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THORIUM STABILITY IN RARE-EARTH PROCESSING

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ABSTRACT

In rare earth (REE) deposits, the presence of radioactive elements is evident, as they are commonly found as a solid solution with REE-bearing minerals. During the intense pre-treatment and leaching conditions, these elements will also solubilize. Hence, downstream separation steps are needed to ensure proper control of product and waste material radioactivity. Thorium, a tetravalent radioactive element, is a radionuclide common to many REE processes, and present at significant concentrations in most Australian deposits, yet often not discussed in process descriptions. Different methods for thorium removal are described in the literature, which involve high-temperature acid baking, selective precipitation/dissolution, or solvent extraction. However, the assumptions on thorium control are based on the final element concentration in solution, and the characterization of the final residue is complex and often neglected.

Using chemical-thermodynamic simulation is a powerful tool for predicting and exploring reactions and behaviour of species in different relevant process systems without the need of lengthy experimental work. For instance, speciation, stability and solubility diagrams were developed for thorium in water, phosphate, sulfate, nitrate, and carbonate systems. Thorium has a high coordination number, which is demonstrated by the complex and numerous hydrated species in water. At acidic environment, thorium tends to form polynuclear species, and the Th:OH molar ratio increases at high pH. Hence, thorium hydroxide ($Th(OH)_4$) solubility regions vary and are attributed to the formation of amorphous compounds, which can directly affect process viability in terms of phase stability and waste management control. In phosphorus-rich systems, $Th_2(PO_4)_2(HPO_4).H_2O_{(s)}$ was found to be in accordance with thermodynamic predictions and experimental work from different studies.

In sulfate, thorium has high solubility, with the formation of a solid phase occurring only in acidic conditions, and $Th(SO_4)_3^{2-}$ is the thermodynamic aqueous species stable at $pH > 1$. Considering $-PO_4-SO_4$, phosphate phases are predominant over sulfate, with solid thorium phosphate forming at $pH = 2.5$. Regarding nitrate, aqueous species are restricted at $pH < 4$, and precipitation occurring at high concentrations. In the case of carbonate, it shows an interesting feature in enhancing thorium solubility at $6 < pH < 11.5$. Therefore, two approaches can be highlighted, such as in the formation of the solid phase of thorium phosphate with a slight increase in pH, precipitating along with the main impurities in REE processing (e.g., iron, calcium, aluminium). Thus, reducing the overall thorium concentration in the waste radioactivity. Secondly, the selective dissolution of thorium in carbonate could be used for purifying the REE-products and, if appropriate, as a concentration method (i.e., to be used in thorium-based nuclear plant).

Keywords: thorium stability, thermodynