

Many gold ore bodies contain high concentrations of mercury which when extracted with cyanide, co-extract with the gold and other metals. This mercury is carried through the process with the gold, posing environmental and technical issues when it is separated from the doré. This paper details and describes the selective adsorption of mercury from the gold recovery circuit while it is in a soluble form, leaving gold to be processed as normal. This selective and quantitative removal of mercury from the circuit, before the mercury is converted from the ionic solution to free metal, eliminates mercury from the doré retorting process and so reduces the potential worker exposure and environmental impact of fugitive emissions of elemental mercury.

The JM process for mercury removal is based on the quantitative adsorption of mercury on a solid phase thiol-based resin or silica composite. The resins and silicas developed by JM have the capacity to reduce the mercury concentrations in both HL and EWP solutions to undetectable levels (by ICP-OES) whilst having no measurable effect on the gold concentration. The control of selectivity and quantitative removal of mercury ensures that no precious metal value is lost in the mercury removal process. The process has been shown to be applicable to both batch and continuous operation, allowing the process to be applied to a variety of flow rates and applications.

Development of the selective adsorption process has extended the technology to include mercury desorption, producing a stable and insoluble mercury salt. Desorption takes place at high pH, and is compatible with cyanide gold extraction flow-sheets. Mercury is retained in the ionic form throughout, never being present as the free metal. The adsorption medium is regenerated during desorption and can be recycled multiple times.

GOLD EXTRACTION TECHNOLOGY

In modern gold mining processes, typically it is necessary to extract gold from complex ores which comprise gold in addition to other metals, including mercury. A common technique for extracting gold from its ores is the cyanide process, where leaching of gold is achieved by the addition of cyanide at alkaline pH following the Elsner equation (Equation 1). Cyanide is a strong extractant for gold, and so leaches the gold out of the ore into solution[1]. The gold is typically present in the leaching solution as a gold cyanide complex.

Equation 1: Elsner equation for dissolution of gold in cyanide[2].

$$\mathbf{4Au + 8CN^- + O_2 + 2H_2O \rightarrow 4[Au(CN)_2]^- + 4OH^-}$$

The cyanide ion is an also a strong extractant for mercury which is also leached into the solution. The mercury may be present in the leach solution as a variety of complex anions with the general formula $[Hg(CN)_{2+x}]^{-x}$ (where x is 0, 1, or 2) but typically it is present as $[Hg(CN)_4]^{-2}$. The removal of mercury from mining waters is very important on health and safety grounds and environmental grounds; mercury volatilisation during extraction processes can be a threat to the health of plant workers, and the presence of mercury in waste waters from mining is a significant environmental concern. Environmental legislation limits the concentration of mercury permitted in waste waters to very low levels in many countries.

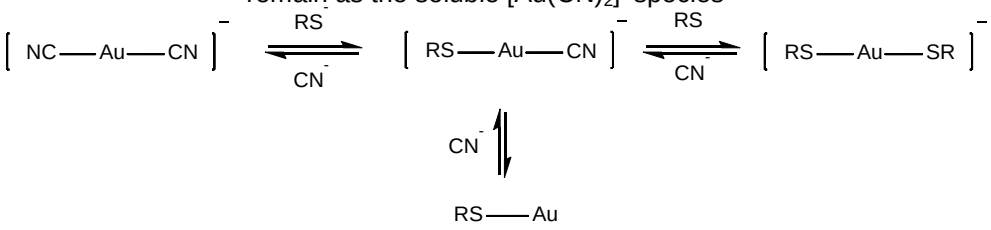
Different methods have been employed for mercury removal, all of which have issues with the long term stability of the mercury compounds produced. Miller *et al*[3] reviewed mercury removal technologies; precipitation with inorganic sulfides or sulfur-based organic compounds; adsorption with activated carbon or crumb rubber; solvent extraction by alkyl phosphorus esters or thiol extractants; ion exchange with isothiouronium groups or polystyrene-supported phosphinic acid; electrochemical cementation. Dithiocarbamates[4] form stable mercury precipitates, particularly in the presence of colloidal hydroxides to aid coagulation[5]. Hutchison and Atwood further reviewed mercury remediation, citing dimethyldithiocarbamate as an effective precipitation reagent. The long term stability has been questioned as mercury leaching and degradation into toxic by-products has been observed over time[6]. Alkyl thiols such as 1,3-benzenediamidoethanethiol can also be used to precipitate mercury[7].

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EXPERIMENTAL

Johnson Matthey Advanced Ion Exchange (JMAIX) produces functionalised fibres, silicas and resins for the selective adsorption of metals under the brands Smopex®, QuadraPure® and QuadraSil®. The starting point for the development of the HgFree process was the recognition that two particular materials, Smopex 112 and QuadraSil-MP, were effective in the adsorption of mercury from model solutions. Both of the materials have functionality based on alkyl thiol which is known to adsorb both mercury and gold in other processes. The equilibrium between thiol and cyanide ligation in gold and mercury is shown in equation 2. This equation shows that, under the right circumstances, a material could be developed that could generate selectivity to the adsorption of mercury in the presence of gold.

Equation 2: Equilibrium of gold cyanide to gold thiolate. Addition of cyanide ions causes the gold to remain as the soluble $[Au(CN)_2]^-$ species[8]



ADSORPTION KINETICS

A set of simple adsorption kinetic tests were carried out using QuadraSil®-MP and Smopex®-11: the results are shown graphically in figure 3. The test was arranged such that a flask containing gold and mercury cyanides (100ml, pH 12, Au 4ppm, Hg 1ppm) was stirred with a charge of 2g of QuadraSil or Smopex adsorbent. Samples were taken at 1,5,15, 30 and 60 minutes and the liquid analysed for Au and Hg. In both cases the initial mercury concentration of 1 ppm fell to <0.01 ppm (instrument detection limit) within 5 minutes. However for both adsorbents gold was also adsorbed in addition to the mercury. Further kinetic measurement was carried out with the same methodology using the QuadraSil adsorbent, but with the addition of an aliquot of cyanide (equivalent to 100ppm CN) added at 30 minutes. The results are shown graphically in figure 4 where the full lines/symbols show the concentration for the standard adsorption without cyanide addition; the dashed line/open symbols show the solution concentration with cyanide addition. In this test gold was at first adsorbed, but on addition of CN the adsorbed gold was rapidly and almost quantitatively desorbed back into solution. No mercury was detected in the liquid 30 minutes after adding cyanide, confirming that the insoluble mercury thiolate is strongly favoured over the soluble mercury cyanide species.

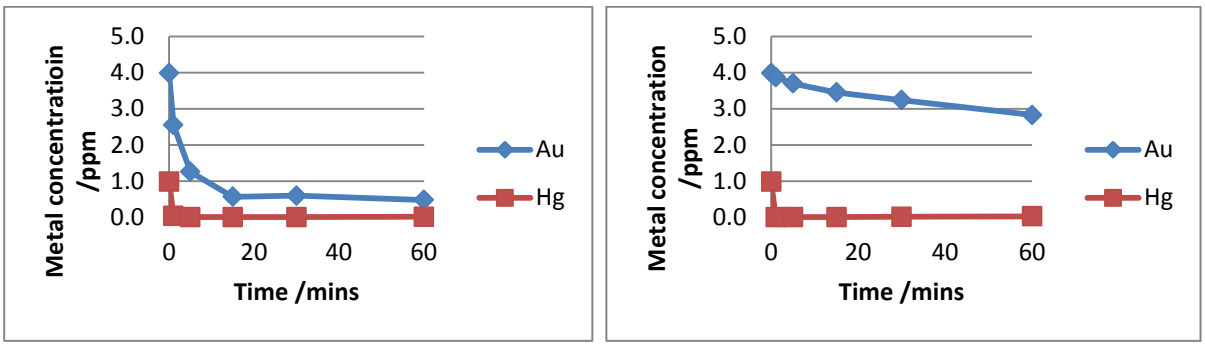


Figure 1: Adsorption kinetics of gold (4 ppm) and mercury (1 ppm) cyanides at pH 12 using QuadraSil®-MP (left); Smopex-112 (right).

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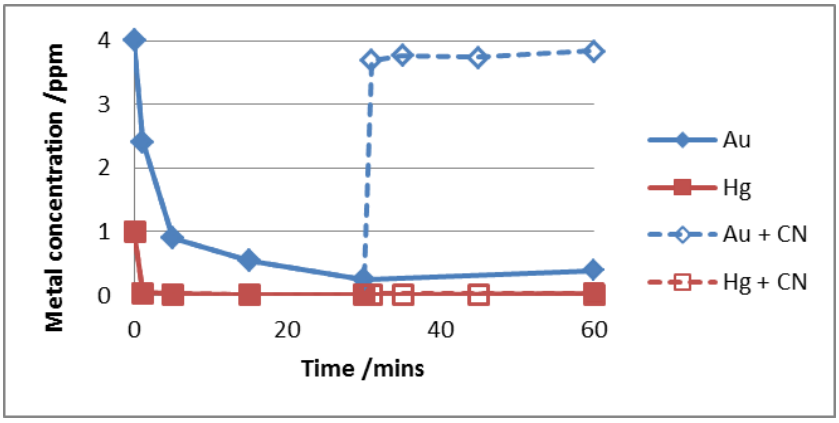


Figure 2: Adsorption kinetics of gold (4 ppm) and mercury (1 ppm) cyanides at pH 12 using QuadraSil®-MP. After 30 minutes an aliquot of sodium cyanide is added, equivalent to 100 ppm.

The addition of CN is key to selectivity, and further development showed that at a ratio of >4:1 [CN] to [Au]+[Hg] the selectivity to mercury over gold was maximised. At CN concentrations below this ratio, gold adsorption was always observed at a ratio that reflected the molar lack of CN. At a ratio of higher than 4:1, gold was never adsorbed, regardless of the gold and mercury concentrations. This data has been used in the drafting of a patent application[9].

COLUMN ADSORPTION TRIALS

Due to the scale of liquid flow at a gold mine the mercury removal process must run continuously, and operation in columns are preferred. Column trials were run with a model solution containing gold (5 ppm) and mercury (5 ppm) at pH 10 with no added cyanide. Figure 3 shows the results of this test: the outlet mercury concentration was below the instrument detection limit (0.01 ppm) during the entire test period; gold was initially adsorbed but then partially displaced by competitive adsorption of mercury as indicated by the outlet concentration going above the inlet concentration ($[M]/[M]_0 > 1$). Figure 4 shows the effect of adding 100 ppm cyanide to the test solution: gold was now not adsorbed by the material whilst mercury adsorption was maintained with the outlet mercury concentration being below the detection limit of the analysis (0.01 ppm).

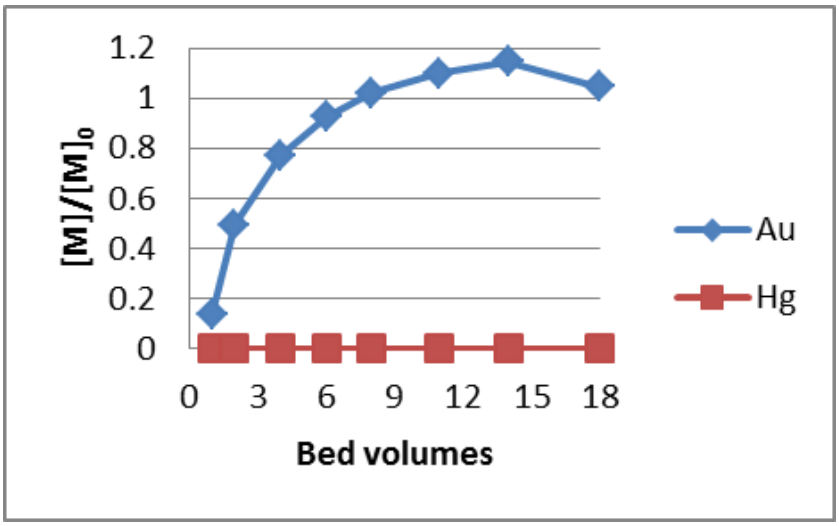


Figure 3: Flow test of adsorption of gold (5 ppm) and mercury (5 ppm) by QuadraSil®-MP at a flow rate of 6 BV/hour.

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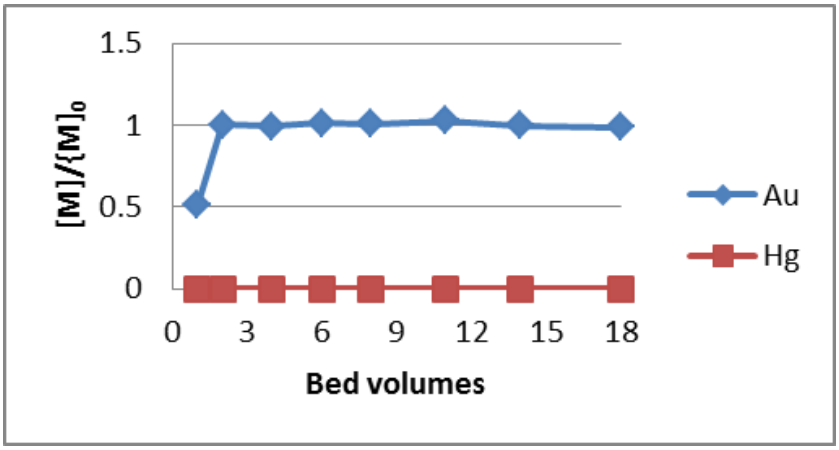


Figure 4: Flow test of adsorption of gold (5 ppm), mercury (5 ppm) and cyanide (100 ppm) by QuadraSil®-MP at a flow rate of 6 BV/hour.

The material used for the test illustrated in Figure 3 was treated by washing with an increasing concentration of cyanide solution at pH 10; the results are shown in Figure 5. Initially, when washed with dilute sodium hydroxide the gold concentration in the eluent rapidly decreases as the load solution is rinsed from the packed bed (BV 1 to 6); when 100 ppm cyanide is added to the wash solution (BV 7 to 12) gold was desorbed from the resin and eluted as soluble gold cyanide. The mercury was retained by the solid even when the cyanide concentration was increased to 1,000 ppm. This result provides evidence that the equilibrium of the gold-thiolate interaction which can easily be perturbed by introducing free cyanide, while the mercury-thiolate interaction is stable under conditions of excess cyanide.

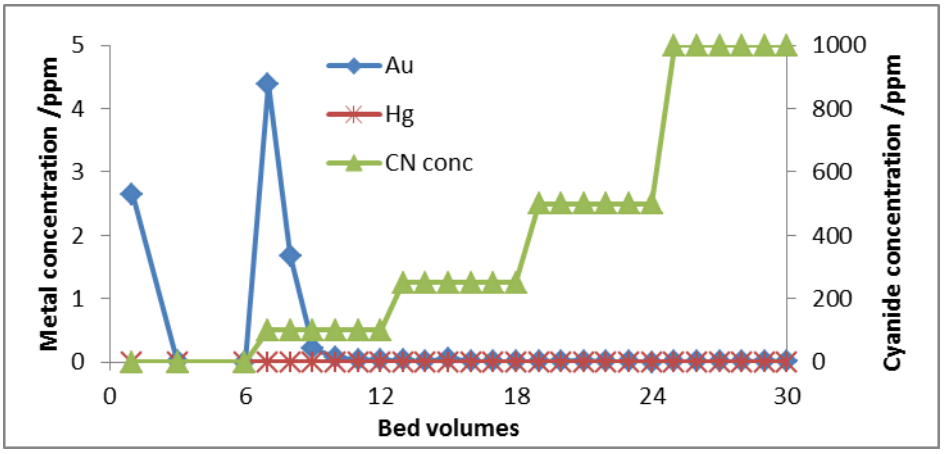


Figure 5: CN treatment of loaded resin from Figure 3.

REAL STREAM ADSORPTION

Due to the complexity of the real solution streams the batch adsorption was repeated using a real sample of heap leach pregnant solution sourced from a Nevada gold mine, containing both gold (1.22 ppm) and mercury (0.31 ppm) at pH 10.0. The solution was tested both as received and with cyanide added at 100 ppm in order to assess whether the addition of cyanide would improve the selectivity of adsorption in a real feed. In the absence of added cyanide, 7% of the gold was adsorbed from solution. When 100pm cyanide was added there was no detectable adsorption of gold adsorbed from solution. In both cases, the QuadraSil adsorbent quantitatively adsorbed the mercury to <10ppb.

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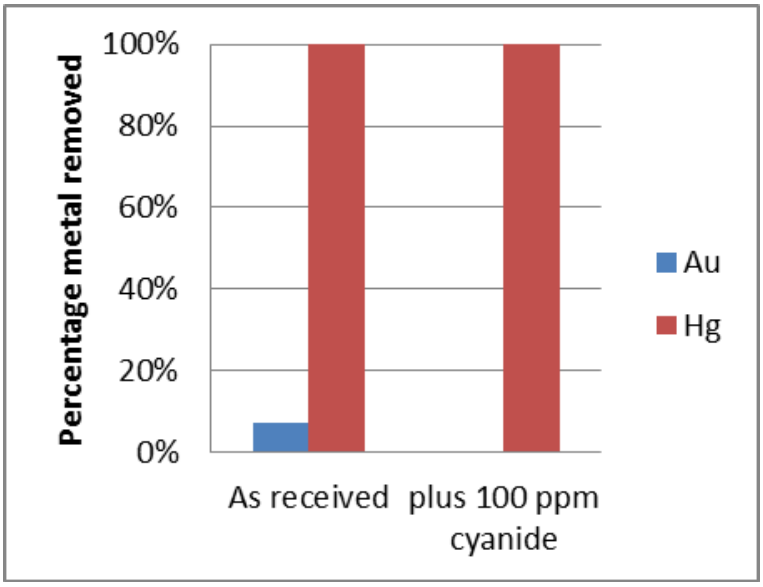


Figure 6: Batch adsorption from real feed (heap leach pregnant solution) containing 1.22 ppm gold and 0.31 ppm mercury at pH 10.0 using QuadraSil®-MP (left); Smopex-112 (right).

CASE STUDIES: PILOT SCALE ADSORPTION

Two case studies of selective adsorption of mercury in the presence of gold are briefly described below. Selective mercury adsorption has been demonstrated at pilot plant scale operation of the HgFree process in two places in the cyanide leach circuit: heap leach pregnant solution, taken directly from the pad, and electrowinning pregnant solution taken directly from the carbon column during the strip cycle. The applications operate under very different conditions – the heap leach pregnant solution contains <200ppb mercury and ~1ppm gold, has a consistent composition, is at ambient temperature from the pad (often as low as 5-10°C). The EW pregnant solution contains up to 200ppm mercury and 40ppm gold, varies in composition of both mercury and gold by a factor of 100, and can have a temperature of up to 85°C.

A number of thiol based adsorbents have been developed and optimised for the different conditions encountered in the heap leach and EW strip. The material developed for the cold, low concentration heap leach case is silica based, with rapid adsorption kinetics and moderate mercury adsorption capacity of up to 5wt%: the rapid kinetics are required to achieve quantitative mercury adsorption at low temperature but limit the overall mercury capacity. The material developed for the EW strip circuit is a polymer resin, has moderate adsorption kinetics at room temperature, and as the high operating temperature gives fast kinetics a very high mercury capacity of over 40wt% can be achieved.

Both adsorption materials can be recycled and reused by eluting the mercury, using a novel eluent that is effective in quantitatively desorbing mercury and producing a neutral, insoluble mercury salt in a single step. Patent applications in process preclude identifying details of the elution step.

Case Study 1: Heap Leach at Marigold Mine

A pilot unit consisting of a single fixed bed, volume 50L, of HgFree adsorbent was used to treat a flow of between 4.5 to 25 litres/minute of the heap leach pregnant solution: no pre-treatment is required before operation. The bed was operated at ambient pressure and samples were taken at regular intervals over a period of ~1800 hours. This is shown graphically in figure 7. The first 1000 hours of pilot operation was carried out at ~5-9 L/min to demonstrate adsorption of mercury to very low levels, target 10ppb. The second period of operation was carried out at 20-25L/min feed flow to speed mercury loading and fully load the adsorbent. After 1800 hours the test was stopped as mercury break-though had been achieved. Total mercury loading on the adsorbent was measured at ~4wt% Hg.

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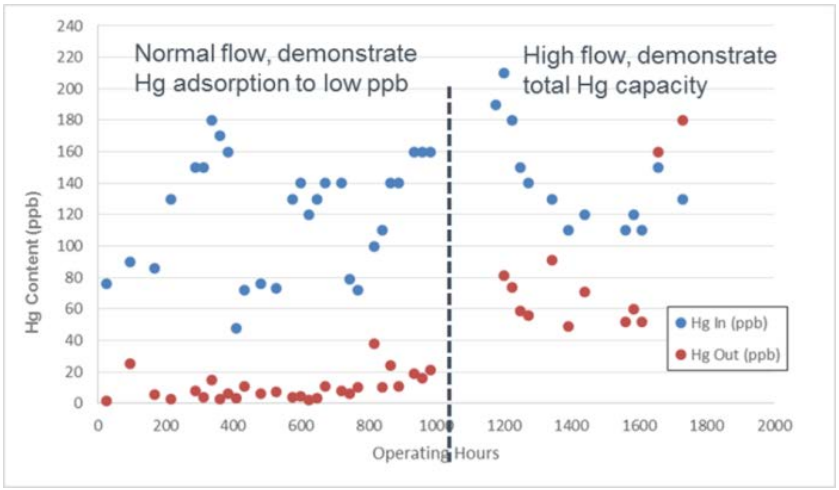


Figure 7: Mercury feed and effluent composition from heap leach pregnant feed

Case Study 2: Electro Winning Pregnant Feed

A similar pilot plant to that used at Marigold mine was set up in the carbon strip – electrowinning circuit of an active gold mine. A single fixed bed of polymer adsorbent, 70 L, was fitted in the feed from the carbon column to the electrowinning cell. The feed flow to the pilot plant was controlled at ~10 L/min and the temperature allowed to vary with the temperature of the feed solution. The carbon strip was carried out periodically, with one or two load/strip cycles taking place in a 24 hour period. Figure 8 shows the concentration in the feed and effluent of mercury (left hand side) and gold (right hand side) for a typical strip cycle. The process and adsorbent achieves close to 100% adsorption of mercury, regardless of the inlet mercury concentration. The apparent adsorption and desorption of gold during the cycle is an artefact of sampling and residence time– over each strip cycle a mass balance of gold was taken and very little gold was adsorbed.

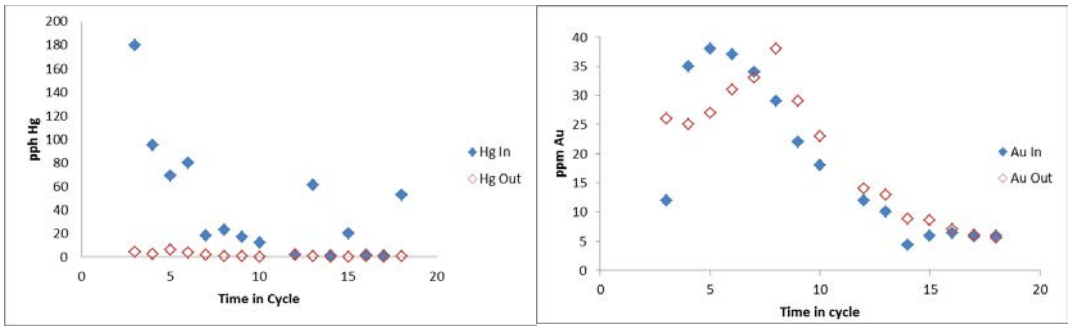


Figure 8: Mercury and gold concentrations during a typical strip cycle

After operating for a period, the resin from the electro-winning pregnant pilot was discharged in sections (14 sections of 5L each) and analysed for mercury and gold. Figure 9 shows the bed profile of mercury adsorption, with peak mercury concentration of over 40wt% at the bed inlet, and a very sharp concentration profile showing the rapid adsorption of mercury in the bed. Gold concentration was constant at <350ppm regardless of position in the bed.

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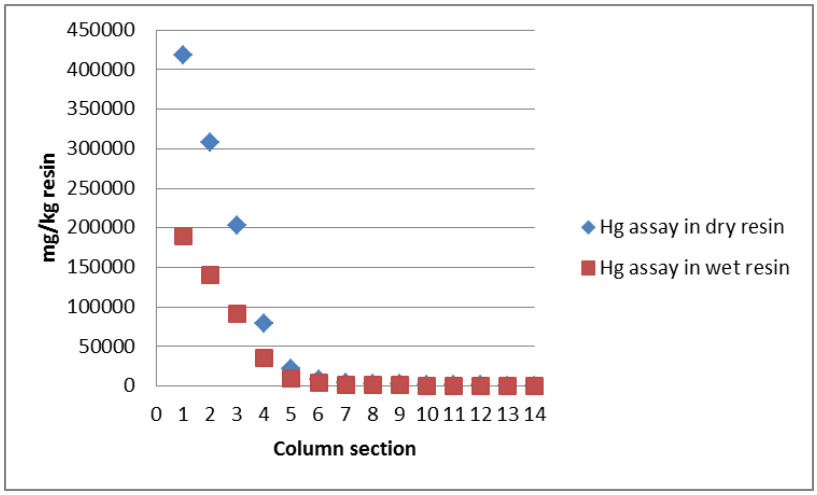


Figure 9: Mercury concentration through resin bed after discharge

CONCLUSIONS

We have described the development of a process for the selective adsorption of mercury in the presence of gold, with selectivity being achieved when using thiol based adsorbents and an excess of cyanide over that required to solubilise mercury and gold. The effectiveness of the adsorption was not influenced by the form of the adsorbent, silica or resin. The mechanism that controls selectivity has been shown to be the presence of a ratio of CN to gold and mercury and that this can be applied to authentic mine feeds as well as synthetic models.

Initial development of the process in the laboratory was transferred to pilot plant scale in two applications – low concentration gold and mercury in a high flow heap leach feed, and high concentration gold and mercury in a low flow carbon strip – electrowinning feed. These pilot studies have confirmed that the high selectivity to selectivity of adsorption of gold, and a very high percentage mercury adsorption observed in laboratory tests is achievable when using the complex feeds that come from an operating mine.

Analysis of a loaded resin have confirmed the very high loading capacities (>40wt% Mercury) achievable when using an optimised adsorbent resin and process, and have also confirmed the very low co-adsorption of gold (<350ppm). Both materials can be regenerated using a novel eluent and produce an inert mercury salt. The eluted materials are regenerated in the process and can be reused multiple times.

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Gold-PM Proceedings

Treatment of Tails/Wastes

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A NEW LEACH SYSTEM OF BASE AND PRECIOUS METALS RECOVERY FROM E-WASTE

By

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ABSTRACT

Electronic waste (e-waste) is accumulating rapidly internationally and pose a significant environmental challenge. One of the ways to pay for the processing of the waste is through sales of valuable metals. In addition, toxic and dangerous metals can be removed prior to incineration of the plastic substrates. E-waste is usually either transported to landfills or processed by pyrometallurgical and hydrometallurgical processes. Recently, a number of hydrometallurgical approaches have been considered in metals recovery from different electronic components. In this study, glycine (amino-acetic acid) in an alkaline environment is considered as a lixiviant for base metals extraction and glycine-cyanide system for precious metals recovery from ground electronic circuit boards. It was found that alkaline glycine solutions selectively dissolve copper, zinc, and lead over precious metals. Gold and silver was then recovered in a consequence step using glycine and low cyanide mixture. In 2-stages glycine leaching system, gold, silver, zinc, lead and copper recoveries were 92.1%, 85.3%, 99.5%, , 91.8%, and 99.1% respectively. The recoveries of precious and base metals by direct cyanidation, direct glycine-cyanide leach, and ammonia were lower than the recovery of these metals using glycine and glycine-cyanide systems.

Outline

- Introduction
- Advantages of Glycine
- Materials Preparation
- Base Metals (BMs) Leaching
  - Effect of Glycine Concentration
  - Effect of pH
- Precious Metals (PMs) Leaching
- Leaching Routes
  - Ammonia
  - Direct Cyanidation
  - Glycine (stage 1) followed by Glycine-Cyanide leach
  - Direct Glycine-Cyanide leach

Introduction

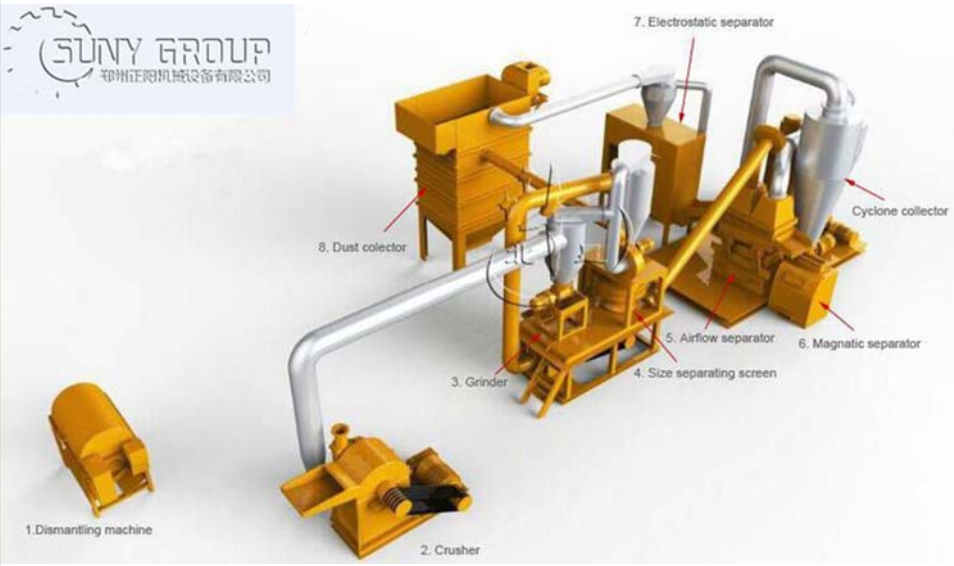
- Electronic waste can be found in many forms, e.g.: computers, photocopiers, printers, faxes, monitors, batteries and mobile phones.
- Worldwide, about 25 million tons/ year of E-waste are generated.
- Australia is one of the world's top ten consumers of electronic devices.
- E-Waste contains valuable resources such as precious metals (Au, Ag), Pt, and base metals (Ni, Zn, Al and Cu). Some can be toxic to the environment such as Pb, Hg, and Cd.
- Recovery of valuable metals from E-waste can be achieved by using both hydrometallurgical and pyrometallurgical routes.

The main aim of this work is to introduce a benign hydrometallurgical system suitable for metals recovery from E-Waste.

Advantages of Glycine

Non-toxic	Ease of reagent recovery and reuse	Operated under dilute and concentrated modes
Environmentally benign	Reagent Cost	Chemical stability
High affinity for Au, Ag, Cu, Zn, Pb, Pd, Cd, Ni, Co	Can be synergistic with cyanide: accelerated Au leach rates	High adsorption of Au, Ag onto activated carbon. Ease of AARL-type elution
No interaction with acid consuming materials	Application to various leaching modes	Cheap materials of construction
Selective over non-sulfide gangue minerals	No transportability & logistics, trade restrictions	Ease of base metals removal / recovery
Thermally stable	Non-volatile	Simple chemistry
Insignificant Fe, Mn, Mg, dissolution	Cu- glycinate good oxidant	No pH swings

Materials Preparation



Plant Layout- Vilytics Company - Egypt

Materials Preparation

no	machine	Photo	input	output
1	Crusher		Complete PCBs	PCBs shredded 4cm*4cm
2	Grinder		Shredded PCBs	Fine powder 1 mm size
3	High Voltage Electrostatic Separator		Mixed powder	Metals powder Non-metals powder

Main Steps

Materials Preparation



Home Appliance PCBs



Cell/Computer/Printer PCBs



PCB Industry Waste Rims

Input



Metal fine Powder



Concentrated substrate Powder

Output

PCBs: Printed Circuit Boards

Metal Contents

Metal	Unit	Content	Value, %
Au	ppm	368	68.9
Pt	ppb	65	
Ag	ppm	557	1.35
Pd	ppm	55	4.59
Al	%	6.4	0.55
Fe	%	2.5	
Pb	ppm	26700	0.28
Cu	%	55.2	12.89
Ni	ppm	3560	0.16
Co	ppm	20	
Cr	ppm	70	
Zn	%	5.8	0.45
Sn	ppm	90500	6.53



Experimental

- The leaching experiments were conducted at ambient pressure and temperature.
- The mixture was agitated using a bottle roller at 100 rpm.
- Leach solutions containing 30 g/L glycine.
- The pH of the solutions was adjusted at pH 11.0 by adding caustic soda.
- Samples were withdrawn and filtered at different time intervals, with the solutions collected for Au, Ag, Pb, Zn, Al, Fe, and Ni, analysis by ICP-MS .
- No additional oxidant other than air through bottle neck.

RESULTS

STAGE 1

Glycine Leaching

Reagent	Units	Amount
Glycine	g	15
Water	mL	500
E-waste	g	2.001
NaOH	g	7.2
pH		11
Temp	C	RT ~23

Sample	Au	Ag	Zn	Al	Pb	Cu	Ni
Time, hour	mg/L	ug/L	mg/L	mg/L	mg/L	mg/L	mg/L
2	0.001	17	23.6	221	113	61.2	<0.1
4	0.002	28	43.2	244	175	404	0.4
6	0.007	95	120	271	230	701	0.8
24	0.005	62	165	283	338	1490	0.8
Ext, kg/t	**0.001**	**0.0155**	**41.2**	**70.7**	**84.5**	**372.3**	**0.2**
Ext, %	**0.34**	**1.73**	**80.94**	**99.05**	**76.50**	**72.52**	**6.49**

Base metals extraction

STAGE 2

Gly-CN Leaching

Reagent	Units	Amount
Glycine	g	15.0
Water	mL	500
NaCN	g	0.15
E-waste	g	0.781
NaOH	g	6.9
pH		11

Element	Total, kg/t	Total Ext, %
Au	0.341	92.1
Ag	0.77	85.3
Zn	50.7	99.5
Al	71.3	99.9
Pb	101	91.8
Cu	509	99.1
Ni	0.60	19.5

Sample	Au	Ag	Zn	Al	Pb	Cu	Ni
Time, hour	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
2	0.302	1.12	4.60	6.50	42.0	114	0.6
4	0.603	1.79	9.80	5.00	65.0	211	0.6
6	0.757	1.82	16.1	4.00	43.6	300	0.6
24	1.36	3.0	38.0	2.50	67.7	547	1.6
Ext, kg/t	**0.339**	**0.77**	**9.5**	**0.6**	**16.9**	**136.7**	**0.4**
Ext, %	**92.08**	**85.07**	**97.77**	**91.90**	**65.21**	**96.88**	**13.89**

Precious and base metals extraction

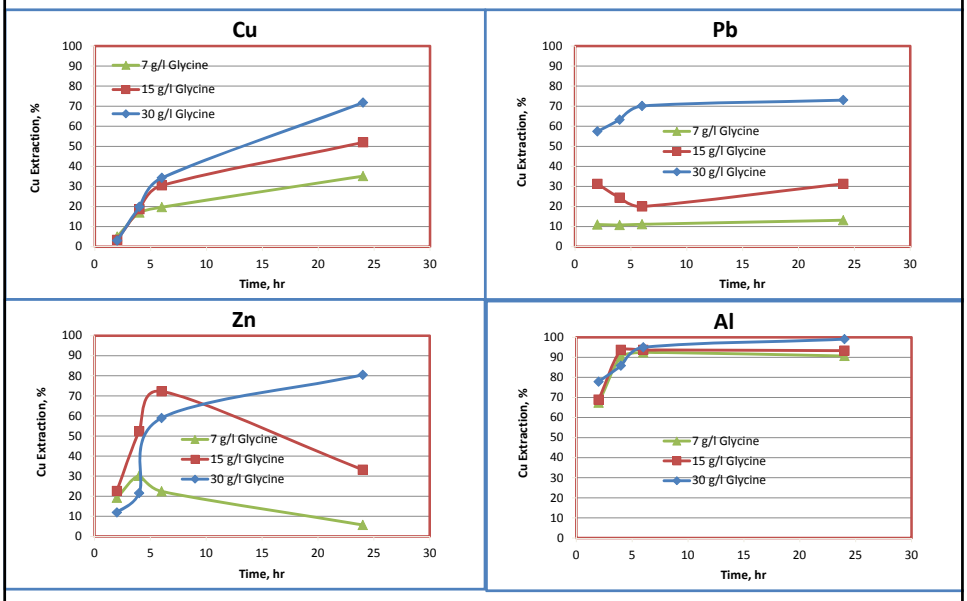
Residue After Leaching



Before Leaching

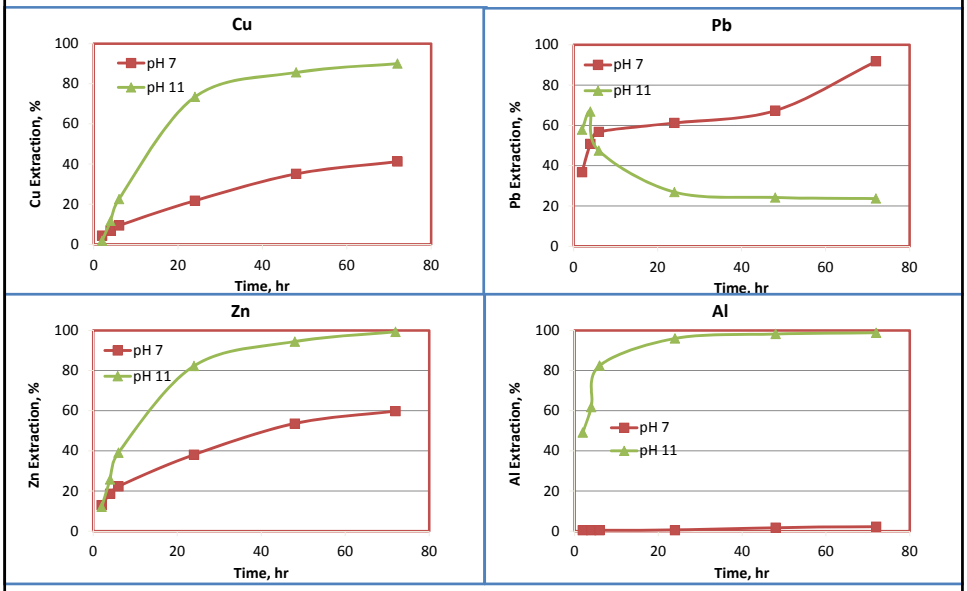
After Leaching

Effect of Glycine Concentration



Glycine, pH 11-12.6, RT

Effect of pH



Glycine 30 g/L, pH, RT

Leaching Routes

Reagent	Units	Amount
Ammonia	M	1.25
Water	mL	500
E-waste	g	2.004
pH		11.5
Temp	C	RT ~23

1. Ammonia

Element	Au	Ag	Zn	Al	Pb	Cu	Ni
Time, hour	mg/L	µg/L	mg/L	mg/L	mg/L	mg/L	mg/L
2	0.002	140	236	249	37.1	1410	1.0
4	0.005	385	326	270	54	1810	1.4
6	0.004	422	347	278	60.7	1930	1.4
24	0.002	1240	335	284	50.1	2050	1.6
Ext, kg/t	0.000	0.3094	83.6	70.9	12.5	511.5	0.4
Ext, %	0.38	58.11	90.15	97.18	22.58	85.33	7.33

Precious and base metals extraction

Leaching Routes

Reagent	Units	Amount
NaCN	g	1.75
Water	mL	500
E-waste	g	2.002
pH		11.0
Temp	C	RT ~23

2. Direct Cyanidation

Element	Au	Ag	Zn	Al	Pb	Cu	Ni
Time, hour	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
2	0.681	1.01	59.1	161	17	602	0.8
4	0.837	1.13	92.8	221	54.8	952	1.4
6	0.884	1.38	93.8	211	54.4	1040	1.2
24	0.868	1.21	94.2	227	64.8	1180	1.6
Ext, kg/t	0.217	0.3022	23.5	56.7	16.2	294.7	0.4
Ext, %	65.35	72.01	25.61	96.90	46.72	54.56	10.24

Precious and base metals extraction

Leaching Routes

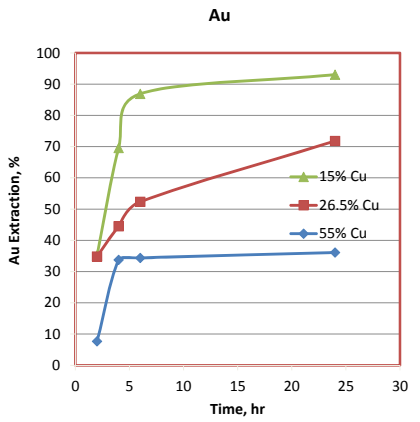
Reagent	Units	Amount
Glycine	g	15
NaCN	g	0.257
Water	mL	500
E-waste	g	2.003
NaOH	g	7.0
pH		11

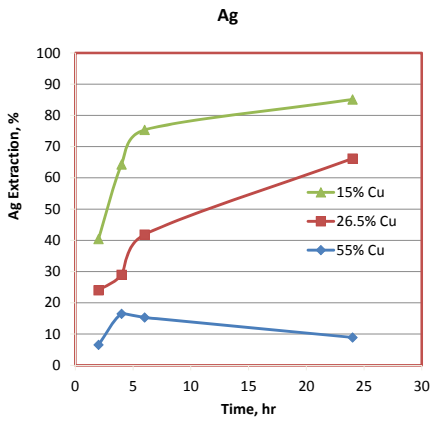
3. Direct Gly-CN Leach

Element	Au	Ag	Zn	Al	Pb	Cu	Ni
Time, hour	µg/L	µg/L	mg/L	mg/L	mg/L	mg/L	mg/L
2	83.7	66	54.5	171	69.7	199	0.5
4	373	168	125	266	99.8	571	1.1
6	380	156	152	286	96.9	739	1.2
24	400	88	258	311	82.2	1620	2.0
Ext, kg/t	0.099	0.0220	64.4	77.6	20.5	404.3	0.499
Ext, %	37.61	8.84	97.78	98.76	24.29	87.65	20.68

Precious and base metals extraction

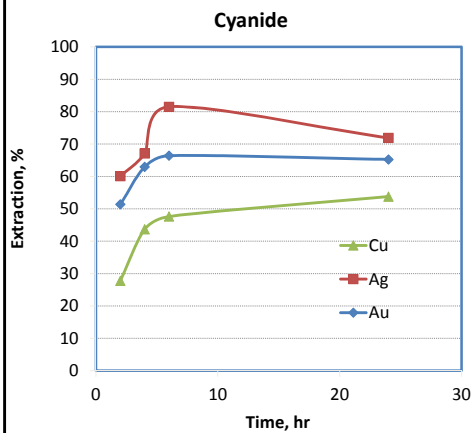
Effect of Cu on Au & Ag Extraction

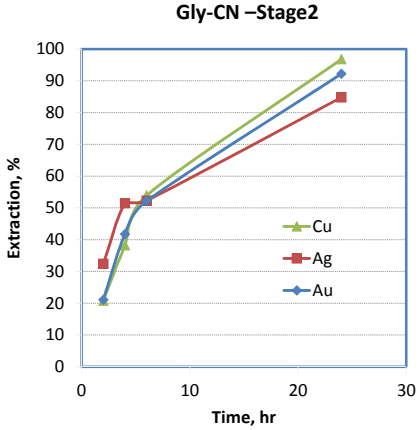




30 g/L Glycine, 500 ppm NaCN, pH 11, RT °C

Cyanide vs Gly/Gly-CN





3500 ppm NaCN, pH 11, RT

30 g/L Gly, 300 ppm NaCN pH 11, RT

Leach Routes

Element	Gly/Gly-CN 2-Stages	Gly-CN Direct	NH_3	NaCN
Au	92.1	37.6	0.40	65.4
Ag	85.3	8.8	58.1	72.0
Zn	99.6	97.8	90.2	25.6
Al	99.9	98.8	97.2	96.9
Pb	91.8	24.3	22.6	46.7
Cu	99.1	87.7	85.3	54.6
Ni	19.5	20.7	7.30	10.2

1. NaCN: 3500 ppm, pH 11

2. NH3: 1.25 M NH_3,pH 11

3. Gly-CN: 30g/L Gly + 500 ppm NaCN, pH 11

4. Gly/Gly-CN: 30 g/L Gly and 30g/L Gly + 300 ppm NaCN, pH 11

Conclusions

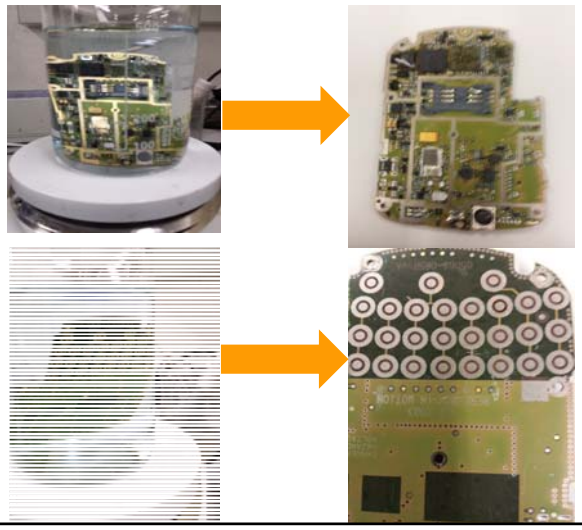
- Results show high potential for the use of alkaline glycine as a new hydrometallurgical leach system for E-waste.
- Significant optimisation potential exists over ambient temperature bottle roll leach tests.
- Glycine leaches most of the base metals (Pb, Zn, Cu) at Room temperature.
- Gold and silver was recovered in a consequence step using glycine and low cyanide mixture.
- In 2-stages glycine leaching system, gold, silver, zinc, lead and copper recoveries were 92.1%, 85.3%, 99.5%, 91.8%, and 99.1% respectively.

Conclusions (Cont'd)

- The recovery of precious and base metals by direct cyanidation and ammonia was lower than the recovery of these metals using glycine and glycine-cyanide systems.
- Metals dissolution increases by increasing glycine concentration and pH.
- Additional work under controlled oxygen leaching is currently conducting.
- **Future work**: Recovery of metals from pregnant solutions.
- The use of a pyrometallurgical step to recover energy from plastic residues and for mass reduction may make a valuable contribution.

Conclusions (Cont'd)

- The recovery of precious metals from mobile boards and Integrated circuits.



3. Gly-CN: 30g/L Gly + 300 ppm NaCN, pH 11

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Gold-PM Proceedings

Process Optimisation

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ONLINE ANALYSIS SOLUTIONS FOR GOLD BENEFICIATION

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ABSTRACT

Gold beneficiation may have many routes depending on the characteristics of the ore. Regardless of the beneficiation method process optimization via online analysis can increase plant profitability through reduced energy consumption, optimized reagent consumption, higher throughput or increased recovery. Four online analysis methods (laser diffraction, x-ray fluorescence, laser-induced breakdown spectroscopy and potential/pH analyser) are introduced for gold process control applications. Carbon pre-flotation, sulphur flotation and pressure oxidation are common pre-treatment methods before cyanide leaching of gold. A new slurry analyser technique based on laser-induced breakdown spectroscopy opens new process control options for this process flow sheet, as it is able to measure carbon and sulphur in the slurry.

Keywords: Online analysis, X-Ray Fluorescence, Laser Diffraction, Laser-Induced Breakdown Spectroscopy, Process Control, Optimisation

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INTRODUCTION

Without online process control beneficiation processes have to be run conservatively to minimize the effect of fluctuating throughput on gold recovery. The processing plant also needs to be run conservatively if the composition of the incoming feed is inconsistent. Without online analysers the process operators generally get the assay information with considerable delay, and the plant must be run without information of the current material passing through. The basis of successful process control is to have a correct analyser for each step of the production chain.

The mineralogy of gold bearing ores plays an important role in the gold concentration process. There may be multiple ways to process gold ores depending on the ore type and how the gold is found in the ore, e.g. solid solution, occluded, liberated etc. Regardless of the gold concentration, process control via online analysis can improve the recoveries, stability and/or yield of gold concentrate. The main gold beneficiation methods include cyanidation, flotation and gravity concentration.

Generally gold bearing ores can be classified as free milling, complex and refractory ores[(1)]. Ores which yield over 90% recovery in conventional cyanidation processes can be described as free milling. Chemical or pyrometallurgical means are used to recover the gold in refractory ores such as roasting, pressure oxidation, or bacterial leaching, which exposes the gold to leaching by a suitable reagent such as cyanide.

GOLD PROCESSES AND ANALYSIS NEEDS

Ore Characterisation

Free milling gold minerals consist of placers, quartz vein gold ores and oxidized ores. These ore types generally require no chemical pre-treatment, and can be concentrated for leaching using grinding and gravity separation methods. Generally free milling ores are depleting globally and more complex and refractory gold ores have to be processed in the future[(2)].

Gold can occur in various forms in ores. Generalized classification can be given as native gold, gold associated with sulphides, gold tellurides and gold in other minerals[(3)]. In other minerals gold generally is associated with arsenic and/or antimony, with copper porphyries, with lead or zinc minerals, and with carbonaceous minerals.

Gold which is atomically distributed in the crystal structure of sulphide minerals, e.g. pyrite (FeS_2) and arsenopyrite (FeAsS), can be referred as solid-solution gold[(4)]. The preferential carrier of solid-solution gold tends to be arsenopyrite, and is generally enriched in the finer end of particles (<20 µm). Pyrite is the most abundant of the sulphide minerals, and can also contain significant gold concentrations in its crystal structure. Solid-solution gold may be a large portion of the total gold in an ore, and in some cases even the main type of gold. Generally the arsenic concentration in these kind of ores shows a good correlation to the gold concentration over different ore morphologies[(5)].

The gangue mineralogy can also have a large impact on the gold recovery. Carbonaceous material can be described as refractory as the carbonaceous matter may adsorb the dissolved gold-cyanide complex from the solution in the leaching circuit, called preg-robbing[(6)]. Most silver present in gold ores usually is within an alloy with gold, called electrum. Electrum can react with sulphur to create a passivating layer on the mineral, thereby preventing cyanide from reaching the gold.

Comminution

Decreasing particle size can improve the dissolution rate of gold in cyanide leaching[(7)]. Smaller particles have a larger surface area for contact between solid and liquid and the larger surface area therefore increases the rate of dissolution (Figure 1)[(8)]. However, increase in fines in the slurry will also liberate cyanide consuming species and hence increase cyanide consumption. Grinding costs also increase with decreasing particle size via higher power consumption. Slurry rheology can also change with decreasing particle size distribution resulting in an increased pumping and mixing power consumption.

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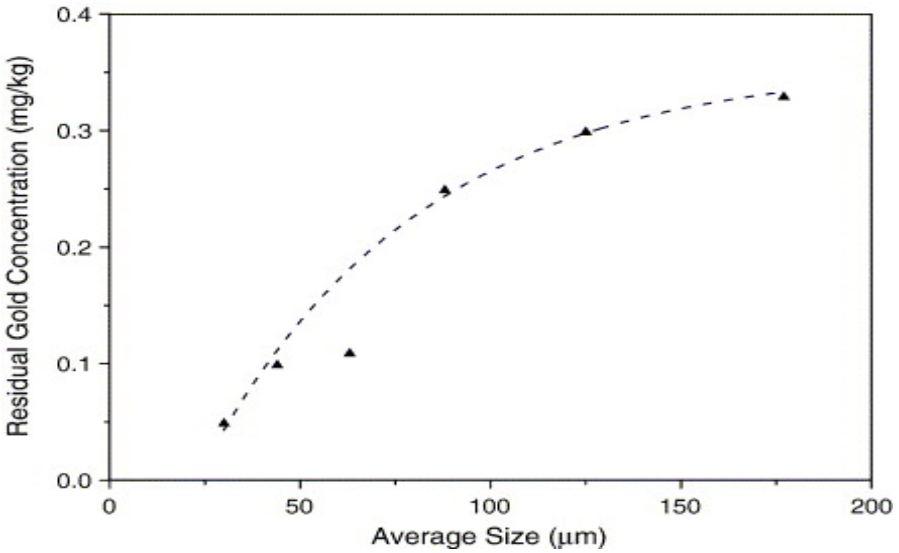


Figure 1: The residual gold concentration versus the particle size of the ore. (de Andrade Lima and Hodouin, 2005)

The main cause of gold rejection in flotation plants is free gold grain losses to the slimes (<5 µm)[4]. The efficiency of gold flotation quickly declines for particles below 5-7 µm. Controlling the particle size distribution of the circuit is therefore important to avoid overgrinding of the material. For this reason there are several operating gold plants where flash flotation is employed in the grinding circuit to recover gold at the coarsest size possible prior to being over ground.

The particle size distribution also has an effect on the flotation reagent consumption and on dewatering of the slurry. Grinding circuit control usually includes target values for the particle size distribution of the grinding product. In most cases the primary control variable is the fresh ore feed rate to the grinding circuit, and there is a trade-off between the tonnage throughput and the fineness of the product. With ore of variable hardness, this gives the opportunity for optimization – the softer the ore, the more tons can be pushed through the mill to achieve the target product size distribution and adequate liberation.

Flotation

In flotation the valuable minerals are made hydrophobic through the use of selected reagents. These hydrophobic particles attach to air bubbles and float to the surface of the flotation tank forming a froth. The froth is continually replaced by new bubbles and hence it transports the floated material to the concentrate launder where it is separated from the rest of the slurry in the tank. Most of the gangue minerals remain hydrophilic and within the rest of the slurry in the tank, which exits through the tank outlet.

Pre-flotation or reverse flotation is the process where the desired mineral is depressed and the naturally hydrophobic gangue material is removed from the bulk slurry by flotation. The floated material is recovered directly to final tailings, with minimum loss of desired minerals. Removing the unwanted material by pre-flotation in the early stage helps in the later recovery of the desired mineral as there will be no naturally floating gangue. An example of pre-flotation practice in the industry is the removal of talc prior to nickel flotation in Western Australia nickel mines.

Mineralogy plays a large role in the separation of valuable minerals from gangue minerals by flotation. In refractory gold ores the sulphide or telluride minerals containing gold are floated (pyrite, arsenopyrite, calaverite, hessite sylvanite, etc), as these minerals need to be further treated prior to leaching with cyanide. Native gold and its alloys, free from surface contaminants, are considered naturally floatable and are normally collected using a mixture of collectors, such as xanthates and dithiophosphates.

The flotation of gangue is a complicated process depending on the gangue mineralogy and its association with the valuable minerals. Excessive use of depressants to depress gangue can have a negative effect on gold recovery though also depressing the target minerals. By measuring the mineral composition of the feed in terms of both valuable and gangue minerals would allow the optimisation of both collector and depressant addition. This shows the importance of knowing what concentration of minerals coming in to the plant on a real-time basis using online analysis.

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Pressure Oxidation

Gold associated with sulphide or telluride ores is encapsulated as submicron particles in the mineral matrix. In order to achieve acceptable recoveries the sulphide minerals need to be broken down chemically to allow the cyanide access to react with the gold surface. The method used for breaking down sulphide minerals is oxidizing the sulphur in the mineral lattice to elemental S, SO_2 gas or SO_4^{2-}. The oxidation method used can be roasting, bacterial oxidation, or pressure oxidation. However it should be noted that roasting is usually not preferred in modern times due to increased environmental regulations.

The ore may be treated with sulphuric acid to reduce carbonate content before the pressure oxidation and the autoclaves may consist of several stages targeting oxidation of different minerals. The oxygen required for each reaction is added to each stage and the autoclave retention times are generally 45 to 60 minutes[9]. The purpose of the autoclave is to oxidise sulphur and/or tellurides and not alter the gold (e.g. passivating layer on surface) entering the autoclave. Hence knowing the quality of the feed entering the autoclave is a critical part of controlling the oxidation process. For process control purposes sulphur and carbonate are the most important for the autoclave operation and if present in the feed, tellurium can also important to monitor.

The overall goal of autoclave control is to minimise operating costs (mainly acid consumption) without decreasing the gold liberation (oxidation of the host mineral matrix). If the carbonate content in the feed is high this can be expensive through down time for autoclave maintenance, and also the amount of acid used to react with the carbonates. Too little sulphur content in the feed will not provide enough sulphur to react and generate heat to sustain the slurry temperature and oxidation reactions, which will mean that an auxiliary heat source must be used such as steam addition to keep the reaction going. Too high sulphur concentration will result in not having enough oxygen for the oxidation reaction and incomplete liberation of the gold for subsequent leaching. Hence it can be seen that monitoring in real time the quality and mineral content of the autoclave feed is very important in optimising autoclave performance while minimising operation costs.

Biooxidation

Biooxidation, or bioleaching, is a process that uses microorganisms to oxidize sulphur in the mineral, and liberate the gold for cyanide leaching. Bacterial oxidation can be performed in heaps or in agitated reactors. The microorganisms obtain energy by oxidation of ferrous iron (Fe^{2+}), chemically reduced sulphur compounds, or both, to produce ferric iron (Fe^{3+}) and sulphuric acid (H_2SO_4)[10]. The organisms used in bioleaching are normally acidophilic, and require a low pH 1.0 – 2.5.

A smaller ore particle size distribution in bioleaching increases the surface area available for oxidation, thus increasing the rate of the oxidation. However, if the particle size is too fine, it may increase the viscosity of the slurry and hence decrease the rate of oxygen transfer. For agitated tanks, the preferred particle size Dv(80) is 53 to 75 µm. The most important factor in controlling biooxidation is the redox potential. As Fe^{2+} is oxidized, the Fe^{3+}/Fe^{2+} ratio is increased, increasing the redox potential. Sulphide oxidation consumes Fe^{3+} and decreases the redox potential. For rapid oxidation of the sulphide minerals, the redox potential should be kept as high as possible that the bacteria can withstand. Redox potential optimization is achieved when providing optimal conditions for the bacteria in the tank (O_2, CO_2, pH and T).

Cyanide Leaching

Gold is classified as a noble metal due to its inertness to chemical reactions. It is not completely inert, and will react with some reagents, e.g. cyanide, thiosulphate. Cyanide leaching is the main concentration method in the gold industry. It is used due to its relatively low cost and high effectiveness in gold dissolution. The gold surface needs to be liberated before the leaching step to allow the cyanide to react with the gold.

Gold requires oxidation as part of the dissolution process in an alkaline cyanide solution. Generally gold is considered to be inert to oxidation, but in the presence of suitable complex agent, e.g. cyanide, gold can be oxidized and dissolved forming a stable complex ion $[Au(CN)_2]^-$. Unfortunately, alkaline cyanide solutions also dissolve many other elements and minerals as well, with other dissolution reactions competing with gold for reagents. This usually increases reagent consumption and decreases the recovery effectiveness of gold.

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The consumption of cyanide can be considered as a function of process variables such as temperature, Eh, plus the concentration of dissolved oxygen, free cyanide, and compounds that react with cyanide[8]. Such species include various sulphur containing species e.g. pyrite (FeS) and chalcocite (Cu_2S). The iron in pyrite can form a stable ferrocyanide ion $[Fe(CN)_6]^{4-}$. Copper can form a large number of complex ions with cyanide, such as CuCN and $[Cu(CN)_2]^-$. Several pre-treatment methods, e.g. pressure oxidation, may be applied to the ore prior to cyanidation to reduce cyanide and oxygen consumption.

Cyanide leaching is generally performed in an environment with a pH of 9.5 to 11 to minimize the production of HCN gas, which is toxic to humans. The leach pH is controlled by addition of a pH modifier, normally lime. The ore properties determine the amount of lime added to the leach, with typical values of lime consumption being in the range of 700 – 1500 g/ton of 100% CaO equivalent[11]. Pulps which contain oxygen consuming components reduce the leaching kinetics. For this reason tanks with mechanical agitation may have oxygen sparging added as a reagent to the process, or alternative sources of oxygen (e.g. liquid oxygen, peroxide, etc).

Carbon Adsorption

There are three carbon adsorption methods used to recover the dissolved gold, carbon-in-pulp (CIP), carbon-in-leach (CIL) and carbon-in-columns (CIC). The CIC method is used mainly to treat solutions from heap leaches, and the CIP and CIL methods to recover gold from slurries. Prior to carbon adsorption methods, the main gold recovery method was the zinc cementation method, known as Merrill Crowe. The Merrill Crowe method is not suitable for all ore types, e.g. clays do not filter well and gold is lost at the residues and base metals require high consumption of cyanide and zinc which add to the total reagent cost.

Typically the dissolved gold cyanide ion is loaded on to activated carbon by a reversible adsorption mechanism without any chemical transformation[12]. In CIP most of the leachable material is leached before the addition of carbon. The carbon addition is done in separate tanks after the leaching process. In the CIL method the adsorption is done simultaneously with the leaching, and the carbon can be added to the leaching tanks.

ANALYSIS METHODS

Laser Diffraction

The PSI500® particle size analyser is based on laser diffraction analysis of the sample. The analyser gives a consistent volumetric particle size analysis without any external calibration. Small difference between other particle size methods can be noticed. However, the repeatability and precision over a wide particle size range are the most important features in process control applications.

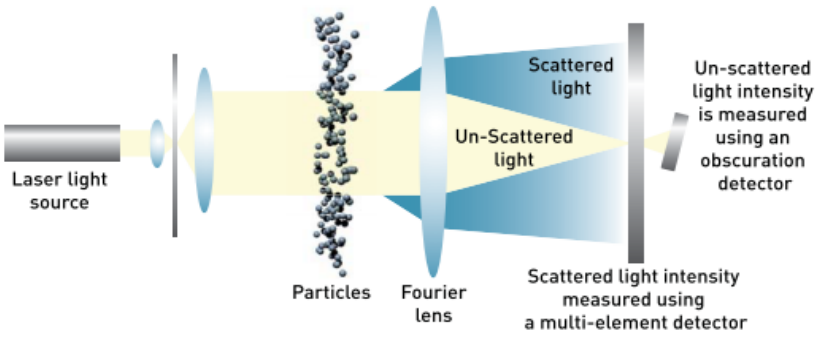


Figure 2: Principle of laser diffraction measurement. A laser is directed through a measurement cell, where particles scatter the laser radiation. The particle size distribution is calculated from the scattered laser intensities.

The size analysis is based on the intensity distribution measurement of coherent laser light scattered by particles (Figure 2). When the laser beam interacts with particles, their size distribution can be calculated from the scattered light distribution based on Mie theory. The speed and robustness at ambient conditions make laser diffraction ideal for online slurry applications.

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Consider the potential impact of improved control in gold production where ore is milled to produce a feed for extraction by cyanide leaching. Extraction tanks operate on the basis of a defined residence time, so the particle size distribution of the slurry entering the tank has a direct impact on the amount of gold liberated. If the milling circuit, and the associated process steps upstream of the extraction tanks, produces a relatively coarse material then gold recovery can decrease due to poorer gold liberation and hence insufficient time for the gold to be leached and recovered in the circuit. A finer particle size distribution enhances gold recovery, but requires higher energy consumption per unit of ore and normally results in lower mill throughput. Once the optimum particle size has been determined from an economic recovery analysis, drift in either direction will compromise profitability. Consistent milling to the specified particle size maximizes profit, and this is where an online particle size distribution instrument, such as the PSI500, can add value to the process plant profitability.

X-Ray Fluorescence

X-Ray fluorescence (XRF) and Courier® online analysers have been the preferred online elemental analysis method for slurry applications for decades. The principle of XRF analysis is presented in Figure 3. XRF analysers have short measurement times and can measure elemental concentrations in the ppm levels. There are two types of XRF detectors, energy dispersive (ED) or wavelength dispersive (WD). Energy dispersive channels measure the amount of different energy X-Rays reaching the detector. The incoming X-Rays can then be plotted to a spectrum. A wavelength dispersive channel uses a fixed crystal which diffracts the incoming X-Rays and allows only the desired wavelength to enter the detector. Older types of ED channels use Si(Li) detectors, which require cooling with liquid nitrogen, and the consumption can be 1 L per day. The sensitivity of counts and the resolution of peaks of the ED channel is much lower than the sensitivity of the WD channels (Figure 4).

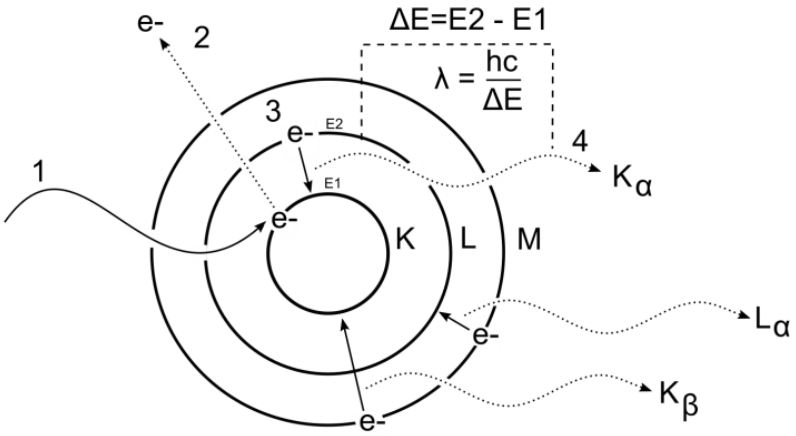


Figure 3: X-Ray fluorescence principle. Incoming X-Ray radiation (1) has correct energy to eject an electron from the inner shell of the atom (2). Electron in a higher energy state occupies the vacancy (3) by emitting a photon with specific energy/wavelength, corresponding to the energy difference of the shells (4).

L lines are preferred for gold measurement due to the high energy of the K lines (Kα 68.8 keV and Kβ 77.99 keV) which would require high power X-ray tube. Gold L lines Lα and Lβ have energies of 9.71 and 11.43 keV, respectively. The detector used for gold measurement needs to have high resolution as Zn (Kα 9.57 keV), Ge (Kα 9.89 keV), As (Kβ 11.73 keV) and Se (Kα 11.22 keV) need to be resolved from the gold line. Typical ED channel resolution (0.15 – 0.60 keV) might not be high enough to resolve gold from the interfering lines.

Courier X-Ray analysers generally use WD element channels to ensure maximum sensitivity of the measurement. In cases where high sensitivity is not required, the analyser can be equipped with new generation SDD multi-element detectors. These channels are Peltier cooled and do not require liquid nitrogen. The analyser is equipped with a 200 W x-ray tube which generates excitation radiation at 0 – 50 keV.

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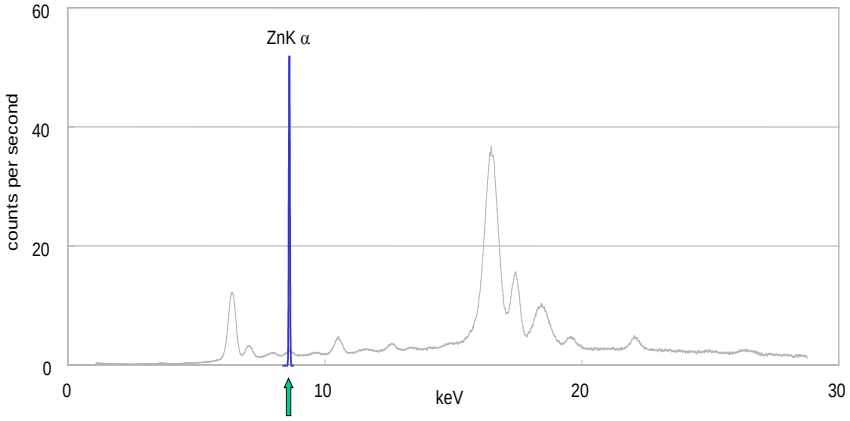


Figure 4: WD (blue) and ED (black) spectrum comparison of Zn Kα line at 8.64 keV of sample containing 0.12% Zn. The X-axis represents the energy (keV) and the Y-axis represents the measured counts per second.

Gold concentrates usually have relatively high gold content and are relatively easy to measure. However, the feed and tailings streams may have gold concentrations even sub ppm level, which are usually too low for XRF measurement. If the feed has >4 g/t Au, the measurement can done, but this requires longer measurement times. A gold feed measurement using two WD Au channels and a 5 minute measurement time is presented in Figure 5.

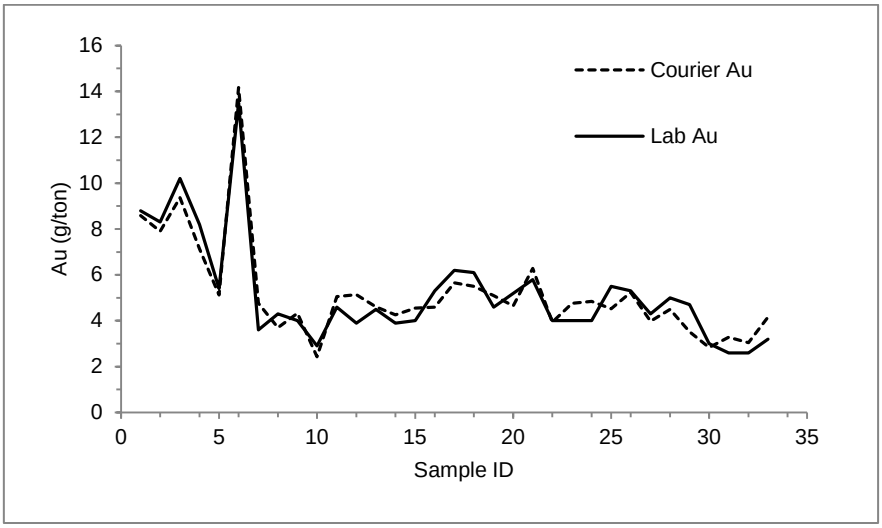


Figure 5: Courier online Au analysis and laboratory Au analysis compared. The measurement was done using two WD Au channels and a 5 minute measurement time.

Due to the random nature of radiation process, the XRF measurement has an inherent statistical error (Equation 1). This random error requires longer measurement times for smaller concentrations to achieve acceptable pulse statistics.

$$\sigma_I = \sqrt{\frac{I}{T}} \qquad \text{Equation 1.}$$

Where I is the measured intensity and T is the measurement time. For streams which have low Au contents, sometimes an indirect measurement can be made. In the case where the gold is carried by arsenopyrite, an assumption can be made that when As starts to increase in the tails, so does Au (Figure 6). The correlation is not perfect, but is enough for process control purposes. In low Au concentrations the laboratory assays also have a relatively large error. The online analyser can never be more accurate than the laboratory assays against which it is calibrated.

Another case where indirect Au measurement can be used is where gold is the by-product of copper ore. Figure 7 presents a case where the recoveries of Au and Cu were calculated using the two product formula (Equation 2). The actual gold concentration was too low to be measured, but following copper recovery, the gold recovery could be followed.

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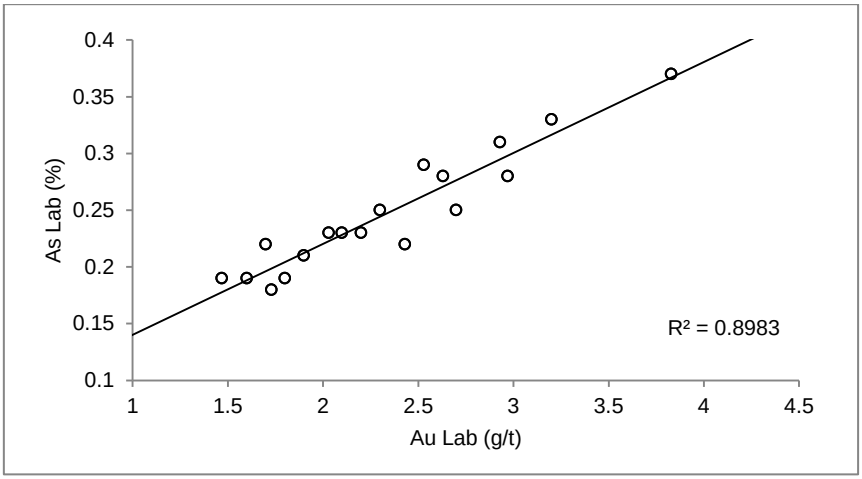


Figure 6: Arsenic correlation with gold in a feed stream.

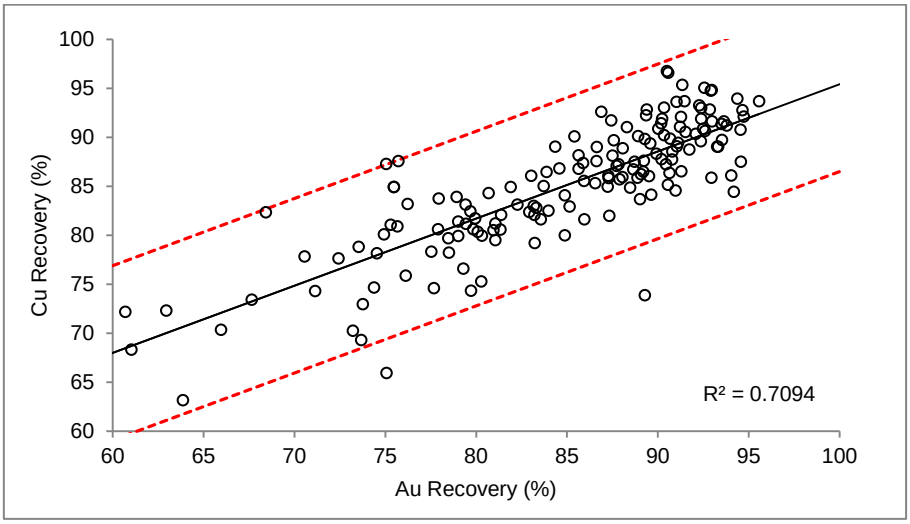


Figure 7: Cu recovery versus Au recovery. The dashed lines represent the 95% confidence interval.

$$\text{Recovery}\ (\%) = \left[\frac{c}{f}\right]\left[\frac{f-t}{c-t}\right] \times 100 \qquad \text{Equation 2.}$$

Where c is the metal assay in concentrate, f is the metal assay in feed, and t is the metal assay in tails. The true metallurgical recovery also takes in account the mass flows, and thus will differ from the two product formula.

Laser-Induced Breakdown Spectroscopy

Courier 8 analyser is based on Laser-Induced Breakdown Spectroscopy (LIBS) which is a variant of optical emission spectroscopy (OES). OES methods e.g. ICP-OES are routinely used in laboratories to determine elemental concentrations of samples. The basic principles of any OES are:

1. Atomization of the sample to produce free atomic species
2. Excitation of the atoms
3. Detection of the emitted light
4. Calibration of the measured intensity to concentration
5. Determination of concentrations

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A high energy laser (10 – 1000 mJ) is used to vaporize part of the sample and to form a cloud of plasma. The atoms in the plasma are excited to higher energy levels. In the beginning of the plasma the temperature is extremely hot and the emission spectrum is dominated by continuum emission, as local thermodynamic equilibrium does not exist. As the plasma cools down, the atoms return to lower energy states by emitting photons at characteristic wavelengths, as illustrated in figure 8.

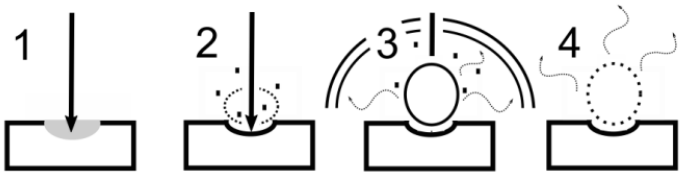


Figure 8: High energy laser pulse is directed to the sample, which absorbs the energy of the laser pulse (1). Small volume of the sample is ablated (2) High luminous plasma and a shockwave are formed and the ablated material is dissociated into excited ionic and atomic species (3). As the plasma cools down the excited species return to lower energy states emitting photons at characteristic wavelengths (4).

The light emitted by the plasma is measured using an Echelle spectrometer equipped with CCD camera. The intensity measured at a wavelength characteristic for the analysed element is proportional to the concentration of the element in the plasma. As the amount of sample vaporized by one laser pulse is small, several hundreds of pulses are averaged in one spectrum. Generally 300 – 1500 laser pulses are measured per sample. The frequency of the laser is 5 Hz, making the total measurement time per sample 1 – 5 minutes.

ALIBS analyser is not able to measure as low concentrations as XRF analysers. The advantage of a LIBS analyser is its ability to measure elements below Ca in atomic number (Ca Z=20). As refractory gold flotation processes can generally be considered as pyrite and arsenopyrite flotation i.e. sulphur flotation, the ability to measure S is beneficial for process control purposes. Another advantage of low atomic number element analysis in gold flotation is the ability to measure carbon (or aluminosilicates) in pre-flotation to optimize the carbon flotation and minimize the product losses.

The analyser was installed in a sulphide flotation circuit. The measurement parameters were 200 laser pulses averaged four times. The energy of each laser pulse was 120 mJ +/- 1 mJ. A calibration sample from each measurement was collected for laboratory analysis. The calibration model is presented in Figure 9.

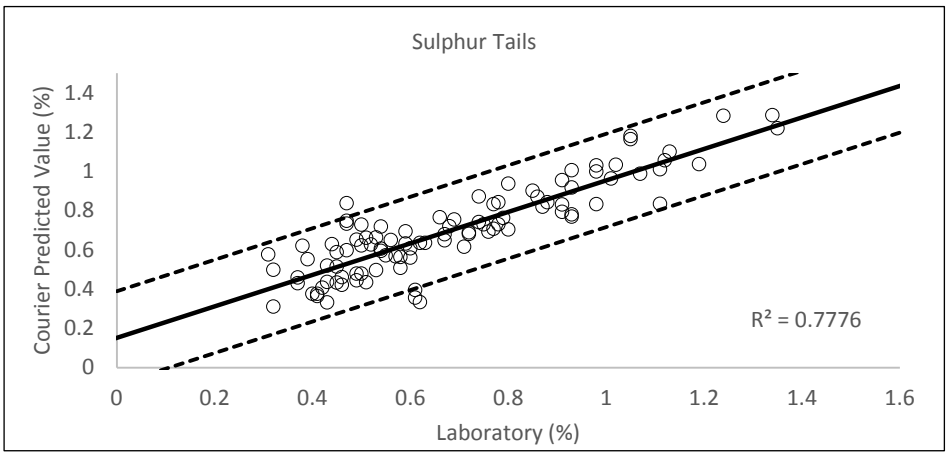


Figure 9: Sulphur calibration model. The X-axis represents the sulphur values and the Y-axis represents the Predicted values. The dashed lines represent the 95% confidence interval.

Solution Analyser system

Solution analyser systems are designed to analyse dissolved species in hydrometallurgical applications. The analyser system is designed around the sampling system, and has a variety of measurements which can be made from the solutions. A sample multiplexer enables measuring of several streams per one analyser, and minimizes the cross contamination of the streams by keeping them separate. The elemental concentrations are analysed using the Courier XRF

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analyser. Additional analyses, including titrations and voltammetry, can be made with the system, depending on the application, e.g. free acid could be measured by titration after pressure oxidation to control the acid used to treat the carbonates; the cyanide leaching circuits could be analysed for cyanide, gold, and cyanide consuming species.

One noteworthy case example of solution analyser system is a gold concentrator which has a noticeable amount of copper in the ore. The site consists of crushing and milling, pressure oxidation, counter current decantation circuit, iron removal circuit and a copper precipitation circuit. In the copper removal stage highly toxic hydrogen sulphide (H_2S) is used to precipitate copper as copper sulphide in acidic conditions according to Equation 3.

$$\mathbf{Cu^{2+} + H_2S\,(g) \rightarrow CuS\downarrow + 2H^+} \qquad \text{Equation 3.}$$

For safety and minimum environmental impact, H_2S feed is controlled in stoichiometric amount to minimize H_2S consumption and emissions. To ensure high quality of the product, some Cu (5 mg L^{-1}) is left in the solution. In low concentrations of Cu, impurities of Zn and/or Cd can precipitate as well. The main consumption of H_2S in the circuit are Fe^{3+} (approx. 0 - 50 mg L^{-1}) leftovers from the iron removal circuit and Cu^{2+} (approx. 100 - 200 mg L^{-1}).

The Cu precipitation feed and tails are analysed for Cu, Fe, As and Cr using the XRF elemental analyser. The Fe^{3+} content is analysed using an automatic titrator in the analyser system. Cr and As are measured as they might interfere with the titration, and the titration results can be corrected by measuring their concentrations. The H_2S feed to the Cu precipitation circuit is controlled by the Cu and Fe^{3+} concentrations, flow rate and the H_2S concentration of the gas.

Electrochemistry Analysis

The development of hydrophobicity of sulphide minerals and metals arises from anodic process of collector. The collector is coupled with a cathodic process e.g. reduction of oxygen. The anodic reactions give the hydrophobic character to the surface of the minerals[13]. The potential of the minerals and the flotation recovery have a clear relationship in many flotation applications (figure 11).

The reduction potential (Eh) and pH can be measured using a Chena electrochemical analyser. The reduction potential tells the tendency of a chemical species to be reduced i.e. acquire electrons. Generally the electrodes are made of platinum or other noble metal. More sophisticated measurement is possible by using electrodes made from pure minerals or minerals of the particular orebody[14].

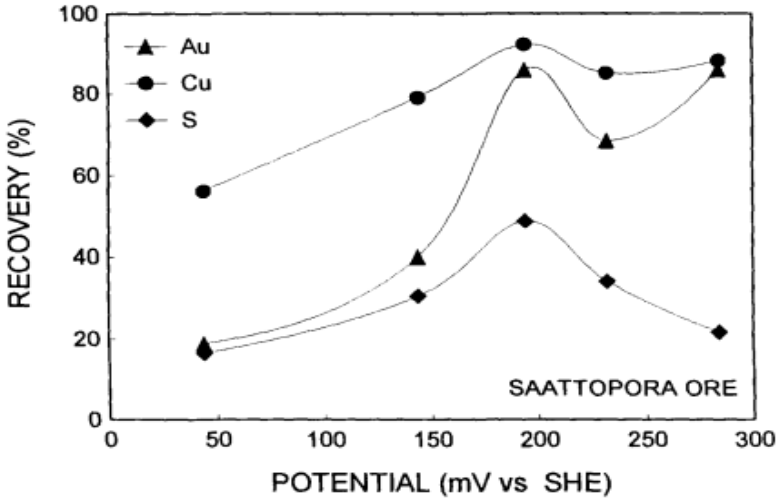


Figure 11: The relationship of flotation recovery and the potential energy in gold ore sample. (Hintikka and Leppinen 1995).

Several factors affect the Eh and pH values of the process. Reducing reagents, such as Na_2S and SO_2 decrease the Eh. Oxidizing reagents, such as O_2, $KMnO_4$ and H_2O_2, increase the Eh. Acidic solutions decrease the pH and alkaline solutions increase the pH. Correct electrochemical state is essential for best possible metallurgical performance. The optimum state of the process is

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determined through combined analysis of the electrochemical measurements and data collected from plant operation.

CONCLUSIONS

Continuous online measurement technologies provide almost instant knowledge of the state of the process. The online measurement can be used to take immediate actions to the process to prevent gold losses in flotation tailings and high energy or chemical consumption. The online analyser can also reduce the cost of on-site laboratory assays. If assays used for process control are based on strongly filtered or averaged results over a long time period, they no longer represent the true process conditions. A long time delay from actual process changes to control action makes feedback control unstable.

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REAL WORLD DEVELOPMENT AND APPLICATION OF A GOLD LEACHING AND REAGENT CONSUMPTION MODEL TO OPTIMISE CIP/CIL PROCESS PROFITABILITY

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ABSTRACT

Real-life use of gold cyanidation models is currently limited to a small number of sites, due to the following main reasons: site specificity of each model, reliance on specialised measurements, and the exhaustive set of parameters required to describe the many competing reactions occurring in a continuous leach process. More general models are of interest in academic circles but tend to be verified on a limited range of ore samples and require input information that rarely mirrors real-life data collection practices on gold mines.

To address these shortcomings, a gold cyanidation model (LeachPRO) was conceptualised and developed by Orica Ltd to display the following characteristics:

- Data inputs are principally, commonly collected measurements on gold processing plants
- Other regularly available measurements (i.e. Bottle Roll extended leach results, Free & WAD cyanide measurements, Diagnostic leach results) can be used to enhance the fit of the model if available
- Outputs allow for manipulation of the most commonly varying process optimisation parameters (throughput, head grades, reagent dose rate and location etc) and reporting results in terms of gold dissolution and reagent consumption
- The model must be adaptable across a wide range of sites via inclusion of deleterious elements such as copper and sulphur, and allow further development to include additional elements.

The development path included modification of previously published models to change data input sources, adapt for continuous operation, and include real-life impacts such as HCN volatilisation and tank bypassing. By undertaking a ‘calibration’ process for each site, fitting the model to the real process measurements & performance before scenario analysis, the model is usable for a wide range of processing operations and configurations.

The real world performance of the model on operating sites is included to evaluate its performance in optimising recovery by manipulating pH, Cyanide, DO, residence time and other variable process parameters.

Keywords: LEACHplus, gold recovery optimisation, Orica PRO Service, CIL optimisation, CIP optimisation, gold leaching, cyanide optimisation, leach process modelling, process simulation, gold recovery improvement

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INTRODUCTION

Gold Leaching Models

Modelling of the leaching process of gold with cyanide goes back many decades. Habashi[1] introduced his model, which proposes an electrochemical mechanism for the leaching reaction of gold and silver, in the sixties. He considered the diffusion mechanism of oxygen and cyanide through the boundary layer as the controlling step. Brittan and van Vuuren[2] considered a variety of factors like gravity concentration, cyanide concentration, fineness of grinding, pH and others in the 70's. Others followed – Prosser[3] studied gold dissolution kinetics in dump leaching in the 80's – he proposed that diffusion of reagents through particle pores is the rate-controlling step. In the 90's Ling et al.[4] proposed a model that considered the dissolution reaction slow-down as a consequence of reduction in available gold surface area. Also in the 90's, Crundwell et al.[5] introduced a mechanism that explained gold dissolution kinetics reduction as a consequence of a passivating layer forming on the surface of gold during leaching, influence of the gold particle size distribution was introduced by Rubisov et al.[6], influence of ore particle size was studied by De Andrade Lima and Hodouin[7] in 2000's, with others introducing their improvements to this complicated phenomenon.

Behavior of cyanide didn't receive as much attention in regards to modelling probably because of the sheer number of possible reactions of cyanide in a gold-bearing slurry. De Andrade Lima and Hodouin[7] proposed a model that takes into account particle size and free cyanide concentration as the main variables affecting cyanide reactions. Bellec et al.[8] proposed a model that considers copper and sulphide minerals separately from other cyanide consumers, as they are usually the main cyanacides.

Despite all these efforts over the decades, adoption of the cyanidation models at the 'coal face' has been very limited. It is hard to find a mine site, where these models are used extensively to optimize their cyanide set-points, DO and leach particle size in an effort to improve gold and silver recovery and/or lower processing costs. This is probably due to a number of factors:

- The models require large sets of data that are sometimes not readily available on a mine site, e.g. Bellec et al. require gold particle size distribution as an input in their leaching model, which is costly to acquire, and can have a large error due to a small sample that the test is based on
- The models are usually validated by a very small set of data based on 1 or 2 ores available to researchers at the time and their predictions are not tested extensively
- There is also a psychological barrier – some if not most metallurgist don't consider these models to be of any more value than performing individual experiments/trials to optimize their processes

We think that we can address most of these barriers. Orica has a large customer base, so potentially have visibility into a large number of data sets based on a large number of different ore types with different leaching behavior. During the development of Orica's LeachPRO model, a particular emphasis was placed on availability of data – the model uses inputs that are readily available at most mine sites. The model is also adaptable to the types of data usually available – although the model is usually improved with the amount and types of data that is supplied, modelling can start with data that is usually collected on daily and weekly basis for metallurgical accounting purposes. Helping customers generate valuable insights from existing operational data is a driving principal behind Orica's PRO Service suite of tools and services, of which LeachPRO is a critical element.

LeachPRO

The dissolution model used by LeachPRO is based on the model proposed by Bellec et al[8], which in turn is based on the electrochemical reaction with diffusion mechanism proposed by Habashi[1] and later supplemented by Rubisov et al.[6] who considered a reduction in oxygen efficiency at the reaction surface. The overall reaction rate is below:

$$\nu_{Au} = \frac{4RD_{CN}[CN^-]D_{O_2}[O_2]}{\sigma_0\left(D_{CN}[CN^-] + 8RD_{O_2}[O_2]\right)}$$

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where

ν_{Au} – rate of dissolution of Au
R – oxygen efficiency coefficient
D_{CN} – diffusivity of cyanide
$[CN^-]$ – concentration of free cyanide
D_{O2} – diffusivity of oxygen
$[O_2]$ – concentration of oxygen in the liquid phase
σ_0 – thickness of the boundary layer

This reaction equation is then applied to four types of gold particles based on their liberation: fully liberated, exposed, available through particle pores, and locked. The proportions of the four types of gold are calculated, for each ore particle size range and based on model estimated gold particle distribution, with the following equations:

$$P_{Au_L} = \frac{{d_g}^3 + 2.25{d_g}^2\,(d_p - d_g)}{{d_p}^3}$$

$$P_{Au_\infty} = \frac{(d_p - d_g - 2\sigma_p)^3}{{d_p}^3}$$

$$P_{Au_P} = \frac{(d_p - d_g)^3 - (d_p - d_g - 2\sigma_p)^3}{{d_p}^3}$$

where:

P_{AuL}- proportion of liberated Au
$P_{Au\infty}$ - proportion of inaccessible Au
P_{AuP} – proportion of Au accessible through pores
d_g – diameter of gold particle
d_p – diameter of ore particle
σ_p – distance from the surface of the ore particle to the surface of the gold particle

Proportion of particles exposed on the surface is calculated as the difference between total gold and the sum of liberated, accessible via pores and locked. These equations were derived by Bellec et al[8] through geometric analysis by assuming that gold particles were regular cubes within ore particles approximated as regular cubes. For other assumptions and detailed procedure, please go to Bellec et al.[8]

The cyanide consumption model follows approach taken by De Andrade Lima and Hodouin[7], later modified by Bellec et al.[8] The cyanide consumption rate is:

$$\omega_{CN}(d_p) = K'_{C_1}[CN]^{\alpha_1}[Cu]^{\beta_1} + K'_{C_2}[CN]^{\alpha_2}[S]^{\beta_2} + \frac{K_d[CN]}{\sigma_0 {d_p}^{\theta_3}}$$

where

$$K'_{C_1} = \frac{K_{C_1}}{d_p^{\theta_1} - k_{c_{11}}}\left(1 + \frac{[Au]_s}{[Au_0]_s}\right)^{\lambda_1}$$

$$K'_{C_2} = \frac{K_{C_2}}{d_p^{\theta_2} - k_{c_{22}}}\left(1 + \frac{[Au]_s}{[Au_0]_s}\right)^{\lambda_2}$$

and

ω_{CN} – rate of cyanide disappearance
[Cu] – concentration of copper in the ore
[S] – concentration of sulphur in the ore
K'_{C1}, K'_{C2}, K_d – respective reaction rate coefficients
K_{c1}, K_{c2}, k_{c11}, k_{c22}, α_1, α_2, β_1, β_2, θ_1, θ_2, θ_3, θ_s – fitting parameters

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Modifications

As mentioned in the introduction, leaching and cyanide consumption models attracted low amount of interest by the intended users – metallurgists at the gold mines. To make Orica's model more relevant to end users, the following changes have been made:

1. LeachPRO contains mechanisms that are very relevant to CIP/CIL processes that were not included previously: effect of pH on free cyanide concentration and loss of cyanide through volatilization (dependent on pH and cyanide concentration and also other factors like temperature, air/oxygen sparging), loss of cyanide through the reaction with oxygen catalyzed by activated carbon, which is especially relevant for CIL processes or when leaching is a major factor in adsorption stages in CIP processes
2. LeachPRO was adapted to continuous leaching process with non-ideal behavior like by-passing, which is often experienced in the large CIP/CIL tanks
3. Additional data, which is normally routinely collected by sites, was included in the model to exclude irrelevant parameter sets as possible solutions and to produce a better fit. The data includes extended tail leaches (bottlerolls), diagnostic leaches, and cyanide speciation tests on the plant tails.
4. The software performs a check for degrees of freedom – is the amount of data sufficient to perform a successful calibration, before calculations are attempted. Insufficient data will prompt the user to disable certain functions like considering cyanide consumption due to copper and sulphides separately or to reduce the number of parameters allowed to perform optimization.

Once calibration of the model is performed, the parameters are stored and the user is able to create scenarios to predict process behavior (gold recovery, cyanide consumption) based on changes to following variables:

- Leaching throughput
- Particle size
- Residence time (or changes to number of leaching tanks)
- Cyanide addition rates, pH, DO and carbon concentrations at every stage/tank
- Changes to by-passing ratios also at every stage/tank

RESULTS

LeachPRO model was used with a number of sets of data that have been collected over time for the purposes of providing technical support to Orica's Sodium Cyanide customers.

Below is an example of fast leaching oxidized ore. We can see that the model fits the data very well for both cyanide and gold on solids profiles (see **Figure *1*** and **Figure *2***). Fitted locked Au and cyanide consumed by Cu are also very close to data (0.17ppm fitted vs. 0.16 ppm, and 51 ppm fitted vs. 52 ppm, for $[Au]_s$ and [Cu-CN], respectively). Whilst this could theoretically be achieved due to the number of fitting parameters used by the model, the additional data provided (gold not accessible, cyanide consumed by Cu estimated from WAD CN) lowers the degrees of freedom and thus increases confidence in the applicability of the solution. The type of data provided for the model is shown in **Table 1**:

Table 1: Data for the model - Gold Mine 1

Feed	Tank profiles	Tails
Tonnage, sizing, %solids, $[CN^-]$, $[Au]_s$, $[Cu]_s$, $[S]_s$,	%solids, $[Au]_s$, $[CN^-]$, pH, DO, carbon concentration, cyanide addition rate (kg/t), residence time, by-passing %	%solids, $[Au]_s$, $[CN^-]$, pH, WAD CN, $[Au]_s$ locked

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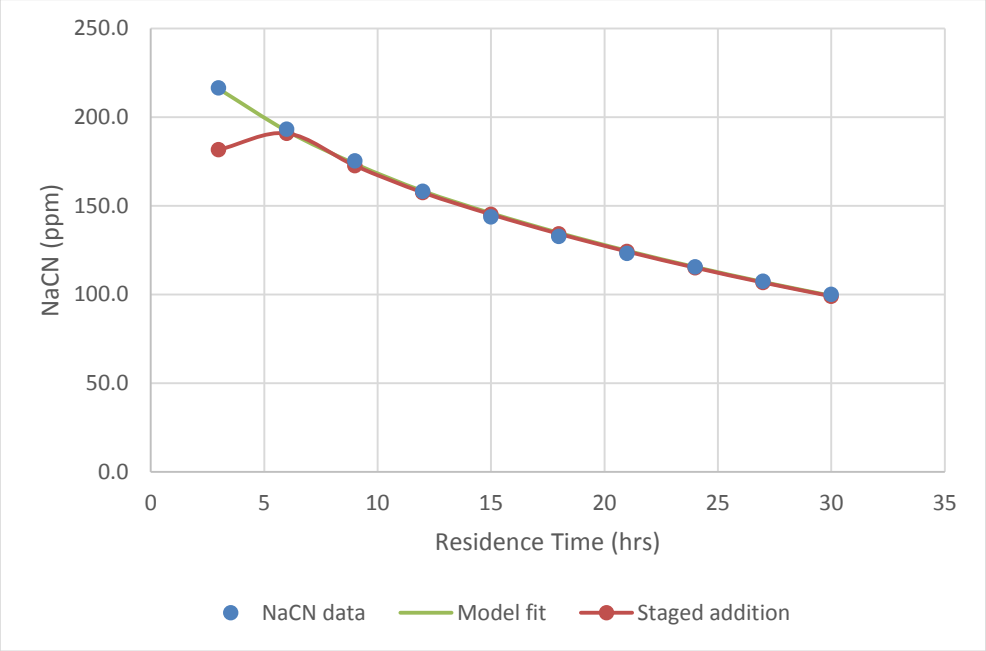


Figure 1: Cyanide profile - model vs. actual plant data and model prediction for cyanide staged addition

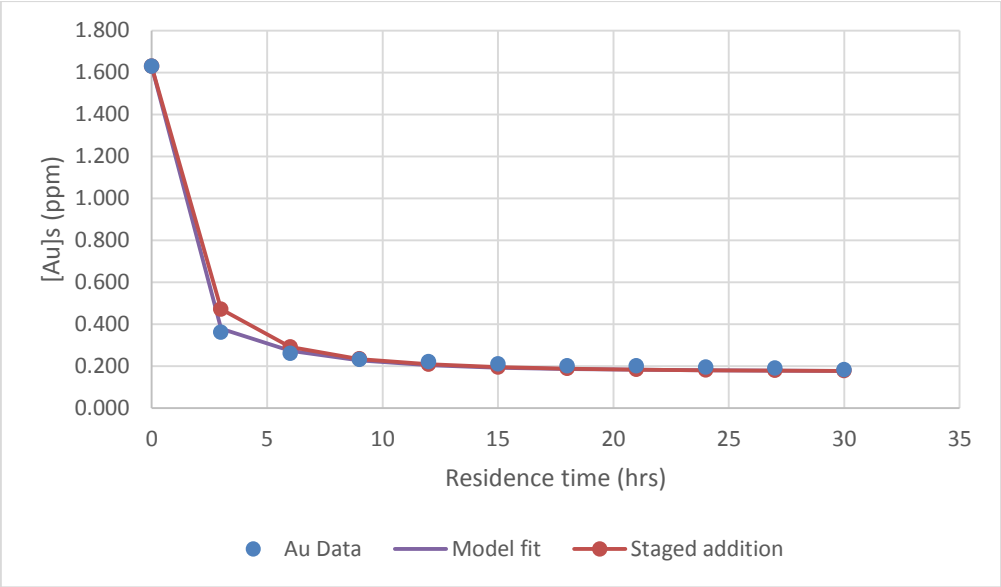


Figure 2: Gold profile - gold data, model fit and simulated staged addition for Gold Plant 1

The data provided is still not enough to completely specify the problem, so the model fit is one of the number of solutions possible. This is especially true for the parameters which specify the gold particle size distribution and the thickness of the boundary layer – these parameters were fitted based on the estimated typical thickness of the boundary layer in typical leach tanks. The model fit and its predictive power clearly can be further increased by providing the gold particle size distribution as an optional input.

One other way of increasing confidence in the model is to make a prediction and use the actual results to recalculate the parameters based on two or more data sets. On the above data set, the current model predicts a 5-10% drop in cyanide consumption when cyanide is controlled in two leach tanks, instead of just one – commonly called staged addition of cyanide. This enables a lower cyanide set-point in the first tank, while controlling the set-point in the second tank at a level, which produces similar cyanide concentration in the last tank. The prediction of 5 – 10% savings is in line with previous estimated savings in systems, where cyanide is controlled in two

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or more leach tanks vs. one[9]. The model also predicts virtually the same gold recovery (increase in gold on solids of 0.001 ppm). This prediction will be tested in near future at the site in question, and we are highly confident, as the model has already been used to accurately hind-cast the results of another trial at this site.

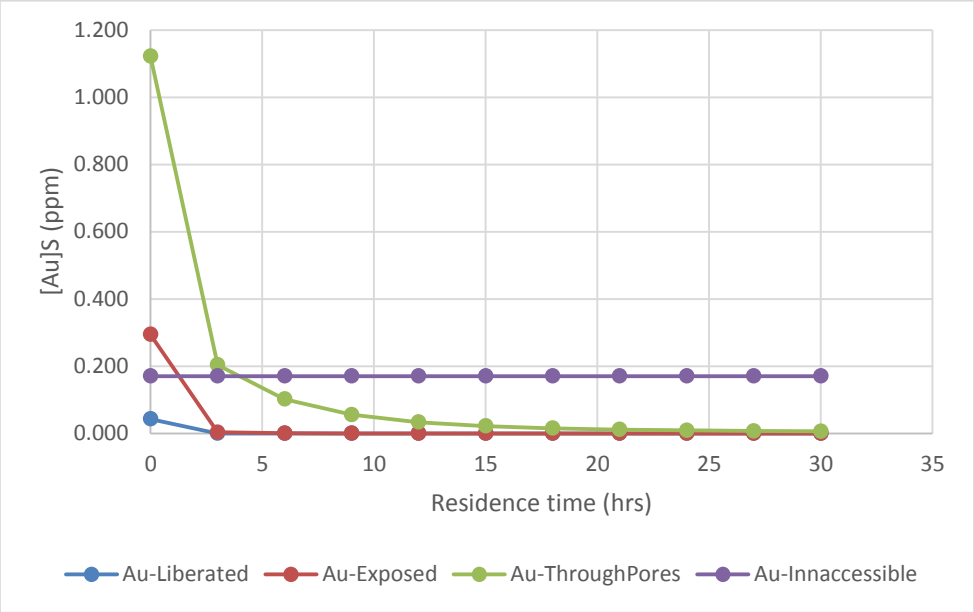


Figure 3: Individual gold types vs. residence time as predicted by the model

Below is another example of a leaching process, this time a sulphidic ore with very high cyanide and oxygen consumptions and high refractory component. The data used to fit the model is the same as in Table 1, with addition of concentration in the tails of cyanide consumed by sulphides.

Again we can see a very good fit to the supplied data (see Figure 4)

The model fit is close, although the system contains a complication - pre-conditioning tank, where the cyanide concentration is very low as compared to the rest of the circuit. Again, due to the addition of extra data in the form of insoluble gold (based on bottle roll results) and Cu and S cyanide in the tails, this solution is the best fitting possibility out of a number of possible solutions.

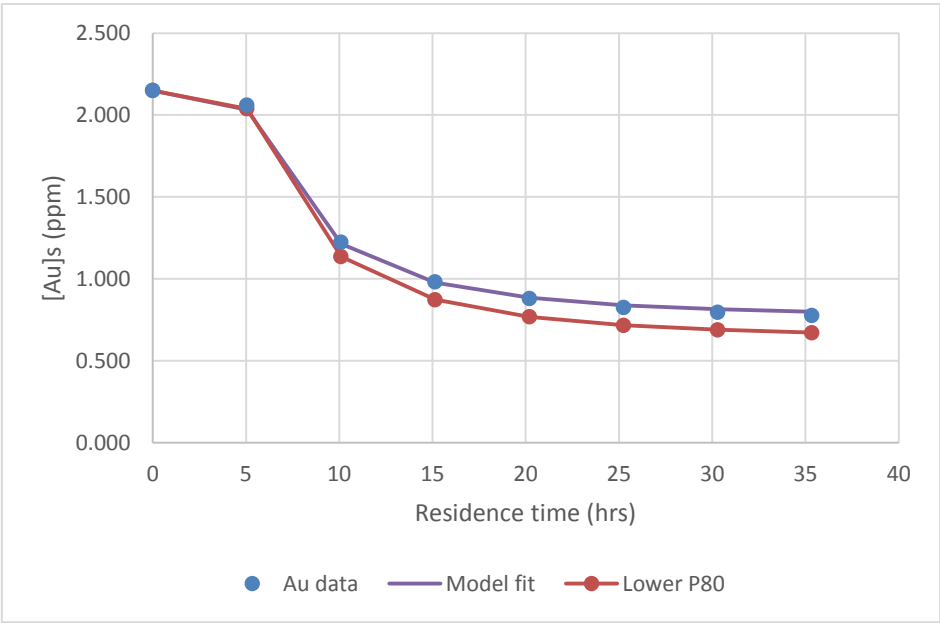


Figure 4: Gold Plant 2 – gold data, model fit and simulated effect of lower P80

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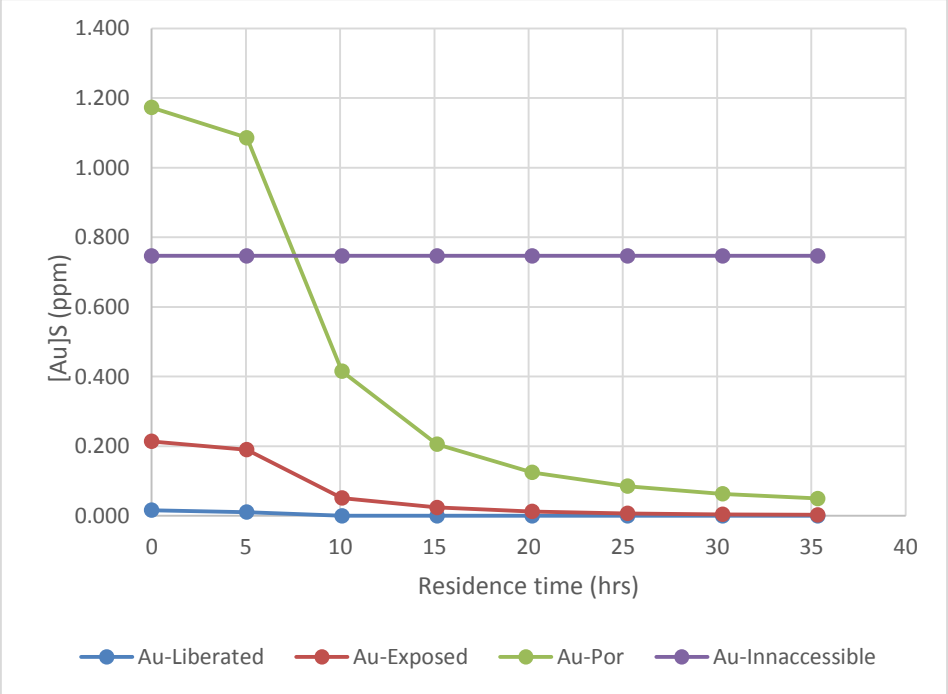


Figure 5: Gold Plant 2: Individual gold types vs. time – based on original data

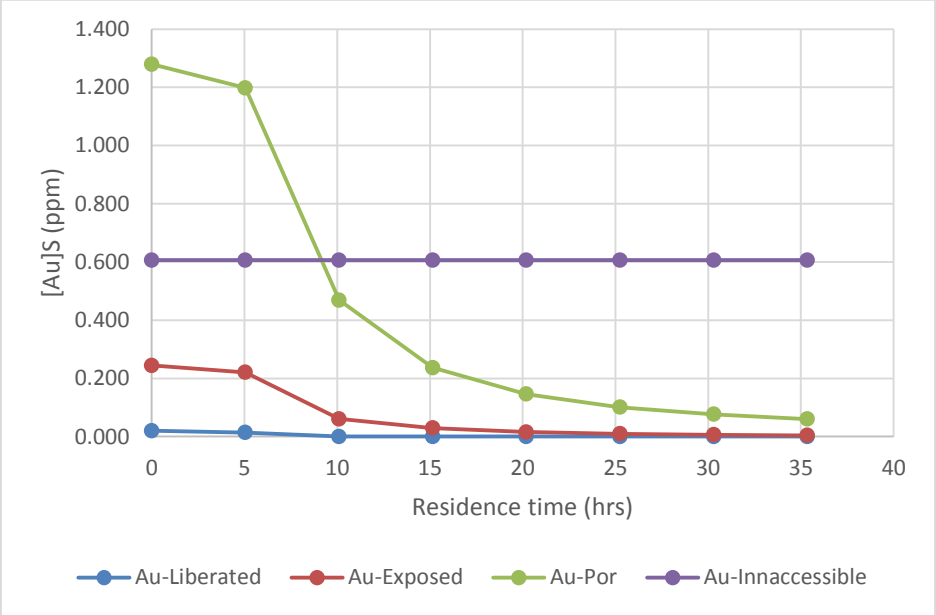


Figure 6: Gold Plant 2 – individual gold types as predicted by the model for lower P80

Based on the current set of fitted parameters, it should be possible to increase gold recovery by a decrease in the grind particle size. According to the model and the current optimised parameters, size reduction from 60% passing 75 micron to 71% passing 75 micron could result in lowering gold on solids in the tails by about 0.1 ppm, mainly due to lower concentration of inaccessible gold. Cyanide concentrations are reduced at the same addition rate, as shown in Figure 7, however the concentration of leachable gold in the tails in unaffected (see Figure 5 and Figure 6). Although unclear at this stage, if the benefits will outweigh the costs of finer grinding, it is certainly an incentive for the plant management to invest in further testwork (or gold particle size distribution analysis to improve this model), so that the net benefit could be estimated with a higher degree of confidence.

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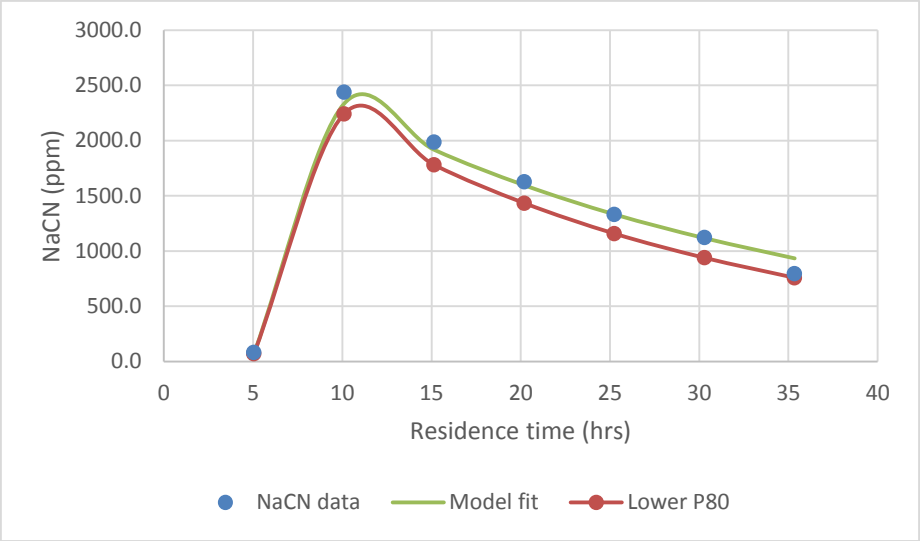


Figure 7: Cyanide profiles, data vs. model and prediction for finer grind, for Gold Plant 2

Below is another example – underground free milling ore with low cyanide consumption and low refractory component. We can see that the cyanide profile fits very closely with the model, however the gold concentration is underestimated in the front tanks. The reason for this error is as yet unclear and could be a simple agitator wear and/or reduction in tank volume due to sanding up, but it could also mean a deficiency of the model to describe a lower initial leaching rate due to a number of possibilities, e.g. gold surface passivation. The reason behind this error will be further investigated, so that this phenomenon can be modelled successfully. The input data was of the same type as in Table 1.

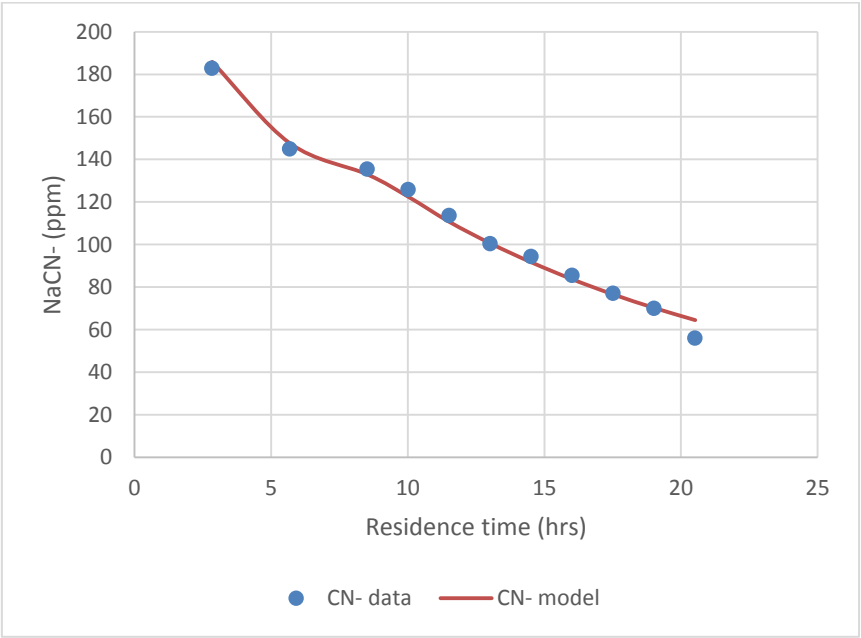


Figure 8: Cyanide profile data vs. the model fit.

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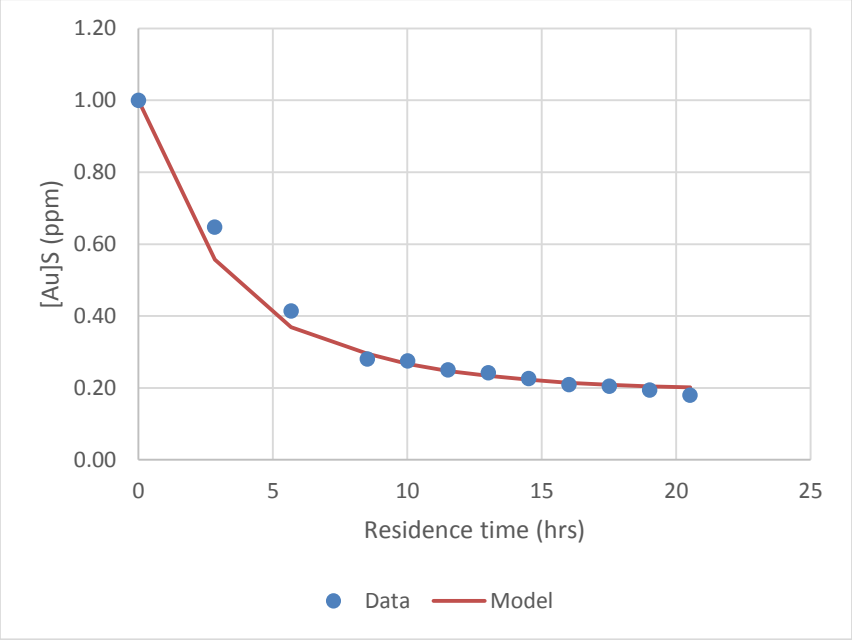


Figure 9: Gold on solids profile data vs. the model fit.

CONCLUSIONS AND FUTURE DEVELOPMENT

Despite being in the early stages of application, the existing cyanide consumption and leaching model is already a useful addition to the set of tools available to optimize gold leaching plants. Although it requires a large data set, most of the data required for the model is routinely collected for gold accounting and reagent control purposes, and 'additional' data such as cyanide speciation in the tails is routinely collected for environmental purposes. There are also some routine tests that are not performed on the whole circuit, e.g. DO is usually performed in the leaching tanks, but sometimes its measurements are not performed in the adsorption tanks. For process optimization and control purposes, it is strongly recommended to perform DO measurements in adsorption tanks, even if the rate of gold leaching in those tanks is very low.

The leaching and cyanide consumption models can be enhanced in the following ways:

- Support for multiple data sets – parameter estimation could be greatly improved, if more than 1 data set is used, especially if the data sets are based on different set-points for cyanide, pH, DO and others.
- Batch data sets – these could be used to evaluate any behavior due to agitator and/or baffle wear, lower tank volumes due to sanding up, and bypass and dead zones.
- Providing more detailed cyanide speciation data in the tails – not only Cu and S, but also other metals and other cyanide species, e.g. cyanate could be used to estimate cyanide consumption in the presence of activated carbon.
- Enhancing the leaching model with effects of sulphide galvanic coupling and surface blinding.
- Enhancing the leaching model with effects of preferential grinding of either gold-bearing minerals or gangue minerals.
- Further validation and improvements based on more data sets.

These improvements will be assessed and implemented in the near future.

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A PRELIMINARY EVALUATION OF ALKALINE GLYCINE AS AN ALTERNATIVE TO CYANIDE FOR GOLD EXTRACTION

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ABSTRACT

This paper presents an evaluation of alkaline glycine chemistry as an alternative to conventional cyanidation for processing a copper-gold ore. Process modelling is used to build numerically rigorous mass-energy balances for two circuits processing a chalcopyrite-bearing gold ore, one using conventional cyanide chemistry and the other using alkaline glycine. The balances are used to calculate estimates of capital and operating costs for the two circuits. The results are used to compare the alkaline glycine circuit to the cyanide circuit using simple financial modelling.

The results indicate that the alkaline glycine chemistry appears to be competitive against cyanide chemistry.

Keywords: Arithmetek, gold extraction, alkaline glycine, alternative to cyanide, process evaluation, financial modelling

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INTRODUCTION

Although dominant in current gold extraction technology, cyanide is extremely toxic. It has been banned in some jurisdictions and in others it is subject to strict environmental regulation. This has resulted in the evolution of technology for destruction of cyanide species in effluents, such as the air-SO_2 technique[1,2] originally developed by Inco. In some applications, such as processing copper bearing gold ores, the consumption of cyanide is unacceptably high, leading to enhancements such as the SART process[3], developed by Lakefield Research (now SGS Canada) with support from Teck Corporation, for the recovery and recycle of cyanide.

The toxicity of cyanide has also led to the exploration of non-cyanide technologies, such as leaching with thiosulphate[4,5,6]. A new approach was recently proposed[7, 8, 9, 10] using alkaline glycine as the lixiviant.

This paper presents the results of a process modelling exercise done to generate a preliminary evaluation of the alkaline glycine chemistry in terms of capital and operating costs in a circuit using this chemistry, compared to the equivalent costs for a cyanide circuit processing the same ore.

FEED

The feed chosen for this study is one used in previously published work[11] done by SGS in Lakefield, Ontario, Canada. Table 1 shows analysis of the feed and a corresponding suite of minerals used to represent the ore.

Table 1: Feed and mineralogy

Element	ppm	Element	ppm	Mineral	mg/kg	Mineral	mg/kg
Au	44	Mn	450	Au	44	MnO	581
Ag	11	Na	5990	Ag	11	Na_2SiO_3	15902
Cu	2300	Ni	92	$CuFeS_2$	6643	NiO	117
Al	49900	P	375	Al_2O_3	94284	P_2O_5	859
As	13500	Pb	119	As_2O_3	17824	PbO	128
Ba	1990	Sb	170	BaO	2222	Sb_2O_3	204
Be	0.9	Sr	215	BeO	3	SrO	254
Ca	14100	Ti	2400	CaO	19729	TiO_2	4004
Co	30	V	158	CoO	38	V_2O_5	282
Cr	138	Y	8.5	Cr_2O_3	271	Y_2O_3	11
Fe	82000	Zn	187	Fe_2O_3	114348	ZnO	233
K	13700	S	4000	K_2SiO_3	27030	SiO_2	679011
Mg	9630			MgO	15969		

The process model of the cyanide circuit assumes the gold dissolution and cyanide consumption measured in the previously published work[11]. The process model of the alkaline glycine circuit assumes the same dissolution of gold.

CYANIDE

A conventional carbon-in-pulp cyanidation circuit was modelled as a baseline against which to compare the alkaline glycine circuit. Figure 1 is a diagram of the cyanide circuit, the main sections of which are:

- Incoming ore is slurried with recycled and fresh water.
- The pH of the feed slurry is raised with lime and cyanide is added to leach gold and silver.

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- The leached slurry is contacted with activated carbon to capture dissolved gold and silver.
- The barren slurry is treated with air and sodium sulfite to destroy the residual cyanide.
- The slurry after cyanide destruction is thickened, the supernatant being recycled to the leach and the underflow leaving the circuit as tailings.
- The loaded carbon is eluted with a solution of sodium hydroxide and sodium cyanide.
- The eluted carbon is washed with hydrochloric acid and rinsed with water.
- After thermal regeneration the washed carbon is returned to the CIP section.
- The solution from the carbon elution step is electrolysed to recover metallic gold and silver.
- Part of the spent electrolyte is bled back to the leach to control impurity levels.
- The remaining spent electrolyte is replenished with sodium hydroxide, sodium cyanide and water and recycled to the carbon elution step.

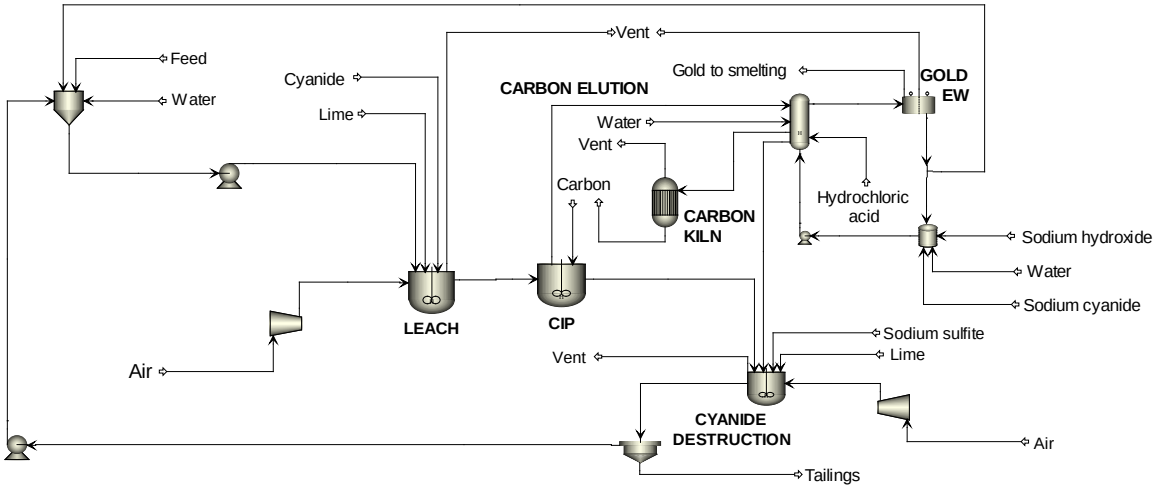


Figure 1: CIP cyanidation circuit

Chemistry

Table 2 shows the leach stoichiometry assumed for the cyanide circuit. The numbers in the right hand column are the fractional conversions of the first reactant listed for each reaction. The experimental work done on the cyanide leach only measured the extents of dissolution of gold and copper. Silver was assumed to mimic gold. The amounts of cyanide and lime used in the experimental work were assumed for this model.

Table 2: Cyanide leach stoichiometry

Reaction	Conv.
$4Au^{o} + O_2 + 8CN^- + 2H_2O \rightarrow 4Au(CN)^- + 4OH^-$	0.850
$4Ag^{o} + O_2 + 8CN^- + 2H_2O \rightarrow 4Ag(CN)^- + 4OH^-$	0.850
$CuFeS_2 + O_2 + 2H_2O + 5CN^- \rightarrow Fe(OH)_3 + 2CNS^- + Cu(CN)_3^{2-} + OH^-$	0.766

The stoichiometry used to represent the adsorption of gold and silver onto activated carbon is shown in Table 3. Bold denotes adsorbed species. The model manipulates the amount of activated carbon to make the loaded carbon carry 5 grams of gold per kilogram of carbon.

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Table 3: Adsorption and elution stoichiometry

Adsorption
$Ca^{2+} + 2Au(CN)_2^- \rightarrow \mathbf{Ca[Au(CN)_2]_2}$
$Ca^{2+} + 2Ag(CN)_2^- \rightarrow \mathbf{Ca[Ag(CN)_2]_2}$
Elution
$\mathbf{Ca[Au(CN)_2]_2} + 2OH^- \rightarrow \mathbf{Ca(OH)_2} + 2Au(CN)_2^-$
$\mathbf{Ca[Ag(CN)_2]_2} + 2OH^- \rightarrow \mathbf{Ca(OH)_2} + 2Ag(CN)_2^-$

The gold and silver electrolysis reactions are listed in Table 4. The extents of the gold and silver deposition reactions are manipulated to give 0.1 g/L gold and 0.1 g/L silver in the exit solution. The third reaction, anodic oxidation of the free cyanide, was assumed to go to completion.

Table 4: Gold/silver electrolysis

Metal deposition
$4Au(CN)_2^- + 4OH^- - 4Au^o + 8CN^- + 2H_2O + O_2$
$4Ag(CN)_2^- + 4OH^- - 4Ag^o + 8CN^- + 2H_2O + O_2$
Cyanide oxidation
$2CN^- + 6H_2O \rightarrow 2NH_3 + 2H_2 + 2CO_2 + 2OH^-$

Air-SO_2 technology was assumed for the cyanide destruction section, with the SO_2 coming from sodium sulfite. The stoichiometry used is listed in Table 5. These reactions were assumed to go to completion.

Table 5: Cyanide destruction stoichiometry

$Na_2SO_3 + H_2O \rightarrow SO_2 + 2Na^+ + 2OH^-$
$2Cu(CN)_3^{2-} + 6SO_2 + 6½O_2 + 23H_2O \rightarrow 2Cu(OH)_2 + 6CNO^- + 6SO_4^{2-} + 14H_3O^+$
$CN^- + SO_2 + O_2 + 3H_2O \rightarrow CNO^- + SO_4^{2-} + 2H_3O^+$

ALKALINE GLYCINE

Two conceptual circuits were examined, both using alkaline glycine instead of cyanide chemistry. Circuit 1 mimics the cyanide circuit and allows a portion of the glycine to be lost to the tailings. Circuit 2 uses a more complex and therefore also more capital intensive configuration in which glycine loss to the tailings is essentially eliminated.

Figure 2 is a diagram of the simpler circuit using alkaline glycine chemistry. The main sections in this circuit are:

- The incoming ore is slurried with make-up water and recycled solution. The resulting slurry is leached with air and glycine at pH 11. Steam is added to heat the leach to 60°C.
- The hot leached slurry passes to a carbon-in-pulp (CIP) section in which the dissolved gold and silver are adsorbed.
- The barren slurry is thickened, the supernatant returns to the leach and the underflow leaves the circuit as tailings.
- The loaded carbon is eluted with sodium hydroxide.
- The eluate is electrolysed to recover the gold and silver, which leave the circuit to be smelted to doré.

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- Part of the resulting spent electrolyte is bled back to the CIP section to control the levels of impurities and degradation products. The balance is replenished with sodium hydroxide and water and recycled as eluant for stripping the loaded carbon.
- The eluted carbon is washed with hydrochloric acid. Some of the spent acid is removed and the balance is replenished and recycled.

Figure 3 illustrates the more complex alkaline glycine circuit. The single tailings thickener is replaced by a six-stage counter-current decantation train and the following extra steps are added:

- Sodium carbonate is added to the hot slurry from the CIP section to precipitate calcium as calcium carbonate.
- The hot slurry ex the calcium precipitation step is passed through a counter-current decantation (CCD) train in which water is used to wash the solids and recover glycine into the supernatant.
- The underflow from the CCD train leaves the circuit for disposal as tailings.
- The hot CCD overflow is flashed at sub-atmospheric pressure to generate the steam needed to heat the leach. The sub-atmospheric steam generated is compressed to atmospheric pressure and returned to the leach.
- The cooled solution from the sub-atmospheric flash is pumped back to atmospheric pressure and then sent through a reverse osmosis step to produce the wash water required by the CCD train.
- The concentrated liquid from the reverse osmosis step is split, part returning to the leach and part passing to a step in which sodium sulphide is added to precipitate the base metals (mainly copper) as a sulphide precipitate that is settled from the resulting slurry and removed from the circuit as a by-product. The remaining liquid from the sulphide precipitation step returns to the leach.

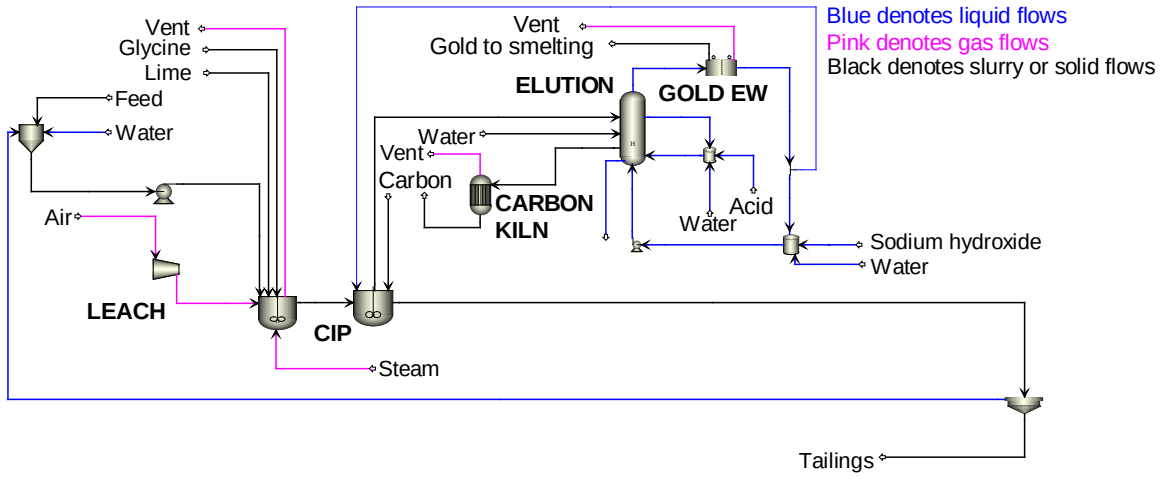


Figure 2: Alkaline glycine circuit 1

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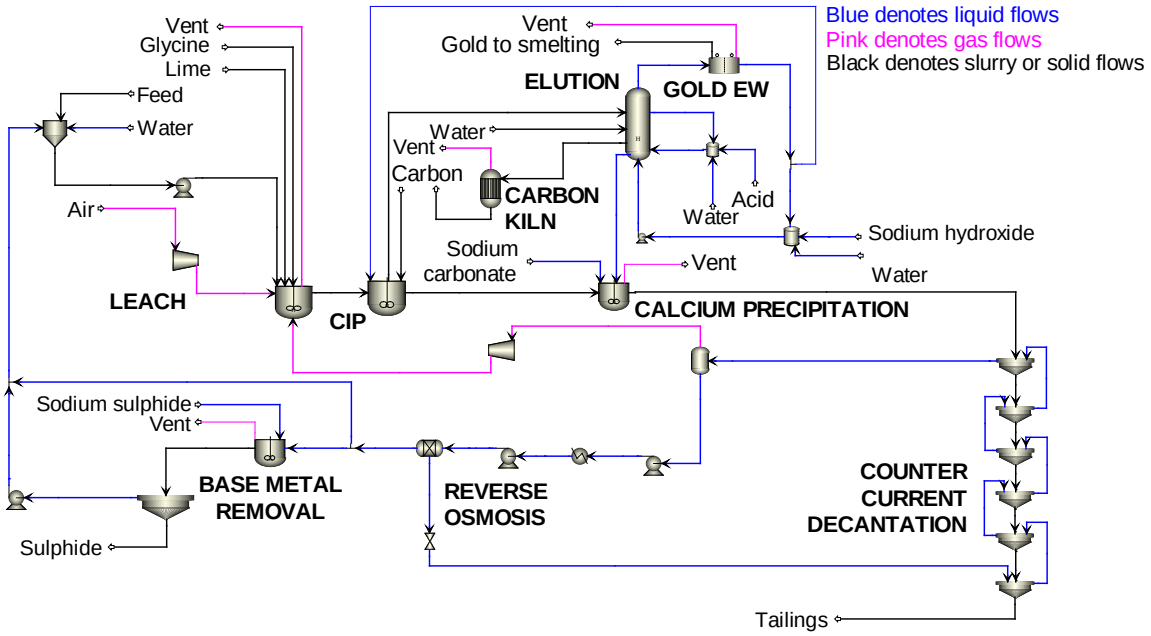


Figure 3: Alkaline glycine circuit 2

Leach

The alkaline glycine technology is still in its infancy and experimental comparisons to cyanide, using the same ore, have not yet been published. For the evaluation presented in this paper, the alkaline glycine chemistry was assumed to give the same dissolutions of gold, silver and copper (chalcopyrite) as were measured in work on cyanidation that was presented previously[11]. In alkaline media, iron, manganese, calcium, chromium and most other lithophile elements do not form glycinate complexes and thus these elements do not leach in alkaline glycine. Glycine does form complexes with gold, silver, copper, zinc, lead, nickel and cobalt. The stoichiometry used to represent the leach chemistry is presented in Table 6. The conversions listed are the fractions dissolved of the first reactant listed for each reaction. The oxide minerals that do dissolve were assumed to dissolve completely. The sulphide sulphur in the chalcopyrite that is dissolved was assumed to become sulphate.

Table 6: Glycine leach chemistry

Stoichiometry	Conversion
$4Au + 8C_2H_4NO_2^- + 2H_2O + O_2 \rightarrow 4Au(C_2H_4NO_2)_2^- + 4OH^-$	0.850
$4Ag + 8C_2H_4NO_2^- + 2H_2O + O_2 \rightarrow 4Ag(C_2H_4NO_2)_2^- + 4OH^-$	0.850
$CuFeS_2 + 2C_2H_4NO_2^- + 1½H_2O + 2¾O_2 \rightarrow Cu(C_2H_4NO_2)_2 + Fe(OH)_3 + SO_4^{2-}$	0.766
$PbO + 2C_2H_4NO_2^- + H_2O \rightarrow Pb(C_2H_4NO_2)_2 + 2OH^-$	1.000
$NiO + 2C_2H_4NO_2^- + H_2O \rightarrow 2Ni(C_2H_4NO_2)_2 + 2OH^-$	1.000
$CoO + 2C_2H_4NO_2^- + H_2O \rightarrow Co(C_2H_4NO_2)_2 + 2OH^-$	1.000
$ZnO + 2C_2H_4NO_2^- + H_2O \rightarrow Zn(C_2H_4NO_2)_2 + 2OH^-$	1.000

Glycinate complexes are larger than the corresponding cyanide complexes, which could make diffusion slower in the alkaline glycine technology. Higher temperatures have been seen to enhance the leach kinetics in the alkaline glycine chemistry[9], which is why the model uses a leach temperature of 60°C instead of ambient temperature as used in cyanide technology. While copper and cyanide have been found to catalyze the dissolution reactions in the alkaline glycine system[10], the appropriate leach time in a system using only alkaline glycine is presently still a matter of some conjecture. Tests have shown that chalcopyrite can be fully leached in 24 hours, after fine grinding and using cyanide as a catalyst[8].

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Recovery of dissolved gold via carbon in pulp was chosen for this exercise. Resin in pulp might also be suitable, but that has yet to be determined. The extents of adsorption and elution were assumed to be the same as in cyanidation. Table 7 lists the stoichiometry used to represent the CIP section of the circuit. Bold denotes the solid phase. The amount of carbon was manipulated to make the loaded carbon carry five grams of gold per kilogram of carbon. For this work the assumption was made that operating the CIP train at about 60°C gives the same extent and rate of adsorption as are achieved in conventional cyanide technology.

Table 7: CIP stoichiometry

Loading	Conversion
$Ca^{2+} + 2Au(C_2H_4NO_2)_2^- + \mathbf{GAC} \rightarrow \mathbf{GAC{\bullet}Ca(Au(C_2H_4NO_2)_2)_2}$	0.999
$Ca^{2+} + 2Ag(C_2H_4NO_2)_2^- + \mathbf{GAC} \rightarrow \mathbf{GAC{\bullet}Ca(Ag(C_2H_4NO_2)_2)_2}$	0.999
Elution	
$\mathbf{GAC{\bullet}Ca(Au(C_2H_4NO_2)_2)_2} + 2OH^- \rightarrow \mathbf{Ca(OH)_2} + 2Au(C_2H_4NO_2)_2^-$	1.0
$\mathbf{GAC{\bullet}Ca(Ag(C_2H_4NO_2)_2)_2} + 2OH^- \rightarrow \mathbf{Ca(OH)_2} + 2Ag(C_2H_4NO_2)_2^-$	1.0

Table 8 lists the stoichiometry used to represent the recovery of gold and silver by electrolysis from the eluate from the CIP section of the circuit. For want of data, the extent of glycine degradation by anodic oxidation was assumed to be 50 percent and the anodic degradation of the formic acid from the glycine degradation was also assumed to be 50 percent. The electrolysis was assumed to reduce the dissolved gold and silver to 0.1 g/L each in the spent electrolyte, hence the conversions shown. The gold and silver in the bleed of spent electrolyte return to the CIP section where they are recaptured.

Sodium carbonate is added to the slurry leaving the CIP step to precipitate enough calcium carbonate to make the supernatant from the CCD train sufficiently under-saturated in calcium (carbonate or sulphate) that the concentrated solution after the removal of water in reverse osmosis is also under-saturated in calcium. This is necessary because otherwise calcium fouling would render the reverse osmosis step inoperable.

Table 8: Electrowinning of gold/silver

Reaction	Conversion
$4Au(C_2H_4NO_2)_2^- + 3OH^- \rightarrow 4Au + 7C_2H_4NO_2^- + H_2O + CO_2 + NH_3 + HCOOH$	0.90
$4Ag(C_2H_4NO_2)_2^- + 3OH^- \rightarrow 4Ag + 7C_2H_4NO_2^- + H_2O + CO_2 + NH_3 + HCOOH$	0.67
$C_2H_4NO_2^- + 3H_2O \rightarrow CO_2 + NH_3 + 2H_2 + HCOOH$	0.5
$HCOOH \rightarrow CO_2 + H_2$	0.5

The sulphide precipitation step controls the level of base metals in the circuit. Table 9 lists the stoichiometry used to represent the sulphide precipitation reactions. Bold denotes the solid phase. These reactions were all assumed to go to completion.

Table 9: Sulphide precipitation

Stoichiometry	Conversion
$Cu(C_2H_4NO_2)_2 + S^{2-} \rightarrow \mathbf{CuS} + 2C_2H_4NO_2^-$	1.000
$Ni(C_2H_4NO_2)_2 + S^{2-} \rightarrow \mathbf{NiS} + 2C_2H_4NO_2^-$	1.000
$Co(C_2H_4NO_2)_2 + S^{2-} \rightarrow \mathbf{CoS} + 2C_2H_4NO_2^-$	1.000
$Pb(C_2H_4NO_2)_2 + S^{2-} \rightarrow \mathbf{PbS} + 2C_2H_4NO_2^-$	1.000
$Zn(C_2H_4NO_2)_2 + S^{2-} \rightarrow \mathbf{ZnS} + 2C_2H_4NO_2^-$	1.000

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The assumptions used in this paper for the alkaline glycine technology will require experimental confirmation or correction in due course, should the alkaline glycine technology be deemed to merit further development. The question addressed in this paper is whether or not this chemistry merits further development.

MODELLING

Commercially available process simulation software known as Aspen Plus was used to develop numerically rigorous mass-energy balances for the circuits outlined above. The process models were adjusted to reproduce the limited available data and the required assumptions. The resulting balances were used in conjunction with estimates of the various unit costs for reagents and utilities to calculate the variable operating cost for each circuit.

Estimates of the capital cost of installed process equipment were generated for each circuit using commercially available cost estimation software known as Aspen Process Economic Analyser. The mass-energy balances were electronically exported into the cost estimation software, the various unit operations in the process models were mapped to the desired equipment (for example agitated tanks in the case of leaching) and material of construction and the required residence time in each item of process equipment were specified. The cost estimation software uses the volumetric flow information from the imported balance and the specified residence time to size each item of process equipment. It calculates the amounts of material and manpower needed to fabricate and install that item, then calculates the fabrication and installation cost from databases of material and manpower costs. The databases are based on a large number of real projects and are updated regularly. The software uses default allowances for process piping, instrumentation, wiring, etc. It also calculates the weight of each item of process equipment, empty and filled with water, and uses civil engineering rules to calculate amounts and cost for structural steel and concrete foundations.

The cost estimates generated thus in this study are not to be viewed as in any way definitive; these are order of magnitude numbers only. They are suitable for no purpose other than the preliminary evaluation of glycine chemistry versus cyanidation presented in this exercise.

RESULTS AND DISCUSSION

The complete balances generated using the process models for the cyanide and alkaline glycine circuits were used to calculate reagent and utility costs and capital costs for the installed process equipment. The capital and operating costs of other parts of the operation, such as mining and other infrastructure, would be the same in both cases and cancel out in comparative analysis. The throughput assumed for this exercise is 200 tonnes of dry ore per hour, and 8400 operating hours per year.

Reagent and Utility Costs

Table 10 lists the reagent and utility costs calculated for the alkaline glycine circuits. In Circuit 1, in which there is no provision for limiting the loss of glycine to the tailings (apart from making the thickener underflow as dense as possible), the cost of glycine is the dominant variable cost. As the underflow from the tailings thickener goes from 60 percent solids to 45 percent solids, the loss of glycine to the tailings rises correspondingly. In Circuit 2, in which there is extra process equipment to essentially eliminate the loss of glycine to the tailings, the cost of fresh glycine is not the dominant variable cost.

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Table 10: Reagent & utility costs, alkaline glycine circuits, $ million/year

Reagent/utility	Unit cost	Circuit 2	Circuit 1, solids in tailings			
			60%	55%	50%	45%
Glycine	$1700/t	4.6	35.7	39.4	43.3	47.2
Lime	$400/t	1.1	3.6	4.0	4.4	5.0
Hydrochloric acid	$700/t	2.4	2.4	2.4	2.4	2.4
Sodium hydroxide	$350/t	0.7	-	-	-	-
Sodium sulphide	$500/t	2.1	-	-	-	-
Sodium bicarbonate	$250/t	0.9	-	-	-	-
Water	$1/t	0.2	0.1	0.1	0.1	0.1
Steam	$10/GJ	-	1.1	1.1	1.1	1.1
Electricity(48 h leach)	$14/GJ	8.4	5.7	5.7	5.8	5.8
Electricity(24 h leach)	$14/GJ	7.1	4.3	4.4	4.4	4.4
Total (48 h leach), $ million/y		20.4	48.6	52.7	57.0	61.5
Total (24 h leach), $ million/y		19.1	47.2	51.3	55.6	60.1

While a typical leach time in a cyanide circuit would be 24 hours, the leach time in alkaline glycine was assumed to be 24 or 48 hours. The required leach time affects the size and thus the capital cost of the leach reactors, and also the energy required to agitate the reactors. Assuming 0.25 kW per cubic meter of active reactor volume for agitation and 48 hours for the leach translates to a total agitation power in the leach of 6.2 MW, costing $2.6 million/year at $0.05/kWh. At 24 hours for the leach the cost of power to the agitators in the leach reactors becomes $1.3 million/year. The electricity cost for circuit 2 includes the power required for pumping in the reverse osmosis section and for steam compression after flashing the supernatant from the counter-current decantation section.

Table 11 lists the reagent and utility costs calculated for the cyanide circuit. In this case the dominant variable costs are those associated with replenishing the cyanide in the circuit and destroying cyanide in the slurry ahead of thickening and removal of the tailings.

Table 11: Reagent and utility costs, cyanide circuit

Reagent/utility	Cost, $	$ million/y
Sodium cyanide, as 100% NaCN	2500/t	34.67
Lime, as 100% CaO	150/t	1.48
Sodium hydroxide, as 100% NaOH	350/t	0.33
Hydrochloric acid, as 36% HCl	350/t	4.47
Activated carbon	2000/t	0.17
Sodium sulfite, as 100% Na_2SO_3	400/t	13.48
Process water	$2/t	3.04
Power for agitation and air compression	0.05/kWh	2.57
Total reagent & utility cost		60.20

Capital Costs

Table 12 lists the calculated capital costs of the installed process equipment for the alkaline glycine and cyanide circuits. For a leach time of 24 hours, the simpler glycine circuit has a capital cost that is essentially the same as that of the cyanide circuit because its process equipment is very similar to that of the cyanide circuit.

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Table 12: Capital cost for installed process equipment, US$

Process	Glycine Circuit 2		Glycine circuit 1		Cyanide
	48 h leach	24 h leach	48 h leach	24 h leach	
Equipment	50,602,176	41,536,276	32,746,087	18,100,836	17,023,181
Piping	9,591,963	8,535,590	5,633,294	3,874,841	3,960,261
Civil	3,957,285	2,808,544	3,604,903	1,953,110	2,283,827
Steel	1,922,213	1,442,164	1,728,747	978,014	860,639
Instruments	4,646,790	4,137,691	3,513,964	2,489,714	2,671,759
Electrical	6,395,881	5,959,178	5,273,145	4,367,065	4,264,068
Insulation	3,302,474	2,367,532	2,923,549	1,503,225	1,592,265
Paint	419,645	362,940	289,851	192,525	176,474
Direct Field Costs	**80,838,428**	**67,149,914**	**55,713,541**	**33,459,329**	**32,832,474**
Indirect Costs	**8,105,400**	**6,545,500**	**6,410,500**	**3,893,900**	**3,984,300**
Total Field Costs	**88,943,828**	**73,695,414**	**62,124,041**	**37,353,229**	**36,816,774**
Freight	2,953,601	2,462,301	2,007,300	1,204,200	1,175,700
Taxes and Permits	4,615,101	3,847,301	3,136,401	1,881,600	1,837,100
Engineering & HO	5,447,401	5,140,501	3,388,301	2,765,800	3,059,100
Other costs	6,262,732	5,216,326	4,537,204	2,805,019	2,809,048
Contingency	19,480,076	16,265,134	13,534,783	8,281,772	8,225,591
Non-Field Costs	38,758,911	32,931,563	26,603,989	16,938,391	17,106,539
Total Costs	**127,702,739**	**106,626,977**	**88,728,030**	**54,291,620**	**53,923,313**

Figure 4 shows the distribution of equipment costs for the more complex glycine circuit as pie charts, assuming 24 or 48 hours for leaching. The dominant capital cost item in the more complex glycine circuit is the slice labelled Recycle, the equipment keeping the glycine in the circuit, i.e. carbonate precipitation, counter-current decantation, reverse osmosis, sub-atmospheric flash and steam compression. This equipment accounts for almost 40 percent of the total equipment cost in the variation assuming a 24 hour leach. In the variation assuming a 48 hour leach, the extra hardware accounts for just over a third of the total installed equipment cost.

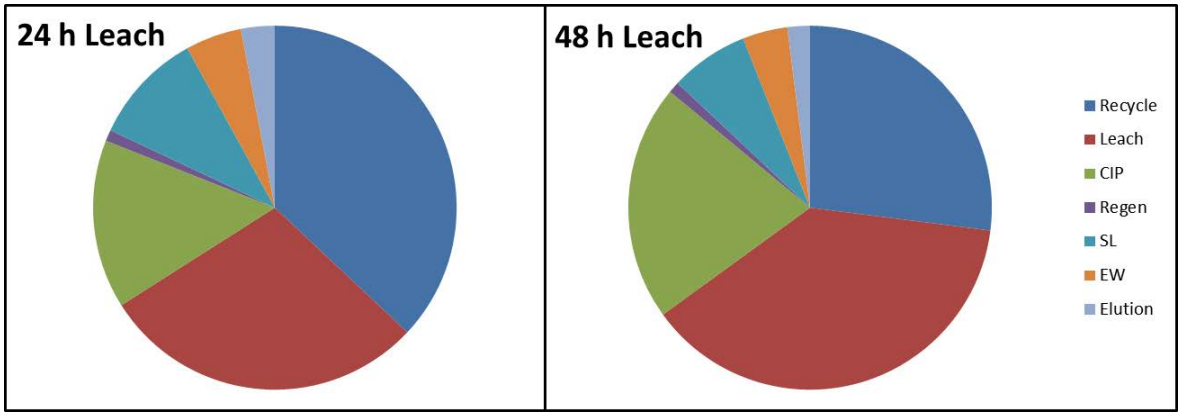


Figure 4: Capital cost breakdown, glycine circuit 2

Table 13 and Table 14 list the results of differential cash flow calculations between the more complex alkaline glycine circuit and the cyanide circuit. The cost is the difference between the installed equipment cost of the alkaline glycine circuit and that of the cyanide circuit. The gain is the difference between the reagent and utility costs of the glycine circuit and those of the cyanide circuit. The calculation assumes that the cost is incurred in the first year and the gain in each of the following nine years. The resulting internal rate of return (IRR), at 67% or 93%, indicates that the more complex alkaline glycine circuit may very well be attractive, economically, compared to the cyanide circuit.

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Table 13: Differential cash flow, $ million, alkaline glycine 2 (48 hour leach) versus cyanide

Year	1	2	3	4	5	6	7	8	9	10
Cost	74									
Gain		48	48	48	48	48	48	48	48	48
Margin	-74	48	48	48	48	48	48	48	48	48
IRR	65%									
NPV, 10%	$184 million									

Table 14: Differential cash flow, $ million, alkaline glycine 2 (24 hour leach) versus cyanide

Year	1	2	3	4	5	6	7	8	9	10
Cost	53									
Gain		49	49	49	49	49	49	49	49	49
Margin	-53	49	49	49	49	49	49	49	49	49
IRR	93%									
NPV, 10%	$209 million									

Table 15 and shows the results of differential cash flow calculations between the simpler alkaline glycine circuit and the cyanide circuit, assuming that the tailings from the alkaline glycine circuit contain 60 percent solids. In the variation assuming a 24 hour leach, the calculated IRR is not meaningful because the differential capital cost is very small. Even so, it would appear that the simpler alkaline glycine circuit is also economically attractive, compared to the cyanide circuit.

Whether or not the more complex alkaline glycine circuit is merited would be difficult to determine from the calculated IRR numbers because, for the 24 hour leach, the simpler case has almost no cost differential against the cyanide baseline, which makes that IRR number meaningless. Table 17 lists the differential net present values calculated for the more complex alkaline glycine circuit and for the simpler circuit with various tailings densities. These numbers indicate that even if the leach requires 48 hours, at anything above 45 percent solids in the tailings, the simpler alkaline glycine circuit could very well offer superior economics to the cyanide circuit. The more complex alkaline glycine circuit, with the extra equipment to eliminate glycine loss to the tailings, also appears to offer superior economics to conventional cyanidation, at least for the ore used in this study. From the net present value numbers, it appears that the extra capital cost associated with eliminating glycine loss to the tailings is justifiable, although there may be scenarios in which capital cost reduction is more important and the extra equipment would thus be omitted.

Table 15: Differential cash flow, $ million, alkaline glycine 1 (48 hour leach) versus cyanide

Year	1	2	3	4	5	6	7	8	9	10
Cost	35									
Gain		20	20	20	20	20	20	20	20	20
Margin	-35	20	20	20	20	20	20	20	20	20
IRR	57%									
NPV, 10%	$74 million									

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Table 16: Differential cash flow, $ million, alkaline glycine 1 (24 hour leach) versus cyanide

Year	1	2	3	4	5	6	7	8	9	10
Cost	0.4									
Gain		22	22	22	22	22	22	22	22	22
Margin	-0.4	22	22	22	22	22	22	22	22	22
IRR	5859%									
NPV, 10%	$113 million									

Table 17: Differential net present values, $ million, 10% discount rate

Leach time	Circuit 2	Circuit 1, different solids in tailings			
		60%	55%	50%	45%
48 hours	190	74	53	30	7
24 hours	209	113	91	69	45

CONCLUSION

The results of the process modelling work indicate that alkaline glycine chemistry may well be competitive with, if not superior to, established cyanide technology, at least for the feed assumed for this exercise and assuming that the assumptions used are valid. A caveat is that the modelling is based on the results of minimal laboratory work on cyanidation of the feed used in this work, and on assumptions for the glycine chemistry. These assumptions are presently thought to be reasonable but are still assumptions that require experimental confirmation or correction. The sizing of thickeners was based on assumed settling rates because the relevant measurements have yet to be done. Solid-liquid separation can significantly affect the capital cost of the processes examined.

The circuit configurations assumed for this exercise may not be the configurations ultimately adopted. Further optimisation would be inevitable as the alkaline glycine chemistry is developed.

The purpose of this exercise was to produce a preliminary high-level evaluation of alkaline glycine chemistry against conventional cyanidation, to help researchers make rational decisions on further development of the alkaline glycine chemistry. The numbers generated indicate that, at least for ores similar to the one selected for this work, alkaline glycine chemistry does appear to merit further development. Appropriate future work would include more detailed laboratory work on the glycine chemistry, in particular on elution of activated carbon loaded with gold and silver glycine complexes and the subsequent electrolysis step, comparative work using cyanide and alkaline glycine on the same feed materials, refining the models with the data generated, re-evaluating the predictions generated from the refined models, scale-up and piloting work, etc. Appropriate future work could also cover expanding the models to examine other approaches such as heap leaching and to comparing the alkaline glycine chemistry with cyanidation when cyanide recovery technology such as the SART process is used.

ACKNOWLEDGEMENT

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DEVELOPMENT OF A SELF-CONTAINED BROMINE/BROMIDE PROCESS FOR LEACHING AND RECOVERY OF GOLD FROM GOLD ORES

By

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ABSTRACT

The AuBrLSX bromine/bromide process for leaching and recovery of gold was developed to improve recoveries and reduce operating and capital costs for new gold processing plants. It also provides an alternative to the use of cyanide for leaching due to increasing legislative pressure on licensing cyanide installations. The AuBrLSX process is also applicable to some ores which are refractory to cyanide.

Halide leaching has been in use since the late 1800's, but bromine/bromide leaching has not been adopted on a wide scale to date mostly due to the simplicity and efficacy of using cyanide.

The new AuBrLSX Process includes atmospheric and ambient leaching, solid liquid separation, solution purification and concentration by solvent extraction, gold recovery by electro-winning followed by electro-regeneration of the bromine lixiviant. The process is a completely recycled system with minimal reagent bleed and make-up. The tailings residue is washed filter cake.

Leaching tests conducted on several types of ore revealed equal or superior gold recovery compared to cyanide recoveries.

This paper outlines the testing of the process in a series of successful bench-scale tests of various ore types. A continuous mini-pilot scale test set-up for on an oxidized ore is currently being designed and will become operational during 2016.

Keywords: AuBrLSX Process, Gold Leaching, Bromine, Bromide, Solvent Extraction, Electro-winning, Electro-regeneration, Process Development,

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INTRODUCTION

History

Bromine was discovered independently by two chemists. Carl Jacob Löwig isolated bromine from a mineral water spring from his hometown Bad Kreuznach in 1825 and Antoine Balard found bromine chemicals in the ash of seaweed from the salt marshes of Montpellier in 1826.

Bromine's usefulness in leaching precious metals patented 50 years later by Charles Schaeffer[1]. Further US Patents for gold leaching from ores with bromine were awarded to Bertrand C. Hinman in 1895 and 1897[2,3]. His process involved leaching in a covered circuit with excess bromine, stripping the bromine with air, steam or chlorine gas and re-using it. The MacArthur-Forrest cyanide process was patented around the same time[4] and took precedence over halides as the process of choice for leaching gold from ores. In 1942 Colin Fink et al[5] improved on the bromine process by adding bromide or chloride ions to the lixiviant, thus reducing its volatility.

In the 1990's Great Lakes Chemical Co, produced a lixiviant called "Geobrom", which was dibromodimethylhydantoin (54.5% active bromine) mixed with CaBr in the ratio 1:2. The Great Lakes patent[6] covered almost every permutation of leaching, generation and regeneration with bromine and halides, claiming to have produced a low vapor pressure mixture. Unfortunately for Great Lakes Chemical, their first published gold application for Geobrom (1990) was on a Nova Scotia ore-body, both oxide ore and sulfide concentrate[7]. In simple bottle roll tests at pH ~ 6.5, the ore leached very well, with 94% gold recovery after 6 hours. The sulfide concentrate, however, reached only 15% Au recovery. After comparing the costs with cyanide, and finding them basically the same for oxide ores, and with no advantage over cyanide for sulfidic concentrates, the North American gold industry lost interest.

At the same time, a US Patent was awarded to Australian inventor Guy Kalocsai of Kaljas Ltd[8]. His process was acquired and further developed by BHP and Dead Sea Bromine. As well as test work carried out by Kaljas, Dead Sea Bromine (DSB) conducted its own research in Israel on various gold ores[9]. There were plans to partner with various mining companies to build a 300kg/hr pilot plant. The plans were shelved due to the gold price being in the doldrums for most of the late 1990's and early 2000's. DSB work focused on difficult ores (high sulfide, high copper and refractory ores) because that was the interest of the industry. They established that leaching of calcined ore (and by extension, oxide ores) was quite straightforward.

Process Development Approach

Recent research[10] has used a largely theoretical approach, using pure minerals and synthetic solutions, The present work follows a deliberately empirical approach, using actual ore samples to generate leach data and material for downstream processes.

The process development was divided into 4 research areas

- Leaching,
- Gold Recovery,
- Lixiviant Regeneration and
- Environmental Stability.

Three teams were established to work in parallel on the first three areas, with the environmental stability intended to be a joint project once the process waste streams are defined.

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LEACHING

Introduction

Summarized below are the results achieved from three different ore samples and one sample of tailings. The materials tested were

- Roaster calcine
- Oxide ore
- Free milling sulfidic ore
- Sulfide flotation tailing

Most of the work though, has been focused on the roaster calcine sample for which the process was optimized for efficiency and cost. The various ores were examined and specific process parameters were determined, with an emphasis on the most critical of pH & leaching time. At a later stage, additional types of ores will be analyzed and tested.

Experimental Method

Preparation and Characterization of the Leaching Solution

The leaching solution requires active species that can penetrate the ore, react with gold and complex it into solution. In the case of bromine based solutions, the active species can differ; however, the most common species would be Br_2 and Br_3^- (polybromide, which is a bromine molecule complexed by Br^- ion).

$$3Br_2 + 6e^- \longrightarrow 6Br^-$$

$$2Au + 8Br^- \longrightarrow 2AuBr_4^- + 6e^-$$

$$2\,Au + 2Br^- + 3Br_2 \longrightarrow 2AuBr_4^- \qquad \text{EQ 1}$$

The quantitative ionic distribution of bromine species in the solution varies with pH, reagent type and reagent concentration. Bromine has a high vapor pressure that will decrease with the concentration of bromides in the solution, due to the formation of larger complexes such as Br_3^-. A series of diluted Br_2/Br^- solutions were tested, using $CaBr_2$ or NaBr as a Br^- precursor, within pH range of 3 – 12.

Analysis of bromine was carried out by iodometric titration and bromide concentration was measured using argentometric titration.

Leaching Experiments

Leaching experiments were carried out at ambient temperature in 500ml jacketed glass reaction vessel hermetically sealed with FEP-Silicone O-Ring and a 5-neck reaction vessel lid. In a typical experiment, the homogenized ground ore was introduced into the Br_2/Br^- leaching solution in the reaction vessel. The slurry was stirred by a mechanical Teflon coated stirrer rotating at a range of 250-500 RPM. Three additional modules were attached to the reaction vessel:

- Cooling condenser to prevent bromine vapor elimination
- pH electrode for on-line measurements
- Reference Redox electrode for ORP (oxidation reduction potential) measurements.

Figure 1 shows a photograph of the reaction vessel.

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Figure 1: Leach Reactor

The experiments were carried out using a solid to liquid ratio between 33% – 50% with retention times ranging between a few minutes to 24 hours. Some of the experiments required pH control, where a Metrohm titrino measured and maintained the pH.

The slurry was filtered using closed 500mL filter funnel with a 90mm Microfiber Glass filter. The depleted cakes were washed and vacuum filtered and dried at 110°C and sent for gold analyses by fire assay (F.A.). The bromine/bromide Pregnant Leach Solutions (PLS) were analyzed for bromine and bromides, as stated before, and for trace metals by ICP method.

Another type of measurement, for understanding the process, was the kinetics study, where the ore was placed in laboratory scale roller bottles with the bromine leaching solution. The samples were agitated using a Tube Roller for up to 24 hours. Samples were removed periodically, separated by centrifuge, and the solutions sent for analysis.

Results and Discussion

Preliminary Leach Tests

Table 1 shows preliminary leach results. Leaching solutions contained up to 10% (w/w) of bromides and bromine. These solutions showed good leaching recovery (>90% gold recovery). The high concentration of bromine presented several issues, such as a corrosive vapor above the solution, more expensive construction materials and potentially high expense from bromine consumption. These issues demanded a practical solution to lower costs, decrease process complexity and retain the high gold recovery.

Table 1: Preliminary Leach Tests

Ore	pH	ORP, (mV)	Leach Time, (min)	Au Recovery, (%)
Roaster Calcine	7.3	910	15	87
Oxide Ore	7.0	900	15	92
Free milling Sulfidic ore	1.9	890	15	90
Sulfide Flotation tailings	6.8	900	30	70

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Optimization Tests

Using the roaster calcine, two parameters were investigated for process optimization and cost reduction: retention time and pH. The static test conditions were a weight ratio of 2:1 liquid to solid, stirring at a range of 250-500 RPM. Tests were carried out at the native pH of around 8. No pH adjustment was undertaken during leaching.

Residence Time

Table 2 shows the effect of residence time on leach recovery for the roaster calcine.

Table 2: Effect of Residence Time – Roaster Calcine

Leach Time, (min)	pH	ORP, (mV)	Au Recovery, (%)
2	8.0	910	82
12	7.9	910	84
15	7.9	910	86

Although not shown here, other tests were carried out for up to 24 hours. The major portion of the gold was already observed in solution after 2 minutes. The optimum time of leaching was found to be 15 minutes, after which there was no increase in gold concentration. For reactions longer than 15 minutes, bromine may be consumed by slower parasitic side reactions which resulted in a higher bromine makeup.

Effect of pH

Tests were carried out on the roaster calcine sample using up to 10% (w/w) Br_2/Br^- leaching solution for 15 minutes

Table 3: Effect of pH – Roaster Calcine

pH	ORP, (mV)	Leach Time, (min)	Au Recovery, (%)
3.0	903	15	70
6.0	910	15	79
7.7(native)	910	15	86
8.0	870	15	84
10.0	770	15	74

Results show that when the reaction pH was controlled, either by acid or base addition, the gold recovery was lower than that of a native pH, achieved by mixing only the ore and the leaching solution.

Summary and Conclusion

ORP was measured during the leaching stage and it is ore dependent at constant values of 870-920 mV with the same Br_2 concentration. The constant value indicates that active bromine is present in the system throughout the process. The ORP value remained constant even at a wide pH range.

The effect of leaching time was studied in the range of 2 min – 24 hours for oxide ore at all parameters. The results indicate that much of gold leaching occurs in the initial stage. The major recovery of gold, up to 80%, is independent of initial bromine concentration and takes about 2 minutes of reaction. The rate of gold leaching decreases over time for all bromine concentrations. Optimal time for gold recovery was found to be 15 minutes. Beyond this time there is no additional gold leaching, yet there might be additional bromine consumption due to parasitic reactions, which require bromide make up.

Native pH was found to be ideal for gold leaching in different calcine samples. The addition of bromine containing leaching solution lowers the pH; however no pH control is needed. Attempts to control the pH of the reaction in various ores was proven to be less optimal and resulted in lower gold recovery

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GOLD RECOVERY

Introduction

Previous work by ICL and other researchers has shown many possibilities for gold recovery from an $AuBr_4^-$ solution. Although opinions are not universal, contacting a gold halide solution with activated carbon (as used in the cyanide process) causes the gold to be precipitated as metallic gold[13]. The gold loading on carbon has been reported to be as high as 60%. However, if the process is carried out in pulp, mechanical abrasion of both the gold metal and the carbon particles could conceivably lead to losses. Therefore the contact needs to be in solution. Once loaded, the carbon requires ashing and the ash leached with the gold finally recovered by precipitation or electro winning.

Many researchers have examined gold halide recovery by ion exchange resins and a plethora of anionic resins have been shown to adsorb gold[12]. Desorbing gold from resin has proven to be more problematic[13]. Destroying the resin to recover the adsorbed gold brings the same problem as ashing the carbon, only more-so as the resins are more expensive and the substrates can be toxic. Fascinating research has been carried out to recovery gold with naturally occurring resins, which may alleviate that aspect[14].

Other researchers have looked at solvent extraction to recover gold halides from solution. Tenova decided to focus on this as well.

Experimental Method

The aim of the solvent extraction process is to recover gold from the bromine/bromide Pregnant Leach Solution (PLS) in order to purify the stream and to concentrate the gold ions for subsequent recovery as solid. The deportment of the bromine species in the SX process is very important as the economics and environmental impact of the process depend upon recovering and recycling the bromine leach solution.

As mentioned, the experimental method was empirical. The following steps were followed

- Research the literature to short-list possible extractants
- Source the extractants
- Shake-flask tests with $NaAuCl_4$ solutions made from gold chloride stock solution and deionized (DI) water
- Dissolve jewelers gold in bromine/bromide solution to make stock synthetic solutions
- Shake flask tests for extraction and stripping with the most promising candidates from the chloride gold tests
- Shake-flask tests with elevated levels of bromine/bromide added
- Eliminate those extractants that smelled bad, cost too much or produced unusual precipitates and solution colors or did not strip well.
- Choose cheapest and cleanest from the remaining candidates
- Commence testing in earnest, extraction isotherms, strip isotherms, bromine deportment

Results

Table 4 shows some results from the preliminary screening tests using synthetic PLS, either gold solution in DI water or gold solution added to bromine/bromide solution.

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Table 4: Preliminary Extraction Screening Tests with Synthetic PLS

Extractant	PLS			Ext.	Observation
	[Au] ppm	[Br2] gpL	Br- gpL	% Rec	
10% Tripropylene glycol n-butyl Ether	2.9	0	0	71	Pink raffinate
	9.5	0	0	88	Blue/grey ppte, pink raffinate
	3.7	0	0	99	Stirred beaker, pH control with HBr, black ppte
Esther alcohol	3.0	0	0	98	LO Mauve, black ppte
	10.7	0	0	100	LO Mauve, black ppte
	3.7	0	0	65	Clear, no ppte, heated for phase sep
Organophosphorous compound	3.0	0	0	98	Clear phases
	10.7	0	0	100	Clear phases
Trialkyl phosphine oxide	3.3	0	0	98	Clear phases
Guanadine	3.3	0	0	49	Clear, no ppte, heated for phase sep
	10.7	0	0	36	Aq phase turbid, heated for phase sep
Quaternary amine & nonly phenol	3.7	0	0	49	Aq. Phase turbid. Clear, no ppte, heated for phase sep Persistent white emulsion
	10.7	0	0	88	
Amine	3.7	0	0	99	Clear phases
Acetic acid n-amyl esther	3.0	30	3	88	Odourous, clear phases
Diethylene glycol dibutyl ether	3.0	30	3	80	Odourous, clear phases
Diethylene glycol dimethyl ether	3.0	30	3	n.d.	Phases completely miscible
Triisobutyl phosphine sulfide	3.4	0	0	98	Clear phases
	5.5	33.7	1.8	99	Clear phases
	5.2	31.1	1.0	99	Clear phases

Stripping tests were completed for the most promising of the above tests. In most cases, the mechanism of extraction was not well understood, so several stripping solutions were tried. Table 5 shows some selected stripping tests results.

Table 5: Preliminary Stripping Screening Tests

Extractant	Strip Solution	Strip Rec %
Esther alcohol	2M HCl Wash followed by 80°C DI Water	56
Organophosphorous compound	1 gpL Na_2SO_3 solution, natural pH	0
	1 gpL Na_2SO_3 solution, basic pH	82
	1 gpL Na_2SO_3 solution, acid pH	0
	1M NaOH solution	40
	DI water adjusted to basic pH	35
Trialkyl phosphine oxide	40°C DI Water	2
	DI water @ pH 1	2
	DI Water @ pH 11	2
	1 g/L Na_2SO_3 solution	2
	1M NaOH	57
Guanadine	DI Water @ pH 10	0
Diethylene glycol dibutyl ether	2M HCl Wash followed by 80°C DI Water	80
Triisobutyl phosphine sulfide	0.5M $Na_2S_2O_3$	~100

Following the screening tests, one reagent was chosen for further study. The other promising extractants have not been discarded, merely that the work to date focused on a single reagent.

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Loading Tests

A various concentrations of extractant in diluent were contacted with Synthetic PLS. Figure 2 shows that 15% extractant seemed to the optimum strength. Notwithstanding, subsequent experiments were conducted at 25% extractant in order to ensure that this parameter was not a factor in results.

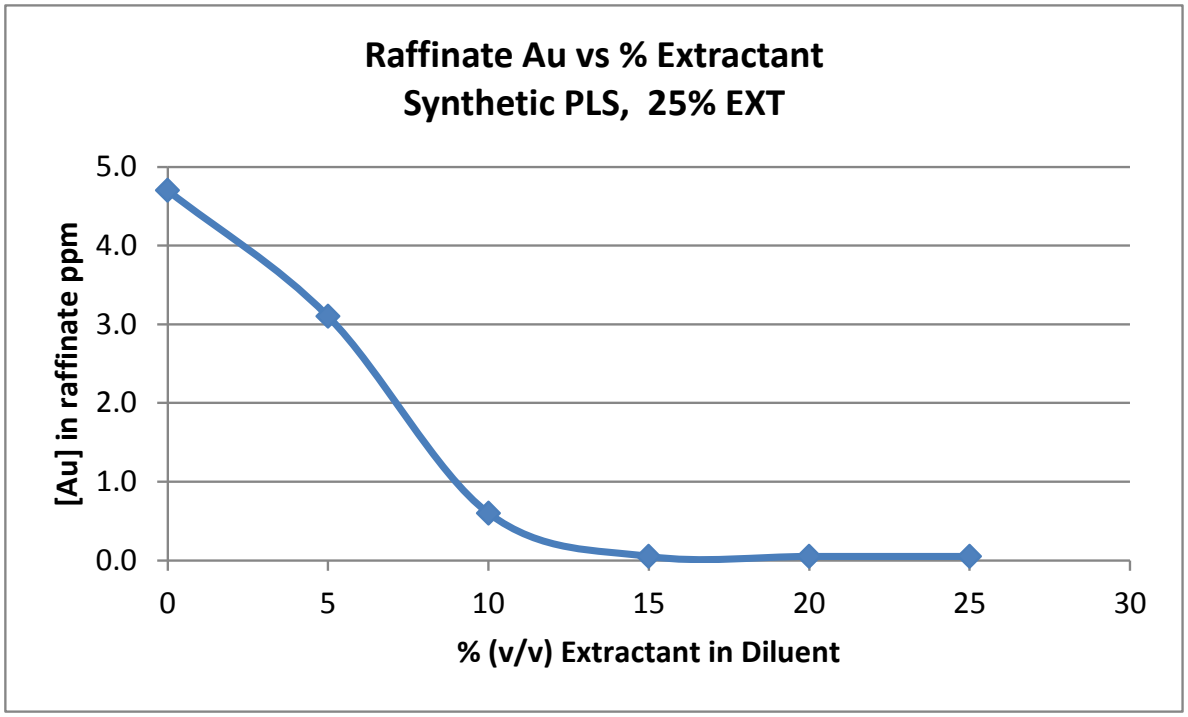


Figure 2: Extractant Strength vs Raffinate

The same synthetic PLS was contacted with 25% extractant at various O:A ratios. Figure 3 shows the gold in raffinate from that experiment. However, the higher O:A ratios resulted in the formation of a deep red third phase which detached itself from the organic layer and sank below the aqueous phase. Analyses of the gold in this third phase were as high as 330 ppm Au.

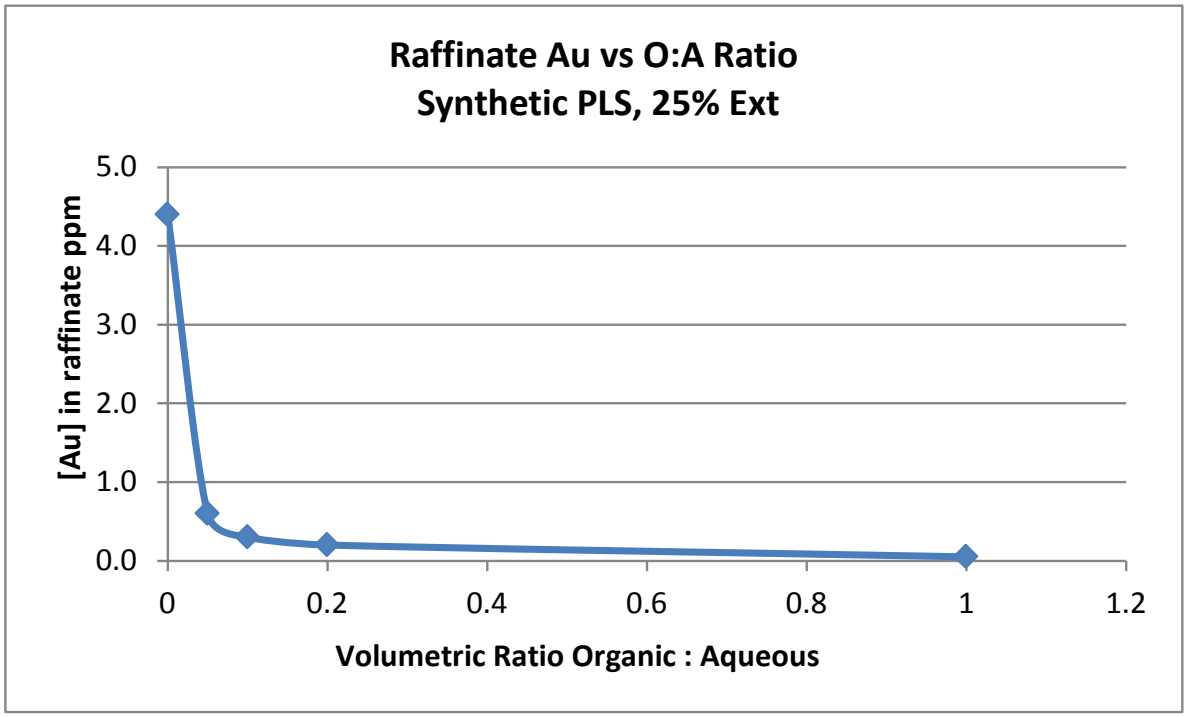


Figure 3: O:A Ratio vs Raffinate

An extraction equilibrium curve was attempted with synthetic solution by increasing extraction phase ratios. As mentioned, at O:A phase ratios beyond 1:2 a heavy organic third phase formed.

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The third phase was eliminated by the addition of 1- decanol to the extractant. Figure 4 shows the isotherm constructed from the data with added decanol.

Subsequently another equilibrium curve was constructed with actual oxide ore PLS using 25% reagent in diluent, without decanol.

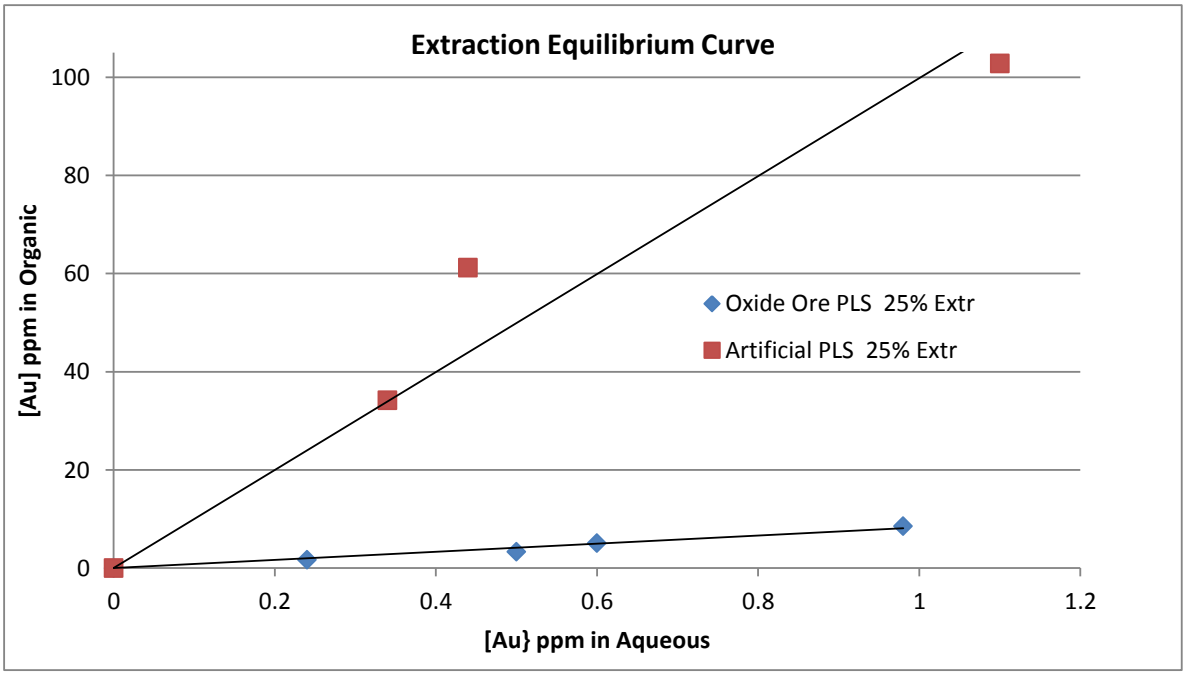


Figure 4: Extraction Equilibrium Curves
Synthetic PLS, [Au] 4.6 ppm, [Br2] 3 g/L, [Br-] 30 g/L,
Oxide Ore PLS, [Au] 1.9 ppm, [Br2] 3 g/L, [Br-] 6 g/L.

Stripping

After many tests, it was shown that stripping could be performed in around 5 stages at a high O:A ratio (~10:1). However, a matrix experiment which attempted to simulate 5 stages of stripping in a counter-current fashion showed that the gold was reabsorbed by the organic in the first stages. The counter current and cross current stripping profiles from the experiment is shown in Figure 5.

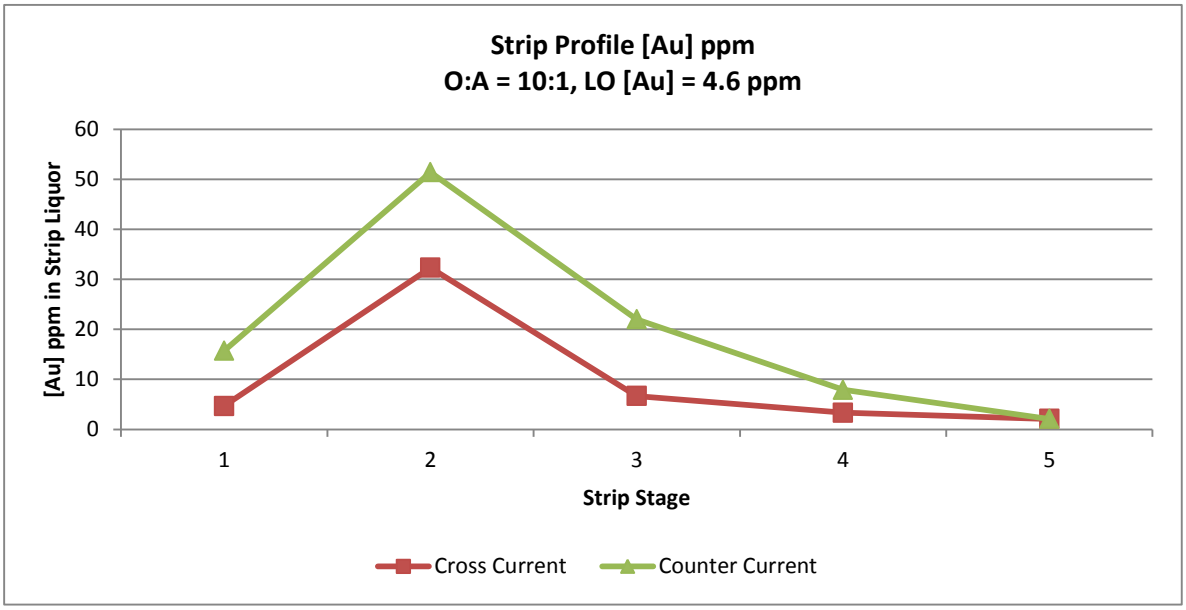


Figure 5: Stripping Profile from Matrix Experiment

Loaded organic prepared using Oxide Ore PLS, 2 g/L Br2, 8 g/L Br- at O:A ratio 1:1. Stripping tests at O:A 10:1.

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From the results it can be seen that a hybrid cross-current stripping is indicated with the liquor from the final two stages being conditioned and reused as strip solution for Strip stages 1 and 2.

Electro-winning

A simulated strip solution at approximately 50 ppm Au concentration was used to provide proof-of-concept that electro-winning of gold could be included in the process. A primitive cell was constructed with a stainless steel wool (kitchen scrubby) cathode contained in a membrane chamber and lead anodes. A rectifier supplied 4 V. The current slowly fell from 1.4A to 0.6 amps. Solution was continuously recycled to the cell for a total of 12 hours. From Figure 6 it can be seen that the solution was depleted in 12 hours. About half of the physical gold was recovered by vigorous water washing of the cathode and the remainder by complete digestion of the steel wool by hydrochloric acid. Both residues were digested in aqua-regia for analysis and the gold accounted for. Figure 6 shows the gold in electrolyte during the operation of the cell and Figure 7 shows the bromine species in electrolyte.

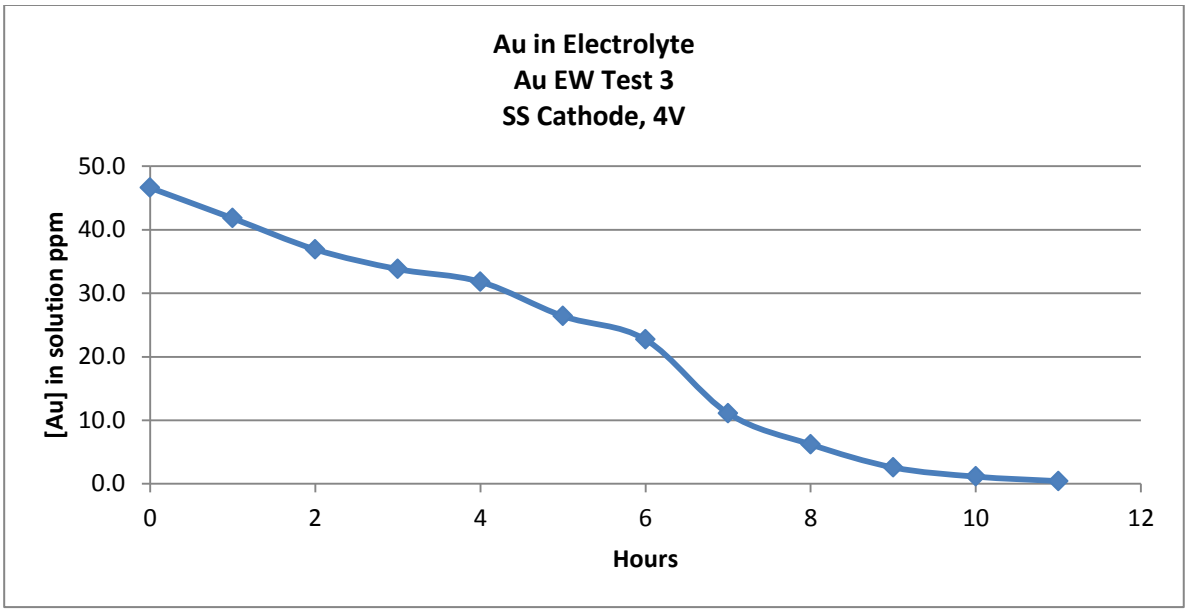


Figure 6: Au in Electrolyte Profile

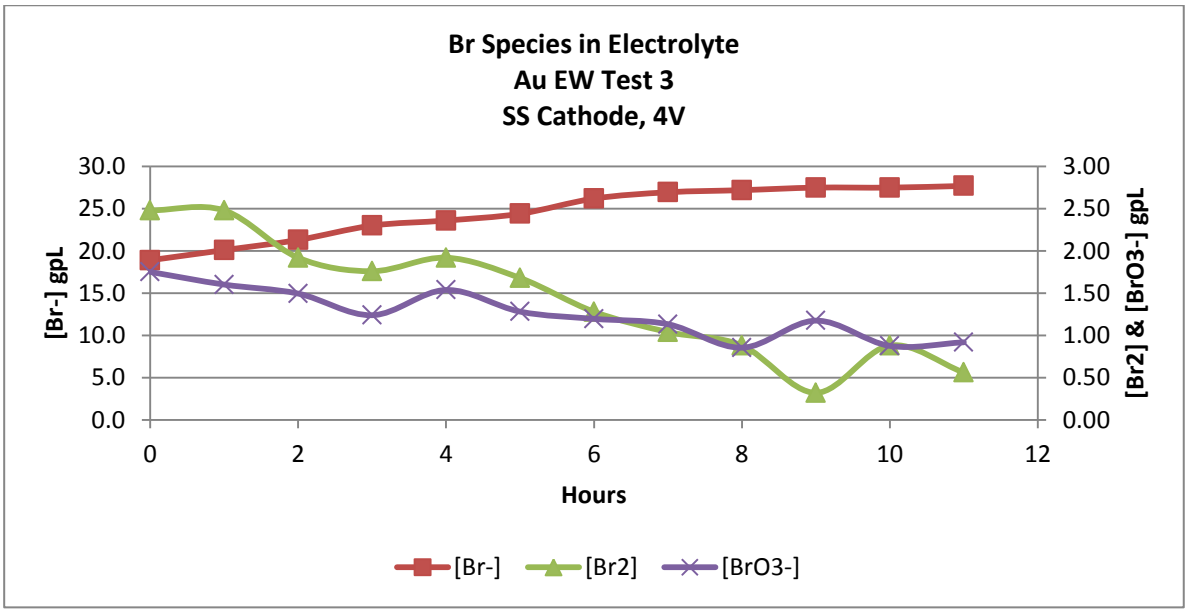


Figure 7: Bromine Species in Electrolyte Profile

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Process Improvements

The experimentation had shown that extraction was indicated at O:A ratio of 2:1 and Stripping in a cross-current fashion at 10:1 using 5 stages. Thus the overall multiplication of gold tenor was 4.

The process was improved by the introduction of a pre-treatment stage for the PLS. Subsequent experiments have shown that with pre-treatment it is possible to extract all the gold in 2 stages at O:A of 1:5 and to strip in a cross current fashion with 5 stages at O:A of 20:1 for a total gold tenor multiplier of 20.

Proposed Flow Sheet

Figure 8 shows a schematic flow sheet for the gold recovery process. This process has been successfully tested in a solvent extraction mini-pilot (4L/hr PLS) using synthetic leach solution, a photograph of which is shown in Figure 9.

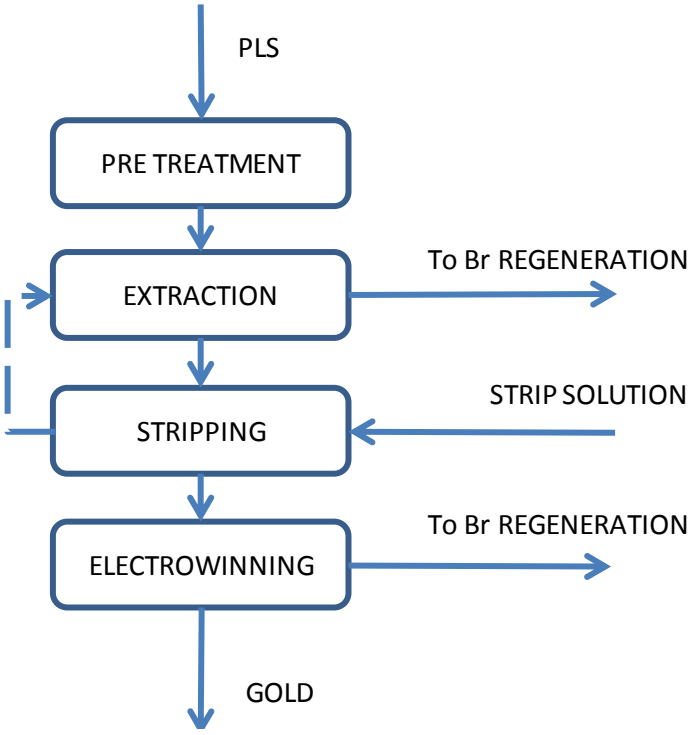


Figure 8: Schematic Conceptual SX-EW Flow Sheet

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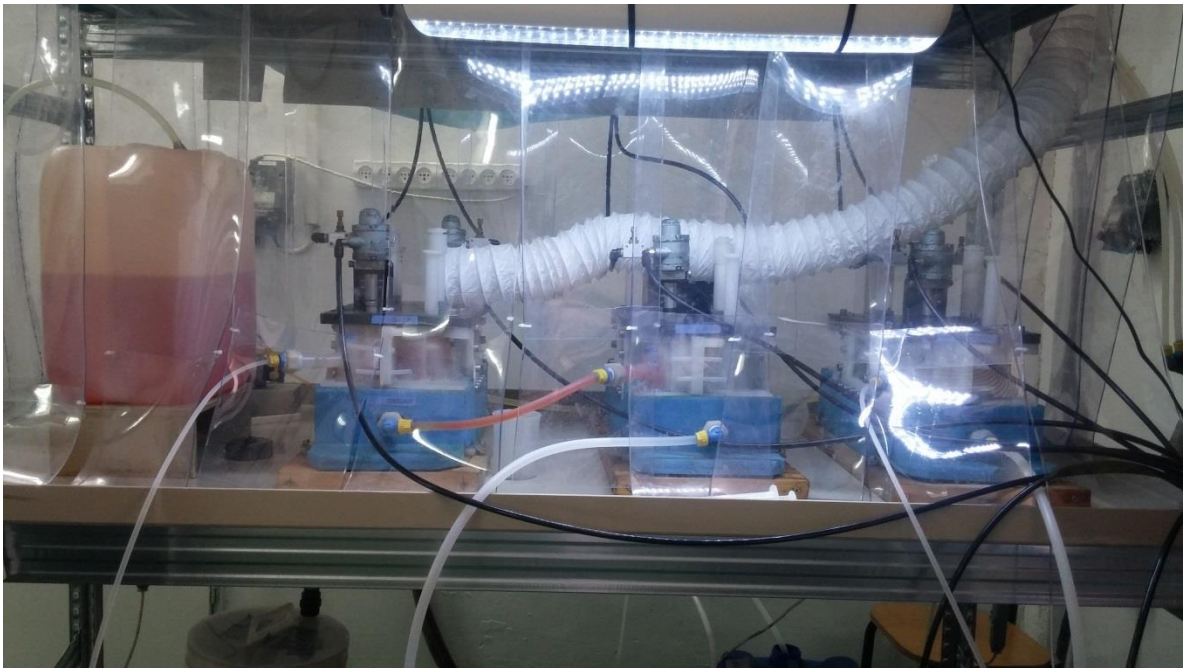


Figure 9: SX Mini Pilot with Synthetic PLS

REAGENT REGENERATION

Experimental

As bromine is consumed during the leaching process, bromide ions are produced. An electrochemical method was developed to regenerate bromine from bromides to regenerate the required amount for the leaching solution. This method, as it recycles the same material, prevents unnecessary bromide bleed into the environment. The electrochemical setup is comprised of a flow cell. This cell has supporting electrolyte solution flowing in the cathode half-cell, producing hydrogen from water as a byproduct, and the process solution flowing in the anode half-cell transforming bromides to bromine. The half cells are separated by a membrane that prevents the crossover of bromine from the anode to the cathode. Figure 10 depicts the experimental apparatus schematically.

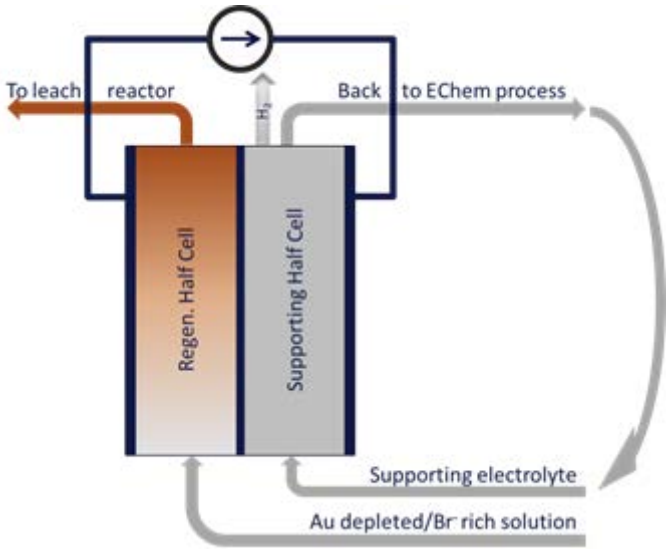


Figure 10: Electrochemical Regeneration Test Cell - Schematic

Experiments were conducted in a galvanostatic mode at 50-100mA\cm^2 current densities, with a cutoff voltage of 4.5-5V. Solutions of 150mL with bromide concentration of 0.8w% - 5w%, and pH values in the range of 1 to 12 were tested. Average time of experiment was 3.5 hours.

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Results and Discussion

The results from the work are shown in Table 6.

Table 6: Preliminary Electrochemical Tests from Bromine from Bromide

Exp. #	Initial Bromide Conc. (w%)	pH	pH control	Current density	Final Bromine conc. (w%)
1	10.0 w%	4	Yes	90 mA cm^{-2}	5.6 w%
2	3.8 w%	6	Yes	50 mA cm^{-2}	2.1 w%
3	2.3w% (+ 4.1w% Bromate)	13.3	No	5 mA cm^{-2}	5.7 w%

Experiments have demonstrated the robustness of the electrochemical process, where pH and ionic concentration had effect on efficiency, but not a detrimental one. The efficiency of the process grows at low pH (below 4) and at high ionic concentrations (above 4w%), yet, pH of up to 12 and bromide concentrations of down to 0.8w% have still yielded the target values of 1:1 bromide to bromine ratios that may be recirculated into the leach reactor.

SUMMARY

Although the work is ongoing, and there are challenges ahead, the authors are confident that a viable, robust process gold recovery process using bromine-based solutions will soon be demonstrated. Figure 11 shows the schematic of the conceptual flowsheet of AuBrLSX process.

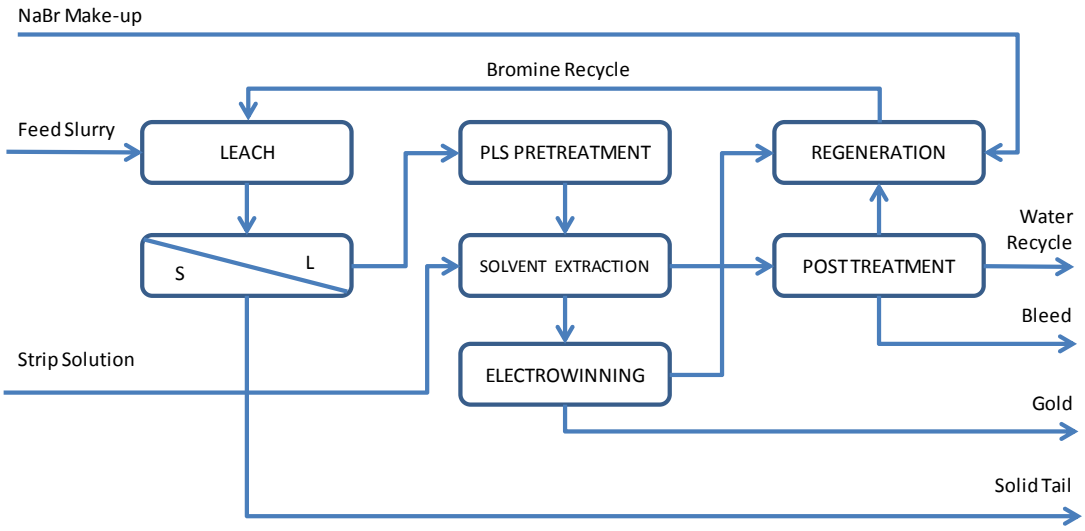


Figure 11: Conceptual flowsheet of AuBrLSX Process - Schematic

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CATALYSED DISSOLUTION OF GOLD IN OXYGEN-THIOSULFATE SYSTEM

By

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ABSTRACT

The research on thiosulfate as an alternative lixiviant to cyanide for gold recovery has predominantly involved the use of copper(II) ammonia as the oxidant. However, the copper(II) oxidises thiosulfate and there have been health and environmental concerns over the use of ammonia. Oxygen can be used as the oxidant instead with much slower loss of thiosulfate, but the resulting oxygen-thiosulfate system is normally very slow to leach gold. The leach rate was found to be significantly enhanced by the presence of certain levels of copper ions, increasing temperature (up to 50 ^{o}C) and galvanic interaction with sulfide minerals. In some cases, gold leach recoveries comparable to or better than cyanidation have been achieved using the oxygen-thiosulfate system, showing promise in treating particularly sulfidic ores. This paper presents some results of the electrochemical study, synthetic gold powder leaching and real ore leaching.

Keywords: gold leaching, thiosulfate, galvanic effect

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INTRODUCTION

The use of thiosulfate as an alternative lixiviant to the highly toxic cyanide to recover gold has been extensively studied for more than two decades. The majority of past research has been carried out on the copper-ammonia-thiosulfate process, in which Cu(II)-ammine acts as the oxidant. This is well documented and a number of reviews are available in the literature[1,2]. Besides the copper-ammonia-thiosulfate system, other systems using different oxidants have also been reported, attempting to avoid the potential health and environmental risks of ammonia/ammonium. These include the iron-EDTA[3] and iron-oxalate[4] systems with the addition of thiourea as a catalyst.

Recently, researchers at Barrick developed a thiosulfate process using dissolved oxygen (as the oxidant) for treating a double refractory (pyritic and carbonaceous) ore following pressure oxidation; success of the process development has led to the recent commissioning of the world's first thiosulfate plant by Barrick's Goldstrike operation in the U.S.A.[4]. In this process pressure oxidation is used as a pre-treatment to release the gold encapsulated in sulfides and the pressure oxidation residue is then leached for gold recovery using the oxygen-thiosulfate system. There are limited studies on using the oxygen-thiosulfate system to treat native gold ores. Recently work has been conducted at CSIRO to treat refractory sulfide ores or concentrates using this system. Although oxygen is normally not an effective oxidant in thiosulfate leaching, the dissolution of gold could be catalysed and some promising results have been obtained under certain conditions for some ores / concentrates. This paper investigates the effect of some factors on the electrochemistry and leaching behaviour of gold in the oxygen-thiosulfate system, followed by gold powder and ore leaching studies using the apparent preferred conditions.

EXPERIMENTAL

Materials and Reagents

The chemicals used in this testwork were of analytical grade and include sodium thiosulfate pentahydrate, copper sulfate pentahydrate, sodium hydroxide, potassium carbonate, potassium dicyanoaurate(I) and sodium cyanide. Calcium thiosulfate solutions were prepared using concentrated calcium thiosulfate solution (20 - 30%) sourced from Tessenderlo Kerley, U.S.A. Concentrations of thiosulfate and polythionates were determined using high performance liquid chromatography (HPLC). The pH of the initial solutions was adjusted using 0.1 M sodium hydroxide. Milli-Q water was used for the preparation of all aqueous solutions used in the fundamental studies described.

REQCM Studies

Electrochemistry and short term leach tests were conducted using a rotating electrochemical quartz crystal microbalance (REQCM), which is described elsewhere[5]. A typical water-jacketed three electrode glass cell was used for the electrochemical studies. A coiled platinum wire was used as a counter electrode (CE), placed in a separate compartment in contact with the solution through a glass frit. The reference electrode was a Ag/AgCl electrode. All reported potentials are converted to the standard hydrogen electrode (SHE) scale. The electrochemical set-up included a PGP 201 potentiostat/galvanostat for experiments involving linear sweep voltammetry in which a scan rate of 2 mV s^{-1} was applied. Prior to each electrochemical gold oxidation experiment, the thiosulfate solutions were deoxygenated by purging for 30 minutes with nitrogen gas.

When investigating the galvanic effect of different sulfide minerals on gold dissolution, a pure sulfide mineral electrode and gold electrode were placed in the same solution and electrically connected externally. Prior to each experiment, the gold electrode was freshly prepared by electroplating gold onto the rotating quartz electrode at 25 A m^{-2} from an alkaline solution containing 0.23 M potassium cyanide, 0.086 M potassium carbonate and 0.02 M potassium dicyanoaurate(I)[6]. The sulfide mineral electrode was polished using Struers silicon carbide paper grit 4000 followed by rinsing with deionised water. Unless otherwise specified, all experiments were carried out at pH 10, 0.1 M thiosulfate, 50 °C, 2 mM copper with a leaching time of 1800 s and a working electrode rotation speed of 300 rpm.

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Gold Powder Leaching

A 1000 mL water-jacketed glass vessel with ports on the glass lid was used, with the mechanical stirrer inserted in the central port. The other ports were used for an oxygen probe and a sampling tube. A water bath with circulating water was used to maintain the cell temperature during the leaching process. Industrial oxygen or air was added at a flow rate of 10 mL min^{-1}. A solution sample of 2 mL was taken from the reactor at predetermined intervals during the dissolution of gold. The solutions were filtered and analysed for gold using atomic absorption spectroscopy (AAS). Unless otherwise specified the leaching experiments were carried out at 50 ^{o}C, pH 10, with an agitation speed of 300 rpm using 0.2 M thiosulfate and gold powder (particle size range from 3.0 µm to 5.5 µm). The effects of background cation and pyrite addition were investigated separately. For comparison, the gold powder was also leached in 10 mM sodium cyanide solution with air added at flow rate of 10 mL min^{-1} at room temperature.

Ore Leaching Tests

The leaching tests were carried out using a bottle roller and 1000 mL high density polyethelene bottles containing 250 mL leach solution at 35% pulp density. In all the leach tests, 0.3 M calcium thiosulfate was used and pH was maintained at about pH 10 using hydrated lime. Industrial oxygen or air was added through an opening in the lid of the bottle and the flow rate was maintained at 10 mL min^{-1} (unless otherwise stated) using a flow meter. Test samples, about 5 mL of the reaction slurry was withdrawn at predetermined intervals, filtered and analysed by AAS for gold and copper and by HPLC for thiosulfate and polythionates. After the leaching period of 48 hours, the solid residue was filtered and dried. The residue was digested in hot aqua-regia and analysed for gold. Cyanide leaching of the ore was also performed for comparison.

RESULTS AND DISCUSSIONS

Electrochemistry

The dissolution of gold in thiosulfate solutions with oxygen as the oxidant is an electrochemical reaction which consists of the simultaneous oxidation of gold and reduction of oxygen. Hence, the anodic and cathodic half-reactions were studied separately. Thiosulfate leaching of gold is well known to be accompanied by other side reactions such as thiosulfate oxidation, therefore the conventional RDE electrochemical technique was not the most suitable tool for studying the gold oxidation half-reaction. The REQCM has the capability to differentiate the reactions involving mass change (i.e. gold oxidation) from other reactions that do not involve mass change, and was therefore considered more suitable for this study. The mass changes were converted to a calculated current density (i_{calc}) using Faraday's law.

Gold Oxidation

It was found that during the anodic oxidation of gold in a thiosulfate solution, the calculated current density based on mass change closely matched the measured current density within the potential region of 100 to 300 mV (data not shown), indicating that the gold oxidation is the sole oxidation reaction occurring. At potentials above 300 mV, however, the measured current density deviated from the calculated current density due to oxidation reactions other than gold oxidation, likely thiosulfate oxidation in this instance. The results shown below are for 50 mV to 200 mV only where gold oxidation is the sole oxidation reaction.

Figure 1 shows the oxidation of gold in a thiosulfate solution at 50 ^{o}C in the absence and presence of copper. As can be seen, in the absence of copper the gold oxidation in a sodium thiosulfate solution is very passive in the potential region of interest (between 50 mV and 180 mV), with the oxidation current being more than an order of magnitude lower than the oxygen limiting current of a cyanidation process (typically approximately 5 A m^{-2} in an air saturated solution). As a result, the leach rate of gold in an oxygen-thiosulfate system is very slow without any additives, even at elevated temperature. The use of calcium thiosulfate instead of sodium thiosulfate resulted in enhanced gold oxidation (higher current density). Senanayake[(2)] attributed this effect to the high Lewis acidity of Ca^{2+} facilitating gold dissolution by stabilizing the gold as a $Au_2(S_2O_3)_2Ca$ intermediate species at the interface prior to the formation of $Au(S_2O_3)_2^{3-}$.

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The rate of gold oxidation is enhanced markedly by the addition of 2 mM copper, regardless of the thiosulfate salt used (Figure 1). It is interesting to note that in the presence of copper the gold oxidation is similar in both sodium and calcium thiosulfate solutions in the potential region of interest. It was also found that further increases in copper concentration above 2 mM had a detrimental effect, which is possibly due to the formation of copper sulfide and/or copper oxide at the gold surface that inhibits the oxidation of gold.

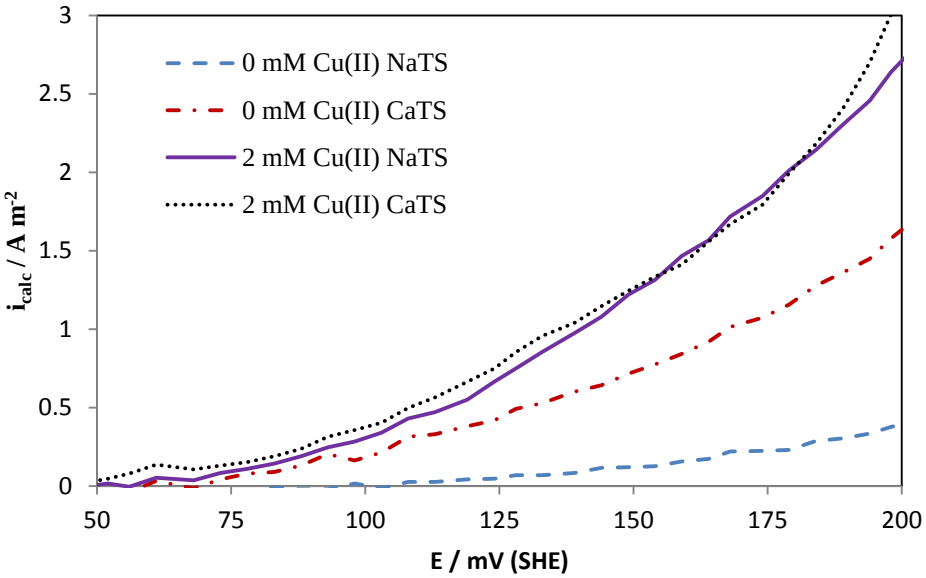


Figure 1: Calculated gold oxidation rate from the measured mass change of a REQCM electrode showing the effect of cation and copper in 0.1 M thiosulfate solution at 50 °C in the absence of oxygen.

Besides copper, the effect of thiosulfate concentration and temperature on the oxidation of gold was also investigated. Not surprisingly, the rate of gold oxidation increases with increasing thiosulfate concentration and temperature (data not shown). Using the gold oxidation rates obtained in 0.1 M sodium thiosulfate and 2 mM copper at different temperatures at 110 mV, an Arrhenius plot was generated by plotting ln(rate) vs. 1/T to estimate the activation energy. From the linear fit, an activation energy of 46.9 kJ mol^{-1} was obtained which indicates that the gold oxidation in the potential region of interest is chemically controlled. The increase in temperature, however, could also increase the rate of thiosulfate degradation (at temperatures higher than 60 °C thiosulfate becomes highly unstable[7]). The highest temperature used in this study was 50 °C.

Oxygen Reduction

The reduction of oxygen on the gold surface was studied in oxygen saturated sulfate solutions but in the absence of thiosulfate to avoid the potential interference from the oxidation of gold and/or thiosulfate. The voltammograms resulting from this testwork are shown in Figure 2. The results indicate that oxygen reduction on the gold surface is very low at potentials above 50 mV, which is consistent with the observed slow leaching of gold in the oxygen-thiosulfate system. The slow reduction of oxygen on the gold surface may be attributed to the high over potential for the reduction of oxygen[3]. The presence of copper significantly enhanced oxygen reduction on gold in the 50 to 300 mV potential region, but the rate of the reaction was still relatively low.

Figure 2 also shows that oxygen reduction on the surface of two sulfide minerals (pyrite and chalcopyrite) is much more effective than on the surface of gold. Oxygen reduction on the sulfide minerals commences at approximately 270 mV, with the reduction current density increasing sharply as the potential shifts to more negative potentials. Oxygen reduction was also found to occur preferentially on other sulfide minerals such as chalcocite and pyrrhotite[8]. As most of the sulfide minerals are semi-conductive, it is expected that a galvanic interaction between gold and sulfide minerals could occur during the leaching of gold sulfide ores.

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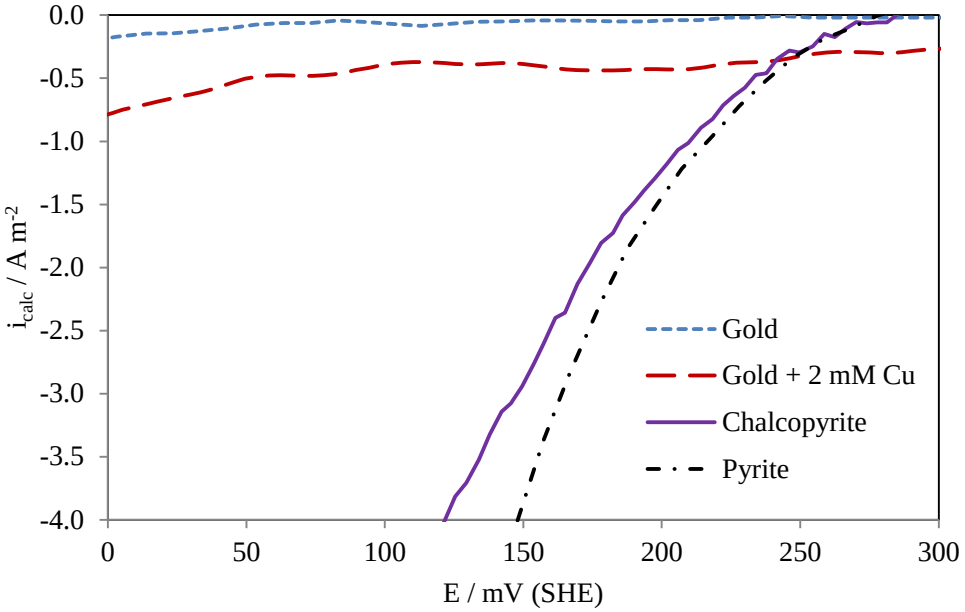


Figure 2: Linear sweep voltammograms using RDE showing the reduction of oxygen on gold (in the absence and presence of 2 mM copper) and sulfide minerals in 0.1 M sodium sulfate at 50 °C and under oxygen saturated conditions.

REQCM Open Circuit Leaching of Gold

Effect of Copper

Initially gold leaching experiments were performed using REQCM to take advantage of the *in situ* measurement of leach rates and fast experimental turnover of this technique. Figure 3 illustrates the effect of copper on the gold leach rate in an oxygen saturated sodium thiosulfate solution. It can be seen that the addition of 1 mM copper increases the dissolution rate by one order of magnitude from 1.9 × 10^{-7} to 2.75 × 10^{-6} mol m^{-2} s^{-1}. Similar gold leach rates were obtained when the copper addition was increased from 1 mM to 3 mM. However, further increases in copper concentration resulted in a decrease in the gold leach rate. This is consistent with the electrochemical study, where the gold oxidation was hindered at high copper concentrations. Thus, for subsequent experiments in this study, 2 mM copper was added to all solutions.

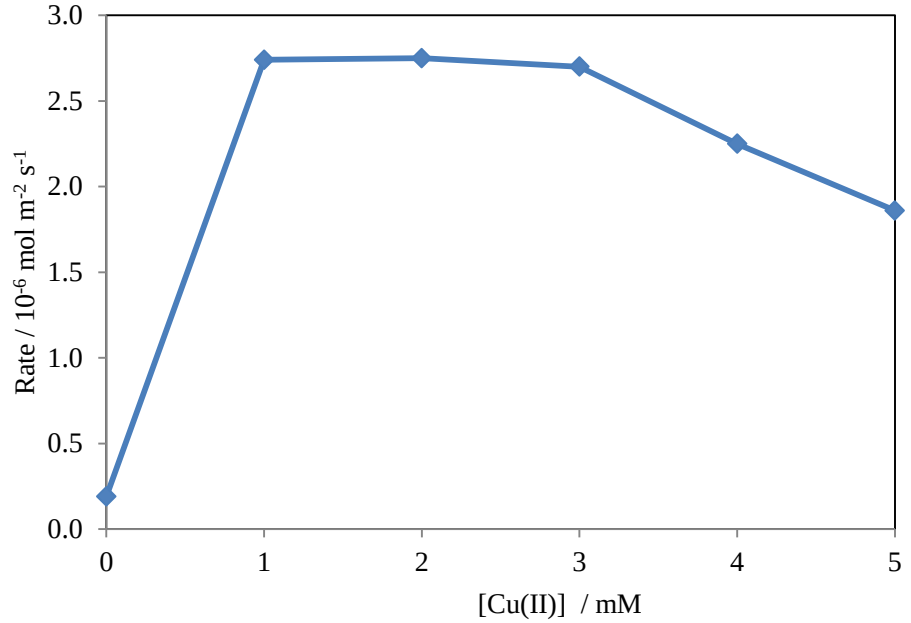


Figure 3: Effect of added copper concentration on the gold leach rate in 0.1 M sodium thiosulfate oxygen saturated solution at 50 °C.

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Effect of Sulfide Minerals

In order to study the galvanic interaction between sulfide minerals and gold, a mineral RDE electrode was placed in the solution along with a REQCM gold electrode during leaching. The REQCM was used to measure the gold leach rate and the corresponding mixed potential. The two electrodes were not connected together electrically until leaching had proceeded for 100 seconds. As shown in Figure 4, when the pyrite electrode was electrically connected to the gold electrode, the gold leach rate increased by almost 3 times. At the same time, the mixed potential increased rapidly from 108 mV to 175 mV. As shown in Figure 4, this is in the potential region where oxygen reduction can occur on pyrite surfaces. Therefore, it is believed that the connected pyrite electrode provides extra surface area for oxygen reduction to occur and, hence, the increase in the total cathodic current causes a positive shift in the mixed potential and an increase in the gold leach rate.

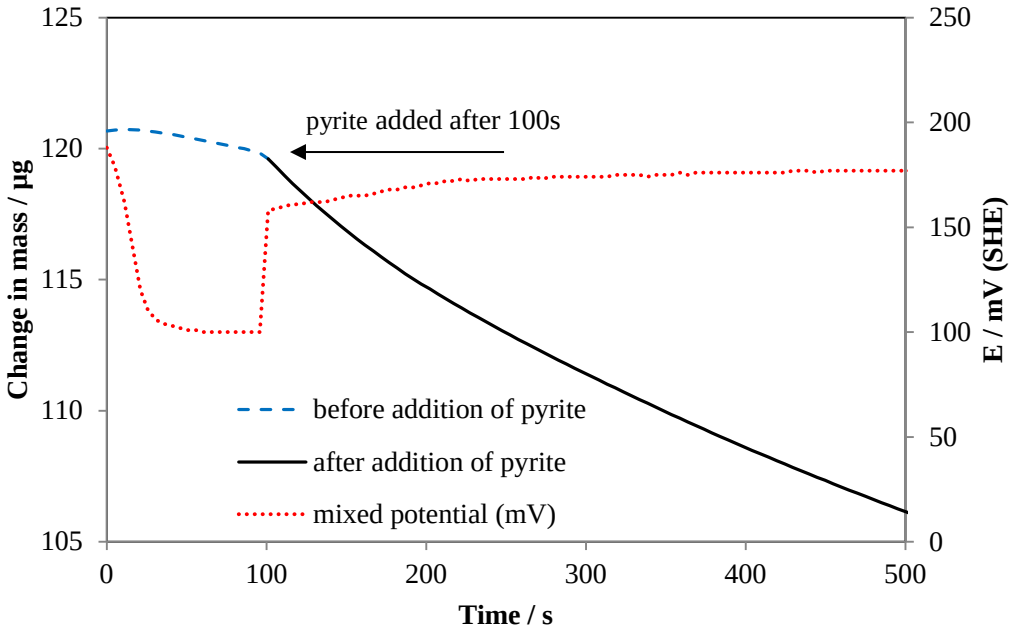


Figure 4: Mass loss of gold RDE due to leaching in 0.1 M sodium thiosulfate, 2 mM copper, oxygen saturated solution at 50 °C with pyrite mineral RDE electrically connected after 100s.

Figure 5 shows the gold leach rate as a function of pyrite : gold surface area ratio for different surface area pyrite electrodes. It is clear that the gold leach rate increases with the ratio up to a point above which further increase in mineral surface area provides little additional enhancement in the gold leach rate. It is most interesting to note that when the pyrite : gold surface area ratio is sufficiently high, which is the case for most sulfidic gold ores, the galvanically enhanced gold leach rate has the potential to reach the rate of 10^{-5} mol m^{-2} s^{-1}, which is in the same order of magnitude as a typical cyanidation rate. In addition to pyrite, other sulfide minerals such as chalcopyrite, chalcocite and marcasite were found to have a similar effect (also shown in Figure 5). The results thus show great promise for the potential use of the oxygen-thiosulfate system for treating sulfidic gold ores. It should be pointed out though, that the oxidation of thiosulfate by oxygen is also catalysed by the sulfide mineral surfaces particularly at pH < 9[9], which could impact the solution chemistry, gold leaching and the downstream gold recovery processes if treating sulfidic ores.

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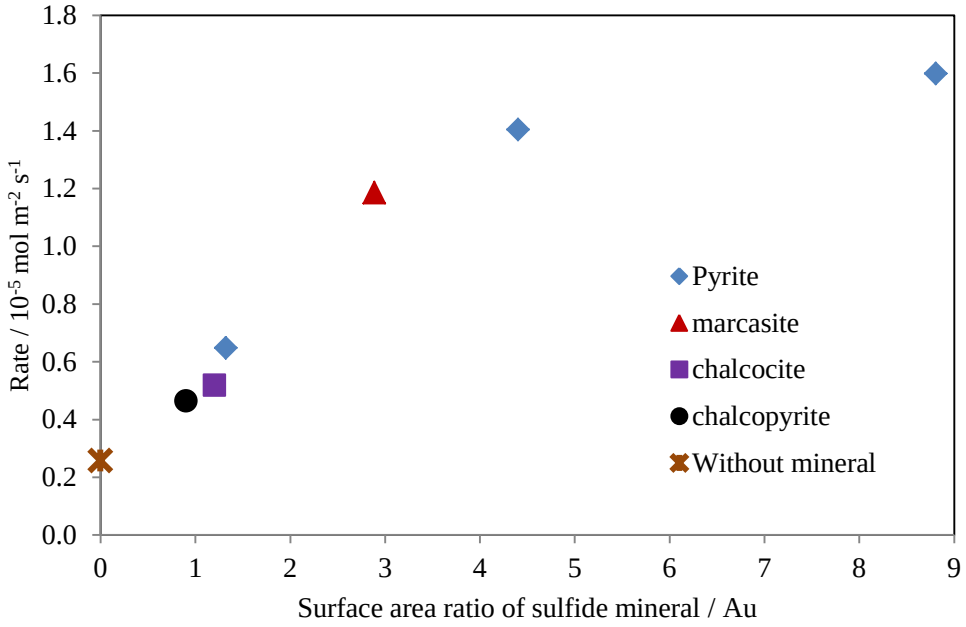


Figure 5: Effect of mineral surface area galvanically connected to gold on gold dissolution in 0.1 M sodium thiosulfate, 2 mM copper, oxygen saturated solution and 50 °C.

Dissolution of Gold Powder

The REQCM offers the advantage of *in situ* measurement of leach rates. However, the leach period is typically short due to a limit on the amount of gold plated on the quartz crystal surface (high gold plating reduces the sensitivity of measurement). Therefore, to investigate the oxygen-thiosulfate system for longer leaching time frames, gold powder leaching was performed. The leaching of gold powder in the presence of pyrite powder also allowed the investigation of potential galvanic interaction.

Figure 6 shows the effect of pyrite on the dissolution of gold powder with results plotted in terms of the shrinking sphere model. The pyrite was added as powder, creating an intimate physical particle-particle contact. Clearly this provides sufficient electrical contact with the gold powder for galvanic interaction to occur, resulting in significantly enhanced gold dissolution rates for the thiosulfate leaches. The enhancing effect of pyrite appeared to increase with increasing pyrite concentration / mineral surface area, which is consistent with the results shown in Figure 5. Also shown for comparison are the cyanidation results obtained using 10 mM NaCN solution with air bubbling in the absence of pyrite. As can be seen, the initial rate of cyanidation is significantly higher than the thiosulfate leaches; the rate, however, decreases with time and deviates from the shrinking sphere model, potentially due to a surface passivation by $AuCN$[10]. Approximately 60% of gold was leached in 24 hours in the cyanide solution. The 24-hour gold leach recoveries are summarised in Table 1. Remarkably, the 24-hour thiosulfate leach recoveries of 1.0% and 2.5% (wt/v) pyrite exceed the cyanidation recovery, approaching complete gold dissolution.

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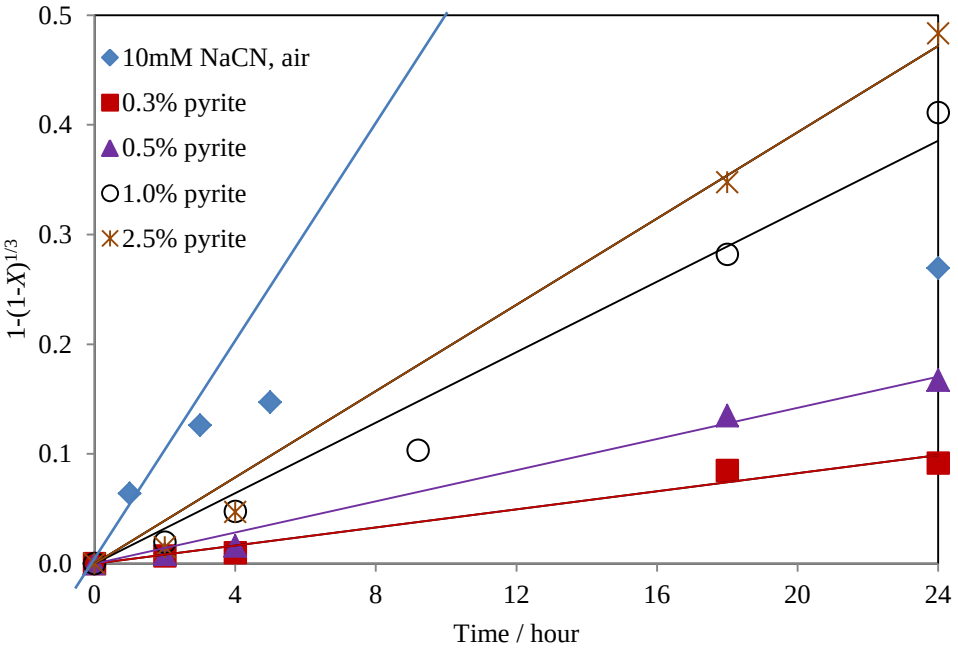


Figure 6: Effect of pyrite mineral on gold powder dissolution (presented as reaction controlled shrinking sphere model where *X* is the conversion rate of gold). Experimental conditions: 2 mM copper, 0.2 M calcium thiosulfate, 10 mL min^{-1} oxygen, 60 mg L^{-1} gold powder, pyrite powder -100 µm.

Table 1: Effect of pyrite on the 24-hour gold recovery.

Pyrite content % (wt/v)	% Au dissolved (24 hours)
0.0	2
0.3	25
0.5	42
1.0	80
2.5	86
Cyanidation	61

Ore Leaching

To confirm the effects observed in the above investigations, leaching experiments were conducted in rolling bottles using different types of ores, including an oxide ore, two copper-gold concentrates and three pyrite concentrates. The leach conditions used were 0.3 M thiosulfate in the presence of 2 mM copper at 50 ^{o}C. Information about the samples is provided in Table 2, along with example gold cyanidation recovery which for the sulfide ores was either low or uneconomical due to very high cyanide consumption.

Table 2: Mineralogical information and cyanidation results of ore samples.

Sample	Description	Size (µm)	Head (g/t)	S^{2-}%	NaCN leachable Au
A	Oxidized ore	P_{100} -90	4.4	0.49	>95%
B	Cu-Au flotation conc.	P_{80} -60	7.7	28.4	62% 24 hr @50 °C + 50 kg t^{-1} NaCN
C	Cu-Au flotation conc.	-	15	-	98% 24 hr @ 241 kg t^{-1} NaCN + O_2
D	Pyrite conc.	P_{80} -26	45	30	90% 48hr intensive cyanidation P_{80} -10
E	Pyrite conc.	P_{80} -36	3.1	42.5	38% 24 hr @ 3 kg t^{-1} NaCN
F	Pyrite conc.	-	45	38	62% 24 hr @ 11 kg t^{-1} NaCN

Figure 7 shows the gold leach recoveries of the above ore samples using the oxygen-thiosulfate leaching system. Leaching of the oxide ore (A) exhibited slow leach kinetics with a gold leach recovery significantly lower than cyanidation. The gold recovery, as well as leach kinetics, was

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significantly better for the copper-gold concentrates (B and C) and pyrite concentrates (D, E and F), indicating a positive impact of sulfide minerals through galvanic effect in the oxygen-thiosulfate leaching system; such results are consistent with the findings of the REQCM and gold powder leaching investigations.

For sample B with a 24-hour cyanidation gold recovery of 62% (under harsh leach conditions: 50 ^{o}C + 50 kg t^{-1} NaCN; Table 2), thiosulfate leaching achieved a similar 24-hour gold recovery and a better recovery in 48 hours, namely 71%. It should be noted that the leaching was still in progress after 48 hours reflecting a slow but steady process. Continued leaching could be possible provided that thiosulfate was still available.

For sample C, a good cyanidation gold extraction could only be achieved using aggressive leach conditions: very high cyanide addition in conjunction with the use of oxygen at high flow rates. The high cyanide consumption is due to the reaction with copper minerals to form copper cyanides as well as the reaction with iron sulfides to form thiocyanate and iron cyanides; high cyanide consumption is a major issue of cyanidation for this concentrate. With thiosulfate leaching, a fairly good gold extraction of 73.2% was achieved in 24 hours. The leach rate slowed down subsequently after this, with only 7% additional gold extracted during the next 24 hours. This could be related to one or more of the following: 1) a decrease in the free thiosulfate concentration (due to the lack of control on leach conditions for these small scale bottle roll tests, the initial 0.3 M thiosulfate was almost depleted by the oxidation of thiosulfate to form polythionates (0.19 M) and the complexation with copper (0.09 M)); 2) the high concentration of copper in the solution (reached 28 mM) passivating the gold surface via the formation of Cu_2S and/or Cu_2O precipitates (see Figure 3) and; 3) a gold thiosulfate instability issue. The loss of precious metals via precipitation from ammonia-copper-thiosulfate leach solutions has been previously investigated at CSIRO. It was found that tetrathionate, a thiosulfate degradation product, is a precursor for the precipitation of gold and silver, particularly in the presence of copper, as a mixed metal sulphide. Both copper and tetrathionate (14 mM) were present at high concentrations in the leach solution. The instability of gold would have been exacerbated by the reduced free thiosulfate concentration.

For sample D, a good cyanidation gold recovery (90%) can only be achieved using 48-hour extensive cyanidation with fine grinding of ore to P_{80} = 10 µm. In comparison, thiosulfate leaching achieved 52% gold recovery in 48 hours without fine grinding; the leach profile also indicates a trend of continuing leaching. Thiosulfate leaching of the fine grinding ore achieved similar results, 51% gold recovery in 48 hours. One potential reason for this lower-than-expected gold recovery is that the fine grinding significantly increased the fresh surface of sulfide minerals, which strongly catalyses thiosulfate oxidation (the thiosulfate concentration decreased from 300 mM to 5 mM in 48 hours).

For sample E, a very refractory sulfidic ore, standard cyanidation only achieved 38% gold leach recovery in 24 hours and little improvement could be made by pre-treatment, lead addition or oxygen enrichment. Notably, thiosulfate leach resulted in a slightly higher gold recovery (41%) within the same time frame. In addition, significantly less copper was extracted (nearly zero additional copper from thiosulfate leaching vs. 30 mM from cyanidation). It was also noted in this study that there is a potential for *in situ* generation of thiosulfate from some reactive sulfide minerals (e.g. pyrrhotite) and therefore the reagent requirement could be reduced/eliminated.

For sample F, the thiosulfate gold extraction was 30% in 24 hours (about half of the cyanidation recovery) and 52% in 48 hours, with no signs of slowing down. A higher gold extraction would be expected if the leaching was allowed to continue for a longer period.

When compared to cyanidation, the thiosulfate leaching of sulfidic ores using oxygen as the oxidant could have slower leach kinetics, but often in the same order of magnitude with fairly good (sometimes better) gold recovery in reasonable time frames. As these were only preliminary evaluations, better gold extractions are expected using optimised conditions and/or longer leach periods. The results hence show some promise in using the oxygen-thiosulfate system for treating sulfidic ores, particularly high copper containing ores where the high cyanide consumption renders cyanidation uneconomic. There are also opportunities for treating carbonaceous, preg-robbing ores where the cyanidation gold recovery is low.

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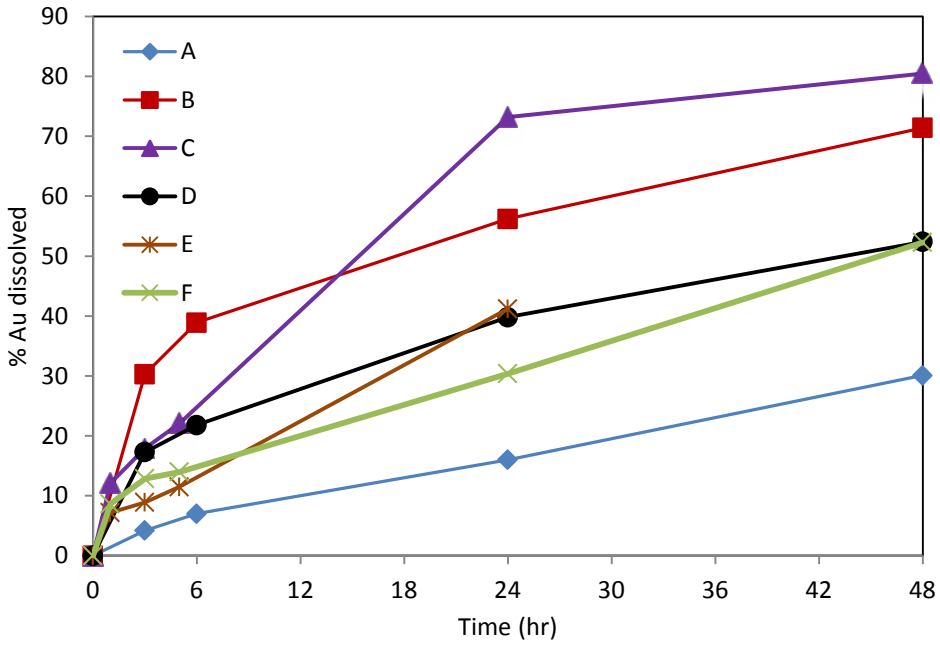


Figure 7: Effect of different ore types on gold leaching in the oxygen-thiosulfate system (0.3 M calcium thiosulfate, 2 mM Cu, pH 10, 50 °C, 10 mL min^{-1} O_2).

CONCLUSIONS

Electrochemical studies have shown that in the potential region of interest for gold leaching in thiosulfate solution, the oxidation of gold is significantly enhanced by the presence of a low concentration of copper. In the absence of copper, the gold oxidation reaction is faster in calcium thiosulfate solutions than in sodium thiosulfate solutions; whilst in the presence of copper, the rate of the gold oxidation reaction is similar in both solutions in the potential region of interest. The oxygen reduction on the gold surface under the tested conditions is very slow and the increase in rate by copper is not to the extent that would allow effective gold leaching. Oxygen can be reduced much more effectively on sulfide minerals, such as pyrite, offering an opportunity for galvanic interaction between the gold and sulfide minerals during the leaching of sulfidic ores.

The gold powder leaching tests confirmed that galvanic interaction between gold particles and sulfide minerals occurs through particle-particle interaction as predicted by the electrochemical study, with significantly enhanced gold leach recoveries in the presence of sulfide minerals. Leaching tests conducted using real gold ores/concentrates achieved, in some cases, gold leach recoveries comparable to or even better than cyanidation. The results hence show promise of using the oxygen-thiosulfate system to leach sulfidic ores, although further work is required to optimise the leach conditions to maintain effective leaching.

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CYANIDE-FREE FUTURE OF GOLD PROCESS SELECTION

By

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ABSTRACT

A tool has been constructed to aid an expert in the comparison of gold processes. Careful selection of a processing method is essential for the profitability of a gold deposit, as deposits vary greatly with respect to mineralogy, size, gold grain size etc. Case-based reasoning (CBR) methodology was selected to be utilized in the comparison of processes and a procedure was created for externalizing and formalizing knowledge from public sources regarding gold extraction processes. An initial case base of existing processes was built and case retrieval algorithms programmed within the CBR tool. Cases are compared according their similarities to a user's query, for example ore description. Similarity based retrieval enables the system to provide results even when no exact match is found. This is an important feature with gold ores and concentrates, since exact matches rarely exist due to the uniqueness of each ore deposit.

Currently, the tool only suggests cyanide based leaching processes, because cyanide is practically the only industrially utilized process for gold ores and concentrates today. However, there is increasing pressure from authorities in many countries to find cyanide-free methods due to environmental and safety risks. Therefore, it is now under investigation whether the knowledge extraction and formalization procedure can be applied for recommending a cyanide-free leaching method for a certain type of raw material. Research is needed to determine and code the similarity models of cyanide-free processes. The task is more challenging, since most of the processes are still in the development phase and there is not as much information available on the new-coming processes.

Keywords: Case-based Reasoning, Gold Leaching

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INTRODUCTION

Gold ore deposits vary greatly with respect to gold content, host and gangue minerals, deposit size and gold grain size to name a few. This variation has led to the use of different combinations of several unit processes, such as flotation, gravity separation, bio oxidation, roasting, pressure oxidation, chlorine oxidation, Merrill-Crowe process, CIP, CIL, RIP and RIL. Combined with all the parameter choices within these unit processes e.g. leaching time, temperature, pH, additives and their amounts, mixing velocity and feed particle size, there is a broad amount of ways to produce gold[1]. When a new deposit is found, rigorous testing and development work takes place before an optimal processing method for that particular deposit is determined and those experiments can be expensive or time consuming. Therefore, if the method of selecting the initial set of processes to be tested could be made more efficient, the economics or time management of the whole project could be improved.

So far the testing procedure is defined by human experts, who have extensive experience in the field. However, the capacity for humans to acquire process knowledge is restricted and the amount of senior specialists in each field is limited. In addition, such deep expertise knowledge can be locally lost due to rapid changes in the mining and metallurgy business. New scientific articles and research reports are published continuously, all contributing to the whole of scientific knowledge and it takes tremendous amounts of manual work for an expert to process all that knowledge and then apply it efficiently.

To aid humans in complex decision making situations, such as the one presented here, several methodologies can be used. These methodologies are, for example model-based, rule-based and case-based reasoning[2]. The use of decision making tools for selecting process chains for gold ores is discussed in the sext section.

REASONING METHODS FOR RECOMMENDING FLOW SHEETS FOR GOLD ORES

The three main reasoning methodologies available are model-based, rule-based and case-based reasoning methods. The selection of the method to be used depends mainly on the nature of the knowledge in the domain and the desired measures. From the knowledge modelling point of view it has been shown that the published knowledge concerning gold extraction from its ores and concentrates is fuzzy and incomplete[2,4]. When the quality of 25 journal articles and industrial reports concerning the results of gold leaching were analyzed, it was observed that gold content and outcome of the process were usually well described. However, the information richness between the publications varied, for example the descriptions of the raw materials, experimental arrangements and results were often described in different levels of detail, which inhibits experiment repeatability. This fuzziness and incompleteness of knowledge and the fact that the knowledge about utilized processes is dynamic and increasing continuously as new publications emerge bring challenges to knowledge formalization. These factors demand a reasoning methodology that can quickly react to changes and that can derive decisions from fuzzy knowledge. Table 1 lists the advantages and disadvantages of model-based, rule-based and case-based reasoning methods regarding process selection for gold ores[2].

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Table 1: The advantages and disadvantages of reasoning techniques recommendation of the gold ore process flowsheets[2]

Reasoning methodology	Advantages	Disadvantages
Model-based	• High precision in the decisions/ recommendations • Broad coverage of domain knowledge	• High initial effort to create the knowledge model • Rigid: once the model is employed it is hard to change to cater for changes in the domain knowledge
Rule-based	• Knowledge model can be expanded quickly • Effective reasoning • Precise decisions/recommendations	• Rigid knowledge model • Knowledge model requires frequent updates of the rules to stay accurate
Case-based	• Possibility to retrieve several cases that are similar to the target problem that allows for alternative recommendations, even if only fuzzy and incomplete queries are used • Easy expansion of the knowledge model by adding new cases • Similarity measures can represent domain knowledge that is otherwise hard to formalise	• Typically high effort in modelling adaptation knowledge to adapt solutions • Similarity measures may require high modelling effort

Properties of these methodologies and their applicability for metallurgical process selection have been compared, and it was shown that the case-based reasoning (CBR) method is suitable for defining similarities between gold processes applied to ores or concentrates[2]. This is due to the fact that CBR makes decisions based on similarity comparison and functions also with incomplete data[3]. The similarity measures employed within the case-based reasoning systems may require a high modelling effort, however, it was selected as being the best method when handling incomplete data related to gold ore/concentrate processing[2].The application of CBR methodology on gold process decision making is discussed further in the following section.

CASE-BASED REASONING

CBR is a decision making method that works in the same manner as a human expert makes decisions, by comparing the problem to previous problems that have been solved. The previous solutions to similar problems are taken as a basis for resolving the current problem. The advantage of CBR is that it eliminates human error and might propose a surprising and promising suggestion that the human expert would not have thought of for various reasons[5].

First, a database of previous cases is required and the knowledge within those cases needs to be formalized. This means defining all attributes and their character as either numerical or descriptive. Different similarity values are assigned for the attribute values ranging from 0 to 1, describing their level of similarity. After this, the user can enter a query containing values of a completely new case. From all the local similarities (sim_i) between weighted (ω_i) attributes (i) of the query case (q_i) and a case already in the system (c_i), a global similarity measure (Sim) is calculated according to Equation 1[6].

$$Sim(q,c) = \sum_{i=1}^{n} \omega_i * sim_i(q_i, c_i) \qquad \text{Eq 1}$$

Based on the global similarities between the query and the existing cases, CBR then provides a number of best matching cases and their solutions. The user can then perform validation tests on the suggested solutions and possible variations of them, eventually finding the optimal one. This results in a new case that can be added into the original case-base, enriching the functionality of the whole mode[6]. This standard process of reasoning in CBR is represented as the CBR-cycle in Figure 1[7].

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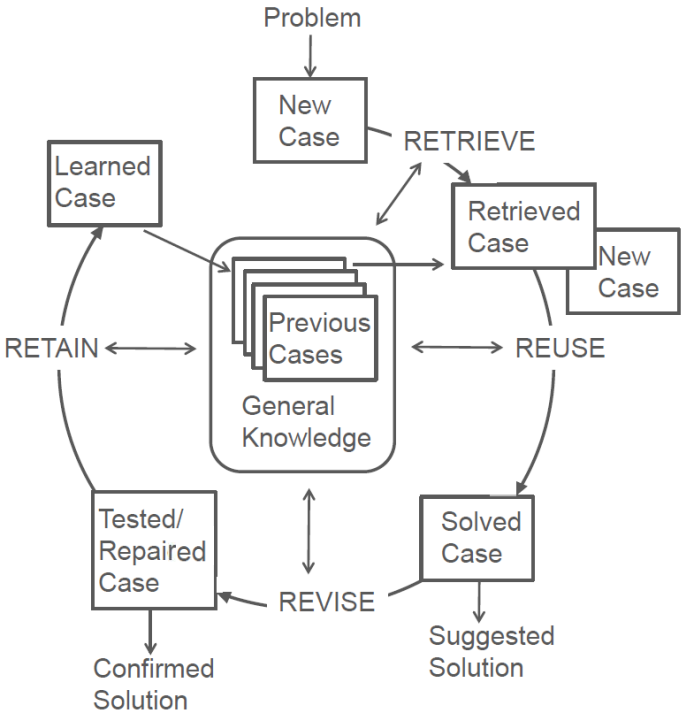


Figure 1: The CBR-cycle adapted after Aamodt et al.[7]

The benefits of CBR, compared to other decision making methods, are that it does not require an exact match to produce results and that it works for incomplete queries. For example, if the gold particle size distribution is not known, it can be left out of the query and the CBR tool makes suggestions based on other queried values. This is beneficial for metallurgical process selection as exact matches for a given raw material are rarely found and there are often gaps in the reported knowledge[2]. There are numerous possible applications for CBR in various fields, such as audio mixing[8] and equipment maintenance[9].

CONSTRUCTED MODEL

A decision making tool based on CBR was constructed for gold ore/concentrate processing methods. First, the attributes to be compared between cases and the similarities between different attribute values needed to be defined. The following attributes were selected to be modelled in this stage of the process selection tool development: *Ore type*, *Gold ore grade*, *Gold distribution*, *Gold grain size*, *Sulfide present*, *Arsenic sulfide*, *Copper sulfide, Iron sulfide*, *Clay present*. Three attribute types: symbol, Boolean and floating point numbers were used in modelling these attributes.

The attributes *Clay present* and *Sulfide present* are examples of attributes modelled by Boolean attribute type. The accepted values for this attribute are Yes and No, the similarity being exactly 0 or 1 for different and similar values respectively.

The attribute *Gold ore grade* was modelled by attribute type floating point by a symmetric distance function presented in Figure 2[2]. The similarity was computed in an interval between 0 (most dis-similar value) and 1 (identical value).

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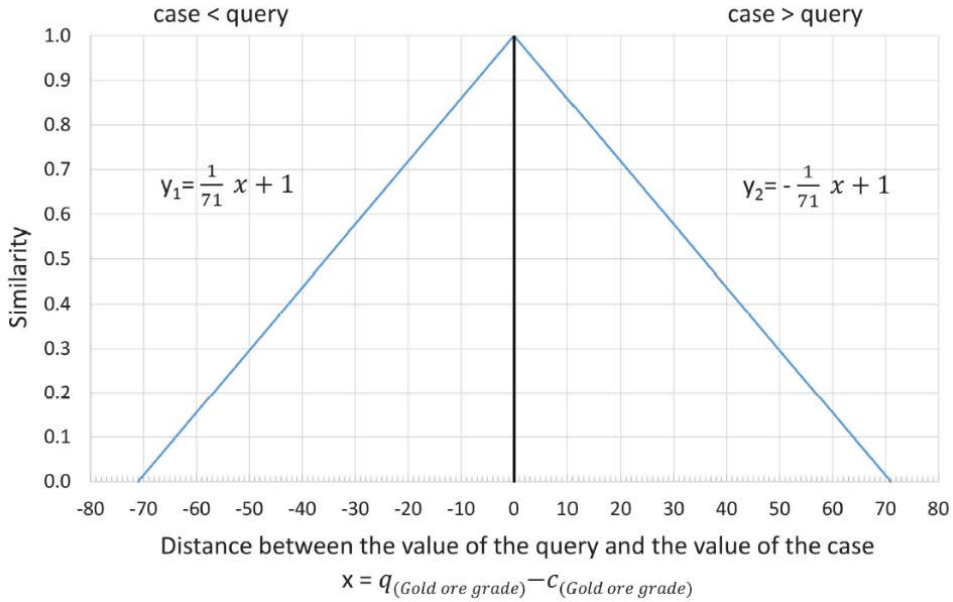


Figure 2: The local similarity model for the attribute Gold ore grade[2]

The other studied attributes (*Ore type, Gold distribution, Gold grain size* and *Arsenic, Copper* and *Iron sulfide*) were modelled by symbols employing comparative similarity tables as similarity measures. These local similarity values were assigned for the attributes based on expert interviews and literature. An example of a comparative similarity table is presented in Table 2[2]. Separate rules were developed for the modelling of the similarities of minerals based on the 10th edition of the Nickel-Strunz classification of minerals[10].

Table 2: Comparative local similarities for the attribute *Arsenic sulfide*[2]

Mineral	Arsenopyrite	Orpiment	Realgar	Any	None
Arsenopyrite	1.0	0.5	0.5	0.5	0.0
Orpiment	0.5	1.0	0.8	0.5	0.0
Realgar	0.5	0.8	1.0	0.5	0.0
Any	0.5	0.5	0.5	1.0	0.0
None	0.0	0.0	0.0	0.0	1.0

The case base for the CBR tool was assembled manually from different sources and is being expanded continuously. With the local similarities defined and the case base compiled, the tool could calculate local similarities for separate attributes of cases. This function was tested by providing the system with several query cases and then evaluating the results against manual similarity calculations. The local similarity calculations were observed to be accurate.

After the tests of local similarity measures, the global similarity calculations were validated with test cases based on existing processes which were not included in the case base. For example, the model was used to suggest a process for a gold ore from Homestake Lead mine located in Lead, South Dakota, USA that is described as follows:

> "Fine free gold and minor silver are associated with a predominantly chloritic-quartzite gangue. Small quantities of pyrrhotite and other minor sulfides occur in the ore"[1]

A test case of seven attribute-value pairs was formulated based on this description and is presented in Table 3.

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Table 3: Attributes and values of one of the test cases that were used in evaluation of the CBR tool – Homestake Lead mine, USA

Test case A	
Attribute	Value
Au grade g/t	4.7
Ore type	Free milling
Gold distribution	Free
Gold grain size	Fine
Sulphide present	Yes
Iron sulphide	Pyrrhotite
Clay present	No

The CBR tool calculated the global similarities between the test case (Table 3) and the cases in the case base according to equation 1. The highest global similarity of 0.86 was produced in relation to East Driefontein mine located in Carletonville, Transvaal, South Africa. The ore from East Driefontein mine is described as follows:

> "The ore is typical Witwatersrand pebble-quartz conglomerate. Fine free gold and electrum are intimately associated with predominantly siliceous gangue but with minor pyrrhotite. Coarse gold present is negligible."[(1)]

The Homestake Lead ore and the most similar East Driefontein ore are relatively analogous; both are free milling ores, gold occurs as fine free grains and the ore contain sulphides, of which pyrrhotite is mentioned. The suggested process based on East Driefontein process was as follows: thickening, alkaline preaeration, agitated cyanide leaching, CIP, carbon elution, electrowinning and gold smelting.

The process flowsheets of the suggested process (East Driefontein) compared to the actual industrial process that has been applied for the test case ore (Homestake Lead) were found to be fairly similar as well, as can be seen from Table 4. Both ores are crushed and ground to somewhat similar size. In both cases alkaline preaeration has been utilised before agitated cyanide leaching. However, the most similar process (East Driefontein) and the actually established process differed – the actual process having also a possibility for gravity concentration and vat cyanide leaching for the coarse fraction. By observing the prioritized list of the most similar cases and not only the first option (East Driefontein), one could find a case where the process includes also gravity concentration. This highlights the principle of using the tool – it provides several different process options for the user to compare and evaluate.

Table 4: Process sheets of the most similar case from the case base and the actual established process of the Test Case[(1)]

Process step	SUGGESTED PROCESS BY CBR	ESTABLISHED PROCESS FOR TEST CASE
Comminution	78% < 75 µm	65% < 75 µm Gravity concentration Coarse fraction vat cyanide leaching
Enrichment	Thickening	Thickening
Pretreatment	Alkaline preareation	Alkaline preareation
Leaching	Agitated cyanide leaching	Agitated cyanide leaching
Recovery1	CIP	CIP
Recovery2	Carbon elution (**ND*)	Zadra elution
Recovery3	Electrowinning	Electrowinning
Refining	Smelting	Smelting

**ND - "type of treatment not defined more exactly"*

KNOWLEDGE MODELLING OF CYANIDE-FREE LEACHING PROCESSES

At the moment cyanide is the most widely used leaching agent in gold processing and also the sole leaching agent in the processes proposed by the constructed CBR tool. However, due to the health and environmental risks cyanide proposes, there is legislative pressure to find alternative gold leaching methods. Currently there are several cyanide-free extraction processes under

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development for gold ores and concentrates, such as the ones based on chloride, thiourea, thiosulfate, thiocyanate, bromine-bromide, iodine-iodide, bromine-chloride[1] and glycine[11]. Only one cyanide-free gold leaching method, thiosulfate, is in industrial use[12].

The research efforts on this topic would benefit greatly if a CBR based tool could be constructed to assist in the selection of cyanide-free leaching methods. This tool could be used for planning preliminary laboratory tests for a given ore, thus eliminating time consuming tests of all alternative methods and enabling focus on the most promising ones. Preliminary case base assembling and knowledge formalization for this tool has begun and professionals have been consulted about their preferences and requirements for such a tool. However, the specific topic of processes that are still in development poses several challenges for knowledge formalization.

Since the cyanide-free gold leaching methods, apart from thiosulfate leaching, have not been applied in industrial scale, the quantity of scientific articles and technical reports is low compared to cyanide leaching. During a literature survey, it was observed that experiments on the leachability of pure gold have been published considerably more than on the leachability of gold ores. Lack of experiments done on diverse ores, produces a problem since the CBR results are improved as the quantity of dissimilar cases increases.

Furthermore, even existing data on the process methods is often incomplete. This problem was discovered already during the construction of the previous model, but has proven to be more distracting in the event of cyanide-free methods. This might be because the level of detail that could be applied in this model is higher than in the previous one with respect to processing conditions. Since this tool should be used to design laboratory scale testing, the processing parameters, such as pH, agitation speed, cell volume etc. play an important role in the model's functionality. The level at which scientific articles report these parameters and ore mineralogy varies greatly.

CONCLUSIONS AND FUTURE WORK

The CBR based tool that was built for selecting conventional gold cyanide processes was shown to compare similarities between the existing gold ore bodies used for conventional cyanide based gold extraction. This model still needs to be improved by increasing the amount of cases within it.

A new selection tool for cyanide-free processes is also being developed along the improvement of the current model. This new tool will eventually aid researchers in acquiring comparable data about cyanide-free gold leaching methods and in designing new experiments on varying gold ore types. The next step is to construct a cyanide-free case base using literature sources, define different attributes related to the various cyanide-free methods and map out local similarities between these attributes. In addition to this, new experimental data will be produced within the scope of this project to increase the number of cases in the case base and simultaneously improve scientific understanding of the cyanide-free gold leaching processes.

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OUTOTEC REFRACTORY GOLD TECHNOLOGIES; COMPARISON AND DISCUSSION OF DIFFERENT PRE-TREATMENT METHODS

By

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ABSTRACT

Outotec is today capable of providing bespoke solutions for the treatment of refractory gold ores or concentrates including the three main pre-treatment processes, viz pressure oxidation (POX), roasting technology (ROAST) and bio-oxidation (BIOX).

This paper focuses on the main aspects effecting the pre-treatment technology selection. The effect of reserves and resources, metallurgical and mineralogical characteristics of the ore, impurities, size and location of the project, local conditions and regulations, utility requirements - especially water consumption and quality and electrical consumption, characteristics of residues and effluents on the technology selection are analyzed based on the data and information obtained from actual Outotec pressure oxidation, roasting and BIOX projects.

Besides the metallurgical performance, the environmental aspects are today of major importance. Today all three Outotec POX, Outotec ROAST and Outotec BIOX technologies can comply with current international environmental regulations.

Outotec can develop a project from conceptual study phase (including testwork execution/supervision) to detailed engineering to ensure the optimum POX, ROAST or BIOX flowsheet. Outotec's scope of supply can vary from single equipment or a full process technology package through to detailed engineering and project implementation. Outotec's scope of supply is also not limited to the refractory treatment process, but covers the whole process chain from ore milling and beneficiation through autoclave oxidation, BIOX or roasting to final gold recovery and effluent treatment.

In this paper Outotec will demonstrate the key process criteria for each of these three technologies and the effect of this on the process selection for a refractory gold project. The best choice of a processing route to treat a refractory ore will in most cases be site specific as demonstrated in this paper.

Keywords: BIOX, POX, ROAST, Outotec, Gold leaching, Design Criteria

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INTRODUCTION

Outotec provides advanced solutions for processing a variety of gold ore types ranging from free-milling to refractory gold ores. Our process solutions include ore sorting, comminution, flotation, refractory ore pre-treatment technologies, i.e. bio-oxidation, pressure oxidation and roasting as well as cyanide leaching and gold recovery with analyzers and automation systems. Tailings and effluent treatment are also an integral part of our solution offering.

Our extensive experience in minerals processing, hydrometallurgy and pyrometallurgy combined with our proven process and equipment technologies make Outotec a unique strategic partner for our customers. The expertise of our two in-house R&D centers with state-of-the-art facilities can be utilized in project development. Our capability to combine process and equipment technology together with automation design is vitally important. The provision of process design, plant engineering, equipment, automation and project management from Outotec eliminates expensive and restrictive interfaces during implementation.

Modern trends in gold metallurgy indicate increasing utilization of refractory gold ores in the future. In refractory ores, gold is locked within sulphide minerals making these ores not amenable to conventional cyanide leaching without pre-treatment. Outotec offers three proven pre-treatment options, bio-oxidation (BIOX), pressure oxidation (POX) and roasting (ROAST), to convert refractory or double refractory ores into easily and effectively leachable form. The addition of BIOX® bio-oxidation technology to Outotec's product portfolio adds to and complements already existing significant experience in the hydrometallurgical industry.

Today Outotec can reliably evaluate all three pre-treatment technologies and develop a project together with a client from a conceptual study phase to the operation. Since our technology portfolio comprises BIOX, POX and ROAST technologies, we have no intention to favor a certain technology but the selection can be made based on the real facts and project requirements.

All three pre-treatment technologies are typically technically feasible for most of the sulphide ores and can be tailored to meet the project requirements. However, based on the specific project drivers, there is an optimal technology for each project that can be found by proper project development including testwork and engineering. Outotec has participated in several refractory gold projects from a conceptual study level to the operation and has gained thorough experience and understanding of the specific project drivers affecting technology selection, including CAPEX and OPEX drivers.

Technology selection is typically done already in the early project development phase, e.g. in the pre-feasibility study phase based on CAPEX and OPEX estimates within +/- 25 % accuracy. Thus Outotec's early involvement in project development is beneficial for a client to secure the best technological fit for a project. We can support the project development team with technology selection in any project development phase and deliver the optimum solution for a client.

TECHNOLOGY FRAME

Declining gold grades and oxide ore resources together with increasing environmental concern set requirements for technologies used in gold industry. When processing a large amount of ores, the efficiency of used technologies start to play a more important role in order to exploit natural resources effectively and in a sustainable manner. Besides increasing throughput rates and tightened environmental regulations, the growing need to utilize refractory ore bodies will increase the complexity of the projects.

Outotec is continuously developing the existing technologies in order to improve the efficiency. We bring new technologies to market that open up new opportunities and allow a totally new approach in project implementation as well as resulting in significant cost savings both in investment and operation phases. As an example, Outotec sensor based ore sorting (SBS) solutions, which are applicable for certain ore types, may significantly reduce down-stream processing and environmental impact. Outotec fine grinding mills provide an energy efficient fine and ultra-fine grinding solution utilizing existing, proven technology. Historically Outotec has put a lot of effort into improving agitation in hydrometallurgical reactors. Outotec has several novel innovations related to reactor technology that improve process performance in roasting, pressure and bio-oxidation as well as in gold cyanide leaching.

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A close association of gold and sulphides, typically pyrite and arsenopyrite, is characteristic of refractory ores. In refractory ores, gold can be in the form of finely dispersed particles of native metal or in the form of solid solution of gold in the crystal lattice of sulphides as well as encapsulated within sulphides. In addition, ore may also contain carbonaceous matter which may cause the preg-robbing effect. The double refractory nature of the ore increases the difficulty of refractory ore treatment.

Roasting, pressure oxidation and biological oxidation are commonly used pretreatment technologies for refractory gold ores. Roasting has been utilized since the late 1940s. Both pressure oxidation and bio-oxidation processes made commercial breakthroughs in the mid 1980s. The first pressure oxidation plant was commissioned in 1985 in the USA and the first BIOX® bio-oxidation plant in 1986 in South Africa, Marsden and House (2006).

Bio-oxidation, pressure oxidation and roasting technologies can be designed and tailored for both refractory and double refractory ores. Pressure oxidation has been successfully applied for sulfidic carbonaceous double refractory ores at Goldstrike, USA (1992), Twin Creeks, USA (Simmons 1996 and Simmons et al 1998), Macraes, New Zealand (Cadzow and Giraudo 2000), Kittilä, Finland (Fleming et al. 2008) and Pokrovskiy, Russia (Zeitsev et al 2013). The BIOX® bio-oxidation process has been successfully utilized for double refractory concentrate e.g. at Ashanti, Ghana (1994), Fosterville, Australia (2005) and Suzdal, Kazakhstan (2005). Fluidized bed roasting for double refractory ore is in operation at Carlin, USA (1994).

All three pretreatment processes can be applied for whole ore treatment. However, if acceptable gold recoveries into the flotation concentrate can be achieved, significant capital savings in downstream processing can be obtained, McMullen et al (2002). In addition, utilization of flotation can result in increased metallurgical performance of the downstream process as illustrated in the following chapters.

Main selection criteria for the feasible processing technology are technical applicability, project profitability and environmental aspects. Capital and operating expenditures together with metallurgical performance form a firm basis for the technology selection. Besides gold recovery, the available by-products may affect the project revenue stream and technology selection. One of the key differences between roasting and bio- / pressure oxidation technologies is that high grade sulphuric acid and high pressure steam (HEROS®) can be produced if roasting technology is selected. High pressure steam can be further converted to electrical power. Both BIOX® bio-oxidation and pressure oxidation processes generate dilute sulphuric acid which in the gold industry is typically neutralized with lime and sulphur reports to tailings area in the form of gypsum. The energy of low pressure steam generated in pressure oxidation process is utilized in some operations. Energy can be used e.g. for water desalination or district heating purposes as designed for the Petropavlovsk Pokrovskiy project, Zaitsev (2013).

The BIOX® process is ideally suited to application in remote locations. The process does not require specialized process equipment and can utilize semi-skilled operators. The modular design of the process also allows for easy expansion of the plant capacity in small increments.

Besides the metallurgical performance, the environmental aspects are today of major importance. Deportment of environmentally hazardous elements such as arsenic, mercury and halides is of great interest during flowsheet development. As demonstrated by several industrial applications globally, all pre-treatment technologies bio-oxidation, pressure oxidation and roasting technologies can be designed to comply with the environmental regulations.

BIOX® BIO-OXIDATION PROCESS

A typical BIOX® circuit for double refractory ores consists of the following main process steps: comminution and flotation followed by BIOX® bio-oxidation, counter-current decantation and neutralization. A block diagram of a typical refractory ore process incorporating a BIOX® bio-oxidation circuit is shown in Figure 1

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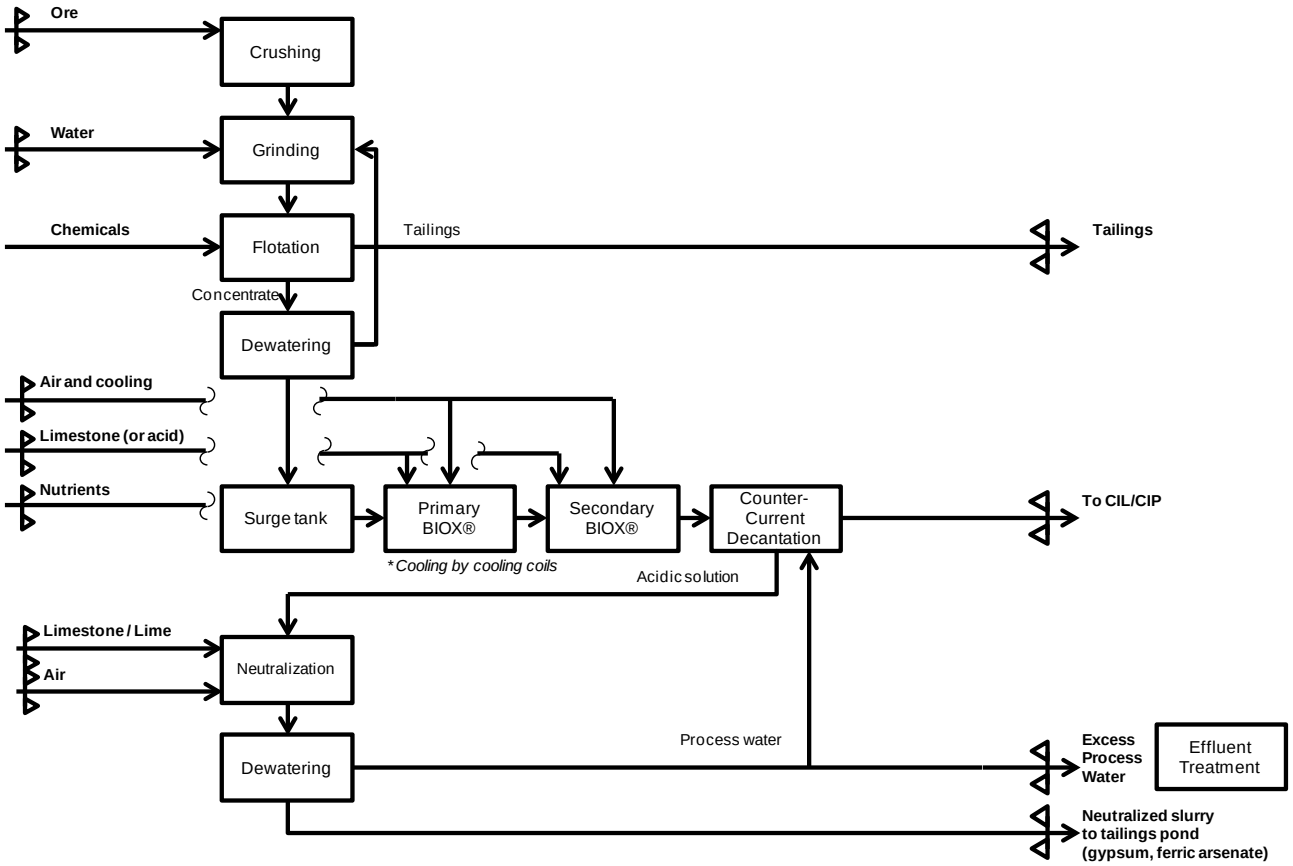


Figure 1: A block diagram of a typical refractory ore process incorporating BIOX® bio-oxidation circuit

The sulphide concentrate from the flotation section of the plant is pumped to the BIOX® stock tank. Flotation concentrate is thickened to a density of at least 50% solids to minimize carry-over of flotation reagents to the BIOX® reactors. A minimum sulphide sulphur concentration of approximately 4 - 6 % is usually required to ensure adequate bacterial activity during the bio-oxidation stage.

A regrind circuit may be included in the circuit before the stock tank, especially when a portion of the concentrate is produced using flash flotation. The feed concentrate to BIOX® would typically be milled to an 80% passing 75 µm with a minimum of plus 150 µm particles. An increase in the grind size would reduce the sulphide oxidation rate and would result in a lower overall oxidation for similar BIOX® treatment periods. Fine grinding to 80% passing 20 µm will enhance the sulphide oxidation rate but may influence the downstream processes negatively.

The bio-oxidation stage comprises two steps, i.e. primary and secondary steps. The BIOX® plant typically consists of six equidimensional reactors configured as three primary reactors operating in parallel followed by three secondary reactors operating in series. The feed concentrate from the stock tank is diluted to 20 % solids by mass before being fed to the primary BIOX® reactors. Slurry density is determined mainly by the oxygen mass transfer requirements of the process. If sulphide sulphur concentration is low, higher solids concentration may be used.

Oxidation reactions of the main sulphide minerals usually present in refractory ores are:

$$2\ FeAsS + 7\ O_2 + H_2SO_4 + 2\ H_2O \rightarrow 2\ H_3AsO_4 + Fe_2(SO_4)_3 \quad (1)$$

$$4\ FeS_2 + 15\ O_2 + 2\ H_2O \rightarrow 2\ Fe_2(SO_4)_3 + 2\ H_2SO_4 \quad (2)$$

$$4\ FeS + 9\ O_2 + 2\ H_2SO_4 \rightarrow 2\ Fe_2(SO_4)_3 + 2\ H_2O \quad (3)$$

$$4\ FeSO4 + O_2 + 2\ H_2SO_4 \rightarrow 2\ Fe_2(SO_4)_3 + 2\ H_2O \quad (4)$$

All reactions above are bacteria-catalyzed.

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Some iron is precipitating in BIOX® stage as jarosites according to the following reaction

$$3\ Fe_2(SO_4)_3 + 12\ H_2O + Me_2(SO_4) \rightarrow 2\ MeFe_3(SO4)_2(OH)_6 + 6\ H_2SO_4 \quad (5)$$

where $Me^+ = K^+, Na^+, NH_4^+, H_3O^+$

It is typical for the bio-oxidation process that a small fraction of sulphide is not completely oxidized to sulfate but remains as intermediate sulphur species such as polysulphides and thiosulphate. These sulphur species are very reactive with cyanide and form thiocyanate according to the following reactions (Luthy 1979):

$$S_xS^{2-} + CN^- \rightarrow S_{x-1}S^{2-} + SCN^- \quad (6)$$

$$S_2O_3^{2-} + CN^- \rightarrow SO_3^{2-} + SCN^- \quad (7)$$

Extensive development work has been carried out in the past focusing both on the pre-cyanidation treatment processes to de-activate the cyanide consuming species (Broadhurst 1996) and on investigation of how the intermediate sulphur species are formed and how the formation could be limited during the bio-oxidation stage.

Although the cyanide consumption following BIOX treatment is typically higher than for POX or Roasting, the consumption can be optimised during the testwork phase resulting in overall operating costs comparable to alternative processes. This is evidenced in the operating cost data form various feasibility studies and operating data from commercial BIOX® plants.

Retention time in the bio-oxidation reactors are typically four to six days depending on sulphide sulphur content and concentrate mineralogy. Half of the retention time is typically designed for the primary reactors to secure a stable bacterial population to be established and to prevent bacterial washout.

The BIOX® process is typically operated at 40 - 45°C. At higher temperatures higher sulphide oxidation rates can be obtained and cooling requirements can be minimized. The oxidation of sulphide minerals is an exothermic process. BIOX® reactors are cooled by circulating water through the cooling coils installed in the reactors. Evaporative cooling towers are typically used to remove heat from the cooling water.

Low-pressure air is injected into the BIOX® reactors to supply oxygen for the oxidation reactions. It is important that dissolved oxygen concentration is maintained above 2 mg/l all the time.

Nutrients in the form of nitrogen, phosphorous and potassium salts are also added to the primary reactors to promote bacterial growth. Low concentrations of nutrients may be present in the concentrate which can reduce the nutrient addition requirements when stable operation has been achieved (Olivier et al. 2000).

Besides air and nutrients, a minimum carbonate content of two percent in the flotation concentrate is usually required to ensure that sufficient CO_2 is available to promote bacterial cell production. If no carbonate is present, limestone or gaseous carbon dioxide must be added to the primary reactors as a source of carbon for cell production.

Depending on the concentrate mineralogy, the BIOX® process can be either acid-generating or acid-consuming. Limestone and sulphuric acid are used to control the pH in the BIOX® reactors within the optimum range of pH 1.2 - 1.8.

The oxidized slurry from the BIOX® bio-oxidation stage is washed typically in a three stage Counter Current Decantation (CCD) circuit before cyanide leaching. The washed BIOX® product would normally contain less than 1 g/l total iron in solution with a pH of 1-3. Iron and copper removal is necessary before cyanide leaching to promote gold recovery and reduce cyanide consumption.

The bacterial oxidation of conventional pyrite and arsenopyrite concentrates produces a solution containing arsenic(V) and ferrous sulphate. Extensive research and development work has gone into the optimisation of the design of the neutralisation section of the BIOX® process in recent years. This was to ensure that the effluents comply with the most stringent international environmental regulations with respect to product stability and residual arsenic concentrations. The most efficient neutralisation flow sheet was found to be a two-stage process effected in a series of

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agitated tanks, usually six or seven. In the first stage the pH is raised to between 4 and 5 with limestone or lime to form ferric arsenate and gypsum. The pH is then further increased to 7.0 in the second stage in order for the effluents to comply with environmental regulations.

In BIOX® bio-oxidation stage arsenic is oxidized according to the reaction (1) to As^{5+} which can be precipitated together with ferric iron as stable ferric arsenate.

$$2\ H_3AsO_4 + Fe_2(SO_4)_3 \rightarrow 2\ FeAsO_4 + 3\ H_2SO_4 \quad (8)$$

$$H_2SO_4 + CaCO_3 \rightarrow CaSO_4{\cdot}2H_2O + CO_2 + H_2O \quad (9)$$

The conventional method for the fixation of arsenic from solution is by lime neutralization, preferably in the presence of excess iron, to produce ferric arsenate ($FeAsO_4$) precipitates. For example, The United States Environmental Protection Agency (US-EPA) considers chemical precipitation of ferric arsenate be the Best Demonstrated Available Technology (BDAT) for the treatment of arsenic bearing wastes (Rosengrant and Fargo 1990).

Pilot plant tests as well as operational results from the commercial plants have shown that a sufficiently stable arsenic precipitate is formed, provided that the molar ratio of iron to arsenic is higher than 3:1. The precipitates, subjected to the standard as well as modified Toxicity Characteristic Leaching Procedure (TCLP) of the US EPA, proved to be stable over a wide range of pH values (5 to 9). Testwork also indicated that continuous dehydration/rehydration of the precipitates, simulating seasonal weathering in a tailings dam, resulted in an increase in arsenic stability.

THE PRESSURE OXIDATION PROCESS

A typical POX circuit for double refractory ores consists of the following main process steps: comminution and flotation followed by carbonate removal, chloride removal, pressure oxidation, vent-gas scrubbing, conditioning, solid-liquid separation and neutralization. A block diagram of a typical refractory ore process incorporating a pressure oxidation circuit is shown in Figure 2. Pressure oxidation technology is applied for both ores and concentrates.

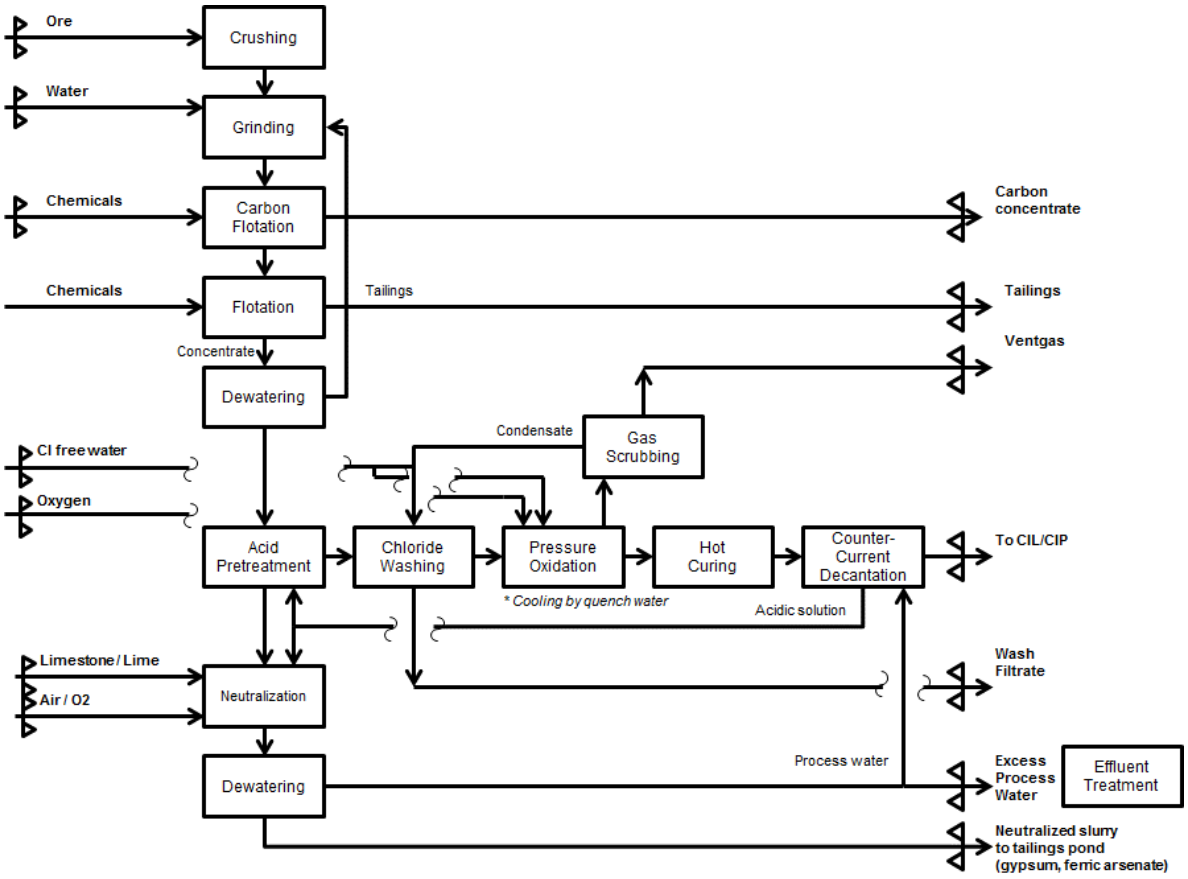


Figure 2: A block diagram of a typical refractory ore process incorporating

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a pressure oxidation circuit

Concentrate, either as thickened underflow slurry or pulped filter cake slurry, is treated in the acid pretreatment step prior to pressure oxidation if carbonates exist in the concentrate. Carbonates are leached by utilizing acid generated in the autoclave to minimize the formation of carbon dioxide and maximize oxygen utilization in the autoclave. Acid pretreatment may also enhance the dissolution of chlorides occurring in the concentrate.

Depending on the concentrate mineralogy, dissolved chloride may have a strongly negative effect on gold recovery in the pressure oxidation circuit. For carbonaceous sulfidic ores i.e. double refractory ores, chloride, even at very low concentrations may affect gold recovery. As an example, the effect of chloride on gold recovery for Petropavlovsk ores is described in more detail by Zaitsev et al (2012) and Zaitsev et al (2013).

Due to the detrimental effect of chlorides, a chloride washing step to remove dissolved chlorides from the concentrate prior autoclaving is applied e.g. in Agnico Eagle Kittilä Mine and Petropavlovsk Pokrovskiy POX Hub.

The purpose of the pressure oxidation step is to oxidize sulphide minerals, e.g. arsenopyrite/pyrite into sulphates and release gold that is encapsulated inside the sulphide crystal structure. Gold will not be dissolved but it remains in the leach residue. Oxidation is carried out typically at 190-230°C and oxygen partial pressure 3-7 bar by feeding gaseous oxygen, with purity above 98%, into the autoclave. Reactions are highly exothermic and the temperature in the autoclave is controlled by cooling water injection to each autoclave compartment separately. The main overall chemical reactions occurring in the pressure oxidation autoclave are shown below.

$$2\ FeS_2 + 7\ O_2 + 2\ H_2O \rightarrow 2\ FeSO_4 + 2\ H_2SO_4 \quad (10)$$

$$FeS_2 + 7\ Fe_2(SO_4)_3 + 8\ H_2O \rightarrow 15\ FeSO_4 + 8\ H_2SO_4 \quad (11)$$

$$4\ FeAsS + 13\ O_2 + 6\ H_2O \rightarrow 4\ H_3AsO_4 + 4\ FeSO_4 \quad (12)$$

$$2\ FeAsS + 13\ Fe_2(SO_4)_3 + 16\ H_2O \rightarrow 2\ H_3AsO_4 + 28\ FeSO_4 + 13\ H_2SO_4 \quad (13)$$

$$2\ H_3AsO_4 + Fe_2(SO_4)_3 \rightarrow 2\ FeAsO_4 + 3\ H_2SO_4 \quad (14)$$

$$Fe_2(SO_4)_3 + 3\ H_2O \rightarrow Fe_2O_3 + 3\ H_2SO_4 \quad (15)$$

$$Fe_2(SO_4)_3 + 2\ H_2O \rightarrow 2\ FeOH(SO_4) + H_2SO_4 \quad (16)$$

Only a small amount of elemental sulphur is formed at temperatures above 190 °C. Ratio of the formation of Fe_2O_3 and FeOHSO4 depends on the operating conditions i.e. operating temperature, acidity and retention time in the autoclave. Basic iron sulphates, $FeOHSO_4$, formed in the autoclave are mainly dissolved in a conditioning process step. These basic iron sulphates decay in the subsequent neutralization and lead to the increased expense of a neutralizer – lime.

Ferrous ion formed in the reactions is oxidized by molecular oxygen back to ferric ion, Reaction (17).

$$4\ FeSO4 + O_2 + 2\ H_2SO_4 \rightarrow 2\ Fe_2(SO_4)_3 + 2\ H_2O \quad (17)$$

Oxidation-reduction of iron plays an important role in the reaction system. Long (2000) has proposed that pyrite is initially oxidized to ferric sulfate by molecular oxygen according to Reaction (17). Long (2000) also reported that ferrous ion oxidation by molecular oxygen (Reaction (16)) significantly affects the reaction rate of pyrite oxidation.

$$4\ FeS_2 + 15\ O_2 + 2\ H_2O \rightarrow 2\ Fe_2(SO_4)_3 + 2\ H_2SO_4 \quad (18)$$

Chlorides have a negative effect on gold recovery if organic carbon is present in the leaching media. In the autoclave, gold may be oxidized e.g. by ferric iron in the presence of chlorides and the formed gold chloride complex is reduced onto organic carbon

$$Au + 3\ Fe^{3+} + 4\ Cl^- \rightarrow [AuCl_4]^- + 3\ Fe^{2+} \quad (19)$$

$$4\ [AuCl_4]^- + 3\ C + 6\ H2O \rightarrow 4\ Au\ on\ Carbon + 12\ H^+ + 16\ Cl^- + 3\ CO_2 \quad (20)$$

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Typically an oxidized autoclave slurry is washed in a counter-current decantation circuit prior to cyanide leaching. Besides acid, detrimental elements for cyanidation, such as iron and copper as washed from the solution.

Acidic solution from the autoclave and from the acid pretreatment step are neutralized with lime. Depending on the local availability, limestone or quick lime may be used. The purpose of the neutralization step is to neutralize the acidic solutions and precipitate components such as iron, arsenic, zinc, lead etc. so that the neutralized slurry meets the local legislation and regulations and can be stored in the tailings pond. The neutralization stage is similar to that in the BIOX® flowsheet.

THE ROASTING PROCESS

A block diagram of a typical refractory ore process incorporating a roasting circuit is shown in Figure 3. Roasting technology is applied for both ores and concentrates.

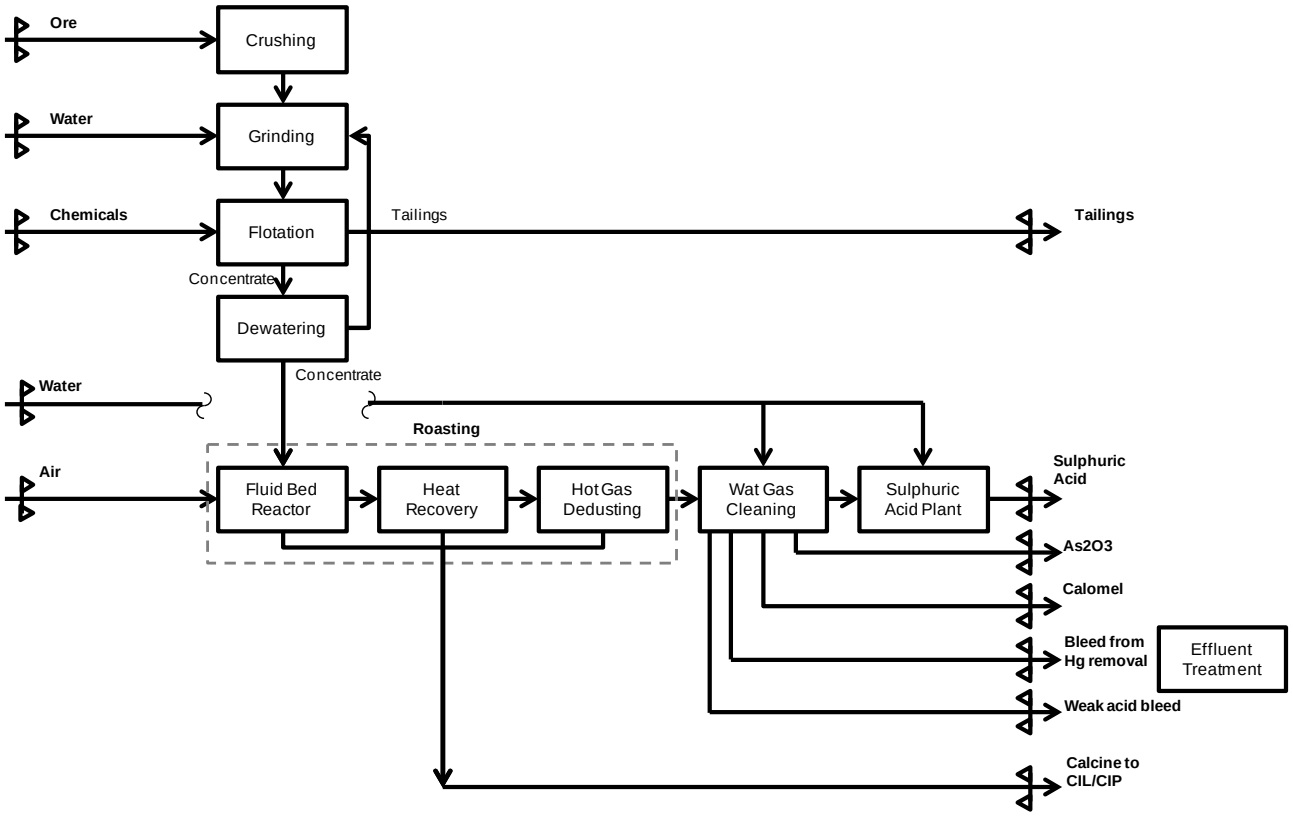


Figure 3: A block diagram of a typical refractory ore process incorporating a roasting circuit

Roasting can be carried out in single or two stages. Selection between the two options depends on ore type. The single stage consists of dead roasting in an oxidizing atmosphere. In the two-stage roasting process, the first stage is operated under reducing conditions for removing impurities such as arsenic and antimony, followed by second-stage roasting in an oxidizing atmosphere to complete oxidation.

Roasting of sulphide ores is an established technology for gold production. As shown in Figure 3 the whole roasting chain needs only water, electricity and air to be operated. Roasting converts a stable and low extractable metal sulphide into a reclaimable oxide compound. The sulphide sulphur serves as fuel for the reaction. In the case of feed material low in sulphur (<8%), feed material pre-heating and oxygen addition can be applied to avoid consumption of extra fuel. Especially for refractory ores, oxygen enrichment is an effective way to reduce process gas volume, which has a significant effect on plant size and consequentially the capex.

The major objective of the roasting process is to eliminate the sulphur and carbon contained in the concentrate, remove impurities such as arsenic and to provide a calcine product as well as SO_2

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containing gas. A roasting temperature of 500-800°C is generally the most suitable range, depending on the process and mineralogical requirements.

Oxidation of pyrite, arsenopyrite and pyrrhotite by molecular oxygen:

$$3\ FeS_2 + 8\ O_2(g) \rightarrow Fe_3O_4 + 6\ SO_2(g) \quad (21)$$

$$3\ FeAsS + 7.25\ O_2(g) \rightarrow Fe_3O_4 + 1.5\ As_2O_3 + 3\ SO_2(g) \quad (22)$$

$$3\ FeS + 5\ O_2(g) \rightarrow Fe_3O_4 + 3\ SO_2(g) \quad (23)$$

$$4\ Fe_3O_4 + O_2(g) \rightarrow 6\ Fe_2O_3 \quad (24)$$

Under reducing conditions pyrite and arsenopyrite decompose as follows:

$$FeS_2 \rightarrow FeS + S(g) \quad (25)$$

$$FeAsS \rightarrow FeS + As(g) \quad (26)$$

Volatilized sulphur and arsenic are oxidized:

$$S(g) + O_2(g) \rightarrow SO_2(g) \quad (27)$$

$$4\ As(g) + 3\ O_2(g) \rightarrow 2\ As_2O_3(g) \quad (28)$$

Arsenic trioxide can be further oxidized and reacted with hematite to generate ferric arsenate:

$$Fe_2O_3 + As_2O_3 + O_2(g) \rightarrow 2\ FeAsO_4 \quad (29)$$

$$FeS_2 + 3\ O_2(g) \rightarrow FeSO_4 + SO_2(g) \quad (30)$$

$$2\ FeS_2 + 7\ O_2(g) \rightarrow Fe_2(SO_4)_3 + SO_2(g) \quad (31)$$

Ratio of Fe_2O_3, Fe_3O_4 and $FeSO_4/Fe_2(SO_4)_3$ depends on the operating conditions, e.g. operating temperature and the excess of oxygen in the roaster.

Decomposition of carbonates and oxidation of organic carbon:

$$CaCO_3 \rightarrow CaO + CO_2(g) \quad (32)$$

$$C + O_2(g) \rightarrow CO_2(g) \quad (33)$$

Oxidation of metal sulphides, where Me is e.g. Cu, Zn and/or Pb:

$$MeS + 1.5\ O_2(g) \rightarrow MeO + SO_2(g) \quad (34)$$

The products gained from the roasting process are calcine and roasting gas. The calcine consists of Fe_2O_3, Fe_3O_4, $FeSO_4$ and gangue material, while the roasting gas has SO_2, SO_3, O_2, N_2 and H_2O as steam. Depending on the chloride content in the roaster feed, HCl may also exist in the roasting gas in corresponding concentrations and removed from the process with the effluent stream from the wet gas cleaning section.

In the case of a high arsenic content in the feed, a special treatment is required using a two-stage roasting process. Typically arsenic occurs in arsenopyrite (FeAsS). Under the usual roasting conditions, with a slight excess of oxygen in relation to the stoichiometric requirement for converting the iron content of the pyrite to hematite, the majority of the arsenic is oxidized to As(V) and will react with the hematite to form stable iron arsenate ($FeAsO_4$). In this way, about 70 – 80% of the arsenic content in the feed becomes bound to the cinder. This conversion can be optimized in a CFB reactor according to special process conditions. The remaining arsenic, which is oxidized to As(III) as shown in Equation (28), is volatilized and entrained by the roaster gas and must be separated in the wet gas cleaning system.

In instances where the cinder is to be used in steelmaking, high arsenic pyrites must be processed in a two-stage fluid-bed roasting system. In the first stage, operating under oxygen-deficient

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conditions, no hematite nor ferric arsenate will form. The arsenic is thus almost completely volatilized and discharged with the roaster gases. In the second fluid bed stage, the separated cinder is oxidized to hematite. This principle is applied on an industrial scale using the Boliden roasting process. Main Chemical reactions in stage 1 (roaster) when roasting a pyrite/arsenopyrite gold concentrate are given in equation (21), (22) and (23). Main Chemical reaction in stage 2 (oxidizer) when roasting a pyrite/arsenopyrite gold concentrate is given in equation (24).

The calcine product from the roaster, heat recovery boiler and hot gas dedusting is collected in one location and further treated in the gold leaching plant. For high arsenic feed material it is possible to separate coarse and fine calcine streams in order to optimize the downstream leaching process.

The gas cleaning section is typically divided into the hot area, which consists of the roasting section and the wet gas cleaning area starting at the quench throat of the Venturi scrubber. The gas is cooled to its saturation temperature by water evaporation. The weak acid bleed is discharged from the gas cleaning section to the effluent treatment plant. The amount of weak acid bleed varies depending on the process conditions and impurities in the concentrate / off-gas.

The SO_2 gas from the gas cooling and cleaning section is conveyed to the sulphuric acid section drying tower. Once the gas is heated up via heat exchangers, it enters the converter facilitating the exothermic oxidation of SO_2 to SO_3. In the absorption section the SO_3 is absorbed by circulating sulphuric acid at 98.5 %. The gas leaving the final absorption tower passes a high efficiency candle type mist eliminator before it is released to the atmosphere via a stack as clean gas. The product acid is cooled in a separate heat exchanger and is discharged to the product acid tank. The heat generated in the acid plant section is recovered and forms together with the waste heat boiler from the roasting plant section an integrated heat recovery system for maximized steam production of the entire roasting plant.

Outotec has built several gold roasting plants, whereas each process concept has been optimized to its specific project needs driven by the feed material chemical and mineralogical composition. The different flowsheets for the roasting process are influenced by operating temperature for maximum gold recovery, oxygen concentration in the roaster off gas, impurity control in calcine product and off gas, requirements for heat recovery and finally the capex aspect for the most economical flowsheet option. Some of the main references reflecting a variety of process scenarios are:

- Syama, Mali: slurry feeding, lowest capex
- Minahasa, Indonesia: low sulphur content in feed, partly heat recovery
- Newmont, USA: optimized heat recovery, ore pre-heating, high capacity
- Tongguan, China: two stage roasting, arsenic removal
- Cengiz, Turkey: conventional dead roasting process, maximum heat recovery

KEY ATTRIBUTES OF DIFFERENT REFRACTORY ORE PRE-TREATMENT TECHNOLOGIES

Key attributes of different refractory ore pre-treatment technologies are summarized in Table 1. Guidelines for technology selection criteria are given in Table 2 and Table 3.

Table 1: Key attributes of different refractory ore pre-treatment technologies.

	BIOX®	POX	ROASTING
Sulphur	- S mainly oxidized to SO_4^{2-} in slurry and basically all sulphur reports to gypsum - S partially oxidized to other sulphur species such as polysulphides, which slightly increase cyanide consumption	- S mainly oxidized to SO_4^{2-} in slurry and basically all sulphur reports to gypsum	- S fully oxidized as SO_2 in gas or partial sulphating - Acid produced via roasting process

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	BIOX®	POX	ROASTING
Iron	- Small amount of jarosites in BIOX® stage, - $FeAsO_4$ and $Fe(OH)_3$ in the neutralization stage - Ref chemical reactions	- Fe_2O_3, $FeAsO_4$ as well as some jarosites in the autoclave - $FeAsO_4$ and $Fe(OH)_3$ in the neutralization stage - Ref chemical reactions	- Fe_2O_3, Fe_3O_4 and $FeSO_4/Fe_2(SO_4)_3$ - less $FeAsO_4$ is formed, since As is removed as relatively pure As_2O_3 - Ref chemical reactions
Carbon Type **- Lignite** **- Anthracite**	- Basically all carbonaceous matter reports to BIOX® residue	- Basically all carbonaceous matter reports to POX residue - Additional chloride washing step may be required prior to autoclave	- Mainly oxidized to CO_2 at >700 °C - Not complete oxidation can be achieved
$MeCO_3$	- CO_3 is beneficial for the bacterial growth, 2-5 % is typically an optimum	- Reduce O_2 partial pressure in the autoclave and is then typically removed prior to autoclave by dilute acid generated in autoclave	- Decomposition to oxides at > 840 °C
Arsenic	- Oxidation to As^{5+} in the BIOX® reactors - Stable $FeAsO_4$ formed mainly in neutralization	- Oxidation to As^{5+} in the autoclave - Stable $FeAsO_4$ formed both in autoclave and in neutralization	- Oxidation and separation to As_2O_3 possible by utilizing two stage roasting - Today As_2O_3 must be typically disposed via ferric arsenate process, i.e. $FeAsO_4$ formed
Antimony	- High levels may inhibit bacterial activity	-	- to roaster gas together with As and collected in effluent stream
Mercury	- Basically all mercury reports to BIOX® residue - Mercury retort is needed in gold plant after cyanide leaching step to remove mercury from gold bullions	- Basically all mercury reports to POX residue - Mercury retort is needed in gold plant after cyanide leaching step to remove mercury from gold bullions	- Almost complete evaporation from roasting - Gas cleaning for Hg with the Boliden Norzink Process - Almost Hg free calcine - Mercury retort may be needed in gold plant after cyanide leaching step to remove mercury from gold bullions
Typical cyanide consumption	10-15 kg/t	0.5-2 kg/t	0.5-2 kg/t
Typical feed	-concentrate	- whole ore - concentrate	- whole ore - concentrate
Operating temperature	40-45 °C	190-230 °C	500-800°C
Operating pressure	Atmospheric	up to 35 barg	Atmospheric
Residence time	4-6 days	0.5 – 1.5 h	0.5 h
Oxidizing agent	Air	Oxygen	Air, Oxygen (optional)
Neutralizing agent	- Limestone and lime	- Limestone and lime	- Lime may be required to stabilize As_2O_3
Energy Recovery	-Typically not applied	-Typically not applied -Heat of reaction can be utilized as hot water and used e.g. in water desalination or district heating purposes	-Excess heat of reaction is used to produce high pressure steam for energy recovery
Sulphuric acid	-	-	High grade sulphuric acid

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Table 2: Guidelines for key selection criteria

	BIOX®	POX	ROASTING
Geographical location	- Advantage for remote locations due to relatively easy operation and maintenance - Availability of neutralization agent	- Availability of neutralization agent - Availability of skilled personnel	- Sulphuric acid market - Availability of skilled personnel
Typical capacity	Concentrates: 50 to 2000 tpd	Concentrates: 150 to 4000 tpd Refractory ores: 2000 to 24000 tpd	Concentrates: 500 to 2000 tpd Refractory ores: 1000 to 15000 tpd
Capex / Opex applicability	Will be clarified in feasibility study	Will be clarified in feasibility study	Will be clarified in feasibility study

The selection of the preferred or optimum process for a specific project will depend on a large number of factors including technical, financial, operational and regulatory aspects. The selection of the appropriate technology supplier is also important. Table 3 lists a number of aspects to take into consideration under each category, but other aspects can be added to the list based on the project specific drivers. A further complicating factor is that technology selection will, in most cases, be completed during the pre-feasibility stage of the project where usually only limited batch testwork data is available and the capital and operating cost evaluation is only done to a +/- 25 % accuracy.

Table 3: Technology selection criteria.

FINANCIAL	TECHNICAL	OPERATIONAL	REGULATORY	TECHNOLOGY SUPPLIER
- Best project NPV - Predicted gold recovery - Capital and Operating cost - Implementation time - Spares Inventory	- Capital and Operating cost risk - Recovery risk - Flexibility - Ease of expansion - Water consumption and quality requirements	- Operability - Maintainability - Level of operator skill required - Ease of start-up/shutdown - Instrumentation & control	-Environmental Acceptability - Safety considerations - Use of local personnel - Footprint - Closure requirements	- Track record - Scope of service - Technical support

The development of the decision framework that will be used to evaluate the different technologies must be done taking the specific requirements of the project into consideration. The weighting given to each criteria selected must reflect the key drivers for the project and address the key risks associated with the project. The decision framework must also identify which criteria will be deemed as fatal flaws where a technology will be eliminated from the evaluation should it not fall within the acceptable limits for the criteria.

It is therefore critical to have an in-depth knowledge of all the processes being evaluated to be able to do a fair evaluation of the processes even at such an early stage of the project. Outotec has extensive experience in the accurate interpretation of the testwork results and extrapolation of the results from batch tests to continuous performance to determine the process design criteria for the design of the plant. Outotec also has an extensive database that can be used to benchmark the testwork results against similar projects and to predict the performance of the commercial plant based on operating plant results.

The final step in the evaluation is to score each technology objectively using the criteria selected and obtain an overall weighted score for each technology. It is also important to understand the sensitivity of the weighted score to changes in the assumptions used in the study. This is not only

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applicable to project economics, resource grade and ore variability or testwork results, but to all criteria for example changes or potential changes in environmental legislation and regulatory environment.

Once the preferred technology is selected, the process will usually be evaluated in more detail as part of a definitive or bankable feasibility study. The DFS study should include a detailed review of the decision framework used to select the technology and clear guidelines must be established when the selected technology will be retained or when it is required to repeat the technology selection process to select a new technology.

SUMMARY

Declining gold grades and oxide ore resources together with increasing environmental concern set requirements for technologies used in the gold industry. Modern trends indicate increasing utilization of refractory gold ores in the future.

Outotec offers three proven pre-treatment options; bio-oxidation (BIOX), pressure oxidation (POX) and roasting (ROAST) to convert refractory ores into easily and effectively leachable form. The addition of BIOX® bio-oxidation technology to Outotec's product portfolio adds to and complements already existing significant experience in the hydrometallurgical industry.

All three pre-treatment technologies are technically feasible for most of the sulphide ores and can be tailored to meet the project requirements. Proper project development including testwork and engineering is required to find the optimal solution for a specific project. Outotec has two R&D centers and can co-operate with other research companies or execute testwork at the customer site. Today all three Outotec BIOX, Outotec POX and Outotec ROAST technologies can comply with current international environmental regulations.

Technology selection is typically done already in the early project development phase, e.g. in the pre-feasibility study phase based on CAPEX and OPEX estimates within ± 35% accuracy. Outotec has no intention to favor either BIOX®, POX or ROAST technologies but the selection can be reliably made based on the real facts and project requirements. Thus Outotec's early involvement in project development is beneficial for a client to secure the best outcome for a project.

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APPLICATIONS OF ADVANCED ANALYTICAL AND MASS SPECTROMETRY TECHNIQUES TO THE CHARACTERISATION OF REFRACTORY GOLD ORES

By

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ABSTRACT

In the current economic environment, the mining industry is focused on reducing costs and improving productivity. The biggest challenges in the future will involve finding new viable gold deposits, the development of viable mining and processing technologies that are able to treat more complex ore deposits, as well as deal with more stringent environmental legislations.

It is well established that mineralogy of the ore dictates the selection of the treatment route and what improvements can be made to a process. General analytical laboratory services can provide bulk metallurgical test work, however issues associated with encapsulation, passivation and deportment of toxic elements are not identified or addressed without detailed mineralogical studies.

The John de Laeter Centre in Perth hosts over $30 million in world-class state of the art analytical and mass spectrometry infrastructure. The Centre's Tescan integrated mineral analyser (TIMA) allows for rapid data acquisition for studies such as precious metal deportment, mineral associations and liberation characteristics of both ore-bearing and gangue minerals. The TIMA can be integrated with some of the Centre's other available techniques, including:

- X-ray powder diffraction for quantitative mineralogical phase analysis;
- Laser-ablation ICP-MS for 2D elemental mapping and the detection of elements in minerals down to the parts per billion level;
- X-ray Photoelectron Spectroscopy (XPS) for surface coating analyses of mineral surfaces for passivation effects;
- FIB-SEM with TOF-SIMS capabilities and Atom probe (Cameca LEAP 4000X HR) for 3D atomic imaging to identify solid solution and colloidal distributions in mineral matrices.

A combination of these techniques allows for the complete identification of all modes of precious metal occurrence in both ore samples and metallurgical process streams. These types of analyses, in conjunction with standard metallurgical test work, can identify causes of reduced gold recovery, or allow for defining improved mineral processing options for recovery and separation of other potential valued components such as copper or cobalt minerals.

This presentation outlines the integrated methodology which can be used, discusses some of the challenges in gold searches and present some studies carried out at the John de Laeter Centre.

Keywords: Gold, refractory ore, automated mineralogy

Status & Challenges

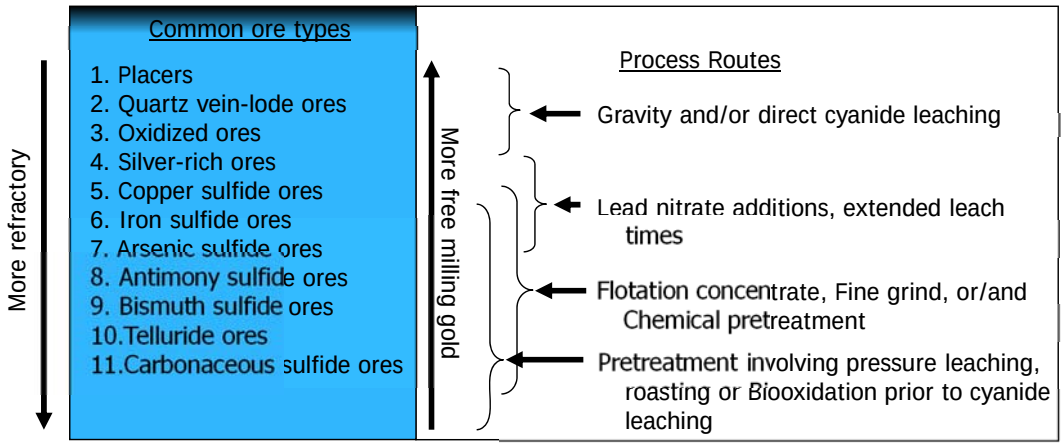
- In the current economic environment, the mining industry is focused on reducing costs and improving productivity.
- The mining industry also require ways to reduce the costs for assessing ore bodies and identifying potential process routes in the early stage of project development.
- The biggest challenges in the future will involve
  - Finding new viable gold deposits,
  - The development of viable mining and processing technologies that are able to treat more complex ore deposits,
  - Deal with more stringent environmental legislations.

1

Role of mineralogy

- Mineralogy of the ore dictates the selection of the treatment route and what improvements can be made to a process.
- General analytical laboratory services can provide bulk metallurgical test work, however issues associated with encapsulation, passivation and deportment of toxic elements are not identified or addressed without detailed mineralogical studies.

Ore Mineralogy



Methods of mineralogical analyses

Method	Advantages	Disadvantages
Bulk assays & microscopy techniques Chryssoulis & Cabri (1990) method	Identify all fractions of gold & their associations	Relies on analysis of gold in refractory mineral grains in polished section Bulk diagnostic cyanidation for free-milling portion.
Amdel method (Henley, 1992)	Identify all fractions of gold & their associations	No microscopic gold associations identified Bulk analysis with no grain analysis
Diagnostic leaching (Lorenzen & Tumility, 1992; Lorenzen & Van Deventer, 1992, 1993)	Bulk analyses, fast suitable identification of visible gold distributions	Minerals dissolution not totally selective No microscopic gold associations identified, only inferred.
Bacteria oxidation (Katsikaros,1991)	Suitable for identification of visible gold distributions	No microscopic gold associations identified
Automated mineralogy & diagnostic leaching (Goodall & Scales, 2007)	Rapid data acquisition - precious metal deportment, mineral associations and liberation characteristics.	Submicroscopic gold inferred from mineral dissolution - not totally selective
Pre-concentration & automated mineralogy, microprobe techniques (Lastra et al., 2005; Cabri et al., 2005; Chryssoulis & McMullen, 2005)	Pre-concentration increase the statistical representation. Rapid data acquisition - precious metal deportment, mineral associations and liberation characteristics. Identification of colloidal and solid solution distributions	Submicroscopic gold determination time consuming & requiring a number of microprobe techniques

The John de Laeter Centre

- The John de Laeter Centre in Perth hosts over $30 million in world-class state of the art analytical and mass spectrometry infrastructure.



Relevant JdLC facilities



Tescan integrated mineral analyser (TIMA)

DIGITAL MINERALOGY HUB FACILITY



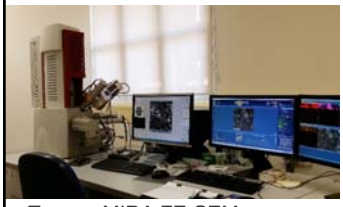
Kratos AXIS Ultra DLD X-ray photoelectron spectroscopy system (XPS)

X-RAY SURFACE ANALYSIS FACILITY



Resonetics S-155-LR 193nm excimer laser ablation system coupled to an Agilent 7700x quadrupole ICPMS.

GEOHISTORY FACILITY



Tescan MIRA FE-SEM with EBSD/EDS system



Bruker x-ray diffractometers



Tescan LYRA FIB-FESEM with ToF-SIMS



Cameca LEAP 4000X HR atom probe microscope

MICROSCOPY AND MICROANALYSIS FACILITY

GEOSCIENCE ATOM PROBE FACILITY

Instruments used to determine gold/silver carriers

Deportment of gold and silver	Study	Technique
Free gold and silver mineral grains • native gold and electrum – readily CN-able • Silver sulfur salt minerals - slow leach in CN	Size Distribution Composition	**Optical/SEM** **TIMA** **LA-ICPMS**
Exposed associated & encapsulated gold & silver minerals • attached native gold and electrum - readily CN-able after re-grind • enclosed silver minerals - moderately CN-able after re-grind	Size Distribution Composition Mineral associations Liberation	**TIMA** **LA-ICPMS** **FIB-FESEM**
Sub-microscopic gold and silver **Types:** • colloidal-sized micro-inclusions – potentially leachable • Solid solution Au in the crystal structure of minerals – refractory to CN	Define mineral carriers and concentration Deleterious element distribution (e.g. As, Cd, Sb) Determination of the form and distribution within grains	**TIMA/ EDS** **LA-ICPMS** **FIB-FESEM ToF-SIMS** **FIB-FESEM / Atom probe microscopy**
Preg-robbed gold and silver • Cemented or adsorbed on mineral particles • Gold compounds in carbon material	Mineral associations Gold species in matrix Surface coatings	**SEM/TIMA** **FIB-FESEM ToF-SIMS** **XPS**

Challenges associated with mineral analyses

- **Preparation of samples** :
  - Obtain represent samples of the ore body.
  - Liberate precious metals & other accessory minerals from rocks for analyses with minimal breakage - permit a better understanding of the grain-size distribution and integrity of grains.
  - Choose a methodology which increases the chances of identifying precious metal content and carriers.

- **Analytical methods**
  - Use of reliable search and characterisation methods to identify phases of interest.
  - Set suitable scan search routine(s) to detect fine grains.
  - Develop simple methodology that allows interchanging between different analytical techniques.
  - Minimise time and cost.

JdLC Analytical Workflow Concept



High voltage pulse power to selectively fragment composite materials
- Allows fracturing along grain boundaries
- Liberation of morphologically intact minerals

Sample Selection

Slurry

Rock

Crushed < 1cm (if required)

Pressure filtered

Electrodynamic disaggregation (SelFrag)

Screen -1mm

Split

Characterisation
- Bulk chemical analysis
- Bulk mineralogy (XRD)
- Particle size analysis

Cyanidation (-106µm & -10µm)
- Tank leach
- Monitor & maintain conditions
- Measure CN species
- ICP solution & solids

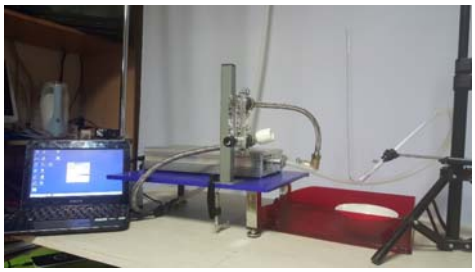
Detailed mineralogy

JdLC Analytical Workflow Concept

Detailed mineralogy

Precious metal deportment

Wet screen sized to five fractions



Hydroseparator

Heavy concentrates
- Hydroseparator
- Magnetic separation

Mineral quantification

Polished mounts (mono layers)

Polished mounts

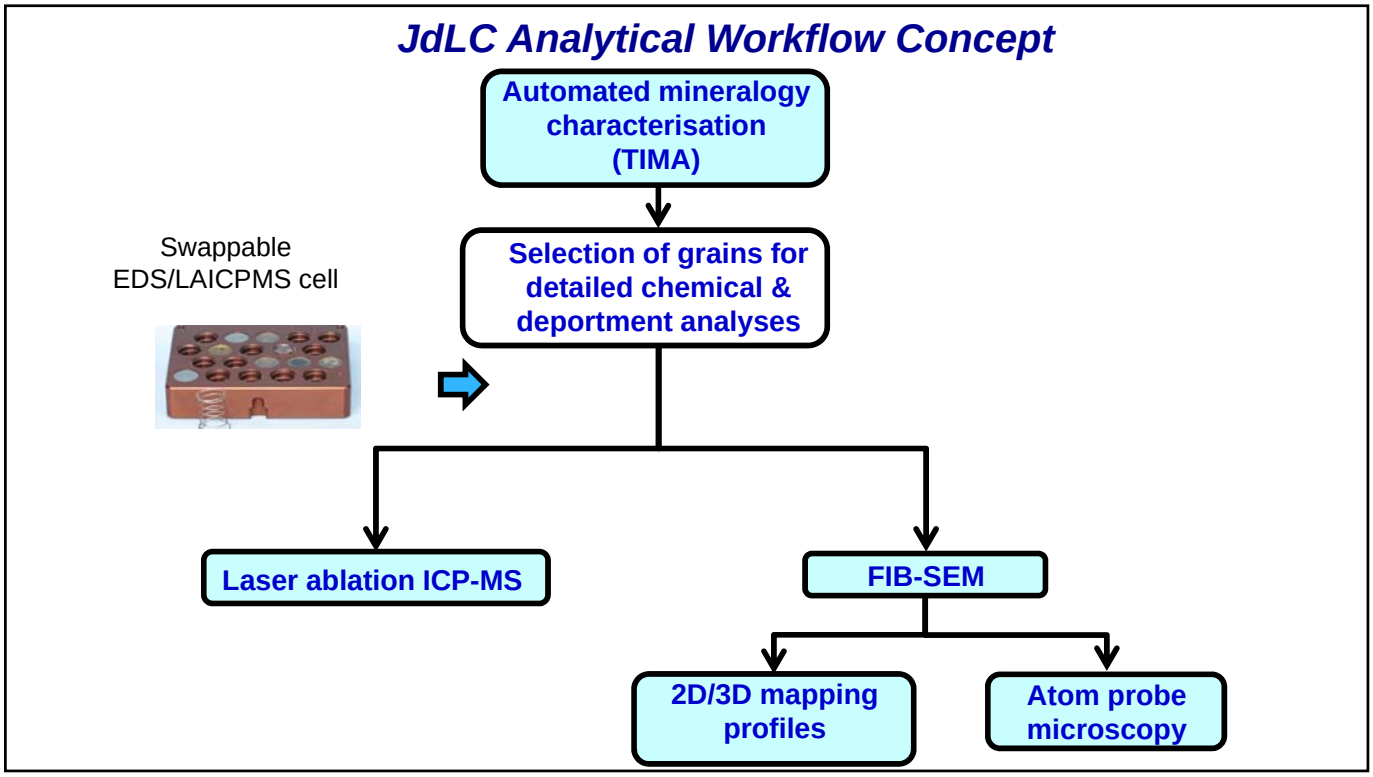


Optical microscopy

Automated mineralogy characterisation (TIMA)

- Sample preparation methodology based on Cabri *et al.,* (2005) approach.

JdLC Analytical Workflow Concept

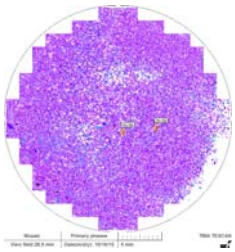




Automated mineralogy characterisation (TIMA)

Colour Cathodoluminescense
- Strain & deformation structures

Bright phase search
- Gold/silver deportment
  - Mineral associations
  - Liberation characteristics



High resolution mapping & Point Spectrometry modes
- Mineral abundance
- Mineral associations
- Liberation characteristics

•**Bright phase search -** BSE image and EDS data are collected on defined mineral phases

•**High resolution mapping** - BSE image and EDS data are collected simultaneously to detect boundaries between phases.

•**Point spectrometry** - BSE image is used to detect boundaries between phases. One spectrum collected per phase.

- Fast acquisition times for data.
- Setting up a suitable mineral library is essential - requires suitable knowledge of mineralogy.

TIMA application - Preliminary assessment of a volcanic massive sulphide ore

Aim

To determine the deportment of gold and silver and their mineral associations in a Pb/Zn/Cu volcanic massive sulphide ore deposit.

Sample

- P_{80} of 90-100 microns.
- Sample composition - 2 g/t Au, 150 g/t Ag, 2% Pb, 15% Zn, 0.4% Cu, 15% Fe, 20% S.

Sample preparation

- Polish sectioned mounts made of a representative sample.
- Heavy minerals concentrated into two heavy fractions by panning. Polished sections made of the heavy panned fractions.

Approach

- Mineral files for precious metal search were prepared.
- Bright field scans were conducted for precious metal content.
- Detailed elemental scans were performed for modal mineralogy ,mineral associations & liberation characteristics.
- Deportment of gold & silver and their mineral associations were then determined.



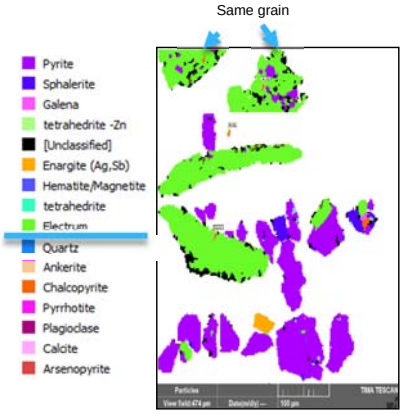
SEM parameters	Operating conditions Bright field	Detailed mapping
Beam energy	25KeV	25KeV
Probe current	6.28nA	6.46nA
Beam intensity	19.6	18.5
Spot size	77.0nm	47.7nm
Working distance	15mm	15mm
Acquisition mode	Hi resolution mapping	Hi resolution mapping
Pixel size	3 microns	2 microns
Field scanned	205	205
Min brightness	60%	15%
Max brightness	100%	100%
X-ray events/pixel	1000	1000

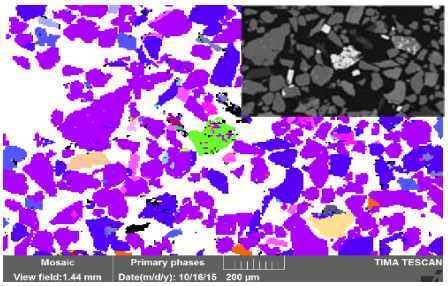
Gold and Silver deportment

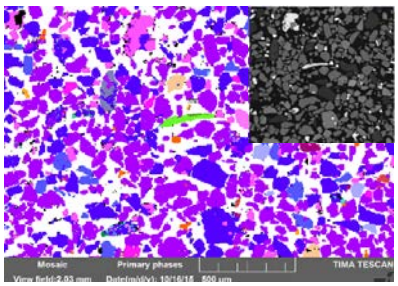
Gold and silver observed in the following forms

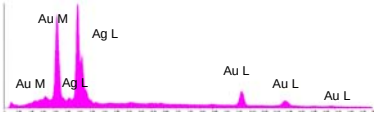
- Gold deportment
  - Electrum (Au,Ag)
- Silver deportment
  - Electrum (Au,Ag)
  - Argentian stibioenargite
  - Argentotetrahedrite
  - Silver and silver sulphide grains (acanthite)

Electrum (Au, Ag)







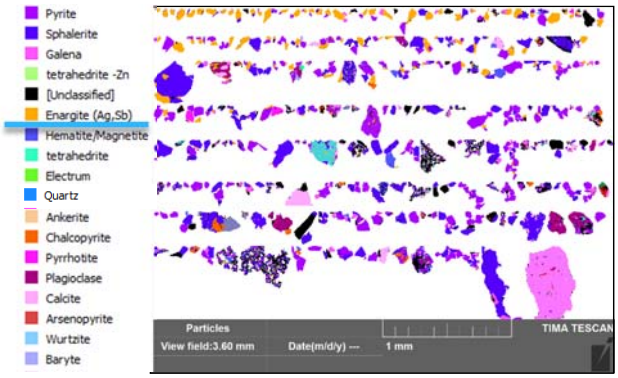


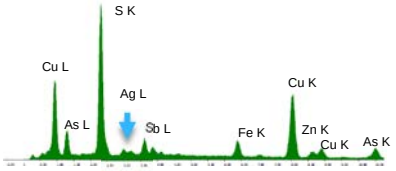
- Electrum detected in heavy fractions only.
- Liberated or associated with pyrite grains (inclusions and attached) .
- Electrum composition varies in silver and gold content.
- The iron content may be surface coatings.

	Electrum (wt%)	Average composition (wt%)	Range (wt%) (8 grains)
Ag	>20	53.8	39.6-63.4
Au	<80	45.4	59.3-36.2
Fe			0-2.5

Argentian stibioenargite

$(Cu,Fe,Ag,Zn)_3(As,Sb)S_4$

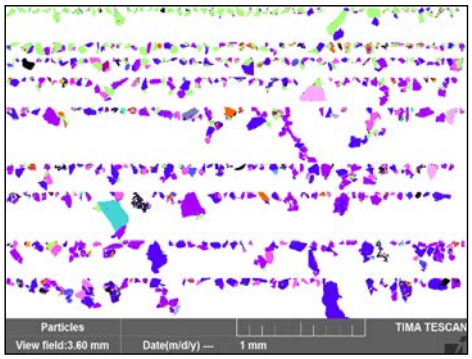


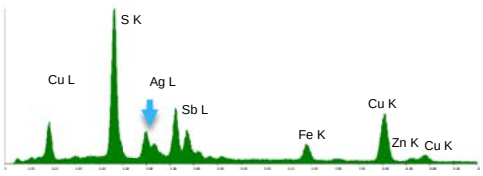


Element	Pure enargite	Average composition (wt%)	Range (wt%) (8 grains)
Cu	48.4	38.1	34.7-39.8
S	32.6	28.6	27.7-29.1
As	19.0	13.2	11.4-13.2
Sb		9.3	7.2-11.1
Zn		4.6	3.8-5.4
Fe		3.7	2.0-4.5
Ag		2.7	1.5-3.7

- Enargite liberated or associated with other minerals.
- Enargite grains contain antimony, iron and zinc impurities.

Argentotetrahedrite





$(Ag,Cu)_{10}(Zn,Fe)_2Sb_4S_{13}$

Element	Pure tetrahedrite	Average composition (wt%)	Range (wt%) (6 grains)
Cu	34.8	31.0	27.6-35.3
S	25.4	26.0	24.9-27.4
Sb	29.6	24.2	22.1-24.8
Zn		4.1	2.9-5.1
Fe	10.2	3.6	3.0-4.4
Ag		10.0	12.9-6.8

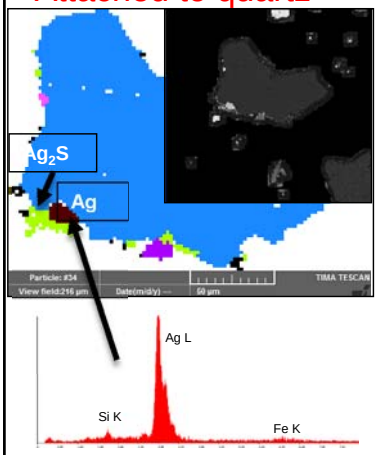
$(Ag,Cu)_{10}Fe_2Sb_4S_{13}$

Element	Average composition (wt%)	Range (wt%) (10 grains)
Cu	22.2	18.6-29.3
S	24.4	23.6-25.7
Sb	26.4	25.4-27.7
Fe	6.1	5.8-6.4
Ag	20.3	11.3-25.1

- Two forms of argentian tetrahedrite identified.

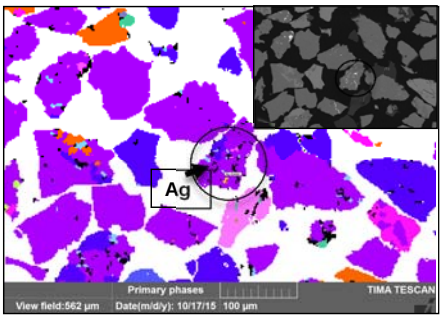
Silver & Silver sulfide

Attached to quartz

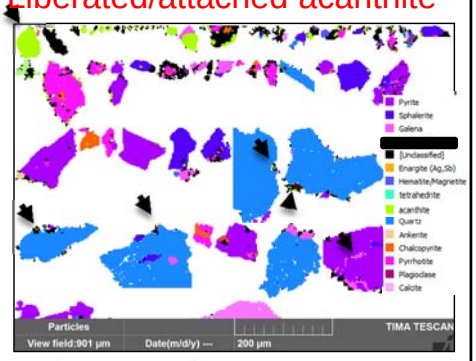


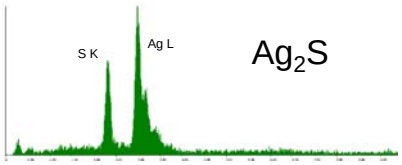
- Fine silver grains present as silver or silver sulphide grains.

Fine silver inclusions in pyrite



Liberated/attached acanthite

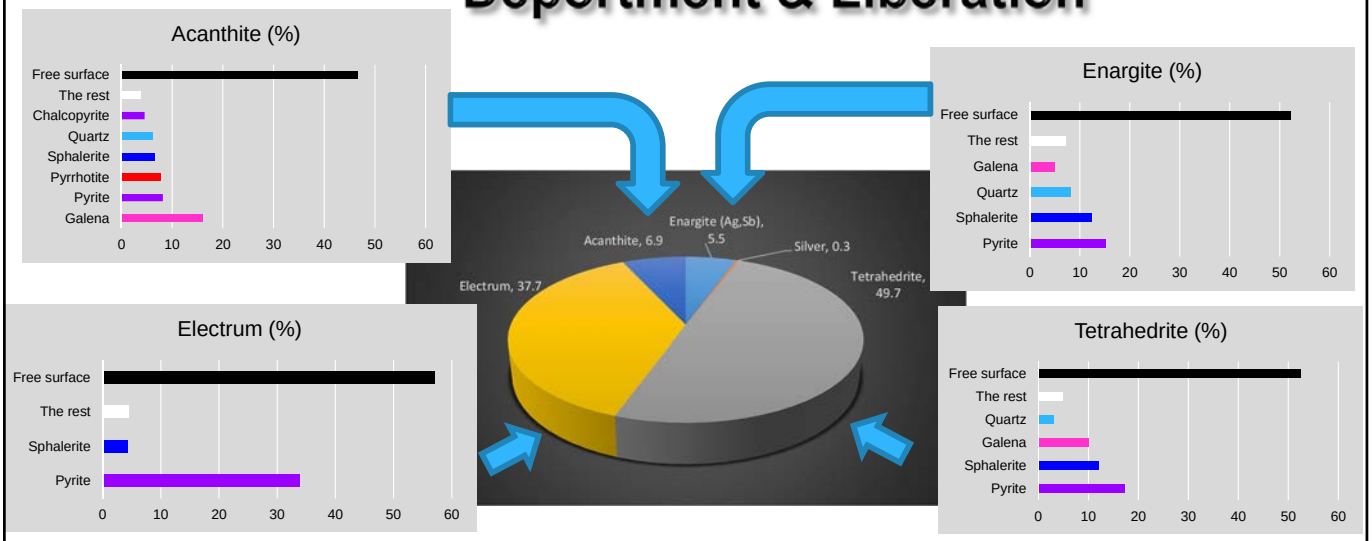




Ag_2S

Element	Pure acanthite	Average composition (wt%)	Range (wt%) (10 grains)
Ag	87.06	81.4	80.2-85.0
S	12.94	18.6	15-19.8

Deportment & Liberation



- Many grains (50-60%) observed are liberated.
- Many fine grains associated with pyrite, galena, sphalerite and quartz.
- Further test work required to determine precious metal distribution in sulfide minerals



Laser ablation ICPMS

Quantification of gold/silver in sulphides & associated minerals
- Gold/silver - ~10ppb

Grain elemental distribution
- Deleterious element contents (e.g. As, Cd, Sb, Hg, Pb, Te)
- Major elements S, Fe, Pb, Zn, Ni

- **Spot analysis 100-500 spot analysis /day**
- **Elemental mapping analysis**.

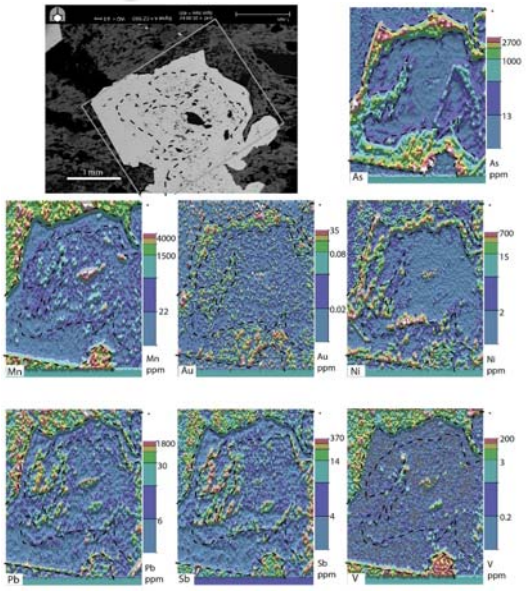
Laser ablation ICPMS application – Arsenian Pyrite

Aim

Ore mineralisation history -
- Study looking into the variations of mineralising fluid compositions and the timing of ore element mobility.
- Investigating chemical variations in trace elements of different growth zones in pyrite grains.

Results

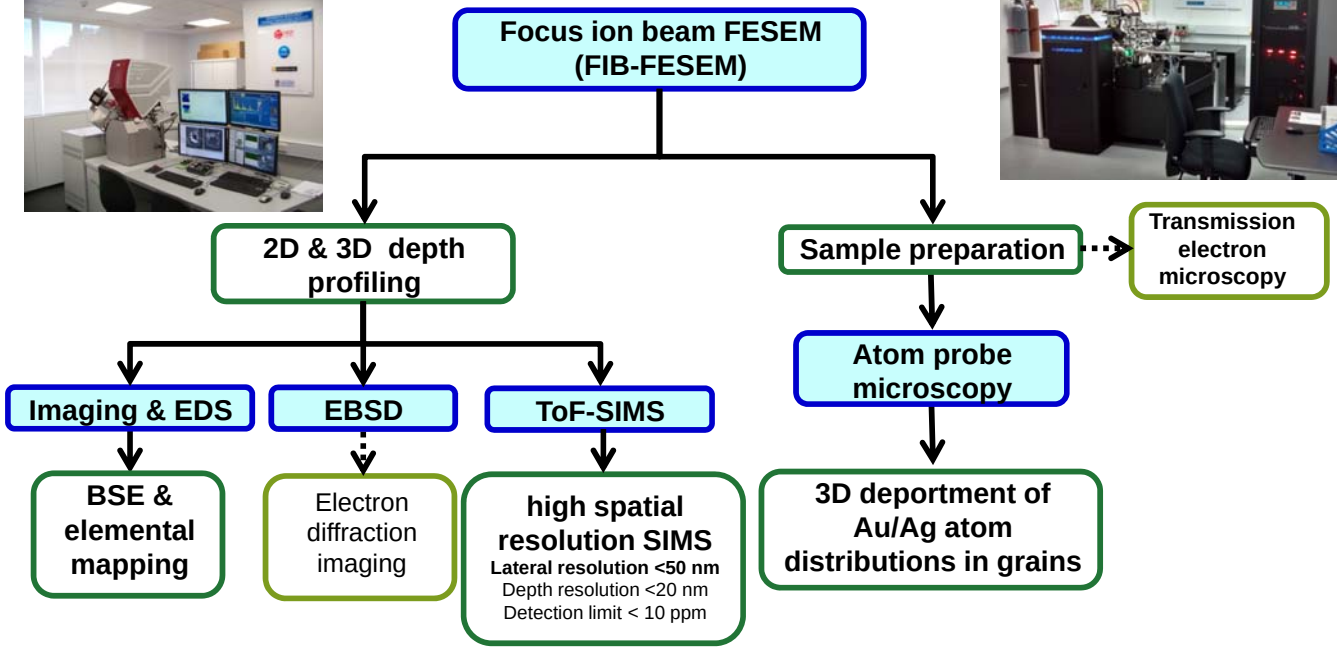
- Core of pyrite grain rich in silicate inclusions, with the rim is more compact (massive textured).
- Low Au concentrations (<1 ppm) mostly concentrated in the rim, which is also enriched in As, Ni compared to the core.



Courtesy of Andrea Agangi



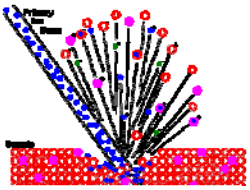




FIB-FESEM application – In-situ morphology of gold grains

Aim

- In-situ analysis of gold grain particles.

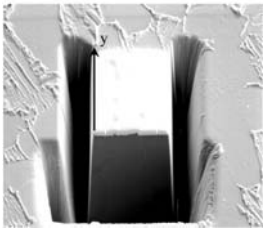


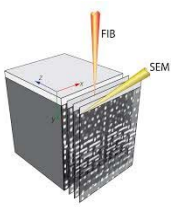
Sample

- Free milling gold ore.

Sample preparation

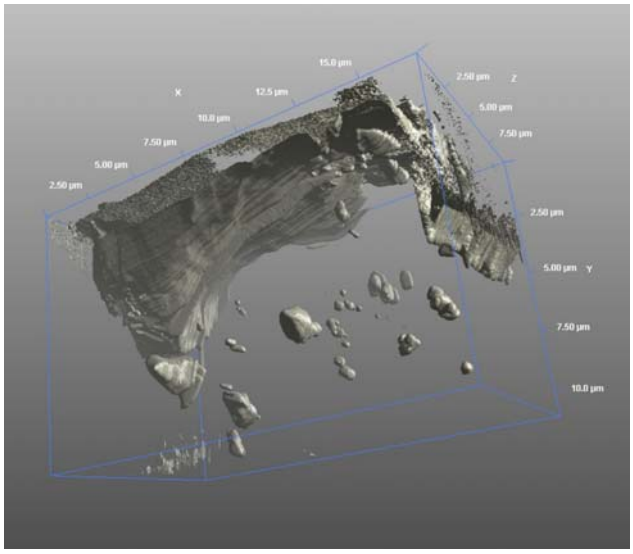
- Using the High resolution Ga^+ focused ion beam (FIB) ablation technique.
  - Area of interest on polished mount is selected and separated.
  - Ion beam rastered across at 50nm slice thickness intervals.
  - 3D model generated from backscatter electron images, energy dispersive analyses or time of flight secondary mass spectroscopy.





Results

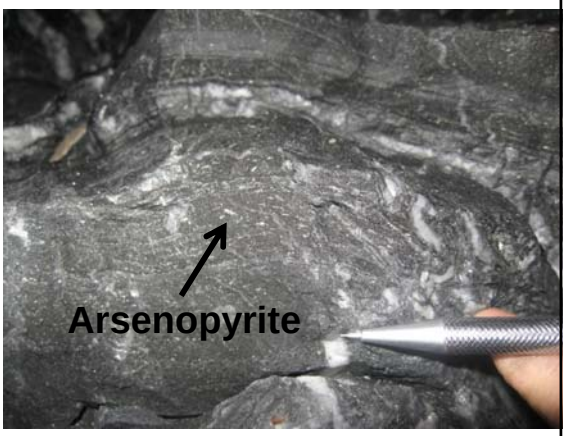
- 3 dimensional iso-surface back scatter electron image of gold grains locked in a silicate matrix (filtered from image).
- Fine particulate gold not amendable to cyanidation without further liberation by fine grinding.



Atom probe microscopy application: Refractory ore from the Obuasi deposit (Ghana)

Aim

- To determine the deportment and distribution of gold in arsenopyrite



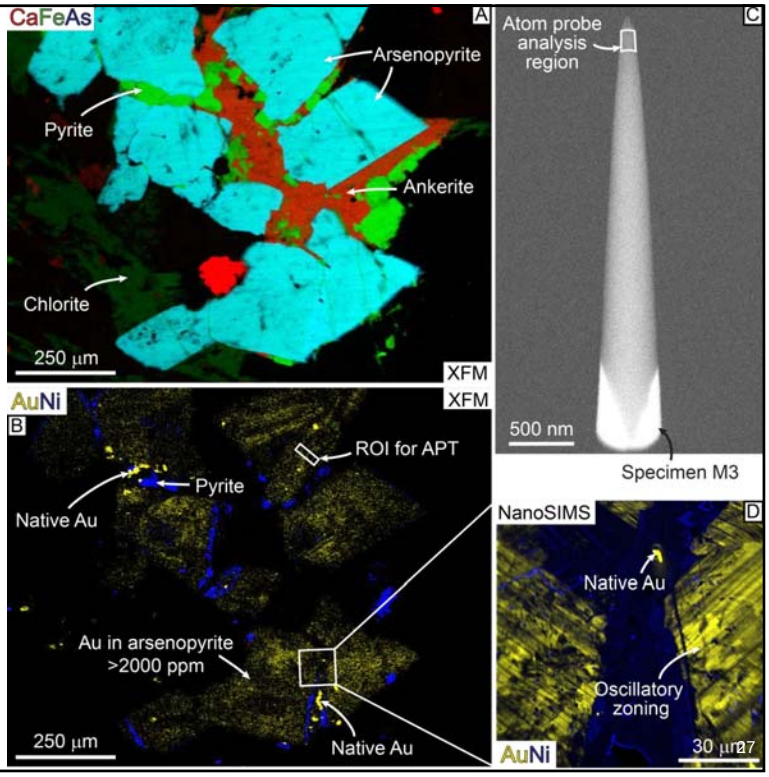
The Obuasi gold deposit:

- 62 Moz of gold (past production + resource)
- Half of the resource is hosted in refractory ores
- Increasing importance of the refractory ores relative to historical production
- Mainly arsenopyrites disseminated in metasediments
- Treated onsite with bio-oxidation plant

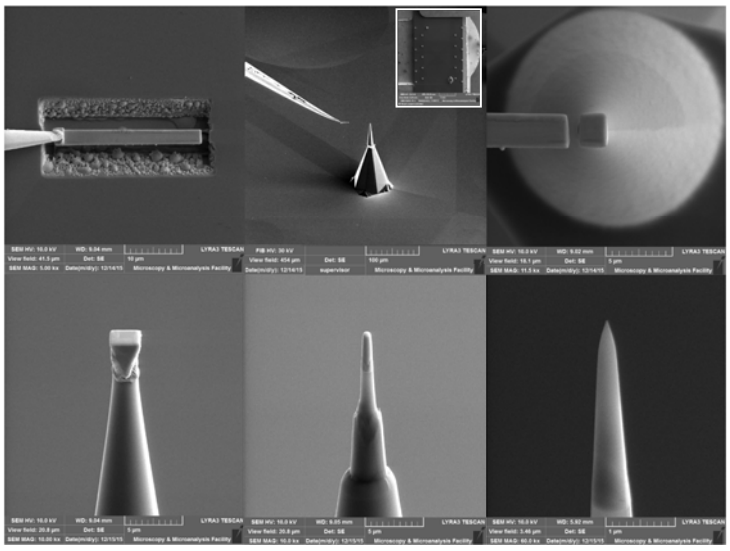
Sample characterisation before atom probe analyses

- Gold is hosted in fine, sub-micron wide oscillatory gold bands.
- Gold is “invisible” - i.e. cannot be distinguished by conventional microscopy between gold chemically bound in the mineral and submicroscopic inclusions.

Fougerouse *et al.,* in press



Atom Probe sample preparation

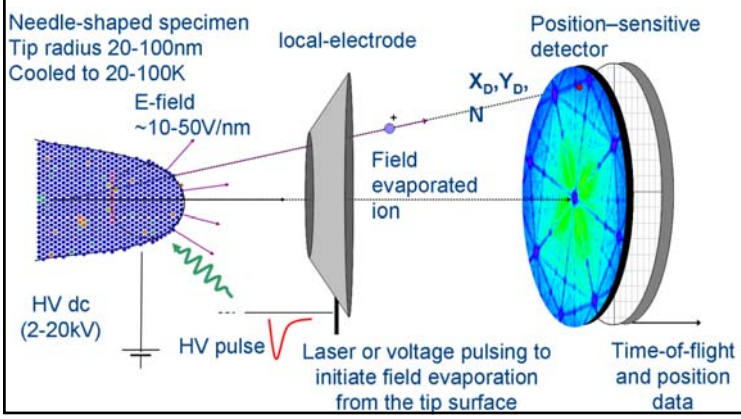


- Tescan LYRA FIB-SEM used to prepare samples for Atom probe.
- High resolution Ga^+ focused ion beam (FIB) ablation is carried out on designated area of a polished mount of interest to produce a wedge which are mounted on stubs.
- Sharp long slender tips (needle-like) are produced and transferred to the atom probe for analysis.

Atom Probe Microscopy

CAMECA LEAP 4000X HR

- 3D chemical imaging
- Position-sensitive time of flight mass spectroscopy
- Sub-nanometre resolution (0.1-0.3 nm)

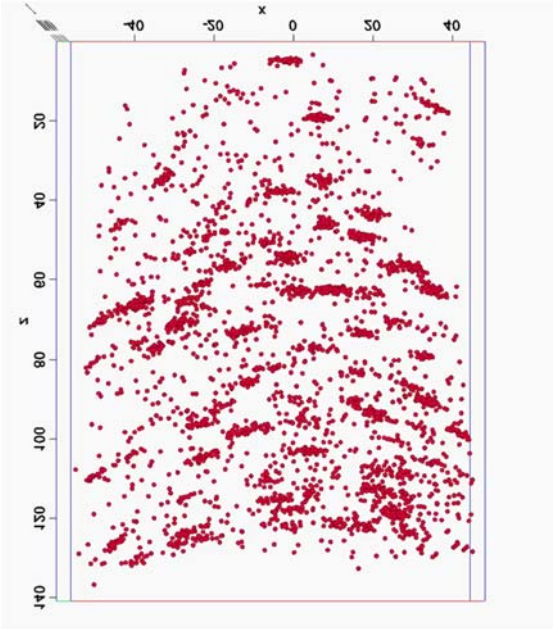




Atom probe microscopy: Results

"Invisible" gold in arsenopyrite occurs in two forms:

- Single discrete atoms – solid solution
- Clusters - ~10nm gold grains



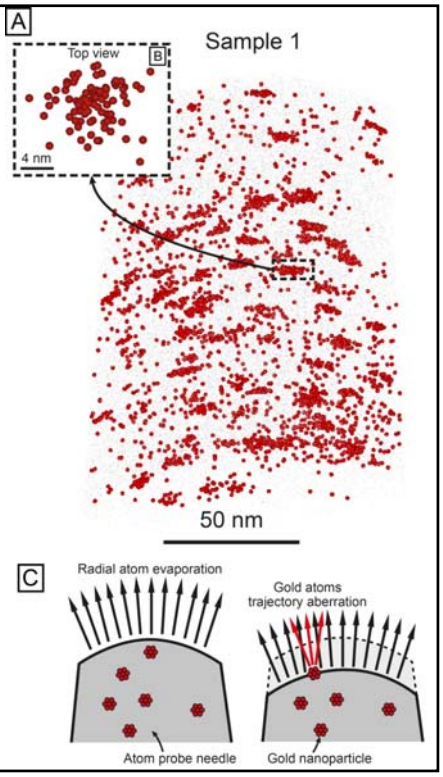
- Gold atom

50 nm

Fougerouse *et al.*, in press

Atom probe microscopy: Results

- Metallic gold (Au^0) nanoparticles
  - 724 ppm Au
  - Field enhanced trajectory aberration (magnification)
- Concentration of nanoparticles gold below the reported maximum gold solubility in arsenopyrite (2% Au).
- To render gold ‘locked’ in the sulfide mineral amenable to cyanidation a chemical pre-treatment process is required.



Conclusions

- Sample preparation methodology important to allow for representative samples to be evaluated.
- A combination of advanced analytical and mass spectrometry techniques available can allow for the complete identification of all modes of precious metal occurrence in ore and metallurgical samples.
- Techniques are suitable for assessing ore bodies and identifying potential process routes in the early stage of project development.
- These types of analyses, in conjunction with standard metallurgical test work, can identify causes of reduced gold recovery, or potentially allow for defining improved mineral processing options for recovery and separation of other potential valued components.

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THE USE OF SPECIAL ADDITIVES TO INHIBIT PREG-ROBBING OF GOLD IN THE PROCESS OF DOUBLE REFRACTORY CONCENTRATES PRESSURE OXIDATION

By

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ABSTRACT

Pressure oxidation is one of the most common and reliable methods of processing gold sulfide concentrates. It allows effective sulfides decomposition, thus eliminating the primary cause of the material's refractoriness to gold cyanide leaching. Nevertheless, the pressure oxidation of double refractory materials containing carbonaceous matter in addition to sulfides results in substantial gold losses due to autoclave preg-robbing. The latter involves sorption of soluble gold compounds by the carbonaceous matter under the POX conditions.

Chloride ion is a common component of POX solutions. It is capable of forming soluble complexes with gold when present in the solution even in an amount of 1–10 mg/L.

The present research aims to study the effect of special additives capable of reacting with chloride ion or carbonaceous matter components, thereby minimizing their negative impact on gold recovery in the process of POX residue cyanide leaching. The salts of silver, bismuth, lead and mercury are among the additives studied.

Keywords: Pressure Oxidation, Carbonaceous Matter, Organic Carbon, Chloride, Gold, Mercury, Silver

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INTRODUCTION

The modern structure of gold resources forces the miners to process primary gold-sulfide ores that are low-grade and have a complex mineralogical composition. Such ores are known as refractory ores[1] due to the complexity of their processing. Gold association with sulfides is a result of either a fine dissemination of gold or a formation of solid solution of gold in sulfides' lattice[2]. This results in the necessity of sulfides decomposition in order to "liberate" gold and make it susceptible to cyanide during the leaching stage.

Pressure oxidation (POX) is the effective and industrially proven technology for sulfides decomposition. High-temperature pressure oxidation is widely used to process refractory gold ores and concentrates[3][4]. The POX is usually conducted at temperatures 190 – 230 °C and oxygen overpressure up to 7 bar. It was noted that a simultaneous presence of a carbonaceous matter in the treated material and ions of halides or pseudohalides (CN^-, CNS^-, metal-cyanide complexes) in a POX solution causes a decrease in gold recovery during subsequent cyanide leaching[5][6][7]. In some cases, even the presence of 3-5 mg/L of chloride ion causes a significant gold losses[8].

The mechanism of gold losses is believed to include formation of soluble gold complexes under the POX conditions with subsequent sorption of these complexes onto the carbonaceous material. It is well known that gold cations Au^+ and Au^{+3} form stable complexes with halides, including chloride ion: $[AuCl_2]^-_{aq}$ и $[AuCl_4]^-_{aq}$. The stability of complex ions increases with temperature[9][10][11]. Besides, gold solubility under the POX conditions also increases with increase of chloride activity and increase of oxidation-reduction potential (ORP) of solution[12][13]. The ORP that is high enough to cause significant gold dissolution and resulting gold preg-robbing onto carbonaceous matter is achieved at the closing stage of sulfides oxidation when the ratio of ferric to ferrous ions is high[8].

The electrochemical kinetics studies showed that ferric ion can conduct the oxidation of gold under the POX conditions when the chloride concentration is high (1 - 5 g/L)[12]. Meanwhile, the special study conducted at SRC Hydrometallurgy demonstrated[14] that the gold preg-robbing under the lower Cl concentrations (up to 30 mg/L) is closely related to the forms of gold in the source material. The authors believe that the extent of metallic gold oxidation under the low chloride concentrations is negligible. Only the gold that is present in the source material in the already oxidized form (e.g., gold in solid solution in pyrite) can be dissolved and subsequently preg-robbed by the carbonaceous matter. A method of oxidized gold content determination based on sulfite leaching was proposed in the same work[14].

The soluble gold-halide complexes tend to interact with natural carbonaceous matter. Mechanism of this interaction under POX conditions is unclear. The same goes for the reason why the gold associated with the carbonaceous matter is not leached by cyanide. On the other hand, the process of gold-chloride complexes adsorption onto activated carbon is well known and studied[15]. Adsorption of gold is accompanied by its reduction to the metallic state in accordance with the reaction:

$$4[AuCl_4]^-_{aq} + 3\mathrm{C} + H_2O = 4Au_{ads}\downarrow + 3CO_2\uparrow + 16Cl^- + 12H^+$$

It is assumed that a similar process causes the loss of gold during the POX of double refractory materials.

The most evident ways to minimize autoclave preg-robbing of gold are: (a) minimization of chloride concentration in the POX solution and (b) minimization of carbonaceous matter content in the feed material. The former could be achieved by adequate water management; the latter – by implementing organic carbon flotation. However, these methods are not always applicable in practice. For example, some ores are partially composed of chloride-containing minerals. In this case, chloride is leached to the solution during POX significantly increasing chloride level. Organic carbon flotation may be restricted due to fine dissemination of carbon within gold-bearing sulfides[16], which may cause significant loses of gold during the organic carbon concentration.

Industrial POX practice evidences that the presence of certain amounts of chloride in the process solutions and organic carbon in the double refractory feed is inevitable. This fact stresses the importance of process parameters optimization in order to avoid autoclave preg-robbing. In most cases, the restraint upon the ORP value by controlling POX parameters is an effective way to decrease gold solubility[8][17]. On the other hand, in some cases tougher conditions of POX and

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increased retention time that promote oxidation/passivation of carbonaceous matter are recommended to increase gold recovery[18][19].

It is known, that some metals can form very stable complexes with chloride ion, or can form insoluble salts with chloride. Both of these processes can decrease chloride activity in solution and subsequently minimize gold solubility. This approach to solve the problem of autoclave preg-robbing was discussed in the patent of Gathje and Simmons[17], but was never tested or proved.

The present research aims to study the effect of special additives capable of reacting with chloride ion or carbonaceous matter components, thereby minimizing their negative impact on gold recovery in the process of POX residue cyanide leaching. The salts of silver, bismuth, lead and mercury are among the studied additives.

MATERIALS

Malomir (Amur region, Russia) ore flotation concentrates were used to test POX technology. Composition of the concentrates is shown in Table 1. The main gold-bearing sulfides are pyrite (30 – 40 %) and arsenic pyrite (15 – 20 %). Concentration of total organic carbon (TOC) in the studied concentrates varies from 0.41 to 1.77 % while the contents of other components and gold are almost the same. The concentrates are refractory: only 4 to 11% of the gold is leachable by cyanide (see Table 2).

The oxidized form of gold was determined using the procedure described in the article[14]. Results confirm that in Malomir most of refractory gold is oxidized (77 – 87 %). The gold unrecovered by RIL of POX residue is probably associated with non-leachable minerals and carbonaceous matter.

Table 1 shows the contents of silver, lead, bismuth and mercury in the studied concentrates. Concentration of silver varies from 7.3 to 12.3 g/t. Concentration of lead is low and varies from 80 to 320 g/t. There are no measurable quantities of mercury or bismuth in the concentrates.

It was shown in earlier studies that the carbonaceous matter in Malomir material has low affinity for gold cyanide complexes both before and after the POX[20]. At the same time, gold losses during POX can be dramatically high and depend on the concentration of carbonaceous matter and chloride ion concentration in the POX solution[8][21]. This property of Malomir carbonaceous matter makes it a suitable object for conducting the autoclave-only preg-robbing study.

Table 1: Composition of Malomir concentrates (%)

Component	Sample of flotation concentrate				
	T21b	M14	M30	T24b	M29
Fe	24.6	28.2	23.7	25.7	20.2
S	23.0	24.2	19.6	23.5	17.4
$S(S^{2-})$	22.8	23.9	19.2	23.3	16.6
As	7.8	12.3	9.8	9.2	8.2
TOC	0.41	0.83	1.06	1.20	1.77
Pb	0.021	0.032	0.027	0.029	0.008
Bi	<0.01	<0.01	<0.01	<0.01	<0.01
Hg (g/t)	<1	<1	<1	<1	<1
Ag (g/t)	8.2	7.3	7.9	12.3	10.5
Au (g/t)	22.0	31.1	24.6	23.8	22.5

Table 2: Forms of gold in Malomir concentrates (%)

Gold state	Sample of flotation concentrate				
	T21b	M14	M30	T24b	M29
Free gold (RIL)	10	7	4	10	11
Oxidized gold Au^{+} (POX-Sulfite leaching)	84	87	81	80	77
Gold in POX-RIL residue	6	8	9	11	18

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EXPERIMENTAL METHODS

The concentrate sample was ground to a P_{80} of 45 microns. The ground sample was acidified and then washed with distilled water to remove acid- and water-soluble chlorides.

Washed cake was diluted with distilled water to a solids concentration in slurry of 14 %. The solids content was calculated using a heat model of the continuous POX process. Slurry was loaded in 1.1 L Büchi Glas Uster (Switzerland) autoclave equipped with temperature control system and oxygen flow and pressure control systems by Bronkhorst High-Tech B.V.

Soluble salts of silver, lead, bismuth and mercury were added to the slurry before heating. Chloride ion concentration in the POX solution was 3 – 5 mg/L. In some experiments sodium chloride was added to the slurry before POX in order to increase chloride concentration by 20 mg/L.

Pressure oxidation was carried out at 225 ± 0.5 °C and total pressure 32.5 ± 0.1 bar. The process duration did not exceed 20 minutes for a P_{80} of 45 microns. Oxygen was fed via an oxygen flow meter, which made it possible to determine the end of the POX process via oxygen consumption.

The POX slurry was cooled down to 95 °C and conditioned for 2 hours (hot curing). The basic iron sulfate is unstable under such condition and mostly dissolves in the acidic POX solution. After the hot cure, the POX slurry was filtered through a Büchner funnel. The solid residue was washed with hot distilled water. The resulting solution was analyzed for chloride ion content. The washed cake was subjected to cyanidation.

The cyanidation process adopted the parameters close to the standard resin-in-leach process (RIL). The RIL feed material was diluted with water to a solids content of 20 wt.%. Lime was added to maintain pH in the range from 10 to 11. 5 vol.% of ion-exchange resin (AM2B) was added to the slurry. Then a 10 wt.% NaCN solution was fed to achieve a concentration of NaCN 2 g/L. The process was conducted under continuous stirring for 24 hours.

RESULTS AND DISCUSSION

Lead and Bismuth

The salts $Pb(NO_3)_2$ and $Bi_2(SO_4)_3$*$3H_2O$ were used as the additives. Salt additives were calculated in order to provide added metal concentration in the POX solution equal to 500 mg/L. Experiments were conducted using T24b concentrate, all results are compiled in Table 3.

The results show that the addition of bismuth salt has no influence on the gold recovery from POX residues. Gold recovery remains stable at 89 % with low chloride level, and about 76 % with chloride addition.

Lead addition showed barely noticeable impact on gold recoveries. In the experiment with low chloride level gold recovery was only 86.8 % (2.2 % drop from base). But in the experiment with chloride addition a slight positive effect was observed, gold recovery increased by 2.8 % up to 78.3 % in comparison with the base 75.5 %.

Pb and Bi additives were deemed ineffective due to the fact that even high concentration (500 mg/L) provided only insignificant increase in gold recovery.

Table 3: Influence of lead(II) and bismuth(III) on gold recovery (flotation concentrate T24b)

Test #	Additives	Addition Me (mg/L)	Addition Cl^- (mg/L)	Gold recovery (%)
1	No add.	0	0	89.0
2	No add.	0	**20**	75.5
3	$Bi_2(SO_4)_3 \cdot 3H_2O$	**500**	0	88.9
4	$Bi_2(SO_4)_3 \cdot 3H_2O$	**500**	**20**	75.8
5	$Pb(NO_3)_2$	**500**	0	86.8
6	$Pb(NO_3)_2$	**500**	**20**	78.3

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Silver

The same concentrate (T24b) was used to test the influence of $AgNO_3$ addition on gold recovery. Experimental results are compiled in 4.

Chloride addition in experiments # 9–11 was 20 mg/L, but analysis of the POX solution has shown that all the silver was deposited in a solid phase, and the chloride level was significantly lower than could be expected considering its addition.

Experiments with addition of silver has showed that the gold recoveries from the concentrate T24b can be increased both at low and high chloride concentration. Significant increase of gold recovery (~5 %) was obtained in the experiment with low chloride level (3 – 5 mg/L). This fact indicates that autoclave preg-robbing causes this loss (~5%) even at such low concentration of chloride ion in solution. The impact of higher concentration of chloride ion on gold recovery can be eliminated by addition of silver (tests # 9–11). The protective effect of silver decreases regularly with a decrease in its dosage.

Table 4: Influence of silver(I) on gold recovery (flotation concentrate T24b)

Test #	Additives	Addition Me (mg/L)	Addition Cl^- (mg/L)	Gold recovery (%)
1	No add.	0	0	89.0
2	No add.	0	**20**	75.5
7	$AgNO_3$	**500**	0	94.1
8	$AgNO_3$	**50**	0	93.4
9	$AgNO_3$	**500**	**20**	92.8
10	$AgNO_3$	**50**	**20**	91.8
11	$AgNO_3$	**5**	**20**	81.4

Presumably, the mechanism of the protective effect of silver is associated with the decrease of chloride ion activity due to the interaction of silver and chloride, which may occur both before and during the pressure oxidation. This interaction can cause the formation of insoluble AgCl, or soluble complex ion $[AgCl_2]^-$.

The idea of formation of the complex ion $[AgCl_2]^-$ is based on the result of experiment # 10. In this experiment the molar ratio of chloride to silver (Cl/Ag) was about 1.5 mol/mol. So there is not enough silver to sediment all the chloride, but it's still enough silver to form stable a chloride complex $[AgCl_2]^-$. In test # 11, the molar ratio of chloride to silver (Cl/Ag) was about 15 mol/mol, a lot of chloride ion remained free in solution, and it affected the gold recovery.

Currently there is no clear proof of the mechanism of the influence of silver. Alternatively to the discussed versions, silver chloride complex may be adsorbed on carbonaceous matter and this may cause a decrease in its affinity for gold chloride complexes.

Mercury

The first series of experiments with Hg was conducted with the same Malomir concentrate (T24b). $HgSO_4$ was used as an additive. Experimental results are compiled in Table Table 5.

The chloride ion concentration in the solution was 3 – 5 mg/L without addition of chloride, and 23 – 25 mg/L with NaCl addition. The analysis determines no mercury in the solution after POX. Mercury addition has no influence on chloride concentration in solution either, even when 500 mg/L of Hg was added. Nevertheless, addition of mercury has significant influence on gold recovery.

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Table 5: Influence of mercury(II) on gold recovery (flotation concentrate T24b)

Exp. №	Additives	Addition Me (mg/L)	Addition Cl^- (mg/L)	Gold recovery (%)
1	No add.	0	0	89.0
2	No add.	0	**20**	75.5
12	$HgSO_4$	**500**	0	95.8
13	$HgSO_4$	**50**	0	95.1
14	$HgSO_4$	**5**	0	94.3
15	$HgSO_4$	**0.5**	0	92.3
16	$HgSO_4$	**50**	**20**	92.6
17	$HgSO_4$	**5**	**20**	92.1
18	$HgSO_4$	**0.5**	**20**	87.9

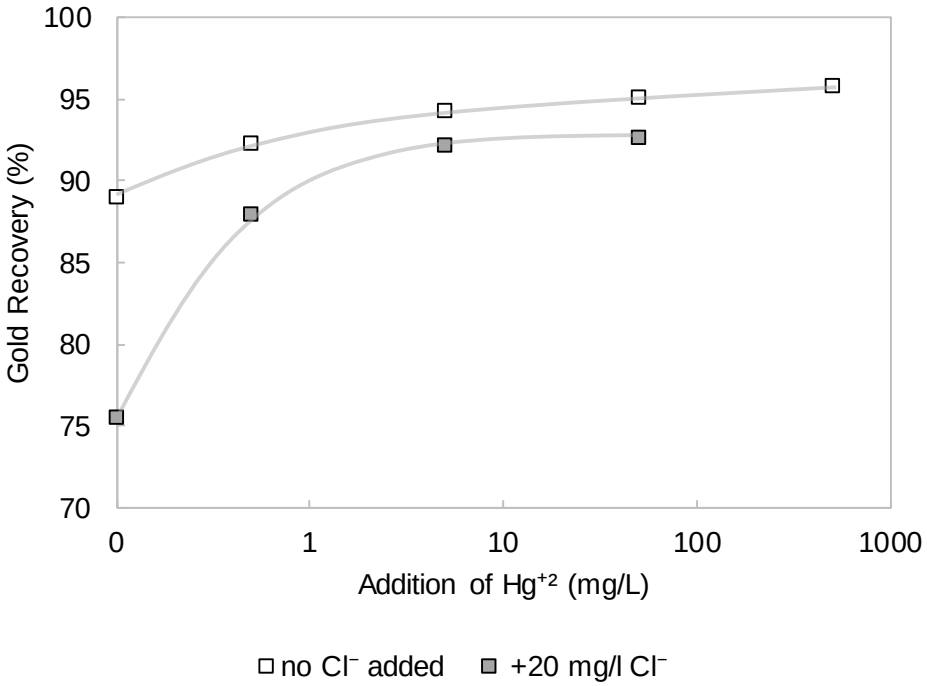


Figure 1: Influence of mercury(II) on gold recovery (flotation concentrate T24b)

Experiments with addition of mercury sulfate has showed that the gold recovery from the concentrate T24b can be increased up to 95.8 %. Such high gold recovery in the experiment with low chloride level (3 – 5 mg/L), again indicates that autoclave preg-robbing causes this loss (~7%) even at such low concentration of chloride ion in solution.

Moreover, addition of mercury can significantly reduce the negative chloride influence at its concentration of about 25 mg/L. In tests # 16 and # 17 gold recovery as high as 92 % was achieved. It is easy to see (from Tables 4 and 5), that the boosting effect of mercury on gold recovery is much stronger in comparison to silver, and that this effect can be obtained at lower addition concentration.

It can also be seen (Table 5, Figure 1) that the gold recovery can be significantly improved by addition of 5 mg/L of mercury(II). Above that quantity, the mercury addition has less significant effect on gold recovery. The addition of 5 mg/L of mercury(II) was considered to be an optimal dosage, and it was used during the second series of Hg experiments.

Concentrates with various amounts of carbonaceous matter were tested with and without mercury addition. All five Malomir concentrates (Table 1) with TOC content from 0.41 to 1.77 were used. Experimental results are compiled in Table 6 and Figure 2.

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The gold recovery regularly decreases with the rise of carbonaceous matter concentration in material. The decrease is noticeably accelerated with increase of chloride ion concentration in the POX solution (Figure 2). This trend persists in the experiments with the addition of 5 mg/L of Hg. At the same time with mercury addition this tendency is much weaker, especially at the higher chloride concentration.

The results show that in all cases mercury addition has a positive effect on gold recovery. The chosen dosage (5 mg/L of mercury(II)) is sufficient to effectively suppress autoclave preg-robbing even at chloride concentration 23-25 mg/L.

Increased mercury reagent dosage does not lead to the increase of gold recovery and reduction in the impact of carbonaceous matter. For example, see the experiments on concentrate M29 with TOC content 1.77 % (6). Increasing mercury dosage up to 10 times from 5 mg/L to 50 mg/L provides only +0.4 % effect on gold recovery.

In some experiments on T24b concentrate mercury were added to the slurry after POX (after cooling and before conditioning), and in an experiment mercury was added at the start of the cyanidation. No mercury influence was registered in both types of experiments. Therefore, it was clearly confirmed that mercury influence occurs during the POX process.

Table 6 – Influence of mercury addition on various concentrates

Concentrate	Exp. №	Addition Me (mg/L)	Addition Cl^- (mg/L)	Gold recovery (%)
T21b TOC = 0.41 %	19	0	0	94.1
	20	0	**20**	85.8
	21	**5**	0	96.7
	22	**5**	**20**	94.1
M14 TOC = 0.83 %	23	0	0	92.5
	24	0	**20**	82.7
	25	**5**	0	95.5
	26	**5**	**20**	92.8
M30 TOC = 1.06 %	27	0	0	91.1
	28	0	**20**	69.5
	29	**5**	0	93.7
	30	**5**	**20**	93.0
T24b TOC = 1.20 %	1	0	0	89.0
	2	0	**20**	75.5
	14	**5**	0	94.3
	17	**5**	**20**	92.1
M29 TOC = 1.77 %	31	0	0	81.9
	32	0	**20**	59.6
	33	**5**	0	86.9
	34	**5**	**20**	85.0
	35	**50**	**20**	85.4

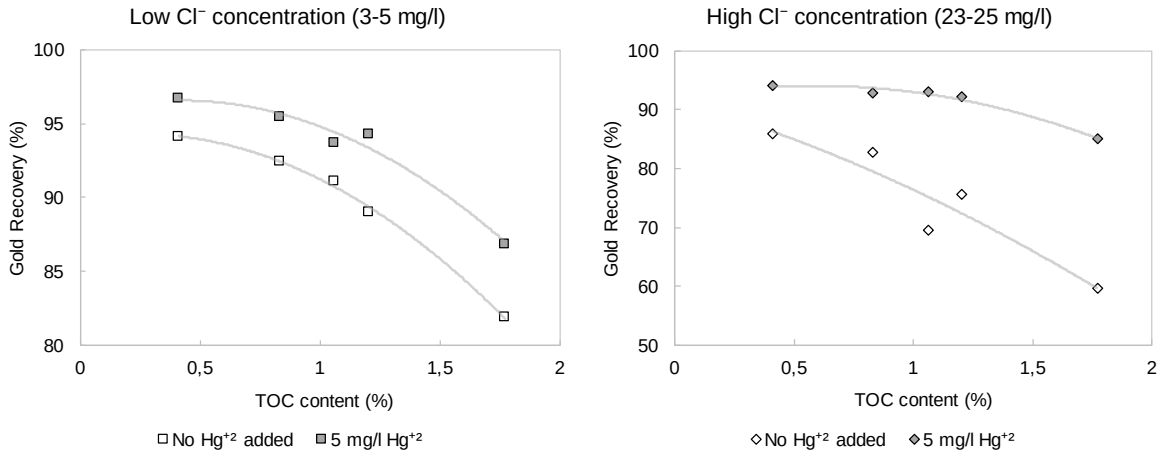


Figure 2: Influence of mercury(II) addition on gold recovery at different levels of Cl^-

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Mechanism of Mercury Effect

All results clearly indicate that a persistent positive effect of mercury(II) addition on gold recovery is obtained with a mercury(II) dosage of 5 mg/L. This addition of mercury(II) is sufficient to effectively suppress autoclave preg-robbing even at chloride concentrations in a range from 3 to 25 mg/L.

The molar ratio of chloride to mercury (Cl/Hg) is about 28 mol/mol in experiments with mercury(II) addition – 5 mg/L and chloride – 25 mg/L. Even if $[HgCl_4]^{2-}$ complex is formed, it will cause a decrease in Cl^- ion activity that is equal to only 15 %. This is equivalent to decrease in Cl^- concentration from 25 mg/L to 21 mg/L, which will have no significant effect on autoclave preg-robbing; thus the mechanism of mercury influence is not associated with decrease in chloride ion activity.

Details of the mechanism of mercury protective influence are not definitely established. One working hypothesis says that added mercury(II) could interact with carbonaceous matter, and thus fill the sorption capacity of carbonaceous matter before the first gold-chloride complexes appear in the POX solution. However, there are some other hypotheses. Some experimental work is now underway in order to understand the influence of mercury.

IMPLEMENTATION OUTLOOK

Silver

Silver is always contained in gold-bearing sulfide ores. Usually silver is extracted from the material simultaneously with the gold in the cyanidation process. Then silver follows gold into the product – dore bar. Potentially silver may be dissolved by nitric acid from the cathode metal. Thus, if the processed material has a sufficient amount of silver then a silver recycle can be arranged in order to increase gold recovery. The schematic diagram is shown in Figure 3.

It must be noted that during pressure oxidation a significant amount of argentojarosite may form. This compound is resistant to the action of cyanide, and will affect the silver recovery during consequent cyanidation. A special operation - Lime Boiling must be added to the flowsheet to solve this problem. Lime Boiling is a well-known process and usually it allows the silver recovery to increase up to 90 - 95 %.

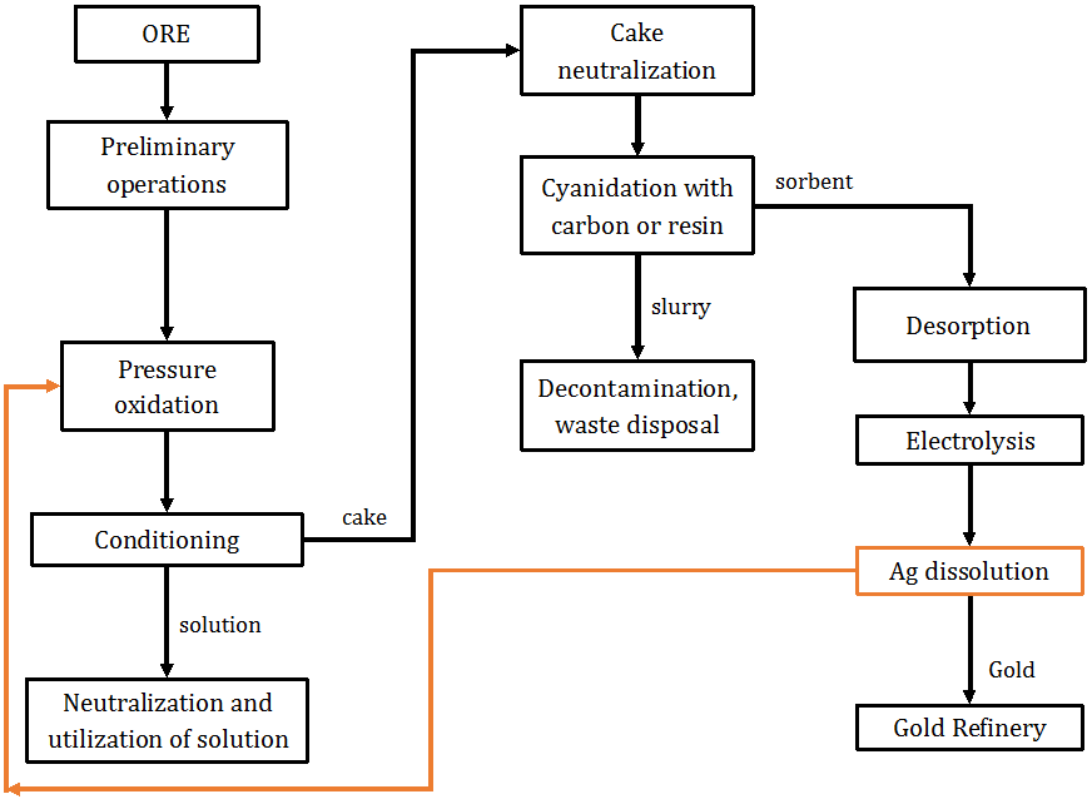


Figure 3: POX technology with recycle of silver (schematic flowsheet)

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It was shown in the experimental section that a silver addition about 50 mg/L is necessary to eliminate the influence of 25 mg/L of chloride ion. For the Malomir concentrates it is equal to silver addition of ≈ 315 g/t, because of high dilution of the slurry due to high concentration of sulfide sulfur in material. At the same time, Malomir has a low silver content (8 – 12 g/t), so it was considered impossible to accumulate 315 g silver per ton by recycle.

This method is more suitable for materials with low sulfide content and with a relatively high silver content. For example, if the material contains only 6 – 8 % of sulfur then 50 mg/L of silver will be equal to 100 g Ag per ton of material. This value is achievable, remembering that the silver content in the feed material may be more than 20 g/t.

Mercury

It was shown in the experimental section that a mercury addition about 5 mg/L is sufficient to eliminate the influence of 25 mg/L of chloride ion. Mercury addition - 5 mg/L is equal to 31.5 g/t. Presumably, the dosage may be reduced in the case of processing of low-carbon concentrates.

There is no mercury in Malomir ores. At the same time, a number of gold-mercury deposits are known[22]. Mercury content in such deposits is usually close to the gold content, and sometimes significantly above it. The practice of processing gold-mercury refractory ores by POX is presented by the Twin Creeks and Gold Strike plants. These plants generate metallic mercury as a byproduct in amounts comparable with the amount of gold bars.

Mercury remains in solid phase during the POX process, and up to 80 % of it will be recovered during cyanidation simultaneously with gold. Mercury content in the cyanidation tailings will be about 5 – 10 g/t. Such mercury content in tailings will have no effect on the hazard class of the tailings. This was confirmed both by calculation and by experimental method - biological testing.

The proposed circuit is shown in Figure 4. It contains a special operation in which the metallic mercury is used to obtain the reagent which contains mercury(II). This reagent is used as addition to the POX process. This method was patented in Russian Federation with Pat. № 2552217[23].

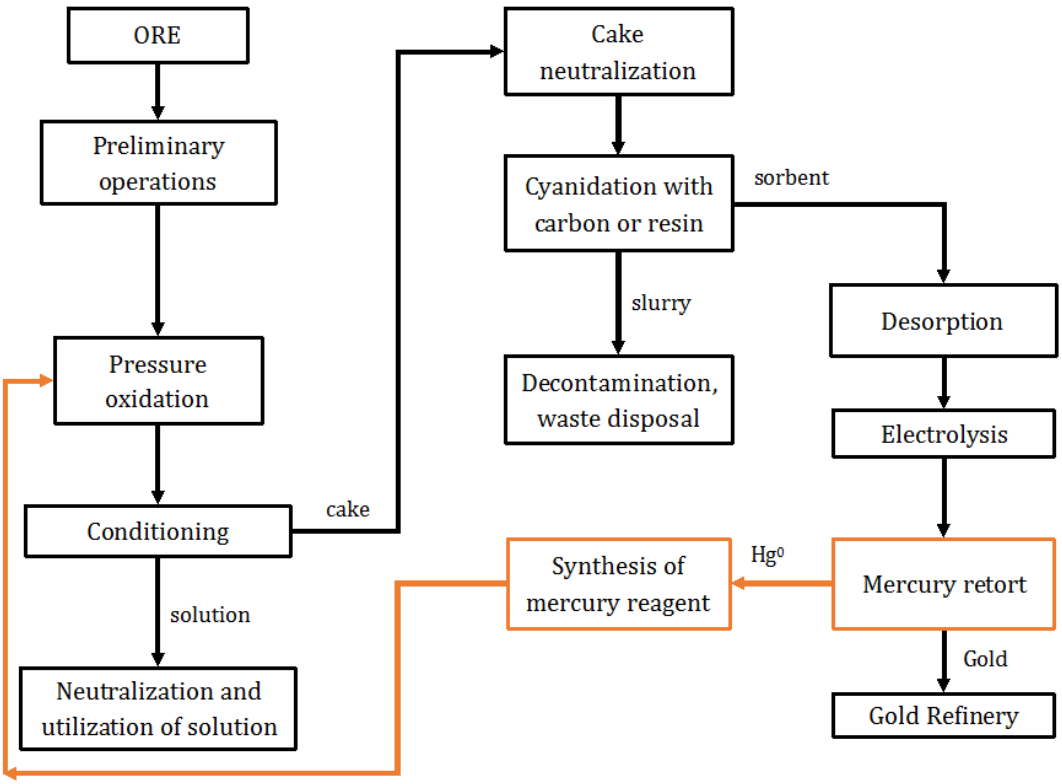


Figure 4: POX technology with recycle of mercury (schematic flowsheet)

The possibility of the simultaneous processing of double refractory concentrates with gold-mercury containing materials may be considered. Significant economic benefits can be obtained by cooperative processing of materials from two different deposits in one plant.

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CONCLUSIONS

The gold recovery from double refractory sulfide concentrates from the Malomyr deposit can be significantly improved by the addition of silver and mercury salts to the POX slurry. Additions of silver in an amount of 50 mg/L (315 g/t conc.) and mercury in an amount of 5 mg/L (31.5 g/t conc.) are sufficient to suppress the negative impact of chloride ion (up to 25 mg/L).

The results of POX tests carried out with the addition of silver and mercury indicate that a significant loss of gold due to autoclave preg-robbing occurs even at low concentrations of chloride ion in the POX solution (3 – 5 mg/L). Gold recovery increases by 7 % in experiments with addition of mercury, and by 5 % with addition of silver. Previously, these losses were considered as unrecoverable.

Despite the fact that both methods are burdened with eco-type difficulties, their industrial use can be justified in the case of processing carbon-containing ores/concentrates with a high natural silver or mercury content in them.

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AUTOGENOUS THIOSULFATE GENERATION AND LEACHING OF GOLD FROM REFRACTORY SULFIDE CONCENTRATE

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ABSTRACT

Under alkaline conditions the oxidation of pyrite generates thiosulfate. The alkaline oxidation of pyrite and autogenous generation of thiosulfate is significantly enhanced by the mechanical energy provided under the conditions of ultrafine milling. The mechanical enhancement to thiosulfate generation requires a minimum energy input to the mill and the generation of thiosulfate preferentially occurs when oxygen transfer into the mill is limiting. Once the hydroxide is consumed the oxidation of the sulfide minerals continues along with the oxidation of thiosulfate which results in the generation of polythionates (trithionate and tetrathionate).

Gold dissolution occurs also as a result of the thiosulfate generation once the hydroxide is consumed and the pH decreases below 10. The mechanical action of the mill was found to enhance gold leaching by the generated thiosulfate during ultrafine grinding under appropriate conditions, but the conditions need to be further optimised to eliminate the observed loss of gold before the majority of the gold is dissolved. However, the milling time required and cost to achieve high gold recovery may be prohibitive.

This study demonstrates the potential for gold recovery from a refractory sulfide concentrate by autogenous generation of thiosulfate during the ultrafine grinding of the concentrate in the presence of hydroxide and oxygen, with the generated thiosulfate used to dissolve gold in a subsequent leaching step.

Keywords: gold, thiosulfate, leaching, refractory

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INTRODUCTION

The recovery of gold from refractory ores and concentrates is a research area in which considerable attention has been focused in recent years as a result of the depletion in ore deposits that are amenable directly to cyanidation. Refractory ores and concentrates generally have physically encapsulated and/or solid solution gold within sulfide minerals. Thus, in order to recover the gold, the sulfide mineral must be broken down either physically or chemically to expose the gold for leaching.

The gold values in these refractory sulfidic ores may be sufficiently exposed by ultrafine grinding and recovery by subsequent cyanidation. The cost of grinding to very small particle size and associated increase in cyanide consumption, however, can make this process uneconomic. Alternatively, oxidation may be used to dissolve some or all of the sulfide components to expose the gold. Oxidation processes that have been developed for the pre-treatment of these refractory sulfidic ores and concentrates before cyanidation include roasting, pressure oxidation (acidic and alkaline), bacterial oxidation or ultrafine grinding with atmospheric oxidation. Notably, thiosulfate can be generated in the aqueous oxidation processes and can act as an alternative lixiviant to cyanide for gold leaching. The gold leach rate in oxygenated thiosulfate solutions is slow, being enhanced by increasing temperature and galvanic interactions[1,2]. Oxidants such as copper(II) and iron(III) are used to achieve similar gold leach rates to that achieved using cyanide.

Thiosulfate is generated from the alkaline oxidation of sulfide minerals[3] during pre-oxidation with alkaline conditions before cyanidation[4] or at elevated temperatures which breakdown sulfide minerals and expose encapsulated gold[5,6]. The work by Melashvili *et al*.[6] at elevated temperatures found that thiosulfate formed under highly alkaline conditions (pH > 12) from the oxidation of pyrite, but itself was oxidised when the pH decreased below 12. In contrast, the dissolution of gold by thiosulfate generated from the alkaline oxidation of pyrite only occurred when the pH was below 12. It was thus apparent from this work that optimisation of conditions was needed for the generation of thiosulfate and subsequent leaching of the gold.

The application of a mechanical force to minerals during grinding can improve the reactivity of minerals or induce mechanochemical reactions such as oxidation or reduction reactions. This includes processes for ultrafine milling of a wide range of ores to render metals more extractable[7] and for treating sulfides through mechanochemical activation to render metals soluble through the formation of soluble sulfates[8,9]. However, the leaching of gold and silver after or during these milling process has required the addition of a gold leaching lixiviant such as cyanide to complex the gold (and silver).

Described in this paper are investigations based on an observed significant enhancement (by mechanochemical activation) of the alkaline oxidation of sulfide minerals during ultrafine grinding to generate thiosulfate. This study investigated the conditions for autogenous generation of thiosulfate during milling of a pyrite concentrate and the ability to leach gold and silver in parallel or subsequently.

EXPERIMENTAL

The ore used throughout this test work was a sulfide flotation concentrate consisting mainly of pyrite with quartz, muscovite, chlorite, albite, ankerite, paragonite and traces of rutile. The concentrate sample contained 51 g/t Au, 12 g/t Ag and 0.14% Cu. Particle size analysis indicated a P80 of 166 µm and a D50 of 65 µm. A significant portion of the gold is locked in the pyrite.

Ultrafine grinding experiments were carried out in a batch 1.25 L attritor (stirred mill). The mill comprised a grinding chamber in which the vertical shaft of an impeller with a series of outwardly directed stirring arms was rotated by means of a drill press. Ultrafine grinding was carried out with the standard conditions outlined in Table 1. Any variation to these conditions are noted in the text and/or within the figure captions. The mill was periodically stopped and samples were taken and filtered. The filtered solution was analysed for thiosulfate, polythionates, gold, silver and copper. The pH and E_H of the filtered solution was also measured.

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Table 1: Standard ultrafine grinding conditions

Parameter	Specifications
Media size and type	~3-5 mm round pebbles
Solids to water ratio	1:2 (300 g ore : 600 mL water)
Ball to sample weight ratio	3:1 (900 g pebbles; 300 g solids)
Impeller tip-speed	4.16 m s^{-1} (1166 rpm)
Atmosphere	500 mL min^{-1} air injected into top of grinding chamber
Hydroxide added initially	0.32 M NaOH (20 mL of 10 N NaOH)

Chemical analyses for gold, silver and copper for all leach solutions were obtained by inductively coupled plasma-optical emission spectroscopy (ICP-OES). Background matrix corrections were carried out using the sample solutions. Thiosulfate, sulfite and sulfate were analysed by a developed anion exchange high performance liquid chromatography (HPLC) method with ultraviolet (UV) and conductivity detection. Polythionates were analysed using a developed reverse phase HPLC method with UV detection.

RESULTS AND DISCUSSION

Autogenous Generation of Thiosulfate

The significant rate of thiosulfate generation from sulfide mineral oxidation during ultrafine grinding is evident in Figure 1. Heat is generated by the grinding action of the mill which increases the temperature within the mill. The temperature in the mill after 90 minutes of grinding for the standard conditions was 45 °C. Controlling the mill temperature at 25 °C using a water jacket did not significantly slow the generation of thiosulfate. After 90 minutes at 45 °C, the generation of thiosulfate stops due to the depletion of hydroxide, which is discussed further below. In comparison the rate of thiosulfate generation from the oxidation of the sulfide concentrate in a stirred tank at 70 °C is shown in Figure 1 to be very slow. Hence, it is the mechanical energy imparted by the mill that overcomes the activation energy barrier for the oxidation of pyrite by oxygen under the milling conditions used.

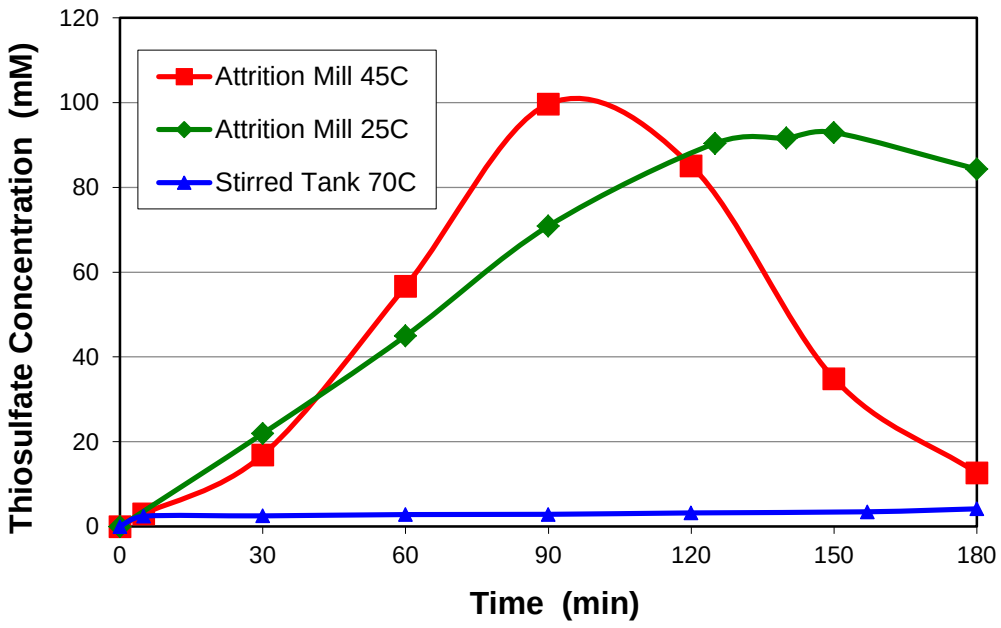


Figure 1: Thiosulfate generation from alkaline oxidation of sulfide concentrate.

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The batch alkaline oxidation of sulfide minerals during ultrafine grinding at 45 °C consumes hydroxide and the pH decreases dramatically once the hydroxide has been consumed (60–90 min in Figure 2). There is also an associated increase in the solution potential (E_H) indicating a change in the solution speciation.

Figure 3 presents the sulfur speciation in the solution during ultrafine grinding under alkaline conditions of the sulfide concentrate. The sulfur balance was found to be within 2% except for the 5 minute sample (5% error) and at times greater than 90 minutes. The latter is due to data from separate runs being combined as both anion and reverse phase HPLC could not be conducted at the same time and the samples degraded with time. Despite this, Figure 3 clearly shows the proportions of sulfur species formed and degraded with time. Under these conditions the major soluble sulfur species generated in the first 90 minutes is thiosulfate. Sulfite is also generated but to a much lesser extent in the first 60 minutes. After 60 minutes the hydroxide is depleted (Figure 2) and the sulfite (and subsequently the thiosulfate) decrease due to degradation reactions which produce trithionate, sulfate and some tetrathionate (detectable and increasing concentrations measured in solution after 90 minutes). The results in Figure 3 also suggest that sulfide mineral oxidation is also ongoing as the total sulfur continues to increase with time.

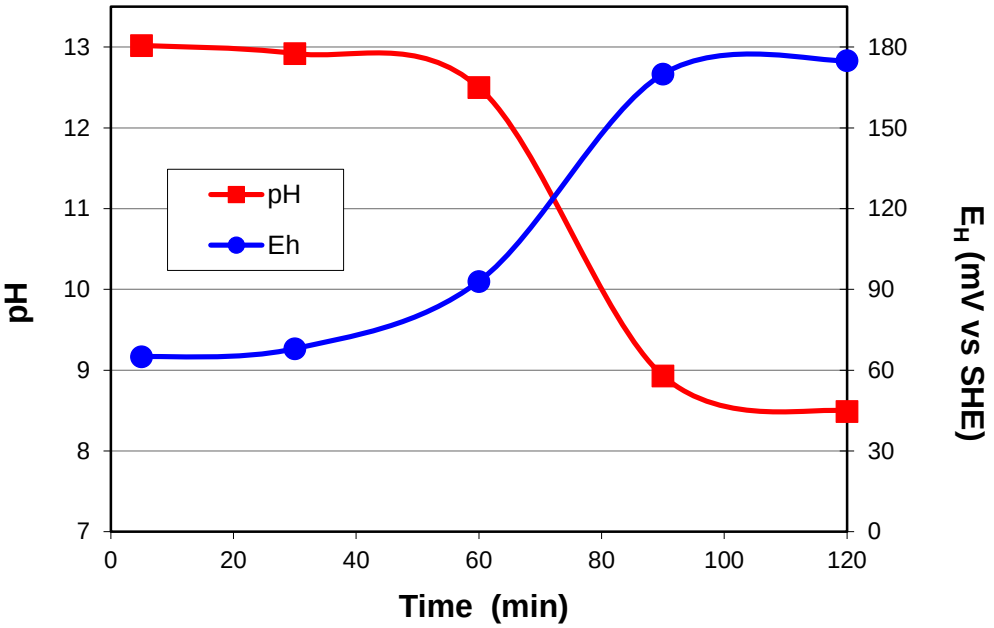


Figure 2: pH and E_H for alkaline oxidation of sulfide concentrate during ultrafine grinding.

For pyrite the overall reactions for the formation of the various oxy-sulfur species are given in Equations 1 to 5.

$$4FeS_2 + 7O_2 + 2H_2O + 8OH^- \rightarrow 4Fe(OH)_3 + 4S_2O_3^{2-} \quad (1)$$

$$2FeS_2 + 4O_2 + 2H_2O + 2OH^- \rightarrow 2Fe(OH)_3 + S_4O_6^{2-} \quad (2)$$

$$12FeS_2 + 29O_2 + 10H_2O + 16OH^- \rightarrow 12Fe(OH)_3 + 8S_3O_6^{2-} \quad (3)$$

$$4FeS_2 + 11O_2 + 16OH^- \rightarrow 4Fe(OH)_3 + 8SO_3^{2-} + 2H_2O \quad (4)$$

$$4FeS_2 + 15O_2 + 16OH^- \rightarrow 4Fe(OH)_3 + 8SO_4^{2-} + 2H_2O \quad (5)$$

The interesting thing to note from these equations is the different ratios of hydroxide and oxygen to sulfur (see Table 2). Not surprisingly, the oxygen-to-sulfur ratio follows the sulfur oxidation state of the oxy-sulfur species formed. Hence, under oxygen limited conditions, thiosulfate will be the likely oxidation product formed, which is consistent with the results observed in Figure 3 for the first 90 minutes. Under hydroxide limiting conditions the formation of tetrathionate and trithionate are the likely oxidation products formed. This is consistent with the results shown in Figure 3 after 90 minutes.

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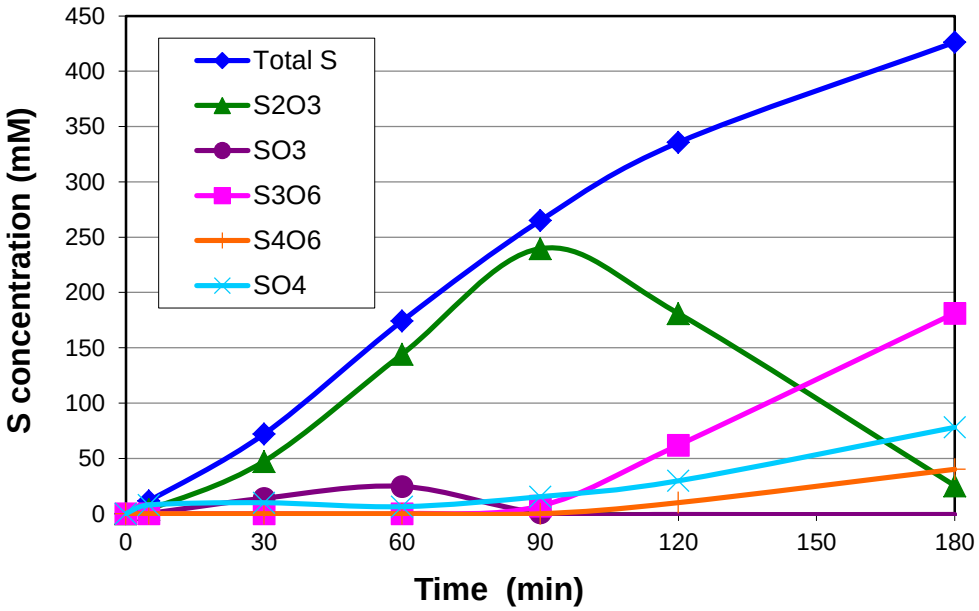


Figure 3: S speciation for alkaline oxidation of sulfide concentrate during ultrafine grinding.

Table 2: Ratios of hydroxide and oxygen to sulfur for Equations 1 to 5.

Oxy-sulfur species formed	S oxidation state	O/S ratio	OH^-/S ratio
Thiosulfate	+2	1.75	1
Tetrathionate	+2.5	2	0.5
Trithionate	+3.3	2.42	0.66
Sulfite	+4	2.75	2
Sulfate	+6	3.75	2

The fact that some sulfite forms in the first 90 minutes (Figure 3) may initially look surprising given the oxygen to sulfur ratios. However, this is possibly due to some tetrathionate actually forming which rapidly undergoes alkaline decomposition[10] with the overall reaction shown in Equation 6.

$$2S_4O_6^{2-} + 6OH^- \rightarrow 3S_2O_3^{2-} + 2SO_3^{2-} + 3H_2O \quad (6)$$

It is also evident from Figure 2 and 3 that the oxidation of pyrite continues even after the depletion of hydroxide. However, the ongoing oxidation of pyrite to tetrathionate or trithionate still requires hydroxide ions (Equations 2 and 3). The fact that the thiosulfate concentration decreases during this time suggests that pyrite oxidation continues due to hydroxide generated from the oxidation of thiosulfate according to Equations 7 and 8.

$$4S_2O_3^{2-} + O_2 + 2H_2O \rightarrow 2S_4O_6^{2-} + 4OH^- \quad (7)$$

$$3S_2O_3^{2-} + 2O_2 + H_2O \rightarrow 2S_3O_6^{2-} + 2OH^- \quad (8)$$

Mill Speed

The effect of attrition energy (mill rotation speed) on the rate of thiosulfate generation is shown in Figure 4. Notably a minimum speed of 950 rpm is required for a significant rate of thiosulfate generation to occur. Below this rotation speed the thiosulfate generation rate decreases sharply with decreasing rotation speed. This decrease in thiosulfate generated was found not to be related to a decrease in the formation of fresh surfaces during grinding as the particle size distribution P80 after 90 minutes grinding was found to be almost independent of rotation rate. The temperature in the mill was also noted to decrease with decreasing mill rotation speed, particularly below 950 rpm. However, this was shown in Figure 1 to not have a significant impact on the thiosulfate generation rate. This suggests thiosulfate generation may have an activation energy barrier. Hence there is a

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minimum mechanical energy input required to overcome the activation energy barrier for the alkaline oxidation of pyrite at atmospheric conditions.

Oxygen Addition Rate

The oxidation of pyrite to generate thiosulfate is shown in Figure 5 to be dependent on the oxygen addition rate to the mill. The generation of thiosulfate increases with increasing compressed air flowrates up to 0.5 L/min which suggests the generation of thiosulfate is oxygen limited up to this air flowrate. At very high oxygen addition rates (industrial oxygen used rather than air) the generation of thiosulfate occurs more rapidly, however the maximum thiosulfate concentration achieved decreased and the thiosulfate was subsequently destroyed faster.

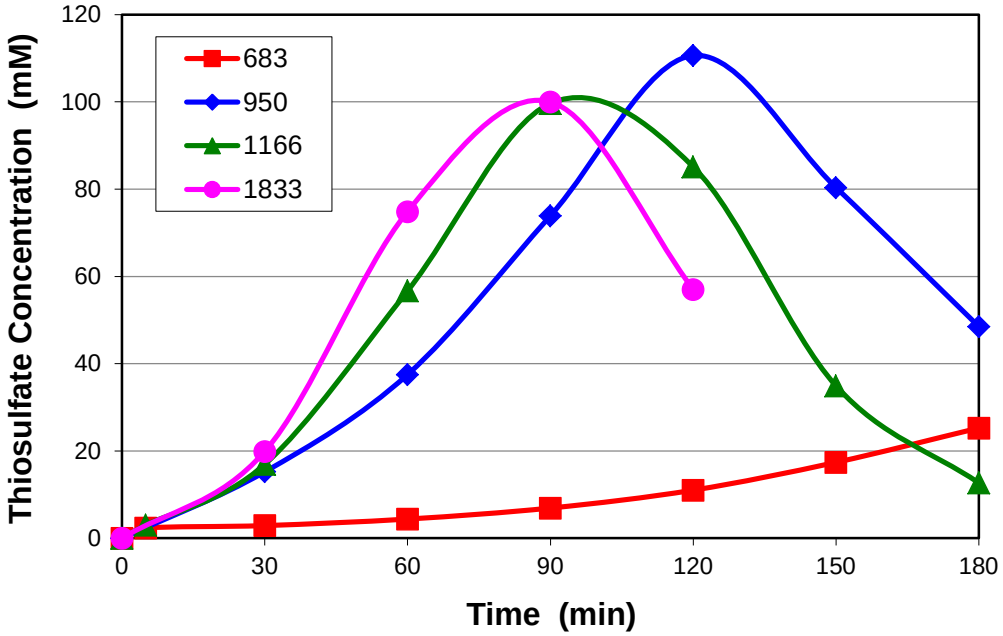


Figure 4: Effect of ultrafine grinding mill rotation speed (rpm) on alkaline oxidation of sulfide concentrate for standard conditions.

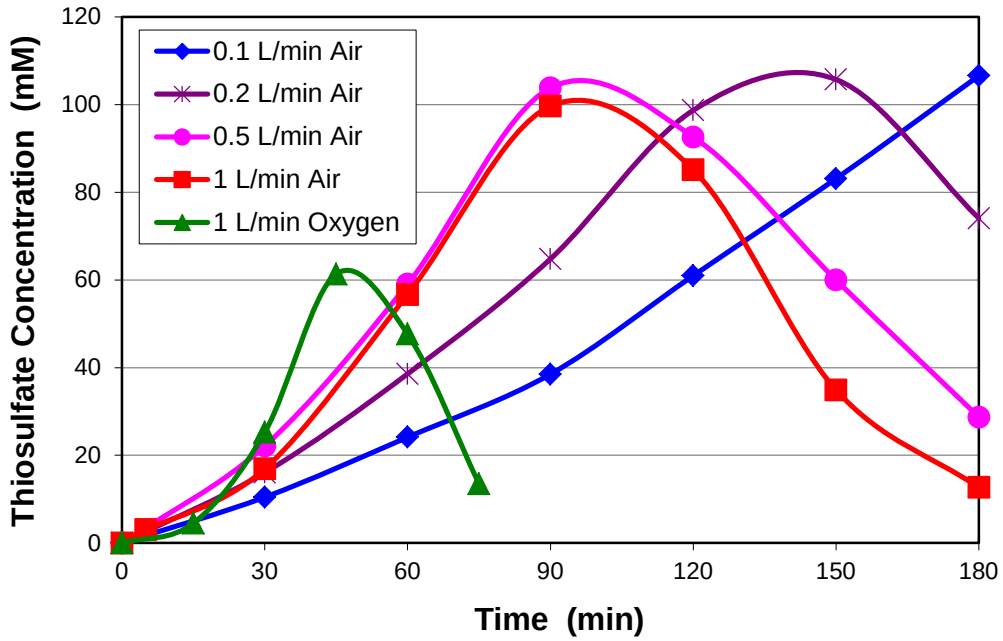


Figure 5: Effect of air/oxygen addition rate on alkaline oxidation of sulfide concentrate during ultrafine grinding for standard conditions.

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An important aspect of this work was to maximise the generation of thiosulfate. The percentage of the dissolved sulfur forming thiosulfate is shown in Figure 6 for various oxygen addition rates. Over 80% of the sulfur oxidised into solution forms thiosulfate at air flow rates at or below 0.5 L/min. Above this rate the oxidation to thiosulfate decreases with increasing oxygen addition rate. This is attributed to the greater formation of higher oxidation state oxy-sulfur species (such as sulfite) when excess oxygen is present.

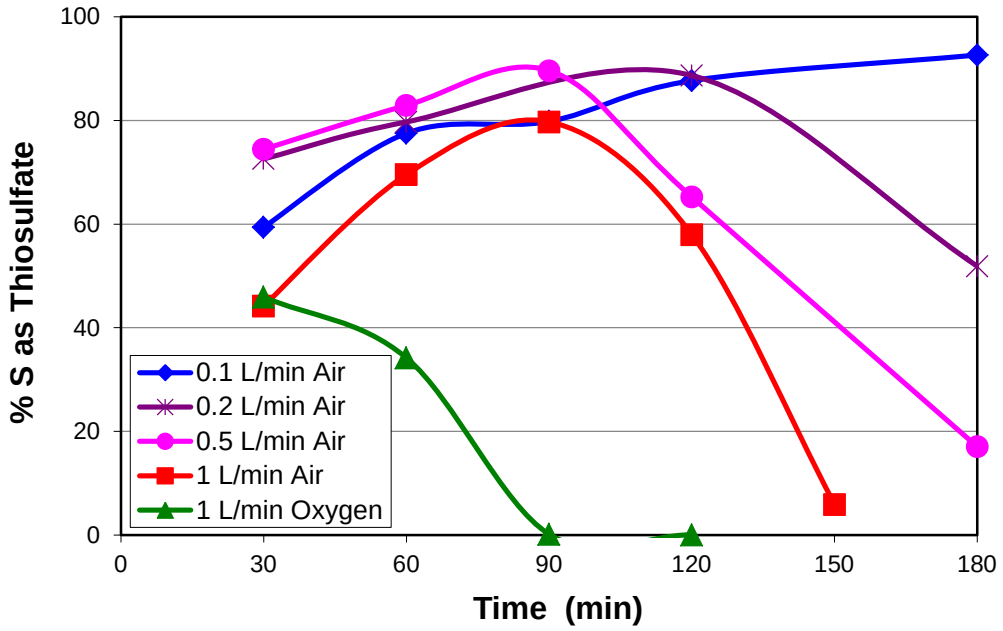


Figure 6: Effect of air/oxygen addition rate on percentage of sulfide oxidation forming thiosulfate during ultrafine grinding for standard conditions.

Alkali Addition

The quantity of thiosulfate generated was found to be proportional to the quantity of sodium hydroxide added. A similar rate of thiosulfate generation is also observed if sodium hydroxide is added constantly to the mill at a rate such that hydroxide is in excess of oxygen (Figure 7). At addition rates below 0.2 mL/min of 10 M sodium hydroxide, the rate of thiosulfate generation is dependent on the rate of sodium hydroxide addition. With no sodium hydroxide addition no thiosulfate generation was observed, however pyrite oxidation still occurred (tetrathionate and other polythionates detected). Lime was found to be less effective as a source of alkali due to the limited solubility; the hydroxide concentration was thus limited as was the rate of sulfide oxidation (similar to the 0.1 mL/min NaOH addition shown in Figure 7). Ammonia was also found to be less effective, similar to lime, due to the limiting hydroxide concentration resulting from the equilibrium with ammonium ions.

Gold Leaching Associated with Autogenous Generation of Thiosulfate

The concentration of metal ions dissolved during the standard batch alkaline ultrafine grinding of the concentrate sample are shown in Figure 8. The metal ion extractions indicate that metal dissolution did not occur to any appreciable extent until after 60 minutes of milling, despite thiosulfate being formed in the first 60 minutes; recalling that for the standard conditions thiosulfate generation reached a maximum at 90 minutes (Figure 1) with a sharp drop in pH between 60 and 90 minutes as a result of hydroxide depletion (Figure 2). Gold extraction measured for varying sodium hydroxide additions confirmed that little gold dissolution (or other metals) occurs whilst the pH is high (pH > 12). The lack of metal dissolution during the initial period is potentially due to the lack of dissolved oxygen as a result of the preferential, oxygen limiting oxidation of pyrite. When the pyrite oxidation becomes hydroxide limited (pH decreases), the dissolved oxygen increases as indicated by the solution E_H (Figure 2) and the gold and other metals begin to oxidise and dissolve. This is consistent with the observation by Melashvili *et al.*[6] at elevated temperatures. The metal extractions attain a maximum after approximately 120 minutes, though the quantity is only a very small fraction (< 2%) of that present in the concentrate. Further milling results in losses suggesting precipitation of the dissolved metals. This loss is attributed to thiosulfate degradation and the

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formation of polythionates (particularly tetrathionate) during this period (Figure 3); tetrathionate, in particular, is known to further degrade to sulfide and elemental sulfur, but no sulfide ions were measured in solution.

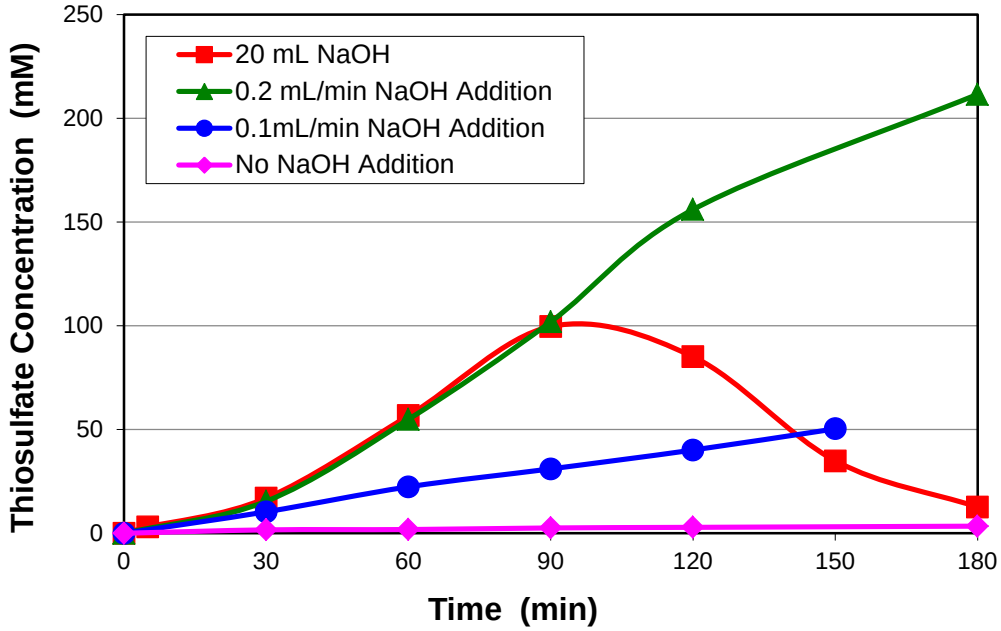


Figure 7: Effect of hydroxide addition rate on alkaline oxidation of sulfide concentrate during ultrafine grinding for standard conditions.

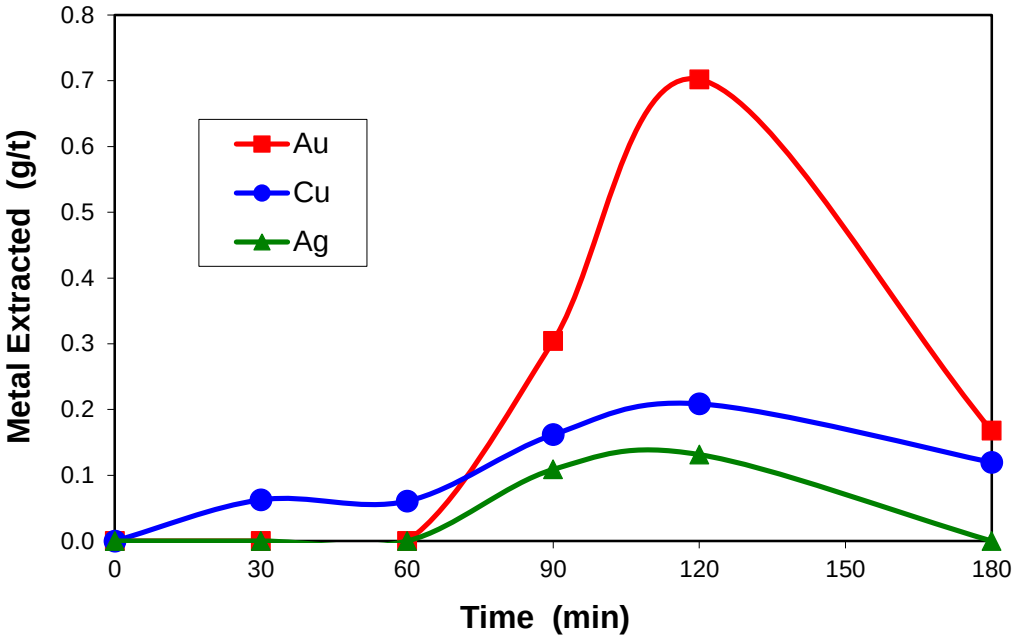


Figure 8: Metal dissolution during ultrafine grinding of sulfide concentrate.

The dissolution of metals subsequent to ultrafine grinding and the autogenous generation of thiosulfate (on depletion of hydroxide) is discussed in the next section. The following discussion describes investigations into the potential of mechanical enhancement (and maintenance of gold dissolution) during ultrafine grinding in conjunction with or subsequent to the autogenous generation of thiosulfate.

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The extent of metal dissolution subsequent to the depletion of hydroxide during ultrafine grinding of the concentrate was found to vary depending on the milling conditions, but in all cases the same profile was observed as shown in Figure 8 with the peak quantity dissolved being less than 5%.

From Figures 1 and 8 it would appear that the milling conditions between 60 and 90 minutes are possibly suitable to parallel thiosulfate generation and metal extraction. Investigations were thus attempted to maintain the pH around 10-11 subsequent to thiosulfate generation. The first approach added 0.2 mL min^{-1} of 10 M sodium hydroxide after 80 minutes and the results are shown in Figures 9, 10 and 11. This approach maintained the pH at ≈10 with continued thiosulfate generation observed. Gold dissolution was improved slightly but was still very low with eventual gold losses observed despite thiosulfate continually being generated. A second investigation shown also in these figures was conducted with 0.1 mL min^{-1} of 10 M sodium hydroxide added after 90 minutes. This maintained a lower pH at ≈9 where thiosulfate generation stopped (with a small loss over time) and a higher gold extraction was achieved.

A further test also shown in Figures 9, 10 and 11 investigated the replacement of some sodium hydroxide by ammonia. Despite the pH being maintained above 10 by the ammonia (Figure 10), this resulted in the thiosulfate generation halting upon depletion of the sodium hydroxide. Most notable also is the significant enhancement to gold dissolution, though the peak extraction is only ≈20%. The presence of ammonia can complex and dissolve copper (final copper concentration was 20 ppm), which potentially assists the gold oxidation and dissolution.

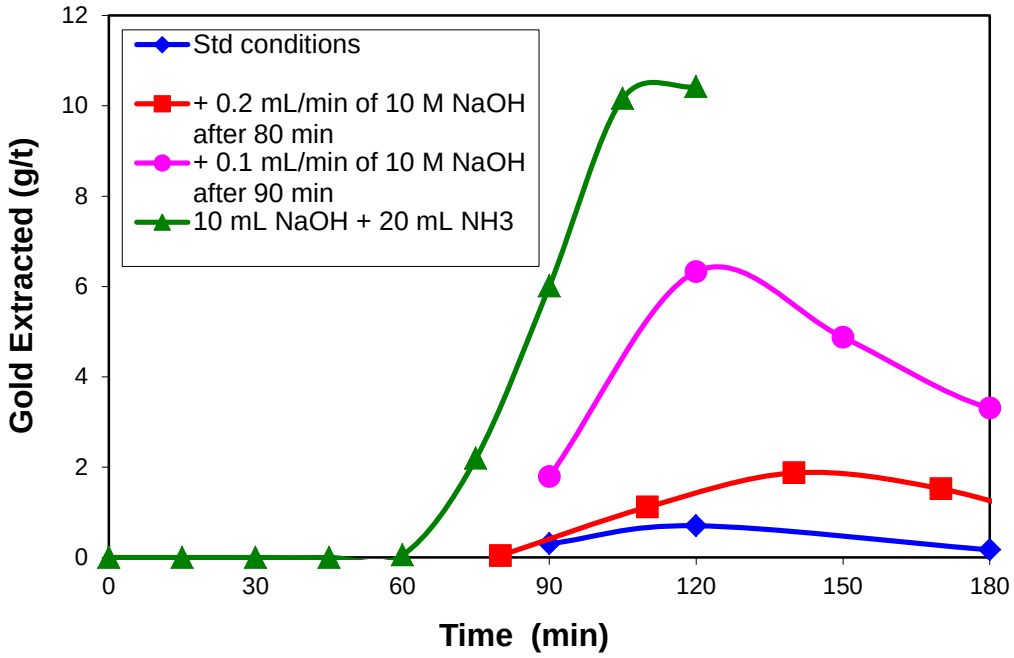


Figure 9: Gold dissolution during ultrafine grinding of sulfide concentrate for varying conditions.

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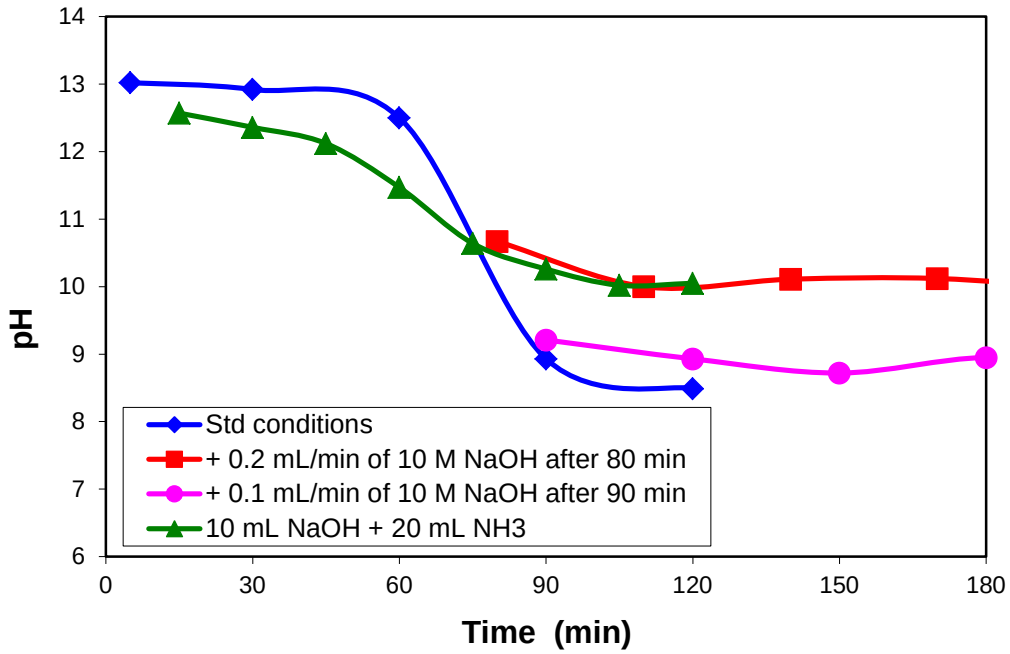


Figure 10: pH during ultrafine grinding of sulfide concentrate for varying conditions.

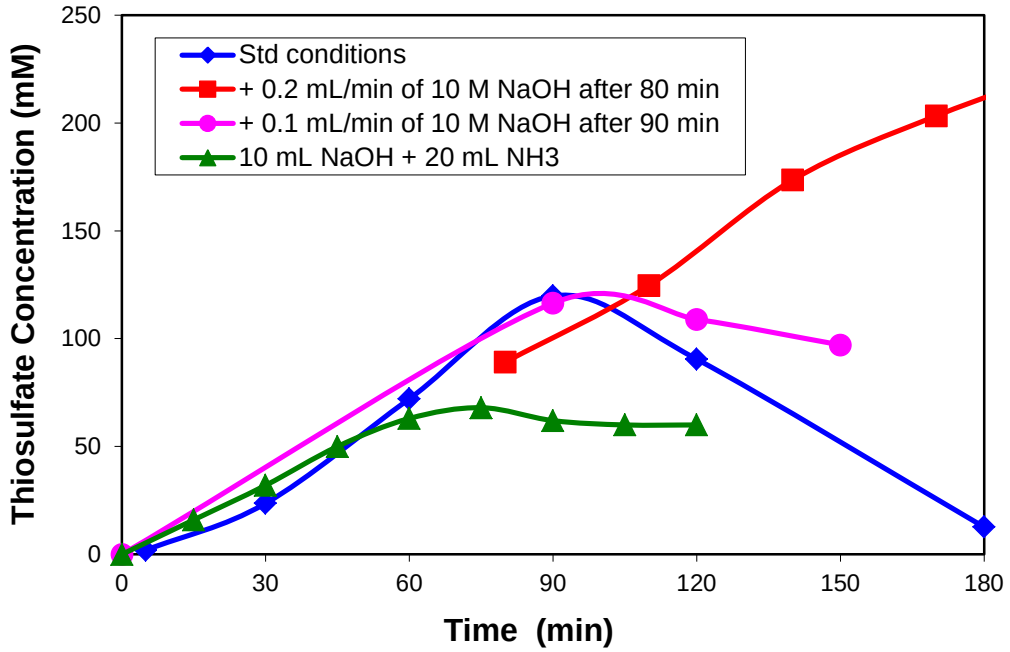


Figure 11: Thiosulfate generation during ultrafine grinding of sulfide concentrate for varying conditions.

Gold Leaching Subsequent to Autogenous Generation of Thiosulfate

The generation of thiosulfate during ultrafine grinding of sulfide concentrates could be used to generate and replenish depleted thiosulfate which is then available in a subsequent leach stage to recover the gold. In this study the slurry from the milling stage was simply agitated in a stirred tank with air addition maintained at the same rate. Shown in Figure 12 is the subsequent gold extraction with time for the standard ultrafine grinding conditions where the milling was stopped at different times around the time where the hydroxide became depleted. Notably gold dissolution did not occur to any appreciable extent if the pH was too high at the end of milling. Where the gold did dissolve, the rates were slow typical of the oxygen-thiosulfate system. Though not investigated, the likely galvanic effect of pyrite on gold dissolution may have been reduced by the formation of iron hydroxide resulting from thiosulfate generation.

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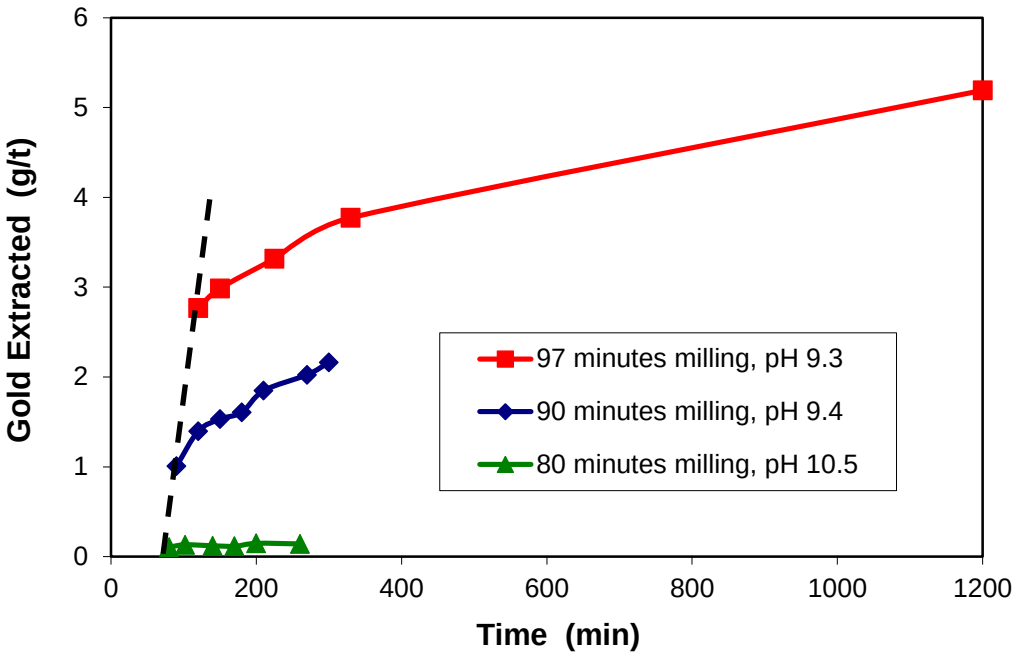


Figure 12: Gold dissolution in stirred tank post ultrafine grinding of sulfide concentrate with autogenous generation of thiosulfate.

The slow leaching of gold indicates that the use of copper and elevated temperature would be required to achieve acceptable gold dissolution rates. On a larger scale (where the heat losses are much less than in the laboratory) the milling process would likely provide the necessary heat to produce acceptable leach rates with the addition of copper.

CONCLUSIONS

This study found that the mechanical energy imparted during ultrafine grinding of a sulfide concentrate provided enhanced oxidation and autogenous generation of thiosulfate under alkaline conditions. The mechanical enhancement to thiosulfate generation required a minimum energy input to the mill and the generation of thiosulfate was found to preferentially occur when oxygen transfer into the mill was limiting. Once the hydroxide was consumed the oxidation of the sulfide minerals continued along with the oxidation of thiosulfate which resulted in the generation of polythionates (trithionate and tetrathionate).

The dissolution of metals was not observed during the milling under alkaline conditions. However, when the hydroxide was consumed and the pH decreased below 10 some metal dissolution was observed. The mechanical action of the mill was found to enhance gold leaching by the generated thiosulfate during ultrafine grinding under appropriate conditions, but the conditions need to be further optimised to eliminate the observed loss of gold before the majority of the gold is dissolved. However, the milling time required and cost to achieve high gold recovery may be prohibitive.

Gold leaching in a stirred tank with air addition (post ultrafine grinding with autogenous generation of thiosulfate) occurs without evidence of any gold losses. The gold leach rate however is slow and would most likely be enhanced with the addition of copper and use of elevated temperature in the leaching stage. On a large scale the temperature generated in milling may be sufficient.

This study has demonstrated that thiosulfate can be generated autogenously during the ultrafine grinding of sulfide concentrates with the addition of hydroxide and oxygen. The generated thiosulfate can then be used to dissolve gold in a subsequent leaching step. The ultrafine grinding conditions may also be beneficial in the regeneration of thiosulfate from the polythionates when leach tails solution is recycled to the mill, but this aspect has not yet been investigated.

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GLYCINE-CYANIDE SYNERGIES IN THE LEACHING OF COPPER-GOLD ORES AND CONCENTRATES

By

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ABSTRACT

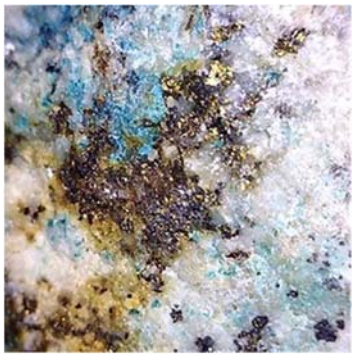
The presence of reactive copper minerals in the cyanidation of copper-gold ores intensively increases the cyanide consumption and deceases the extraction of gold. There are also increasing environmental concerns and restrictions on the discharge copper-cyanide complexes to tailings dams. In addition to that, additional cyanide recovery or cyanide detoxification/destruction processes are required. This research study introduces a new process to extract gold and silver from copper-gold ores and concentrate using glycine-cyanide mixture. The effect of glycine/copper and cyanide/copper molar ratio addition on gold leaching kinetics and recovery was studied. The results show that, in the presence of glycine, gold and silver leaches fast (in comparison to either cyanide or glycine on their own) in solutions containing copper-cyanide species at a very low, or zero, free cyanide concentration. It has been shown that the gold recovery in glycine-cyanide system is almost three times higher than the gold dissolution rate in the conventional cyanidation. Kinetic studies were conducted to evaluate the effects of glycine concentration, pH, CN/Cu ratio on the dissolution of gold and silver. It has also been shown that the gold dissolution rate increases by increasing the glycine concentration up to 7.5 g/L and any further glycine addition has no effect on the dissolution of gold. Increasing leaching pH up to 11.0 enhances gold dissolution in the copper-cyanide-glycine solutions. The main finding from this research is that the presence of glycine in solutions containing different copper(I)-cyanide species can significantly enhance the dissolution of precious metals. It appears as if the glycine is involved in dissolving the passivation layer of both $Cu(OH)_2$ and CuCN formed on the gold surface at low, or zero free cyanide, and re-generating free CN^- ions from CuCN which will be involved in any further gold dissolution. In addition, glycine also stabilises the cupric ion in the system which act as a stronger oxidant for gold leaching.

Outline

- Introduction
- System Mechanism
- Research Aims
- Applications
  - Gold-Copper Concentrate
  - Gold-Copper Oxides Ore
- Glycine-Cyanide vs Cyanidation
- Conclusions

Introduction

- Gold (Au) often associated with Copper (Cu).
  - Cu problems in gold circuits
  - Gravity recovery & smelting
  - Cyanide consumption during leaching
  - WAD production & toxicity
  - Competition with Au in adsorption (Au loss)
  - Problems with electrowinning of Au eluate
  - Costs associated with CN destruction and detox
- CN- consumption: 30kg/t for 1%Cu in ore



Copper-Gold Oxide Ore from Utah, USA

Research Question?

- Can we treat gold-copper deposits at the following merits?
  1. Low Cyanide Consumption
  2. High Gold Recovery
  3. Utilised Low or Zero Free Cyanide
  4. Low WAD Cyanide



Aims

- This research work presents a new leach system of using Glycine-Cyanide catalysed solutions to treat gold-copper deposits at the following merits:
  1. Low Cyanide Consumption
  2. High Gold Recovery
  3. Utilised Low or Zero Free Cyanide
  4. Low WAD Cyanide



System Mechanism

The major roles of glycine in copper-cyanide systems are expected to be one or more of the following:

1. Formation of Cu complexes

$$Cu^{2+} + 2(H_2NCH_2COO)^- \leftrightarrow Cu(NH_2CH_2COO)_2 \ , log\ K = 15.6$$

2. Passivation layer ($Cu(OH)_2$/Cu_2O/CuO, CuCN) dissolution:

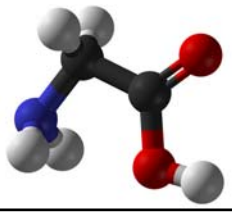
$$2Cu(CN)_2^- \leftrightarrow CuCN + Cu(CN)_3^{2-}$$

3. Glycine can act as an additional lixiviant for gold dissolution

$$4Au + 8NH_2CH_2COOH + 4NaOH + O_2 \leftrightarrow 4Na[Au(NH_2CH_2COO)_2] + 6H_2O$$

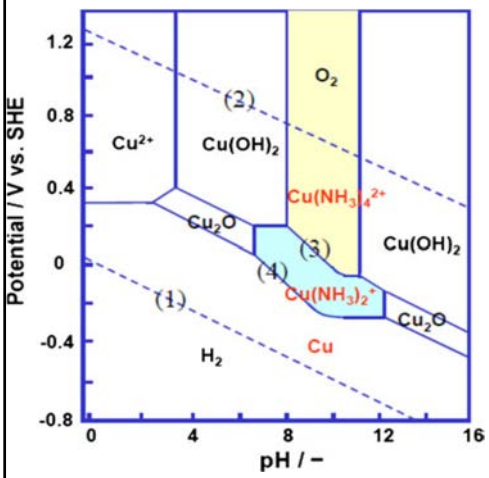
What is an Amino Acid?

- Building block of all proteins
- About 500 different types.
- Simpler amino acids are produced in bulk quantities and available at low prices.
- Glycine is simplest amino acid (amino acetic acid).
- Sweet tasting, non-toxic, occurs in human body.
- Glycine has the following structure:

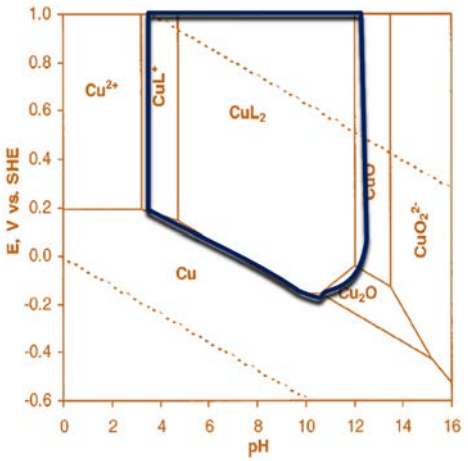


Black: Carbon
White-grey: Hydrogen
Blue: Nitrogen
Red: Oxygen

Cu-NH_3 vs Cu-Glycine



Cu-NH_3

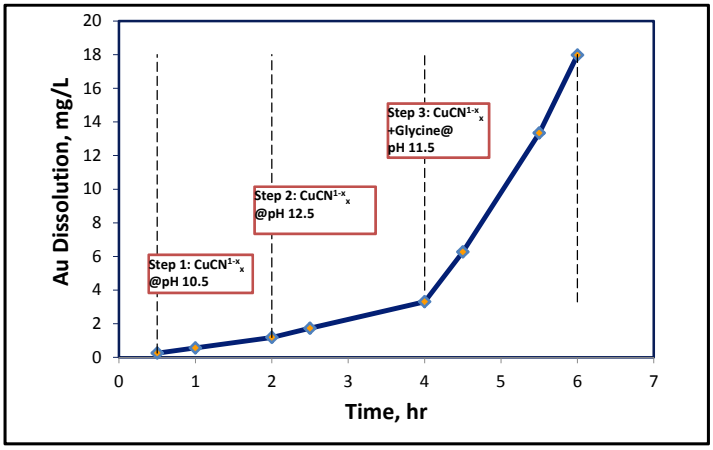


Cu- Glycine

Experimental

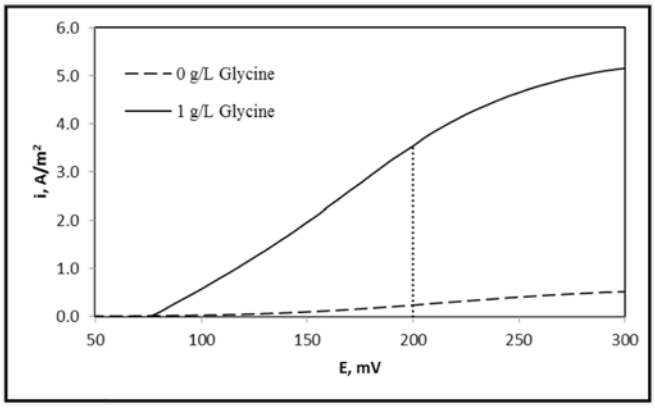
- Purity: AR Grade, Deionised Water
- Particle Size: P_{100} – 75 μm
- Experiments Conducted using:
  - Room Temperature (RT)
  - 2.5 L Bottle rolls (BR) open to atmosphere
  - 150 RPM rotation speed
- Variables: Glycine & Cyanide Concentration, pH
- Solution assay by AAS
- Solid assay by XRF and Fire Assay

Results: Impact on Rate Change



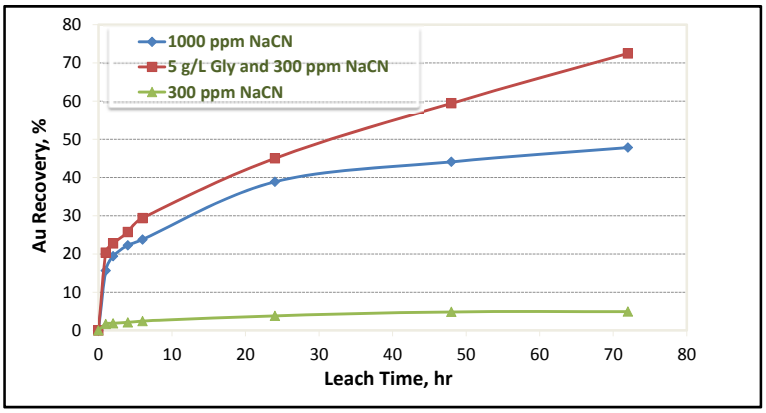
Gold dissolution in 10 mM copper cyanide solutions at room temperature (in step 3, 0.85 g/L glycine added).

Results: Electrochemistry



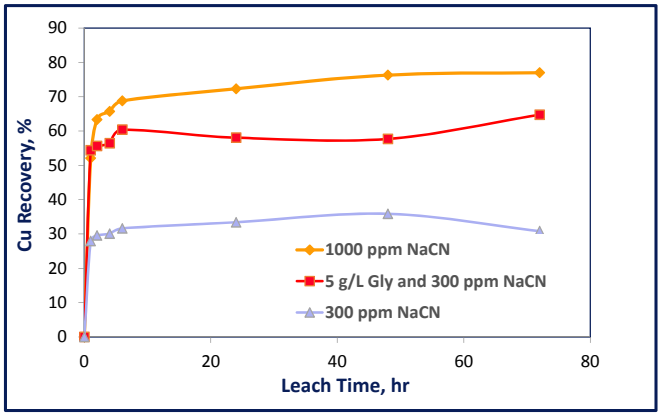
Linear sweep voltammograms showing the oxidation of gold in solutions containing 5.5 mM Cu(I) and 11 mM CN^-, in the presence and absence of 1 g/L glycine.

Results– Gold-Copper Oxides



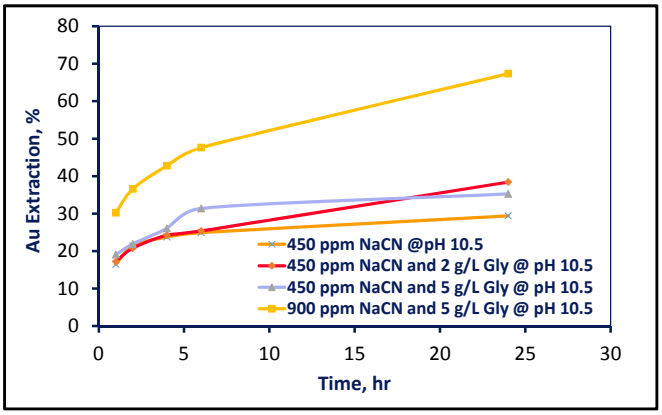
Leaching gold from gold-copper oxides. (100% -75 um, 12.5 g/t Au and 0.04% Cu)

Results– Gold-Copper Oxides



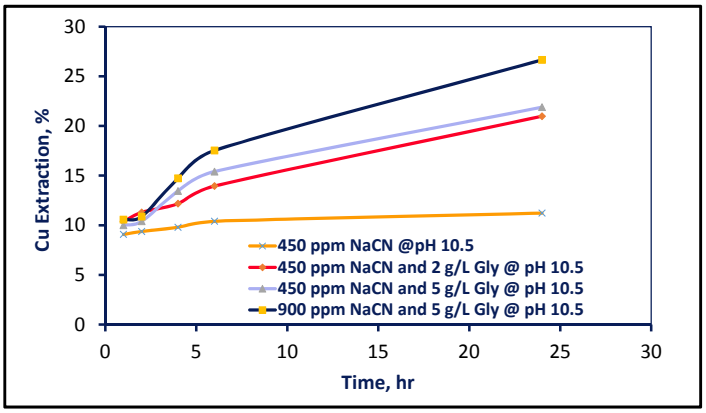
Leaching Copper from gold-copper oxides. (100% -75 um, 12.5 g/t Au and 0.04% Cu)

Results – Gold-Copper Sulfides



Leaching Gold from gold-copper sulfides. (100% -75 um, 0.68 g/t Au and 0.15% Cu)

Results – Gold-Copper Sulfides



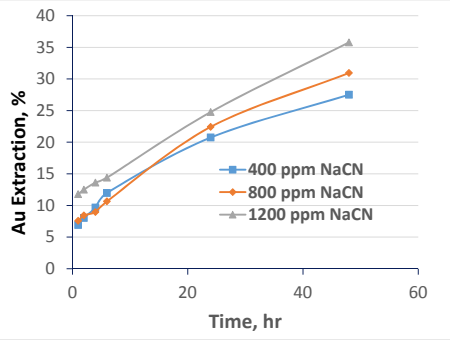
Leaching Copper from gold-copper sulfides. (100% -75 um, 0.68 g/t Au and 0.15% Cu)

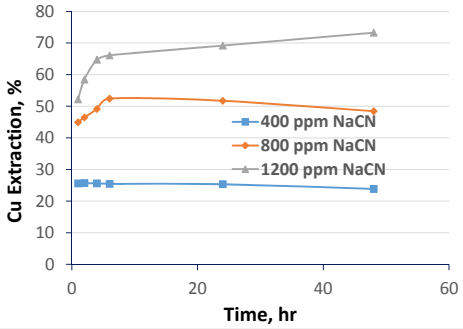
Results– Gold-Copper Concentrate

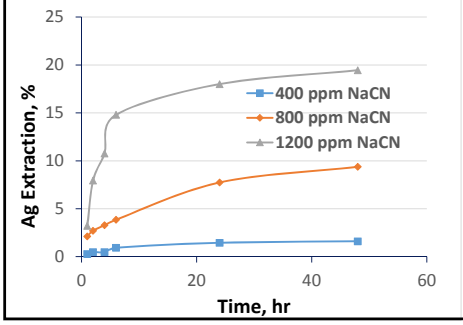
The mineralogical analysis of copper and gangue minerals of the studied copper-gold gravity concentrate.

Mineral	Wt, %	Mineral	Wt, %
Chalcocite/Digenite	0.4	Arsenopyrite	0.00
Cu-metal	0.3	Quartz	87.1
Cuprite	0.2	Feldspar	1.3
Chalcopyrite	0.2	Calcite	<0.1
Bornite	0.1	Dolomite	0.00
Covellite	<0.1	Ankerite/Dolomite	0.2
Exotic complex Cu-sulfides	<0.1	Rutile/Anatase/Ilmenite	0.1
Cu boundaries	0.1	Hematite	0.2
Pyrite	7.1	Goethite	0.7
Pyrrhotite	0.1	Others	1.8

Results – Gold-Copper Concentrate

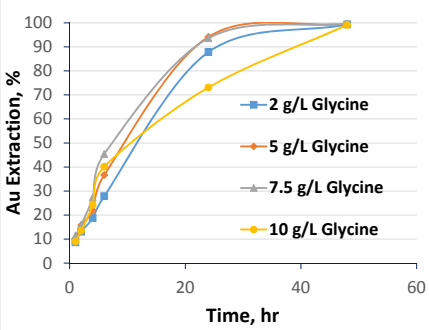


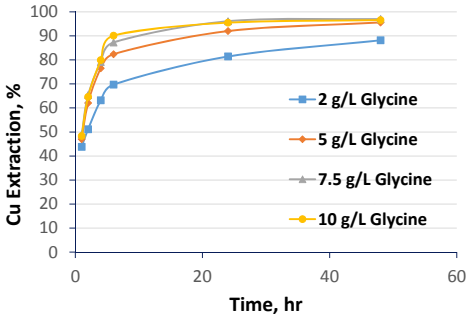


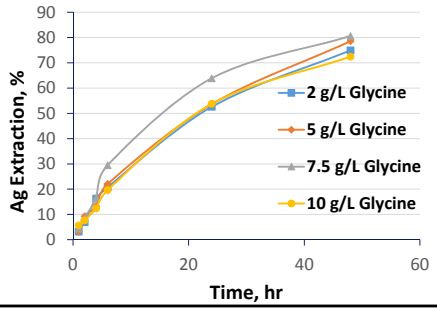


Au, Ag and Cu extraction from Au-Cu gravity concentrate (100% -75 um, 47.5 g/t Au and 0.08% Cu)

Results – Gold-Copper Concentrate

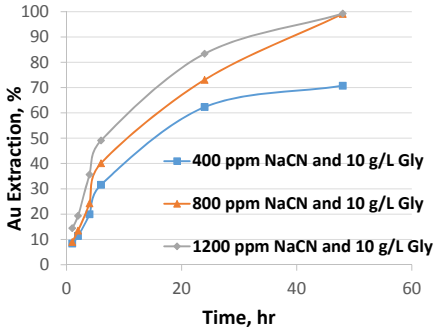


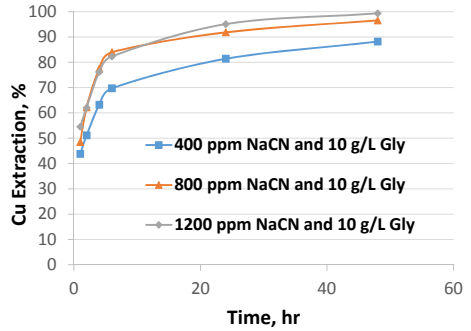


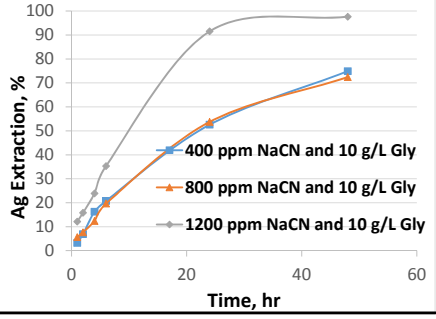


Au, Ag and Cu extraction from Au-Cu gravity concentrate (100% -75 um, 47.5 g/t Au and 0.08% Cu)

Results – Gold-Copper Concentrate

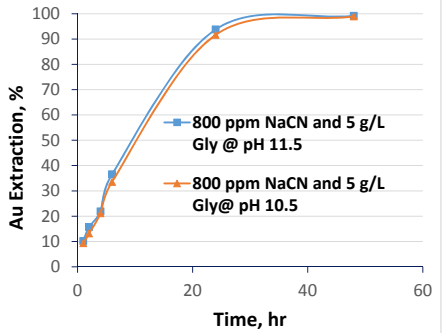


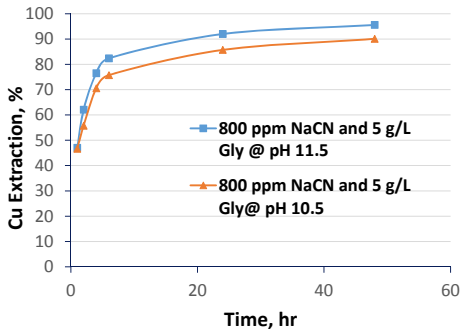


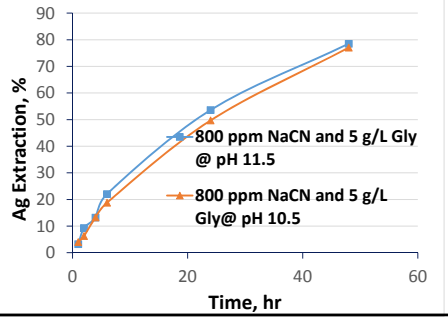


Au, Ag and Cu extraction from Au-Cu gravity concentrate (100% -75 um, 47.5 g/t Au and 0.08% Cu)

Results – Gold-Copper Concentrate







Au, Ag and Cu extraction from Au-Cu gravity concentrate (100% -75 um, 47.5 g/t Au and 0.08% Cu)

Conclusions

- New system (GlyCat): Cyanide Catalysed Glycine leaching useful for Cu-Au deposits
- High Au recovery and low CN consumption.
- Glycine reactivates/releases cyanide ions from copper WAD cyanide at low and zero free cyanide.
- Gold extraction was about 10 times higher in Gly-CN system than cyanide only in treating Au-Cu oxides.
- Gold extraction from gold-copper concentrate reaches 99.1% and 24.2% in the presence and absence of 5 g/L Glycine respectively.

Conclusions (Cont'd)

- GlyCat system improves gold, silver and copper extraction.
- Increasing glycine concentration up to 7.5 g/L enhances gold, silver and copper extraction.
- Increasing leach solution pH from 10.5 to 11.5 has a slight improvement on gold, silver and copper dissolution.
- WAD cyanide in the final leach solution has significantly been reduced.
- Metal recovery from solution (e.g. Precipitation/SX) releases glycine for recycle and reuse.
- Glycine recovery and recycling requires solid-liquid separation: Associated costs need to be considered.

Conclusions (Cont'd)

- In the presence of an air, or O_2, glycine can dissolve copper from chalcopyrite at either an elevated (40-70 °C) or ambient temperature at atmospheric pressure.
- Pyrite remained unreacted during leaching of chalcopyrite and iron concentration in the final pregnant solution was less than 20 mg/L.
- Recovery and reuse potential of lixiviants after SX, electrowinning and NaSH precipitation.
- Sulfides are oxidised to soluble sulfates.
- Applicable to wide range of Cu-minerals (oxide, sulfide, native copper).

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ARSENIC DURING PRESSURE OXIDATION OF REFRACTORY GOLD ORES AND ITS BEHAVIOUR IN DOWNSTREAM PROCESSING

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ABSTRACT

It is widely accepted that pressure oxidation (POX) is the most appropriate technology for the processing of arsenic containing gold refractory feeds due to the stabilisation of arsenic in the leach residue. This is of specific interest since the environmental management of arsenic during gold processing has become more critical due to the enforcement of stringent legislation with regard to arsenic concentration in mine or plant effluents.

Detailed investigations into the precipitation of iron-arsenic compounds at typical POX conditions have only been initiated during the late 2000s. The type and stability of these iron-arsenic precipitates is a function of pH, iron-to-arsenic ratio in the solution, sulphate tenor and temperature. The system has however proven to be very complex with conflicting views regarding stability of precipitates and conditions required for specific compounds to be formed. The current paper is therefore targeted at contributing to the current understanding of the impact of iron-arsenic precipitates formed during POX on downstream processing.

Arsenic behaviour during POX and basic iron sulphate (BFS) curing was investigated by evaluating the treatment of a typical refractory gold concentrate containing arsenopyrite at iron-to-arsenic ratios of between 5 and 7. In addition, the impact of the nature of iron-arsenic precipitates formed on reagent consumption during further cyanidation, as well as final residue stability, is evaluated.

It is likely that the majority of arsenic precipitated as a basic ferric arsenate sulphate-type compound in all instances. In terms of arsenic release, the iron-arsenic precipitate exhibited high stability during carbon-in-leach, but environmental stability was much lower. Unlike BFS, the iron-arsenic precipitate did not consume lime or cyanide during cyanidation. Even though curing resulted in significant decomposition of the iron-arsenic compound, no improvement in lime consumption during cyanidation was observed. Cyanidation (at pH > 10.5) impacted the environmental stability of the iron-arsenic precipitates negatively, therefore it is likely that the cyanidation residues cannot be regarded suitable for arsenic disposal and would require a lined tailings pond for storage.

The results obtained during this study provided further insight into expected precipitation products at typical POX conditions and associated behaviour in downstream units.

Keywords: Arsenopyrite, Pressure Oxidation, Conditioning, Iron-Arsenic Precipitates, Precipitation, Reagent Consumption, Residue Stability

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INTRODUCTION

During the oxidation of typical refractory gold ores in an autoclave, a number of iron containing precipitates could be formed depending on the acidity, temperature, sulphate, iron and arsenic tenors as well as residence time [1] [2].

In the case of low arsenic concentrations, it is typically anticipated that either hematite, jarosite, basic ferric sulphate (BFS) or a combination of these precipitates will form during pressure oxidation (POX). It is well-known that the presence of BFS and/or jarosite in the POX residue can result in excessive lime consumption during cyanidation as these compounds react with lime [3]. In addition, BFS and jarosite are viewed as environmentally unstable products, unsuitable for storage in unlined tailings ponds. One of the industrially practiced methods to decompose BFS and jarosite prior to cyanidation is to include a "hot curing" or BFS decomposition stage in the plant flow sheet. During curing, BFS is decomposed to ferric sulphate, rendering a gold-containing residue which does not consume an excessive amount of lime during further cyanidation [3].

Arsenic is often associated with gold-containing sulphidic ores as arsenopyrite and, therefore, the safe disposal and storage of arsenic-containing residues should be highly prioritised by gold mining companies. In the presence of arsenic, it is widely believed that stable scorodite is formed during POX, which does not consume lime during cyanidation and is also considered as an environmentally 'safe' product. However, it has been confirmed that a number of Fe-As compounds could be formed at conditions typical of POX and that scorodite is not necessarily the main As-bearing precipitate [1] [4]. The characterisation of these Fe-As precipitates is inherently complex and, has therefore received considerable attention over the last decade. Little published data exists regarding the stability of these precipitates during cyanidation (i.e., in terms of lime and cyanide consumptions) and whether a curing stage is actually required, as well as whether these compounds are environmentally stable.

In this paper, the autoclave leaching of a refractory arsenopyrite containing material is discussed with specific focus on the behaviour of Fe-As precipitates throughout the gold recovery process. The objectives include:

- characterisation of the Fe-As precipitates formed during POX;
- evaluation of the stability of the Fe-As precipitates during subsequent hot curing and cyanidation processes (i.e., associated lime and cyanide consumptions);
- and the assessment of the environmental stability of cyanidation residues.

The current paper is targeted at contributing to the current understanding of the impact of Fe-As precipitates formed during POX on subsequent gold downstream processing.

BACKGROUND

Precipitates Produced During POX

Under typical oxidation acidities (10 to 50 g/L free H_2SO_4) and temperatures between 180 and 220°C, Fe^{3+} may precipitate as hematite (Fe_2O_3), Fe(III) hydroxy sulphate and/or a range of Fe-As compounds [5].

In the absence of arsenic, the relevant precipitation reactions are described by Reactions 1 to 3 [5]:

$$Fe_2(SO_4)_3 + 3\,H_2O = Fe_2O_3 + 3H_2SO_4 \quad \text{(R.1)}$$

$$Fe_2(SO_4)_3 + 2H_2O = 2Fe(OH)SO_4 + H_2SO_4 \quad \text{(R.2)}$$

$$3Fe_2(SO_4)_3 + 14H_2O = 2H_3OFe_3(SO_4)_2(OH)_6 + 5H_2SO_4 \quad \text{(R.3)}$$

The formation of basic ferric sulphate (BFS) and jarosites (both Fe^{3+} hydroxyl sulphates) are typically favoured at high acidities (>20 g/L) while hematite is precipitated at lower acid concentrations of < 20 g/L [3].

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Precipitates formed during POX in the presence of arsenic are much more complex compared to compounds formed in a purely Fe(III)-SO_4 system and detailed investigations were only initiated in the late 2000s [1] [6] [7]. It was proposed that the following general reaction describes the formation of these Fe(III)-AsO_4-SO_4 phases [8]:

$$Fe(SO_4)_{1.5} + H_3AsO_4 + (w+z/2)H_2O \rightarrow Fe(AsO_4)_x(SO_4)_y(OH)_z.wH_2O + (1.5-y)H_2SO_4 \quad (R.6)$$

Four main arsenic containing precipitates were identified to form at POX conditions: sulphate containing scorodite (Sc), ferric arsenate sub-hydrate (FAsH), basic ferric arsenate sulphate (BFAS) and arsenate-containing basic ferric sulphate (As-BFS). The proposed compositional formulas and precipitation conditions required for these compounds are listed in Table 1.

Table 1: Arsenate compounds precipitated from the Fe(III)-AsO_4-SO_4 system at typical pressure oxidation conditions [2] [7]

Compound Name	Abbreviation	Chemical formula	Precipitation conditions		
			$\frac{Fe(III)}{As(V)}$	T,°C	Time, hr
Sulphate-containing scorodite	Sc	$Fe(AsO_4)_{1-0.67x}(SO_4)_x.2H_2O$ $x \leq 0.20$	0.7-0.87	150-175	2-24
Ferric arsenate sub-hydrate	FAsH	$Fe(AsO_4)_{0.998}(SO_4)_{0.01}.0.72H_2O$	0.69-0.93	200-225	10-24
Basic ferric arsenate sulphate (arsenate containing and sulphate containing)	BFAS	$Fe(AsO_4)_{1-x}(SO_4)_x(OH)_x.(1-x)H_2O$ $0.3 < x < 0.7$	1.67-4.01	175-225	4-24
Arsenate containing basic ferric sulphate	As-BFS	$Fe(OH)_x(AsO_4)_y$	1-4	175-225	not stated

As observed in Table 1, Sc is only thermodynamically stable at temperatures lower than 175°C and the formation of FAsH and BFAS was found to occur at temperatures exceeding 175°C. The precipitation of Sc and FAsH is characterised by a low Fe-As ratio (<1), while BFAS and As-BFS are produced at higher Fe-As ratios. Recently, further differentiation in the type of BFAS compound was established i.e., arsenate containing BFAS and sulphate containing BFAS. It was reported that the arsenate-containing BFAS phase was isotypic with the monoclininc form of pure BFS, whilst the sulphate-containing BFAS consists of a mixture of arsenic-containing BFAS (55 wt%), BFS (43 wt%) and hematite (2 wt%) [2].

From the above, it is likely that BFAS, As-BFS or a mixture of these compounds would be the dominant precipitation products in an As-containing refractory feed, as Fe-As ratios typically range from 2 to 4 and temperatures higher than 180°C are usually employed during POX. However, the formation of pure Fe-containing phases is also expected where excess iron (Fe-As ratio > 4) is available.

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Chemical and Environmental Stability of Iron-Containing Precipitates

The formation of BFS and jarosites during POX is undesirable, as these precipitates react with lime during pre-neutralisation and cyanidation according to Reactions 4 and 5 [3]:

$$Fe(OH)SO_4 + Ca(OH)_2 + 2\ H_2O = Fe(OH)_3 + CaSO_4.H_2O \quad (R.4)$$

$$H_3OFe_3(SO_4)_2(OH)_6 + 2Ca(OH)_2 + 2H_2O = 3Fe(OH)_3 + CaSO_4.H_2O \quad (R.5)$$

Thus, the presence of BFS and/or jarosites in significant quantities could result in lime consumptions exceeding 70 kg/t and in extreme cases could reach up to 200 kg/t [3] [9]. In addition, since BFS continuously consumes lime during cyanidation, the pH control process may become challenging (pH should be maintained above 10.5). From an environmental perspective, the formation of BFS and jarosite is also unfavorable due to the chemical instability of these compounds during storage [3].

The BFS decomposition or “hot curing” process is based on the fact that the hydrolysis reaction that produces BFS in the autoclave is reversible at lower temperatures (60°C – 100°C) [9]:

$$2Fe(OH)SO_4 + H_2SO_4 = Fe_2(SO_4)_3 + 2H_2O \quad (R.10)$$

During the BFS decomposition process, acid and heat that had been generated in the autoclave are used to break down the BFS structure. Thus, the process requires no additional reagent or energy costs and entails only capital expenditure [3].

The formation of hematite is usually targeted in POX operations as hematite is chemically stable in the subsequent neutralisation and cyanidation steps and environmentally stable in tailings storage facilities [9].

Chemical and Environmental Stability of Iron-Arsenic Containing Precipitates

Considering the recent environmental stability tests on Fe-As precipitates, it was found that the stability of BFAS was comparable to the stability of Sc. Both BFAS and Sc were more stable compared to FAsH during short-term and medium-term stability tests conducted at pH values <7. Medium-term leachability studies conducted on the BFAS-type phases have shown less than 1 mg/L As liberation over a period of 8 months [2]. In terms of Fe-As residue stability after cyanidation, very little published information was found. It was however reported that during development stages of the METBA refractory gold project, where a BFAS-type precipitate had formed, that the Carbon-in-Leach (CIL) residues were stable [10]. Similarly, high stability of a BFAS-type precipitate after CIL was reported by Cominco Engineering Services Ltd (CESL) [11].

Conflicting views exist regarding the chemical stability of Fe-As containing residues during cyanidation and associated lime consumptions. It is generally believed that scorodite and Fe-As compounds, similarly to hematite, are stable and do not react with lime during neutralisation or cyanidation [9]. On the other hand, a curing stage was included during the development of the AGA Brazil refractory gold plant to minimise lime consumption due to the presence of Fe-As-SO_4 precipitates [12].

Based on information provided in literature, it appears that the environmental and chemical stability of Fe-As precipitates, as opposed to purely Fe-containing precipitates, are not well understood.

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EXPERIMENTAL

Test Work Program

The test work program followed is displayed in Figure 1.

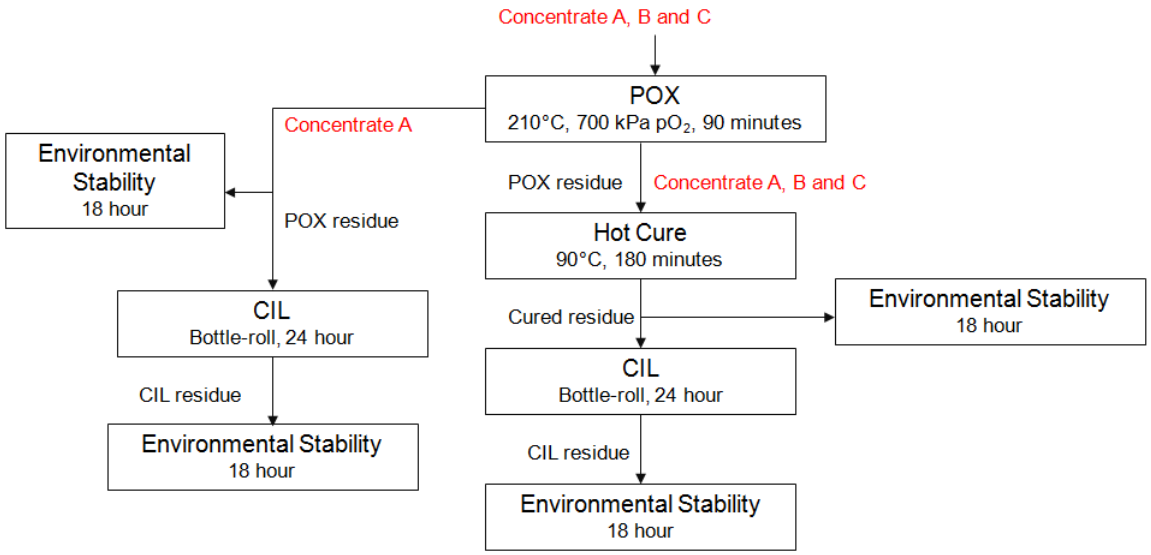


Figure 1: Test work program

Three flotation concentrates, with varying iron, arsenic and sulphide contents, were obtained. These concentrates were subjected to POX, hot curing, CIL and subsequent environmental stability tests. Concentrate A POX residue was also subjected directly to CIL (without curing). In addition, environmental stability tests were conducted on the cured residues and Concentrate A POX residue. All test work, mineralogical and chemical analyses were executed at the research facilities of MINTEK.

Feed Samples Characterisation

Chemical and mineralogical analysis of the three gold-containing flotation concentrates used during the study is presented in Table 2 and Table 3, respectively.

Table 2: Concentrate chemical composition

Element	Units	Concentrate		
		A	B	C
Au	g/t	77.1	74.3	32.8
Fe	wt %	25.28	26.03	15.93
As	wt %	6.51	6.22	3.12
Sulphide S	wt %	18.7	19.7	11.3
Fe/As	mole/mole	5.2	5.6	6.8

Concentrates A and B had very similar composition as well as iron to arsenic ratios. In all samples the iron to arsenic ratio exceeded five. Pyrite, pyrrhotite and arsenopyrite were identified as the sulphide containing minerals for the samples, whilst quartz, muscovite, plagioclase and chlorite as the predominant silicate gangue minerals. Based on the Fe-As ratio in the concentrates and the guidelines included in Table 1, it was expected that a mixture of BFAS and As-BFS would form during POX.

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Table 3: Concentrate Mineralogy

Mineral Name	Chemical Formula	Concentrate		
		A	B	C
Pyrite	FeS_2	Minor	Intermediate	Trace
Pyrrthotite	$Fe_{(1-x)}S$	Minor	Minor	Minor
Arsenopyrite	FeAsS	Minor	Minor	Trace
Quartz	SiO_2	Intermediate	Intermediate	Major
Muscovite	$KAl_2(AlSi_3, O_{10})(F,OH)_2$	Major	Minor	Intermediate
Dolomite	$CaMg(CO_3)_2$	Minor	Intermediate	Minor
Plagioclase	$(Na,Ca)(Si,Al)_4O_8$	n.d	Trace	Trace
Calcite	$CaCO_3$	Trace	Trace	Minor
Chlorite	$Mg_3(Mg_2Al)(Si_3AlO_{10})(OH)_8$	n.d.	n.d.	Minor
n.d. –not detected, trace < 5 mass %, minor 5-15 mass%, intermediate 15-25 mass%, major 25-50 mass%, predominant >50 mass%				

Pressure Oxidation

The concentrates were pulped to 15 wt% and pre-acidification at 65°C with the addition of 800 g/L sulphuric acid (H_2SO_4) to a pH 1 for 1 hour. Pre-acidification was done to ensure carbonated minerals were destroyed prior to the pressure leach.

After pre-acidification had been completed, the slurry was transferred to a 2 gallon Parr autoclave and heated to the target temperature. The slurry was oxidised at 210°C and 700 kPa oxygen partial pressure for 90 minutes. It was ensured that complete oxidation of all sulphide minerals were obtained during the leach. After each leach, the slurry was rapidly cooled to 50°C or to the required "curing" temperature.

The cooled slurry (either directly after POX or after curing) was filtered using a vacuum filter. The POX leach residue was washed twice with deionised water by re-pulping at a wet solids to water mass ratio of 1:5 using hot water at 60°C. The solids were then plug washed once with deionised water in a wet solids to water mass ratio of 1:5. The washing procedure was thorough to ensure that the solids which would undergo gold leaching contained minimal entrainment which otherwise could affect lime and cyanide consumptions in the downstream CIL process. The solids were dried overnight at 40°C. Solids and solutions were submitted for chemical analyses.

Curing

At the end of the pressure leach, instead of cooling the slurry immediately and filtering, the "hot-cure" process was applied to the slurry. This process involved reducing temperature of the slurry to 90°C and maintaining it for 180 minutes.

Before the curing process was started, oxygen was first vented from the reactor head space and the reactor closed again. Kinetic samples were taken after 0, 30, 60, 90, 120 and 180 minutes of curing. On completion of the curing test, the slurry was cooled to 40°C and removed from the autoclave. The final slurry and kinetic samples were filtered and washed (see procedure above under "Pressure Oxidation"), the solids dried and both solution and solids submitted for chemical analyses.

Carbon-in-Leach

Carbon-in-leach (CIL) tests were carried out using the conventional bottle roll method. The POX and/or cured residues were slurried in a bottle to 30 wt % solids using Rand Water Board (potable) water and the pH was controlled at 10.5-11 by the addition of hydrated lime ($Ca(OH)_2$) as a dry powder. 10 kg/t of sodium cyanide (NaCN) was added to the slurry and the bottle was rolled for a

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period of 24 hours. The pH of the slurry was checked regularly and controlled to 10.5-11 by manual addition of $Ca(OH)_2$.

After 24 hours, the slurry was filtered under vacuum and the filter cake was washed once by re-pulping with water at a wet solid to water mass ratio of 1:1.5, and thereafter plug washed twice. The washed filter cake was dried in an oven at 40°C for 24 hours before submitting for chemical analyses.

Lime consumption was determined by conducting a solution lime titration with oxalic acid on a sample of the CIL filtrate. Phenolphthalein was used as an indicator. Lime consumption was then determined by difference (lime added minus lime remaining in filtrate).

The cyanide consumption was determined by conducting a free cyanide potentiometric titration on a solution sample of the CIL filtrate. The solution was titrated with silver nitrate solution and a platinum indicator electrode was used to determine the end-point. Cyanide consumption was then determined by difference (cyanide added minus free cyanide remaining in filtrate).

Residue Stability Testing

The US Environmental Protection Agency (EPA) Synthetic Precipitation Leaching Procedure (SPLP) method was carried out per the instructions given in the EPA Test Method 1312 (1994). Exactly 5 g of the residue was used. The extractant was prepared by mixing concentrated sulfuric acid with nitric acid in a 60:40 mass ratio and adding it to deionised water until the pH was 4.20 ± 0.05. Exactly 100 g of extractant was placed with the solids in a 500 mL Schott bottle and shaken for 18 hours at 140 rpm. It was ensured that the solids were fully suspended throughout the test. The mixture was subsequently separated by vacuum filtration and the filtrate was submitted for chemical analysis.

Mineralogical Characterisation

Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM)

Polished sections were prepared from the selected samples for analysis on the SEM. A Zeiss EVO MA15 scanning electron microscope was used to identify the minerals/phases present in the sample. Elemental maps of the samples were produced by using Energy-Dispersive Spectrometry (EDS). Backscattered and elemental maps images were captured to illustrate the textural relationships of the different phases.

The TEM analysis was done with the use of the FEG_TEM JEOL**2100F @ 200 kV. This microscope was equipped with a Scanning Transmission Electron Microscopy (STEM) detector and an Oxford EDS detector. For the TEM analysis, particles were suspended in alcohol and deposited on a Cu grid. A single tilt holder was used.

X-ray Diffraction (XRD)

Qualitative XRD was performed on a representative sub-sample of selected residues. A Bruker D8 diffractometer was used, with a step size of 0.02º 2 theta and a counting time of 1 second per step, applied over a range of 5 to 80º 2 theta. The method makes use of the net intensity of the main peaks of the phases, and identification is based on the crystal structure of phases. Only crystalline phases in amounts sufficient to diffract are detectable.

Attenuated Total Reflection Infrared Spectroscopy (ATR-IR)

Infrared spectra were obtained using a Fourier Transform Infrared (FTIR) spectrometer. Spectra over the 4000 to 400 cm^{-1} range were obtained.

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RESULTS AND DISCUSSION

Chemical and Mineralogical Characterisation of POX and Cured Residues

Complete sulphide oxidation was achieved within 90 minutes in all POX tests at 210°C, 700 kPa oxygen partial pressure and 15% solids. During the POX tests, 65, 66 and 80% of arsenic was precipitated from Concentrate A, B and C, respectively.

The chemical composition of the POX and cured residues are presented in Table 4 and the results of the XRD scans performed on the residues are presented in Table 5.

Table 4: Chemical composition of POX and cured residues

		Fe	AsO_4	SO_4	Fe/As	Mass loss per step
		wt%	wt%	wt%	mole/mole	%
Concentrate A	Feed	25.28	6.50	n/a	5.2	n/a
	POX Residue	21.0	10.8	13.3	4.8	26
	Cured Residue	19.4	5.3	12.4	9.1	36
Concentrate B	Feed	26.03	6.22	n/a	5.6	n/a
	POX Residue	23.9	10.5	10.3	5.7	n/a
	Cured Residue	20.4	4.9	10.4	10.4	34
Concentrate C	Feed	15.93	3.12	n/a	6.8	n/a
	POX Residue	13.3	4.8	16.0	6.9	n/a
	Cured Residue	11.0	2.6	16.4	10.6	13

Table 5: Qualitative XRD analysis of POX and cured residues

Mineral Name	Chemical Formula	Concentrate A POX Residue	Concentrate A Cured Residue	Concentrate B Cured Residue	Concentrate C Cured Residue
Muscovite	$KAl_2(AlSi_3,O_{10})(F,OH)_2$	Major	Major	Intermediate	Major
Quartz	SiO_2	Intermediate	Intermediate	Major	Major
Anhydrite	$CaSO_4$	Minor	Minor	Major	Intermediate
Hematite	Fe_2O_3	Trace	Trace	Trace	Trace
Plagioclase	$(Na,Ca)(Si,Al)_4O_8$	Trace	Trace	Trace	Trace
Iron sulphate hydroxide	$2Fe(OH)SO_4$	Minor	Minor	Minor	Minor
n.d. –not detected, trace < 5 mass %, minor 5-15 mass%, intermediate15-25 mass%, major 25-50 mass%, predominant >50 mass%					

From Table 4 it was clearly seen that curing resulted in a significant decrease in the arsenic residue concentration while the sulphate and iron content remained roughly unchanged. The arsenic content in the cured residues decreased by approximately two times when compared with the

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compositions of the uncured POX residues. The Fe/As ratios in the residues were much higher after curing which suggested significant arsenic liberation into the liquor during the curing step.

Minor and intermediate portions of gypsum (or anhydrite) were identified in all residues, which indicated that a large portion of SO_4^{2-} (>50%) in the residues was associated with gypsum and not with the Fe-As precipitate.

In terms of the Fe-containing mineral phases, XRD scans detected only trace amounts of hematite and minor amounts of BFS. Given the large concentration of Fe in the residues (~20%) it was highly probable that minerals identified by the XRD scans did not account for all the Fe compounds in the samples. Furthermore, no crystalline arsenic bearing compounds were detected. This could be due to the presence of amorphous Fe-As precipitates which cannot be detected by the XRD technique.

SEM was used to investigate the textural relationships of the phases present in the precipitates and also the arsenic and iron distribution. The arsenic and iron elemental maps of Concentrate C cured residue are presented in Figure 2.

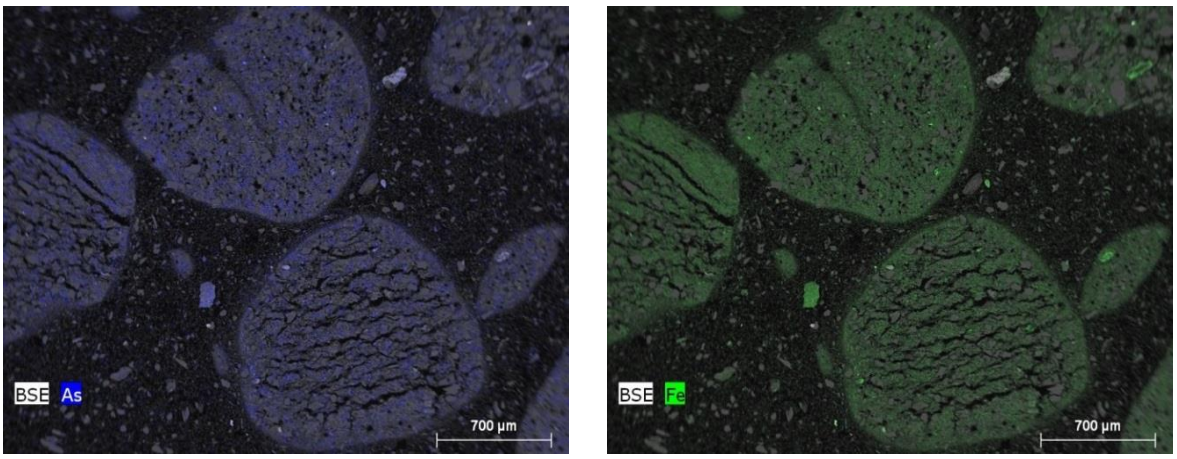


Figure 2: Elemental map of Concentrate C cured residue by SEM followed by EDS

From the images it was evident that iron and arsenic were finely dispersed throughout an amorphous phase. The absence of well-defined crystal structures indicated the nano-crystalline nature of the precipitate. Further analyses were therefore required to identify the type of nano-crystalline iron-arsenic bearing precipitate.

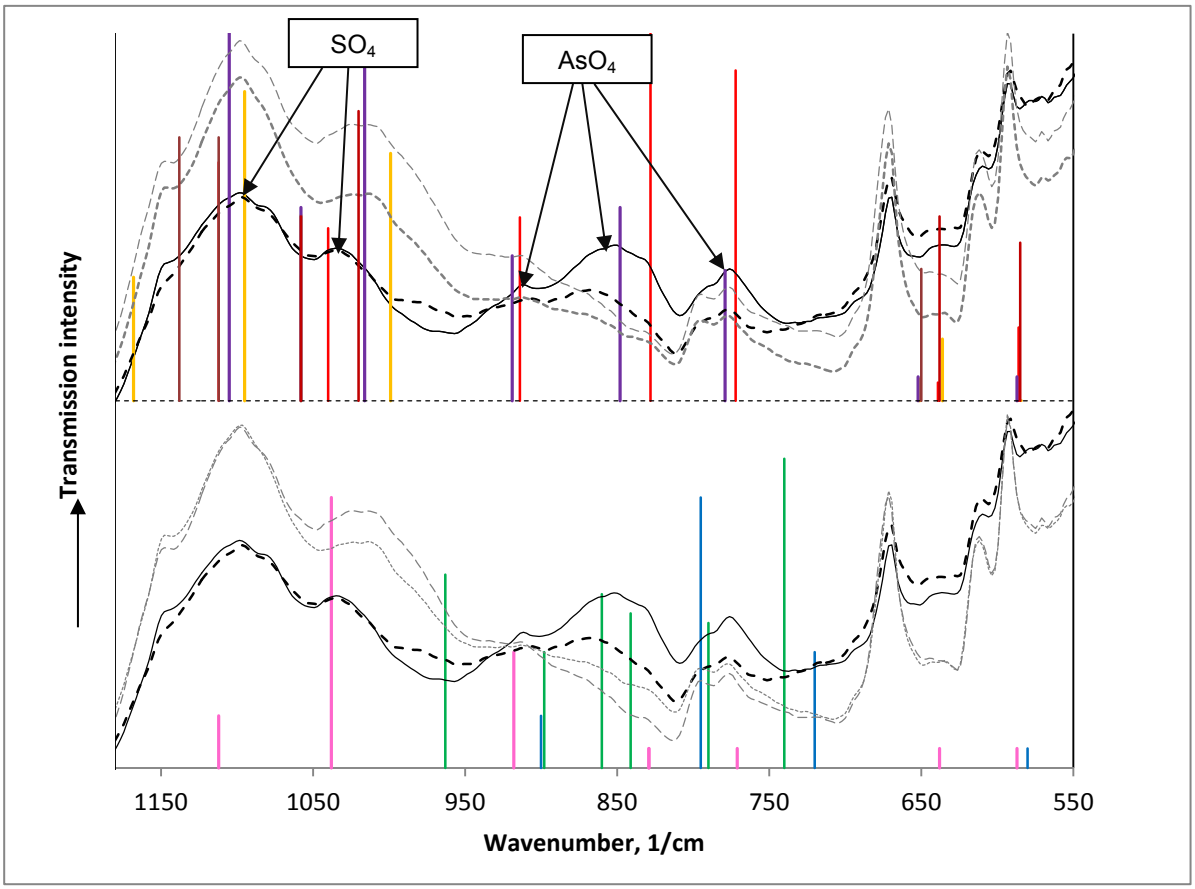
ATR-IR was hence employed to investigate the amorphous precipitates in the residue samples further. The IR-spectra between 500 and 4000 wavenumbers of selected residues were compared with published spectra of Fe-As phases as shown in
Figure 3. Spectral lines of BFAS, sulphate rich BFAS, arsenate containing BFS, FAsH, scorodite and arsenic-rich BFAS were obtained from literature [2] [13] [14].

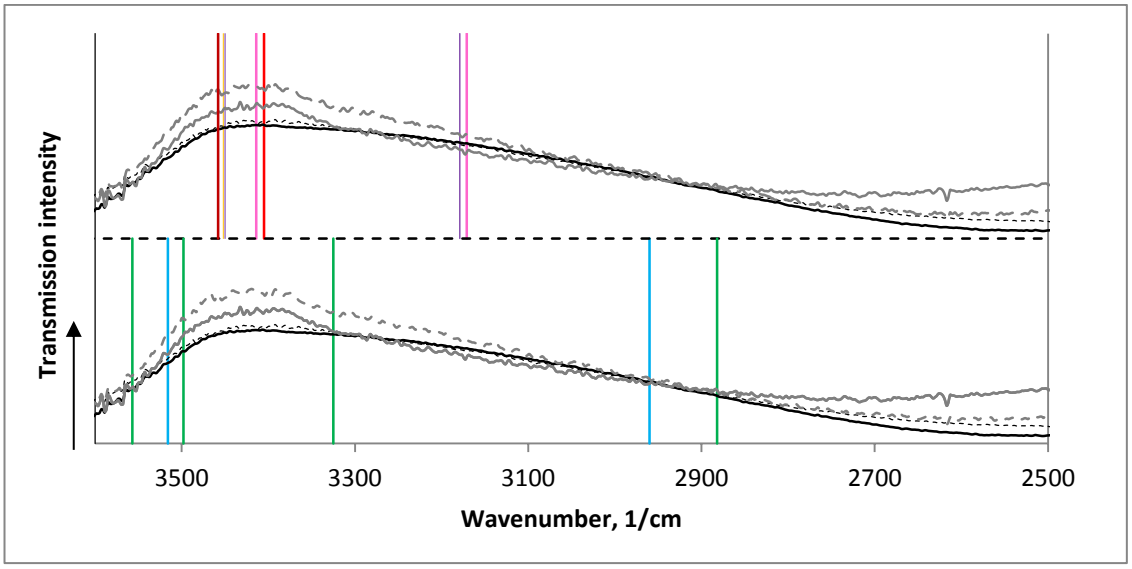
The IR bands of the POX residues (Concentrate A and Concentrate C) exhibited similar signatures which confirmed that the same phase had formed during pressure leaching irrespective of the higher iron to arsenic ratio in Concentrate C. Peaks of cured residues also exhibited high correlation with POX residues, which indicated that no major phase changes had taken place during curing.

As observed, the published spectral lines of Sc, FAsH and arsenic-rich BFAS did not correlate well with the bands of the spectra for the residues. The presence of multiple arsenate bands confirmed that scorodite, which has a single arsenic band, was probably not present in the samples.

From the IR plot, the bands of BFAS (sulphate–rich and arsenic-rich) and arsenate containing BFS exhibited the highest degree of correlation with the residue spectra. Thus, it was evident that BFAS or arsenate-containing BFS had most likely precipitated during autoclaving. It should however be noted that a small amount of arsenic could also have co-precipitated with hematite or other Fe-As phases.

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Concentrate C Cured residue
Concentrate A POX residue
Concentrate A Cured residue
Concentrate C POX residue

Published spectra exhibiting high correlation to spectra of residues:

- BFAS
- Sulphate-rich BFAS
- Arsenate containing BFS
- Arsenic-rich BFAS
- BFS

Published spectra which do not correlate with spectra of residues:

- FAsH
- Scorodite

Figure 3: ATR-IR spectra of POX and cured residues compared to published spectra of Fe-As precipitates (spectra reconstructed from Gomez *et al.* [2] [13] and Powers *et al.* [14])

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TEM analysis was used to obtain the average elemental compositions of selected particles in the residues and results are included in Table 6.

Table 6: Elemental composition of particles from Concentrate A cured residue by TEM followed by EDS

	Fe	As	S	Fe/As
	wt %	wt %	wt %	mole/mole
Particle 1	36.2	25.1	6.1	1.939
Particle 2	37.4	29.5	7.3	1.703
Particle 3	42.3	33.4	6.3	1.698

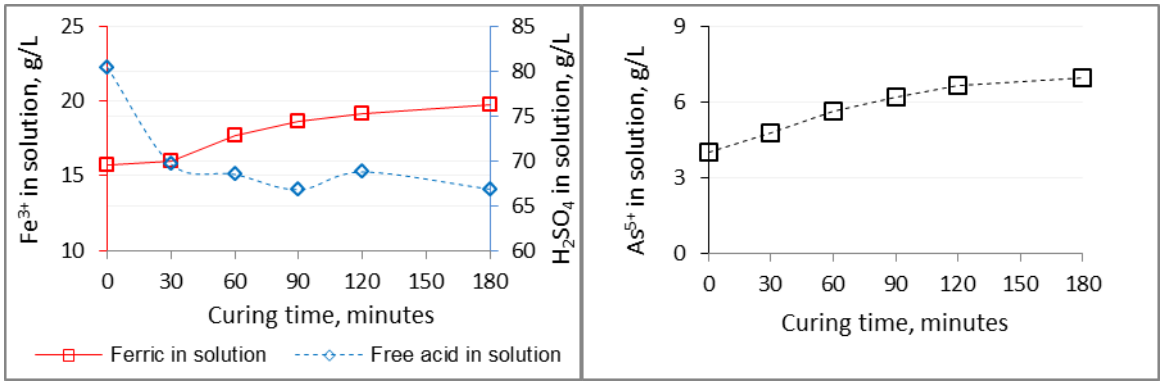
The Fe/As ratio from multiple scans exhibited the highest degree of correlation to the ideal formula of BFAS i.e., where x has a value of 0.4~0.5 in the ideal formula $Fe(AsO_4)_{1-x}(SO_4)_x(OH)_x \cdot (1-x)H_2O$. Although, the presence of other Fe-As compounds could not be neglected as TEM scans were only done on selected areas on particles.

Behaviour of Fe-As Containing POX Residues During Curing

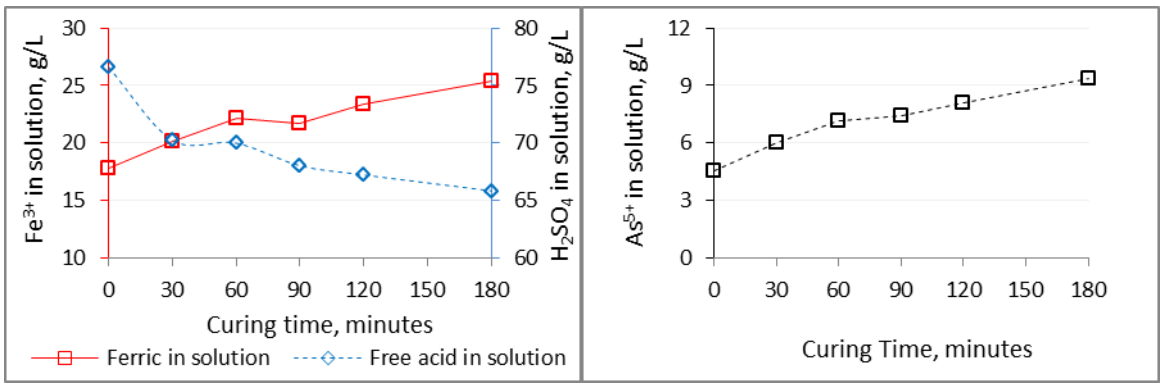
All pressure leached slurries were cured at 90°C for 3 hours to evaluate the stability of the Fe-As precipitates during a typical curing stage. During the curing period, iron, free acid and arsenic in solution were monitored. For the three concentrates investigated, the results are displayed in Figure 4.

As observed, free acid concentration decreased while both iron and arsenic tenors increased during curing, which suggested that the reverse of reaction R.6 had taken place. On average, curing increased arsenic levels from 4 to 7 g/L during treatment of the higher arsenic grade POX residues and from 1 to 2.5 g/L during curing of Concentrate C POX residue. The Fe/As ratio in the cured residues almost doubled in comparison with the POX residue compositions (see Table 4). The trend clearly illustrated the instability of the Fe-As precipitate during the subsequent hot curing step which also suggested that large portions of the Fe-As precipitates had been decomposed.

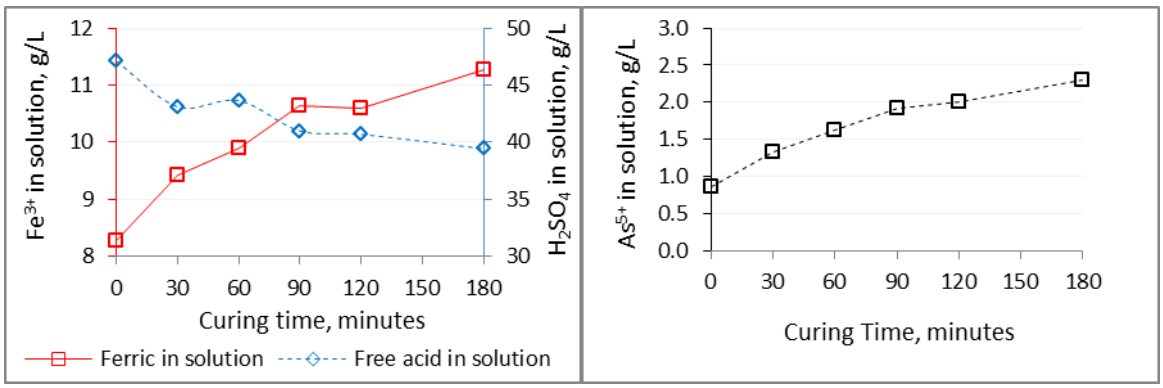
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a) Concentrate A



b) Concentrate B



c) Concentrate C

Figure 4: Behaviour of POX residues during curing at 90°C

Behaviour of Fe-As POX and Cured Residues During CIL

The cyanide and lime consumptions for the residues are listed in Table 7.

As seen, relatively low lime (~10 kg/t) and cyanide (1.3 to 4 kg/t) consumptions were measured during cyanidation of cured and untreated POX residues.

Firstly, the results suggested that the Fe-As compound formed during POX did not contribute to lime and cyanide consumption, as the reagent consumptions obtained for Concentrate A residues were comparable. Since the Fe-As compound had been partially destroyed during curing, a significant difference in lime consumption between the untreated and cured residues were expected, this was however not the case.

Additionally, lime consumptions were relatively low (~10 kg/t), meaning that the precipitate did not react with lime to such an extent to what would have been the case if BFS had formed. Recall that the formation of BFS during pressure oxidation of refractory gold ore via POX typically results in lime consumptions exceeding 70 kg/t during subsequent cyanidation [9].

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It is proposed that these observations could be attributed to one or a combination of the following factors:

- Minor amounts of BFS and/or arsenate-containing BFS had formed during POX
- The majority of the arsenic and iron was fixed in a BFAS-type precipitate
- The BFAS-type iron-arsenic precipitate formed was stable during cyanidation and did not react with lime

Table 7: Results obtained during CIL of POX and cured residues

		CaO Consumption	NaCN Consumption	Fe in CIL Filtrate	As in CIL Filtrate
		kg/t	kg/t	mg/L	mg/L
Concentrate A	POX Residue	8.9	1.3	21.5	<2
	POX-Cured Residue	10.3	3.3	84.5	<2
Concentrate B	POX-Cured Residue	8.7	4.1	137.5	<2
Concentrate C	POX-Cured Residue	7.5	2.2	42.0	<2

The fact that no soluble arsenic (<2 mg/L) was detected in the filtrate at the pH of cyanidation (pH~10.5), further shows that curing may not have had an appreciable effect on the stability of the Fe-As precipitate. As an alternative explanation, any dissolved arsenic may have re-precipitated as calcium arsenate.

Relatively high iron deportment into the cyanidation liquor might have been attributed to the formation of a minor iron phase during POX which becomes somewhat unstable during cyanidation conditions. However, additional investigation regarding this phenomenon should be initiated.

Environmental Stability Testing on POX, Cured POX and CIL Residues

Limits on arsenic content in the mining effluents are usually very site-specific. In most stringent cases, arsenic and iron content should not exceed 0.1 and 2 mg/L, respectively. The Toxic Characteristic Leaching Procedure (TCLP) from the US EPA is often used to determine arsenic stability. The hazardous waste criterion for arsenic using the TCLP method is 5 mg/L [15]. However, the TCLP test was designed to simulate the leaching of heavy metals and organics from industrial wastes to be co-disposed in municipal solid landfills. Hence, this one step extraction process is believed to be inadequate for simulation of the environment typical of gold tailings [16].

The SPLP method was chosen to evaluate the environmental stability of the POX, cured and CIL residues. The SPLP test evaluates the potential for leaching metals into ground and surface waters and was developed to provide a more realistic evaluation of arsenic mobility under actual field conditions compared to the TCLP method [17].

The SPLP environmental test results are included in
Table 8.

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Table 8: SPLP test results on POX, cured and CIL residues

		As	Fe
		mg/L	mg/L
Concentrate A	POX Residue	<2	<2
	POX-Cured Residue	<2	2.4
	POX-CIL Residue	8.7	<2
	POX-Cured-CIL Residue	8.1	<2
Concentrate B	POX-Cured Residue	<2	7.9
	POX-Cured-CIL Residue	9.8	<2
Concentrate C	POX-Cured Residue	<2	7.4
	POX-Cured-CIL Residue	3.8	<2

The arsenic content in the filtrates from the CIL residues were significantly higher compared to the SPLP filtrates of the POX and cured residues, which were well above or close to the hazardous waste criteria of 5 mg/L.

Presumably the higher arsenic release from the CIL residues is attributed to the solubilisation of poorly crystalline ferric arsenate and subsequent re-precipitation of arsenic as a more soluble ferric or calcium arsenate at high cyanidation pH values (pH 10-11). This result contradicts the outcomes of CESL tests (copper pressure leaching technology) where the stability of a BFAS-type precipitate subsequent to CIL was evaluated [11]. Bruce (2012) reported that less than 0.3 mg/L arsenic was found in the filtrate after environmental stability tests performed on CIL residues [11]. However, the BFAS-type precipitate during the CESL campaign was produced at lower temperatures of 150 to 160°C, which is typical of medium-temperature autoclave operations. Moreover, the TCLP method was applied for the samples characterised in their campaign [11].

The POX and cured residues exhibited similar arsenic release (~1 mg/L) for Concentrate A and B indicating that improved environmental stability was not obtained by curing the precipitate. The SPLP filtrate of the cured residue of Concentrate C had slightly lower arsenic content of 0.25 mg/L, however this concentrate had a lower initial arsenic content in the feed.

CONCLUSIONS

The autoclave leaching of arsenic containing refractory gold can result in the formation of various Fe-As precipitates. The current paper was focused at improving the current understanding of the behaviour of these precipitates during CIL and the environmental stability of residues produced. The effect of curing the Fe-As precipitates was also evaluated, since in some cases a curing stage had been recommended for Fe-As precipitates due to high associated lime consumptions during the subsequent cyanidation step.

The Fe-As precipitates formed during the current pressure leach work (210°C, 700 kPa oxygen partial pressure) conducted on samples containing iron-to-arsenic ratios in the range of 5 to 7 exhibited high stability during subsequent CIL tests.

From the characterisation study, it appears that the majority of arsenic precipitated as a BFAS-type compound (most-likely sulphate-containing BFAS). Even though published spectra of As-BFS also showed high correlation with residue spectra, higher associated lime consumptions would have possibly resulted if large amounts of As-BFS had precipitated.

Due to low minimal difference in lime and cyanide consumptions observed during subsequent cyanidation of POX and POX-cured residue the hot curing step can be excluded from the flowsheet, especially if a low variation in feed composition is expected. Curing might in fact result in destabilisation of the residues and affect environmental stability negatively. In addition, arsenic

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dissolved during curing has to be precipitated with lime/limestone which could result in the formation of less stable compounds compared to precipitates produced at high temperatures.

Under the SPLP environmental stability test conditions, which are harsher, compared to the TCLP, it was found that the CIL residues did not meet environmental regulations as arsenic concentrations in the filtrate exceeded or was close to the hazardous waste criteria of 5 mg/L. From the results it was evident that submission of the BFAS residues to a high pH process such as CIL negatively affects their environmental stability and therefore a lined tailings pond would be required for subsequent disposal. The BFAS containing CIL residues are therefore not as stable as scorodite, which is considered to be a “safe” environmental residue.

The results obtained during this study provided further insight into the conditions required for BFAS formation and what could be expected in downstream units once this compound formed.

It is recommended that during project evaluation of high arsenic containing refractory gold feed, conditions favourable to the formation of a stable Fe-As precipitate should be determined by experiment.

Prediction of the Fe-As compounds which will form during pressure oxidation proved to be complex therefore MINTEK is undertaking a comprehensive test work program to enable a better understanding of which compounds will form under specific conditions and to evaluate the behaviour of these iron-arsenic compounds in subsequent hot curing and gold recovery processes.

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ROLE OF POLYTHIONATES ON THE STABILITY GOLD IN THE LEACHING OF DOUBLE REFRACTORY ORES IN THE CALCIUM THIOSULFATE-AIR LEACHING SYSTEM

By

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ABSTRACT

Gold leaching of double refractory ores by calcium thiosulfate (CaTS) and recovery by Resin-in-Leach (RIL) is currently an industrial reality as evidenced by Barrick's Goldstrike operations in Nevada, USA. The performance of the leaching circuit is highly dependent on the management and control of thiosulfate degradation products. It was postulated that the generation of CaTS oxidation products during leaching, notably trithionate and tetrathionate, could affect the gold-thiosulfate complex stability in solution. As such, a series of controlled laboratory tests were devised to investigate the detrimental effects of polythionates and mineral additions on the stability of synthetic gold-thiosulfate complexes in solution. Subsequently, the competitive loading of polythionate species and of gold-thiosulfate onto Purolite A500 resin was investigated.

Keywords: Gold Leaching, RIL, Calcium Thiosulfate, Polythionates

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INTRODUCTION

In November 2014, the Goldstrike mine in Nevada poured its first gold bar produced using their patented thiosulfate leaching technology[1]. This milestone marked the industrial beginning of a new process developed to extract gold from double refractory ores that could not be treated via traditional cyanidation/carbon-in-leach (CIL). Previously, single refractory sulfide ores were pretreated by pressure oxidation using autoclaves to liberate and expose the surface of the trapped gold particles followed by a cyanide leach and gold recovery by CIL. In parallel, the continuing mining efforts and characterization of future mining zones of the deposit predicted an increase in levels of carbonate content and of total carbonaceous matter (TCM) in the forthcoming ore. The former mineral negatively impacts the acidic pressure oxidation pre-treatment to breakdown sulfides by consuming acid. The latter, similar to naturally occurring carbon[2], contributes to the preg-robbing phenomenon observed during the cyanidation of these so-called double-refractory ores by adsorbing the gold onto the fine carbon matter. These gold losses to the tailings make the autoclave-cyanidation process uneconomic. A partial solution to the TCM problem was the commissioning in 2000 of a roaster to destroy the carbon and oxidize the sulfides allowing for economical operation of a gold cyanidation/CIL recovery circuit[3, 4]. However, even with the roaster running at capacity, the Goldstrike mine continued stockpiling about 4 million ounces of gold which would otherwise be processed at the end of the mine's life. As a result, the calcium thiosulfate leaching process was developed to increase gold production from TCM ores[5]. This process' foundation is built on previously existing capital assets, namely the six autoclaves, the retrofitting of the former two seven tank CIL circuits into new RIL circuits for gold recovery and the building of a thiosulfate reagent plant. The ramp up to full capacity is expected to be reached by Q3 2016 at rate of 13,400 tons of ore processed daily[6].

Thiosulfate Leaching Conditions

The thiosulfate-air leaching process is simply represented by Equation 1.

$$2Au+4S_2O_3^{2-}+\frac{1}{2}O_2+H_2O \rightarrow 2Au(S_2O_3)_2^{3-}+2OH^- \quad (1)$$

Typical leaching conditions encountered in the calcium thiosulfate (CaTS) leaching system are 0.1 M thiosulfate, 50 mg/L copper, a temperature of 50°C and a pH of 8-8.5. Copper is added to the system in order to improve the leaching kinetics although its role is not as well understood as in the ammoniacal thiosulfate leaching system where it acts as a catalyst. Addition of copper as cupric sulfate into the thiosulfate leaching system quickly oxidizes thiosulfate into tetrathionate as given by Equation 2. The resulting cuprous ion is then complexed with thiosulfate. The presence of this non-oxidizing species in the CaTS-air leaching system may help reduce or remove the passivation of gold thereby enhancing gold oxidation[7]. Copper can also be present in the pre-treated ore during leaching where this reaction can also occur.

$$2Cu^{2+}+2S_2O_3^{2-} \rightarrow 2Cu^{+}+S_4O_6^{2-} \quad (2)$$

During leaching, the thiosulfate reagent oxidizes over time to produce higher oxidation state sulfur species known as polythionates (PolyTS). A range of products such as trithionate (3T), tetrathionate (4T) and pentathionate (5T) are found in thiosulfate leach solutions. The resulting decomposition products are dependent on pH. Jeffrey and Brunt[8] concluded that tetrathionate and pentathionate are the dominant species in the pH range of 8.5 to 9. At pH of 10.4 trithionate and sulfate are formed.

Gold Stability

Leached gold has been found to be stable as long as thiosulfate is available. It was reported that when the thiosulfate concentration reaches a certain critical low point, gold may be re-precipitated. Gold precipitation can also occur after leaching if the leach slurry or filtrate is left unstirred whereby reducing conditions may develop leading to the formation of sulfide and eventual gold precipitation as a gold sulfide[7]. In an ammonium thiosulfate system, gold can also precipitate if air sparging is ceased[9]. Dissolved gold species may also be adsorbed and reduced on the surface of pyrite[10].

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Effect of Minerals

Several researcher have highlighted problems encountered during the thiosulfate leaching of sulfide minerals[11]. Due to the strong catalytic effect on the surface of the sulfide minerals, rapid oxidation of thiosulfate can occur. A mechanism for pyrite catalyzed oxidation of thiosulfate to tetrathionate (Figure 1 and Equation 3) was proposed by Xu and Schoenen[12]. Thiosulfate adsorbs onto a surface area of pyrite becoming the anodic site. Electrons transfer from thiosulfate to the anodic site and then over to a cathodic site on the same pyrite surface via the conduction band before ultimately being accepted by oxygen.

$$2S_2O_3^{2-}+0.5O_2+2H^+ \xrightarrow{\text{Pyrite}} S_4O_6^{2-}+H_2O \qquad 3$$

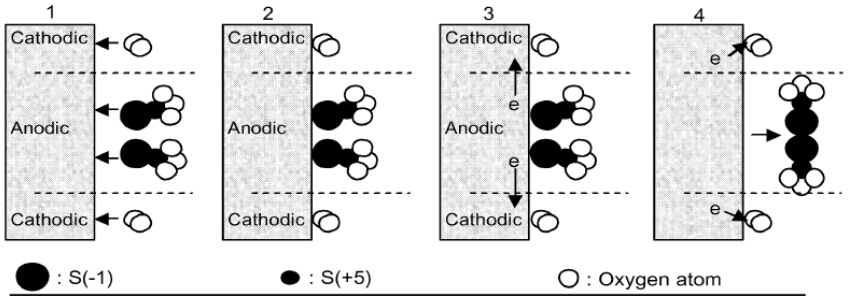


Figure 1: Proposed catalyzed oxidation of thiosulfate on the surface of pyrite by Xu and Schoonen[12] (Figure taken from [10])

Xia and Yen[10] demonstrated that additions of either pyrite or pyrrhotite during the ammoniacal thiosulfate leaching of a gold silicate slurry effectively decreased gold extraction and increased thiosulfate consumption. In a similar investigation, Feng and Deventer[13] found that addition of both pyrite and pyrrhotite also catalyzed thiosulfate oxidation in the presence of oxygen. The degradation products were initially tetrathionate (Equation 3) which quickly decomposed to trithionate in the alkaline conditions of the leaching system (pH 10.3) according to Equation 4.

$$2S_4O_6^{2-}+3OH^- \rightarrow \frac{5}{2}S_2O_3^{2-}+S_3O_6^{2-}+\frac{3}{2}H_2O \qquad 4$$

XPS analysis of the sulfide surface after leaching revealed presence of a thiosulfate-like intermediate species believed to be involved in the catalytic decomposition of thiosulfate.

It was previously shown that gold leaching can however be improved in the presence of sulfide minerals in the CaTS-Air/O_2 system especially at higher temperature and in the presence of copper[7]. This was partially attributed to the galvanic effect of pyrite which increases the mixed potential of the system. In leaching tests (0.3 M CaTS, 2 mM Cu, pH 10, 40°C, 10 mL/min Air) comparing an oxidized ore with ones containing pyrite, higher gold recoveries but also higher losses in thiosulfate were observed in the latter. For the same set of tests, it was reported that the pyrite concentrates contained 20-70 mM trithionate and 1-3 mM tetrathionate after 48 hours which is in line with the expected species at pH 10[14].

The detrimental effects of hematite additions on gold dissolution were investigated in the ATS leaching system. It was found that hematite formed coatings passivating gold dissolution and increasing the thiosulfate decomposition in presence of oxygen[15]. The CaTS leaching system is susceptible to the generation of gypsum which can lead to complications with equipment scaling[16]. The presence of gypsum in the leaching circuit may contribute to gold stability issues and is therefore of interest.

Gold-thiosulfate Recovery Process

Gold Loading on Ion Exchange Resins

Gold-thiosulfate complexes have high affinities for adsorption sites on strong base anion exchange resins. Unfortunately, so do the degradation products of the thiosulfate leaching reagent. This competition for adsorption sites on the resin beads is an important drawback of the recovery

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process. Moreover, the stability of gold thiosulfate complexes is another concern where gold losses over time have been observed during the leaching stages[17]. Adsorption limitations and gold losses can be prevented to a certain extent by applying engineering solutions such as the use of a resin-in-leach (RIL) process instead of resin-in-pulp (RIP)[14] and enhancing the recovery by modifications to the flowsheet such as using a combined co-current and counter-current leaching circuit versus a simpler counter-current circuit resulting in reduced effects of degradations products on gold adsorption[17]. Another aspect used to control polythionate levels in the RIL circuit is the treatment of partially loaded resins from the counter-current portion of the circuit with sulfite to ultimately convert tetrathionate, pentathionate and other higher polythionates into trithionate and thiosulfate while leaving the gold on the resin as depicted by Equation 5[14].

$$R_2S_xO_6+SO_3^{2-}\rightarrow R_2S_{(x-1)}O_6+S_2O_3 \quad 5$$

In this instance, trithionate is not as strongly adsorbed nor as detrimental to gold loading on the resin as other polythionates. The treated partially gold-loaded resin can continue adsorbing gold in the co-current portion of the leach before being eventually removed for gold elution.

Gold Elution

The negative impact of trithionate on resin gold loading can be utilized as a strategy for gold recovery. In the gold elution stage, trithionate, produced through the oxidation of thiosulfate by hydrogen peroxide as given by Equation 6, can be used as a stripping agent along with sulfite to effectively displace the gold-thiosulfate complex from the resin[16].

$$Na_2S_2O_3+4H_2O_2\rightarrow Na_2S_3O_6+Na_2SO_4+4H_2O \quad 6$$

The gold eluate is sent to an electrowinning stage while the barren resin, now loaded with trithionate, is regenerated by addition of sulfide resulting in the in-situ formation of thiosulfate on the resin and in solution according to Reaction 7. The barren resin, free of polythionates, is recycled to the leaching circuit whereas the spent regeneration solution containing thiosulfate is recycled for the next elution after renewed conversion to trithionate by peroxide (Equation 6).

$$R_2S_3O_6+Na_2S\rightarrow R_2S_2O_3+Na_2S_2O_3 \quad 7$$

As was highlighted above, the performance of the leaching circuit is therefore highly dependent on the management and control of the polythionates species.

Although calcium thiosulfate gold leaching is currently an industrial reality, there remain some unanswered fundamental questions regarding the effects and role of polythionates on the gold thiosulfate complex stability and resin adsorption behaviour. This paper intends on describing the observed effects of polythionate additions on synthetic soluble gold-thiosulfate solutions alone and in the presence mineral additions. In addition, the loading rates of gold in the presence of varying amounts of initial polythionate additions as well as their loading behaviours on Purolite A500 strong base ion exchange resin was investigated.

EXPERIMENTAL PROCEDURES

Analytical Methods

Gold Analysis

A method for the analysis of gold in alkaline calcium thiosulfate (CaTS) solutions was developed using a Varian AA420 Atomic Absorption Spectrometer (AAS) with an air (3.5 L/min)-acetylene (1.5 L/min) flame, a gold hollow cathode lamp and lamp current of 4 mA, a wavelength of 242.8 nm and a deuterium lamp in operation for background correction. Previously observed issues with aqueous gold analysis using AAS were low absorption and resulting detection limits and burner flame interruptions due to precipitation of sulfur due to thiosulfate present in the CaTS gold leaching system (0.1 M CaTS) studied in this work. In addition, over time, sample degradation occurred and

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it was therefore important to maintain a stable sample, free of precipitates, that was representative of its time of sampling. As such, upon sampling, filtered (0.22 µm) aqueous aliquots of gold-thiosulfate were converted into a stable aurocyanide complex by addition of an excess of sodium cyanide to thiosulfate before a known volume of methyl isobutyl ketone (MIBK) containing 1 wt% Aliquat 336 was added and vigorously shaken for 10 minutes. The sample was subsequently centrifuged and the separated gold-containing organic phase was transferred into a capped test tube awaiting analysis. To eliminate interferences due to background solutions[18], an organic gold stock solution was prepared in a similar fashion as experimental samples. The organic gold stock was made by pipetting 5 mL of a 1000 ug/ml aqueous AAS gold chloride standard solution (Acros organic) that was pH adjusted to 10.5 using concentrated NaOH before addition of 0.1 M CaTS plus sodium cyanide at a 25 % excess to thiosulfate. The gold chloride (yellow) is expected to be immediately reduced by cyanide to form gold(I) cyanide (clear) in a 0.1 M thiosulfate background. This solution is transferred quantitatively and mixed into a 50 mL volumetric flask from which 25 mL are used for gold solvent extraction into an equal volume of MIBK with 1 wt% Aliquat 336. Working gold standards in MIBK were made by diluting appropriate amounts of this organic 100 ppm gold stock solution.

Thiosulfate and Polythionate Analysis

Sodium-thiosulfate and -tetrathionate are commercially available whereas trithionate was synthesised using the procedure developed by Kelly and Wood[19]. For thiosulfate and polythionate analysis, a simplified procedure by Jeffrey and Brunt[8] was employed for use with a Dionex DX600 ion chromatographer and an AD25 absorbance detector running at a wavelength of 214 nm. A 4 x 250 mm IonPac AS16 anion exchange and 4 x 50 mm AG16 guard column set with a sample loop of 25 µL were used. The mobile phase set at a flow rate of 1 mL/min was made up of a 0.2 M sodium perchlorate solution prepared in 18.2 MΩ deionized water and filtered with a 0.2 µm membrane filter. Sodium perchlorate has a low UV absorbance, provides rapid exchange of strongly adsorbing species and does not have a propensity to degrade polythionates unlike strong alkaline solutions. With this method, thiosulfate, trithionate, tetrathionate and pentathionate could all be detected within 7 minutes with the ability to quantify the former three species using freshly prepared standards.

Leaching Solutions

A 0.2 M copper stock solution as copper sulfate pentahydrate and a 1250 mg/L gold stock solution as gold(I) sodium thiosulfate hydrate in 0.1 M CaTS were prepared in advance and minutes before the start of the experiments respectively. Briefly, a calculated amount of ~24 wt % CaTS solution was added to a 250 mL beaker partially filled with 18.2 MΩ nano pure water before addition of each 1 mL copper and gold stock solutions as well as any extra soluble additives such polythionates. A calibrated pH electrode was used to stir and adjust the solution to the desired pH using 0.1 N NaOH. The solution was then quantitatively transferred into a 250 mL volumetric flask whose volume was quickly made up to the mark. After adequate mixing, the whole content of the volumetric flask was transferred into an Erlenmeyer flask reactor and initial samples (t=0) were immediately taken. For experiments containing mineral additions, calculated amounts of each additive were subsequently introduced into the reactors. The activated carbon used was provided by the Buenaventura mining company. The pyrite sample was prepared by crushing and grinding a pure pyrite cube originating from Huanzala, Peru. Laboratory grade hematite (Fisher Scientific) and gypsum (Alfa Aesar) were used. Experiments involving actual preg-robbing material (ore pre-treated by pressure oxidation provided by Barrick Gold Corporation subsidiary AuTec) were prepared similarly by addition of a predetermined volume of a stock leaching reagent solution (typically 50 mg/L Cu, 0.1 M CaTS and, optionally, 5-8 mg/L gold(I) thiosulfate) to a calculated mass of dry ore of known density giving an overall slurry pulp density of 30 wt %.

Reactor Design

Erlenmeyer flasks were capped with rubber stoppers containing apertures for a pH electrode and a base inlet line. Reactors were submerged into a large temperature controlled water bath sitting atop multiple magnetic plate stirrers for agitation (500 rpm). Where applicable, automatic base addition of 0.1-1 N NaOH was made by a Jenco 3675 pH/ORP controller for pH control.

Resin Loading and Gold Isotherms

Gold adsorption tests in the presence of increased initial polythionate concentrations were conducted in 2 L baffled glass reactors with 500 rpm overhead agitation by a 2 inch diameter 4

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blade pitched impellor. Solutions were prepared in 2 L volumetric flasks by adding calculated amounts of CaTS stock solution and polythionate salts to give the targeted concentrations. Next, a precise volume of concentrated gold thiosulfate stock solution was added to the flask to achieve an 8 mg/L gold solution after making up the volume. Samples for initial gold and polythionate concentrations were taken right before addition of the resin (swollen state in Cl^- form), which marked the onset of the loading test. Intermittent reactor aliquots were taken to monitor the rate of gold and polythionate loadings.

Similarly, for the construction of gold isotherm diagrams, a fixed volume of resin (0.5 mL) was added to reactors containing increasing initial gold concentrations (0.25, 1, 2.5 and 8 mg/L) in 0.1 M CaTS with or without added polythionates. The solutions were accurately prepared using a 2 L volumetric flask before being transferred into the reactors for initial sampling and addition of the resin. The resin was allowed to reach equilibrium overnight and the barren solution was analyzed the next day. The resin was subsequently stripped twice for 1 hour using 50 mL of 0.5 M sodium perchlorate and its gold loading was inferred from the mass of stripped gold per mass of dry resin.

RESULTS

Effect of Polythionate Additions on Synthetic Gold-thiosulfate Leaching Solutions

Initially, the aim of this work was to investigate the stability of the gold thiosulfate complex in artificial CaTS leaching solutions over time containing added initial polythionates. Initial tests were performed without pH control allowing the solutions to drift naturally (Figure 2).

Figure 2

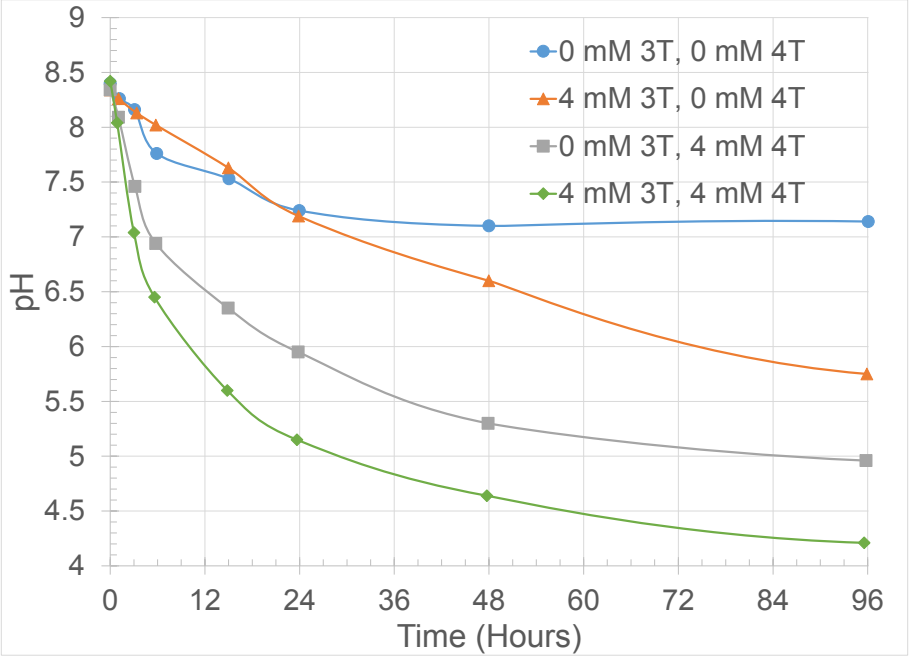


Figure 2: pH profiles of experiments with various polythionate additions ($[Au]_{ini}$ = 5 mg/L, 0.1 M CaTS, 50 mg/L Cu, 25°C)

No changes in gold concentrations (not shown) were observed over the course of 96 hours for each condition. It is evident that initial additions of polythionates decrease the pH over time in the order of no PolyTS<3T<4T<3T & 4T. Subsequent tests used automatic pH control to maintain a constant pH over time. The drawback from these tests were solution dilutions resulting from added dilute base at the expense of worse pH control using concentrated base. To account for this, gold curves were modelled representing expected gold concentrations based on solution withdrawals due to sampling and solution dilution due to base additions. Losses of soluble gold over time resulting from polythionate additions alone are inconclusive.

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Effects of Polythionate and Mineral Additions on Synthetic Gold-thiosulfate Leaching Solutions

Figure 3 shows the measured gold concentration over time in a synthetic leach solution containing gypsum (4 g/L). For the most part, actual gold concentrations for each tests are in agreement with respective gold concentrations represented by the modelled curves. Note lower gold concentrations in tests with added polythionates in the order of 3T & 4T<4T<3T< no PolyTS in line with base consumption data. The only possible drop in gold concentration occurs shortly after mineral additions for each test containing added initial polythionates in particular for the test with both 4 mM 3T and 4 mM 4T.

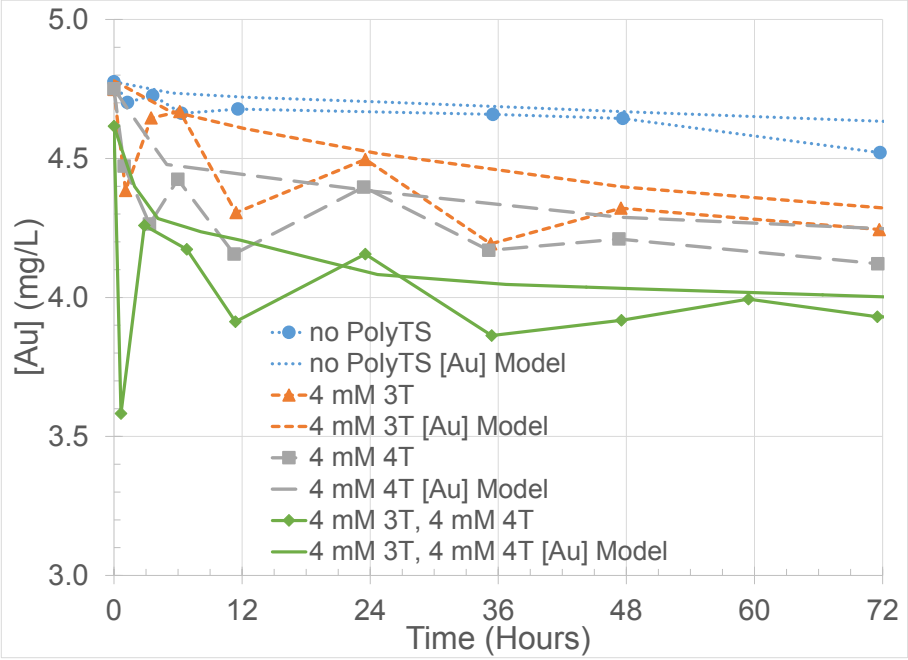


Figure 3: Gold concentration over time in solutions (initial [Au] target 5 mg/L, 50 mg/L Cu, 0.1 M CaTS, 40°C, pH 10) without (no PolyTS) or with additions of 4 mM 3T and 4T separately and together in the presence of 4 g/L gypsum. Modelled [Au] curves represent expected gold concentrations based on solution withdrawals due to sampling and solution dilution due to base additions for pH control

Similarly, initial gold drops were observed for additions of pyrite (8 g/L) (

Figure 4) and activated carbon (1.29 g/L). Hematite additions (8 g/L) showed no suspected drops in soluble gold concentration. After the stability tests, both the filtered gypsum and hematite additives underwent cyanidation in a 2 M NaCN solution for 24 hours. No gold was detected in the cyanide leachate.

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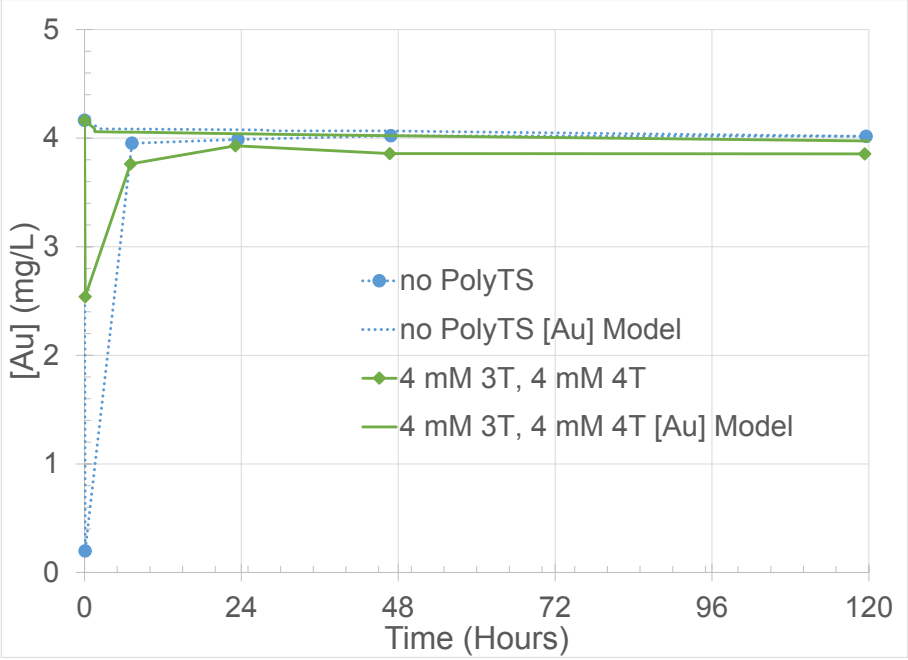


Figure 4: Gold concentration over time in solutions (initial [Au] ~4 mg/L, 50 mg/L Cu, 0.1 M CaTS, 40°C, pH 10) without (no PolyTS) or together with additions of 4 mM 3T and 4T in the presence of 8 g/L pyrite. Modelled [Au] curves represent expected gold concentrations based on solution withdrawals due to sampling and solution dilution due to base additions for pH control

An attempt was made to reproduce the drops in soluble gold observed during the initial stage upon addition of pyrite (

Figure 4) and activated carbon (not shown) in synthetic leaching solutions without initial polythionates. Briefly, to this end, solutions were prepared using a similar procedure as used for the former gold stability tests with the main difference being a focus on duplicate initial gold sampling followed by duplicate gold concentration sampling post mineral addition over time as well as reproducibility (repeats 1 and 2). Only initial pH 10 adjustments were made by base additions and then the solution pH was allowed to drift.

Figure 5 shows that the anticipated drops in gold concentration after pyrite addition (t=0) were not observed. It is possible that the sampling procedure failed to capture the initial gold precipitation from solution right after pyrite addition by allowing enough time for releaching to occur. As a result, the observations made in

Figure 4 still need to be confirmed. However, the addition of as little as 50 mg/L copper seems to accelerate the decrease in soluble gold concentration after extended times (t=168). This is best illustrated by comparing tests Py2 and Py2-Cu and seeing the accelerated decrease in soluble gold for the latter starting at the 68 hour mark.

Figure 5 also shows drops in soluble gold contacted with activated carbon in both repeated tests AC1 and AC2 past the 68 hour mark. This confirms an affinity of $Au(S_2O_3)_2^{3-}$ complexes with activated carbon over extended periods of time. It was previously reported that thiosulfate only slightly adsorbed onto activated carbon hence its suitability as a lixiviant for carbonaceous ores[20].

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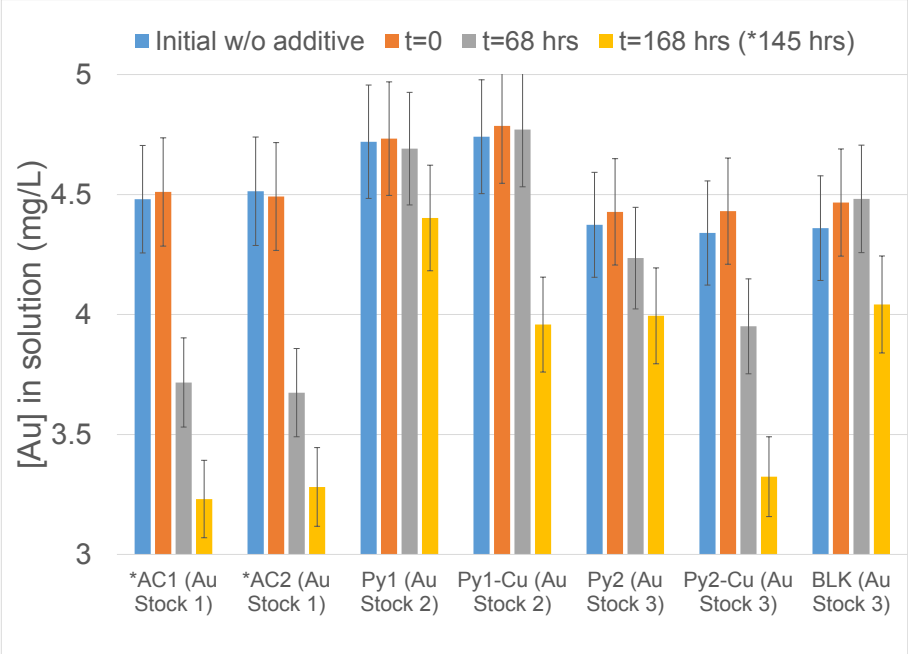


Figure 5: Gold concentrations before (initial) and after mineral additions (t=0). Separate fresh gold stock solutions (1-3) were used for each set of tests. Error bars = 5%. Conditions: Cu = 50 mg/L Cu added, $pH_{ini.}$ = 10

Figure 6 shows the accelerated decomposition of 0.1 M initial thiosulfate when contacted with pyrite compared to little thiosulfate oxidation in the blank experiment. As mentioned earlier, results from other researchers indicated faster gold leaching rates in the presence of pyrite with copper and also higher thiosulfate consumption[10].

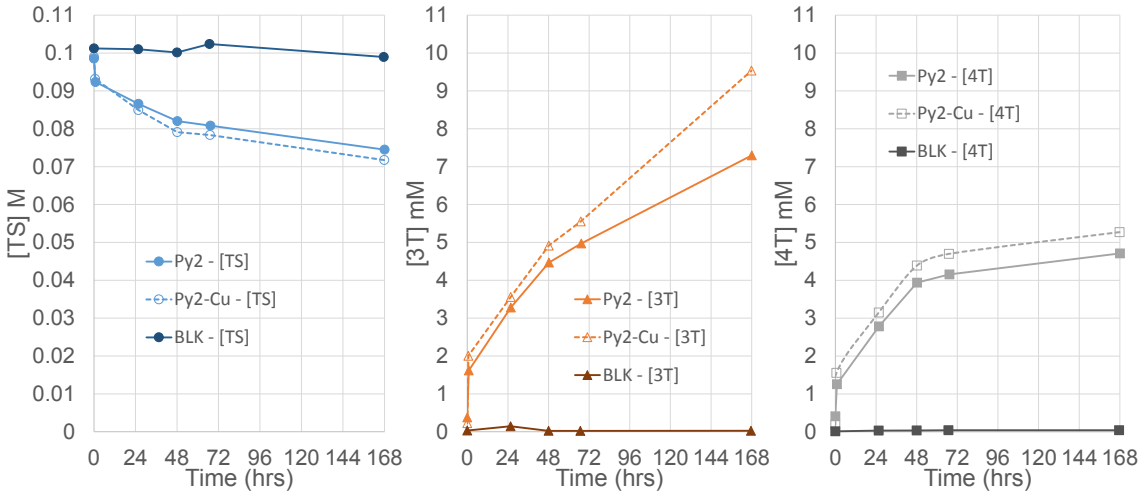


Figure 6: Comparison of thiosulfate decomposition (left) without added pyrite (BLK = blank) and in the presence of added pyrite (Py = pyrite). Resulting formation of trithionate (center) and tetrathionate (right). Cu denotes addition of 50 mg/L copper. Corresponding [Au] given in Figure 5

Effects of Polythionate Additions to a Preg-robbing Ore

Leaching Tests with Added Initial Gold

The next set of trials involved the addition of polythionates to a gold bearing preg-robbing ore (2.96 ppm) at a pulp density of 30 wt % together with an artificial source of initial gold thiosulfate (6-7 mg/L). Polythionate additions of 25 mM as trithionate (Conc3T), tetrathionate (Conc4T) or both tri- and tetrathionate (ConcPT) were made after an initial gold sample was taken.

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Figure 7 combines the soluble gold concentration data of these leaching trials with initial synthetic gold to expose its tendency to be preg-robbed by the ore. Blank experiments (BLK) denote no added polythionates except for the initial presence of tetrathionate due to added copper (Equation 2). Initially, for each blank test, there was a slight increase in soluble gold likely due to fast initial leaching of gold from the ore. Then the gold was preg-robbed to levels below the initially added artificial soluble gold concentration. The preg-robbing behaviour was intensified when polythionates were added where, in all cases, a significant reduction in soluble gold was observed with a minimum gold concentration achieved between 2-5 hours before increasing back to levels similar to the blank tests (

Figure 7). This indicates an interaction between the preg-robbing material and thiosulfate degradation products occur that precipitates gold from solution which can re-dissolve given enough time.

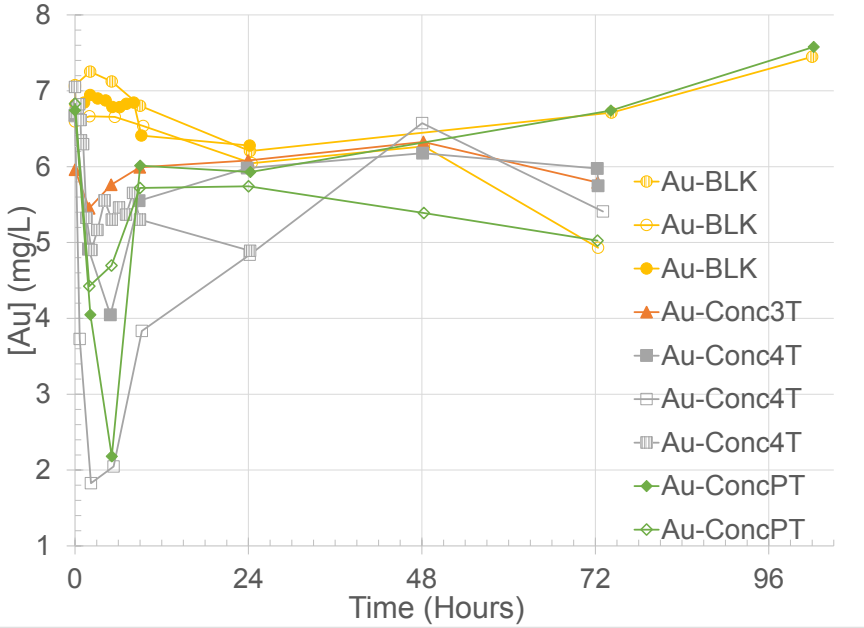


Figure 7: Effect of concentrated polythionate additions to CaTS leaching solutions (0.1 M CaTS, 50 mg/L Cu, 50°C, pH 8.5) containing artificial initial gold-thiosulfate (6-7 mg/L) during the leaching of a gold-bearing preg-robbing ore (2.96 ppm)

The interaction between the preg-robbing materials in contact with initial soluble gold and polythionates was made evident by the gold mass balance for one such test (ConcPT - Figure 8) where drops in soluble gold measured by AAS corresponded to increases in fire assays of solid fractions sampled over time.

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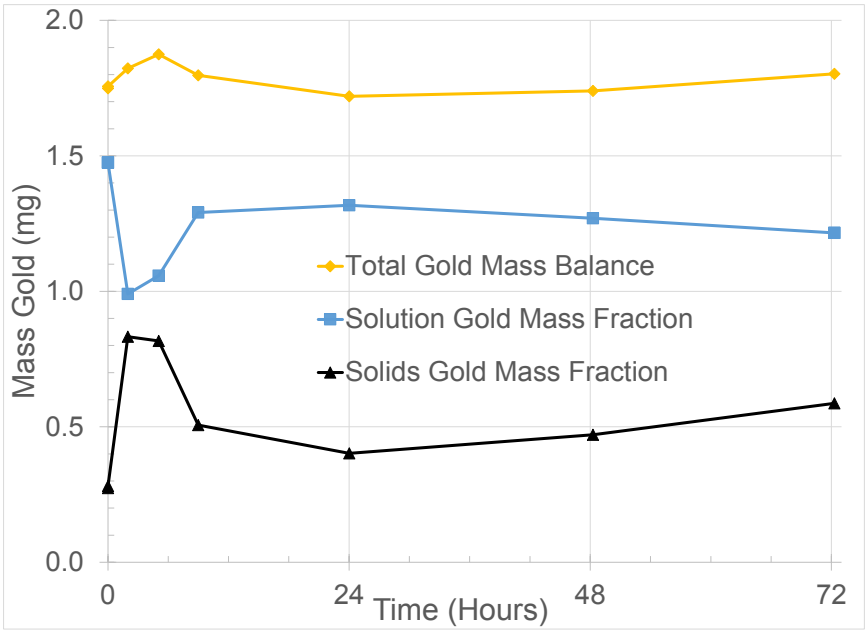


Figure 8: Gold mass balance for test with additions of 25 mM each of tri- and tetrathionate to a CaTS leaching solution (0.1 M CaTS, 50 mg/L Cu, 50°C) containing artificial initial gold-thiosulfate (6.83 mg/L) during the leaching of a preg-robbing gold ore (2.96 ppm)

The re-dissolution of gold over time could be partially explained by an increase in the thiosulfate concentration resulting from the degradation and rearrangement of higher polythionate into thiosulfate as displayed in Figure 9.

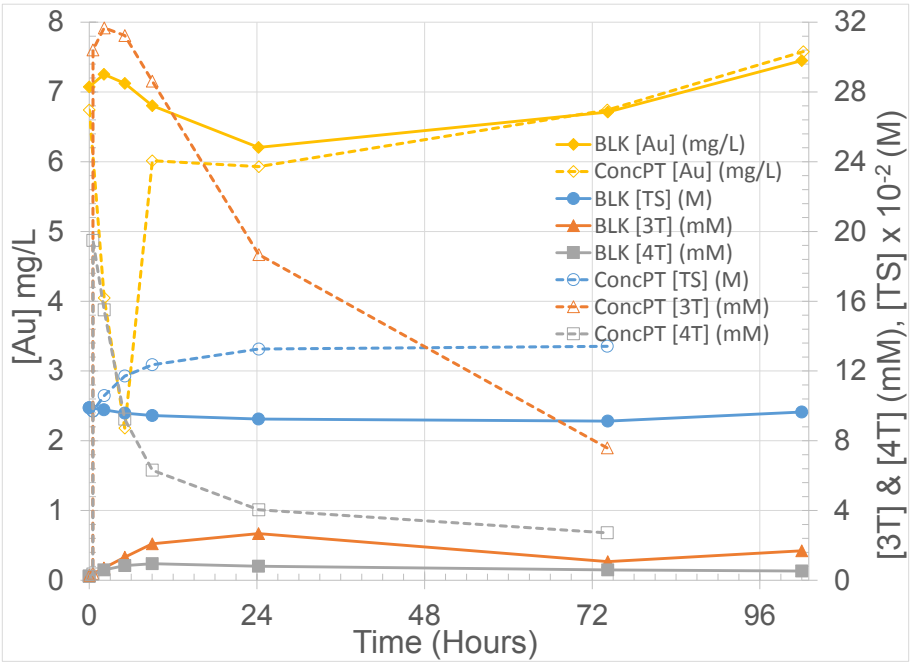


Figure 9: Gold and polythionate concentration profiles of a blank test (BLK = no polythionates) compared to a test with 25 mM tri- and tetrathionate additions (ConcPT) at the 30 minute mark (0.1 M CaTS, 50 mg/L Cu, 50°C)

The first step in the degradation of tetrathionate is considered to be the thiosulfate catalyzed rearrangement of tetrathionate to tri- and pentathionate according to Equation 8.

$$2S_4O_6^{2-} \rightarrow S_3O_6^{2-} + S_5O_6^{2-} \quad (8)$$

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Subsequently, tri- and pentathionate degrade further according to the trithionate hydrolysis and pentathionate degradation reactions based on solution pH, represented by Equations 9 and 10 respectively.

$$S_3O_6^{2-} + H_2O \rightarrow S_2O_3^{2-} + SO_4^{2-} + 2H^+ \quad (9)$$

$$2S_5O_6^{2-} + 6OH^- \rightarrow 5S_2O_3^{2-} + 3H_2O \quad (10)$$

It was shown that at pH values between 8 and 9, subsequent degradation of pentathionate is dominant compared to trithionate hydrolysis[21]. Therefore, for the conditions used in Figure 9, it is reasonable to describe the fast observed degradation of added tetrathionate as the combination of Equation 8 (4T rearrangement) and 10 (5T degradation) resulting in a single reaction given by Equation 11.

$$4S_4O_6^{2-} + 6OH^- \rightarrow 5S_2O_3^{2-} + 2S_3O_6^{2-} + 3H_2O \quad (11)$$

Leaching Tests without Added Initial Gold

Figure 10 displays soluble gold extractions over time for the leaching trials of a refractory preg-robbing ore in the absence of initial gold. All curves show fast initial gold leaching kinetics, however, it should be noted that for the tests with tetrathionate additions, a drop in soluble gold was once again observed as in

Figure 7. Gold dissolution did not taper off after 72 hours indicating higher recoveries than given in Table 1 may be achieved with longer leaching times.

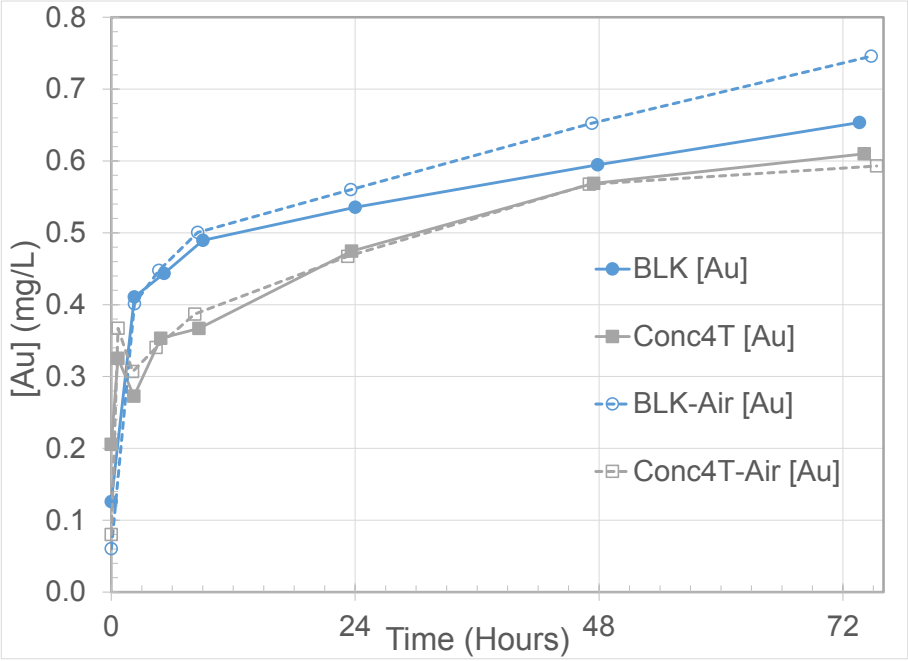


Figure 10: Effect of 25 mM tetrathionate additions and air sparging (0.25 L/min) on gold recovery during the leaching of a preg-robbing gold ore (2.96 ppm) (0.1 M CaTS, 50 mg/L Cu, 50°C, pH 8.5)

Table 1 also shows that, in spite of the drops in soluble concentration, tests with tetrathionate additions have a higher overall gold extraction based on residue fire assays and head assay. It should be noted that tests with added tetrathionate required more base addition than the blank tests contributing to the dilution of the leach solution and lower soluble gold in Figure 10. In addition, tests with aeration were more prone to evaporation of the leaching solution over time although measures

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were taken to reduce the uptake of moisture from the reactor by first bubbling the air in a separate water reactor as a pre-humidifying step.

Table 1: Gold extraction for preg-robbing ore leaching tests

Test	Gold extraction (%) after ~74 hours	Base consumption (mL)
BLK	61.8	2.31
Conc4T	66.9	13.19
BLK-Air	62.5	2.32
Conc4T-Air	63.2	11.75

In the case of added tetrathionate to the leaching of the preg-robbing ore,

Figure 11 shows the aforementioned increase in thiosulfate due to the rearrangement and degradation reactions of higher polythionates into thiosulfate. This increase of the leachant concentration can also explain the re-dissolution of the precipitated of gold due to tetrathionate addition and the overall higher gold extraction.

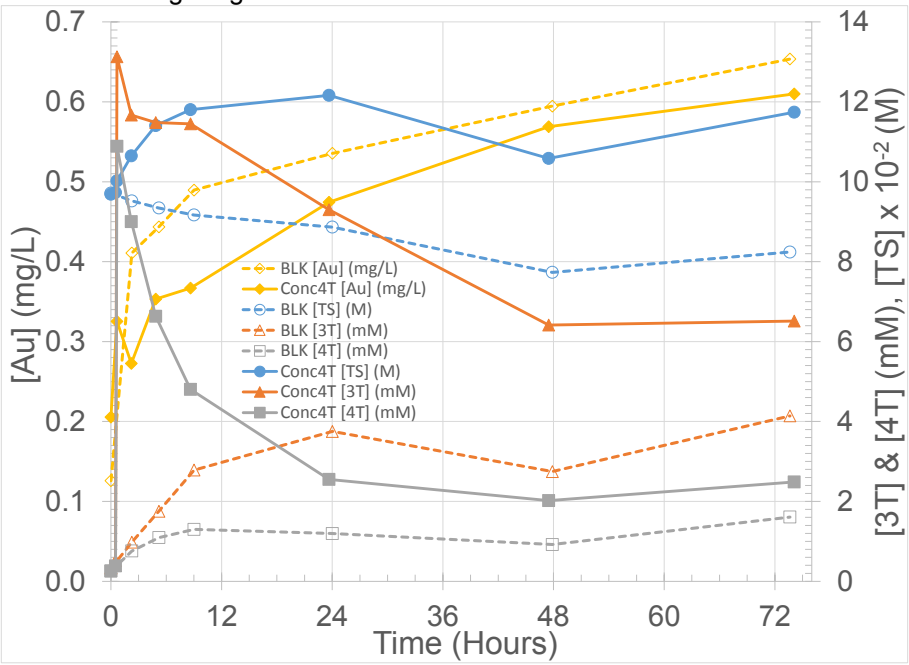


Figure 11: Gold and polythionate concentration profiles of a blank test (BLK -no polythionate addition) compared to a test with 25 mM tetrathionate addition at the 30 minute mark (Conc4T) during the leaching of a preg-robbing gold ore (2.96 ppm) (0.1 M CaTS, 50 mg/L Cu, 50°C)

It appears that surface interactions between preg-robbing minerals and additions of polythionates have the propensity to reduce gold. The mechanism by which this occurs remain unknown and further investigation is required.

Effect of Polythionates on the Loading of Gold onto Anion Exchange Resins

Relevant research was initiated by the work of Jeffrey and Brunt[8] and Muslim et al.[22, 23] to investigate the competitive loading behaviour of polythionates with respect to one another and with respect to the gold thiosulfate complex. As these types of fundamental studies have yet to have been conducted on the CaTS leaching system, an opportunity exists to compare and build upon the limited knowledge regarding the dynamics between thiosalt species and the gold thiosulfate complex.

Figure 12 displays the soluble gold concentration profiles during the loading of 8 mg/L gold onto 5 mL of Purolite A500 resin in a 0.1 M CaTS solution in the presence of increasing concentrations of initial polythionates. At equal molarities, tetrathionate is consistently more detrimental to gold loading than trithionate.

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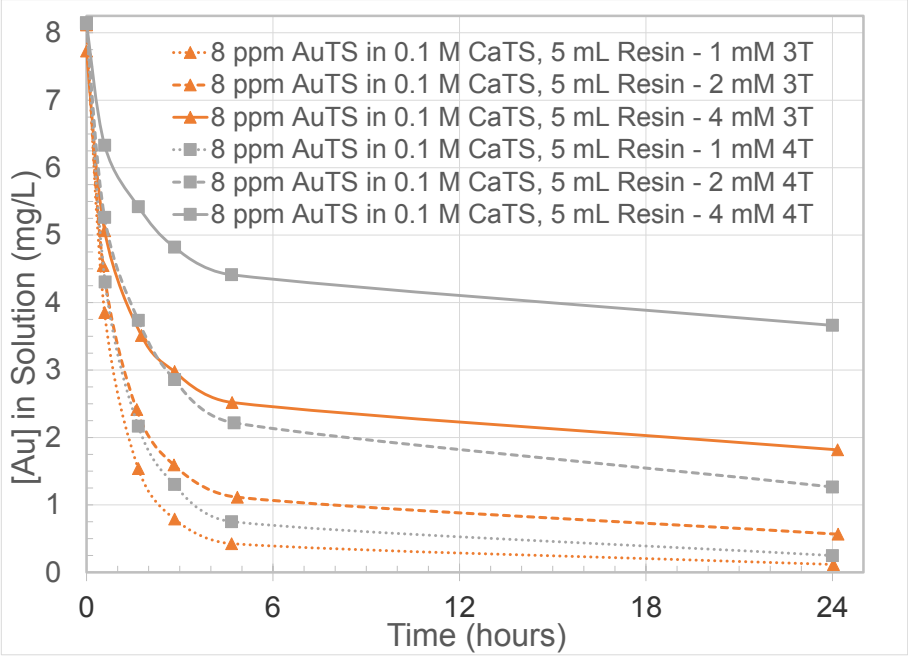


Figure 12: Gold concentration profile in 0.1 M CaTS during adsorption onto 5 mL Purolite A500 resin with increasing polythionate concentrations

Table 2 gives the resulting gold loadings on a dry resin mass basis as well as the remaining gold concentrations in the reactors. It is clear that increasing the initial trithionate or tetrathionate concentration adversely impacts the gold loading on the resin with the latter having a more pronounced effect.

Table 2: Gold resin loading and corresponding remaining gold concentration in solution after 24 hour contact in an 8 mg/L gold solution in 0.1 M CaTS (* 0.4 mM initial TS from AuTS stock only)

Volume Resin (mL)	$[Polythionate]_{ini.}$	Soluble $[Au]_{t=24\ hrs}$ (mg/L)	Resin Loading (mg Au/kg dry resin)	Total Resin Loading (meq/L)
5	4 mM 3T	1.82	5742.74	1184
5	2 mM 3T	0.57	7470.06	1160
5	1 mM 3T	0.12	8089.16	1161
5	4 mM 4T	3.66	4266.64	873
5	2 mM 4T	1.27	6557.64	962
5	1 mM 4T	0.25	7509.39	1073
10	4 mM 4T*	0.04	3459.27	1241
10	4 mM 4T	1.04	2923.40	947
10	2 mM 4T	0.19	3552.45	1054
10	1 mM 4T	0.05	4081.55	1082

For loading tests involving trithionate, an average total resin loading of 1.168 eq/L (resin capacity = 1.15 eq/L) was achieved after 24 hours indicating the resin was at equilibrium. In the case of tests involving tetrathionate, the resin loading was slightly lower on account of the missing pentathionate values (analytical peaks detected but could not be quantified due to lack of a suitable standard) which were significant. The appearance of pentathionate was likely due to the rearrangement of tetrathionate (Equation 8).

Figure 13 shows an example of the loading behaviour of an 8 mg/L gold solution with 4 mM tetrathionate in a 0.1 M CaTS solution. Thiosulfate was quickly loaded initially before gradually being displaced by the loading of tetrathionate (61% of resin capacity). At the same time tetrathionate degrades into trithionate and thiosulfate (Equation 11) which also loads onto the resin albeit to a lesser extent (22 % of capacity) and therefore accumulates in solution.

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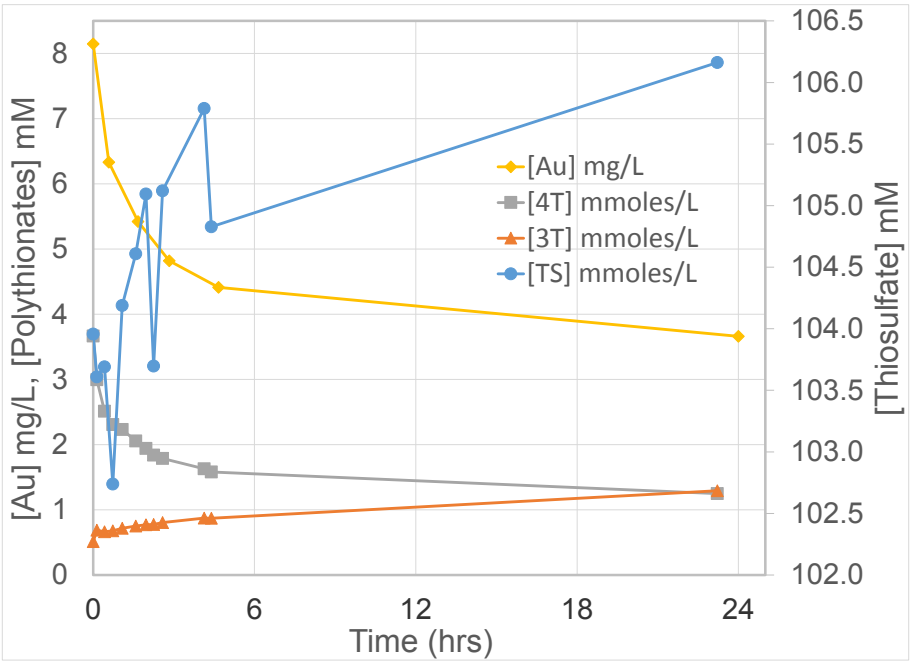


Figure 13: Polythionate and gold concentration profiles during the loading of 8 mg/L gold thiosulfate in the presence of 4 mM tetrathionate in a 0.1 M CaTS solution

Gold Isotherms

Gold loading isotherms in the presence of various total concentrations of polythionates and combinations of polythionates were constructed to elucidate the effect of the thiosalts on gold loading. These loading tests were carried out in typical CaTS leaching solution compositions (0.1 M CaTS, 50 mg/L Cu). Loading isotherms are usually reported in the literature as the mass of gold loaded per mass dry resin (mg Au/kg Resin) versus the equilibrium concentration in solution[8]. These types of graphs can be a useful tool in the design of separation processes in similar systems. Figure 14 contains thee gold isotherm curves each with varying degrees of polythionate additions. It is evident that as little as 4 mM of tetrathionate can have a severe impact on the uptake of gold onto the resin.

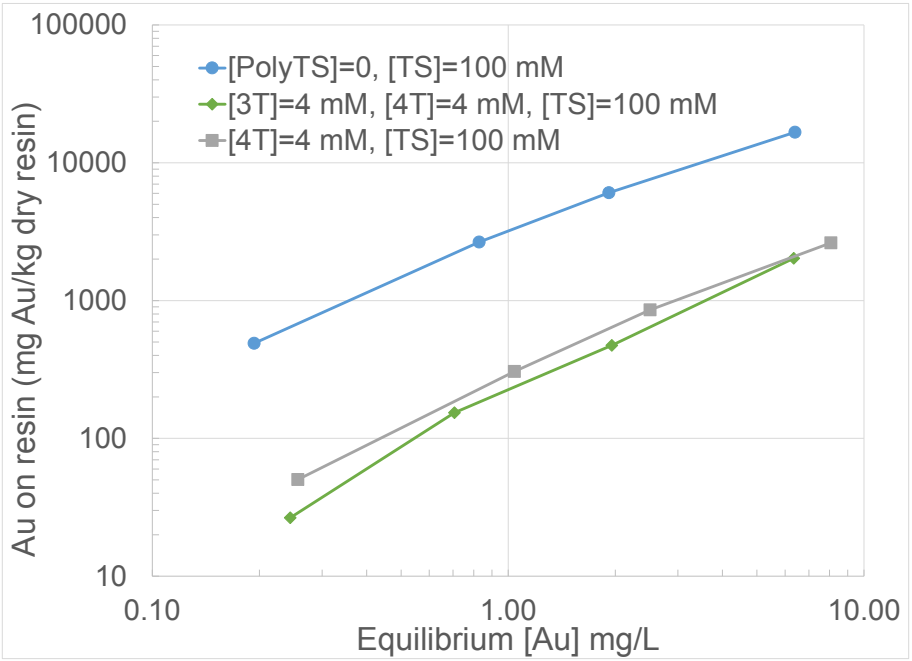


Figure 14: Gold Loading Isotherms at various concentrations of polythionates

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CONCLUSIONS

Addition of hematite into a synthetic CaTS leaching solution with or without the presence of initial polythionates did not reveal any gold stability issues. However, in the case of gypsum, activated carbon and pyrite additions, soluble gold data suggests an interaction with those minerals capable of precipitating gold. The presence of pyrite, in particular, added to synthetic CaTS leaching solutions increased the degradation rate of thiosulfate. This was even more pronounced in solutions containing copper. Final dissolved gold concentrations suggest a decrease in the long term gold stability for solutions containing both pyrite and copper.

During CaTS leaching of a gold bearing ore with initial gold, it was shown that new gold leaches quickly before being preg-robbed together with initial gold. The addition of polythionates enhanced the observed preg-robbing phenomenon. Solids fractions sampled during leaching and analysed for gold via fire assay showed that gold precipitated onto the ore material. Similarly, in the absence of initial gold, leaching tests of the preg-robbing ore once again showed momentary decreases in soluble gold following additions of polythionates. These observations lead to the conclusion that an interaction between polythionates and soluble gold at the surface of the mineral exists whereby gold precipitation can be facilitated.

The detrimental effects of polythionates on gold adsorption onto strong base anion exchange resins was re-affirmed this time for the CaTS system. Lastly, gold loading isotherms for this system in the presence of polythionates were constructed which compare well with other such diagram available in the literature for the ATS[8] and non-ATS[22] systems.

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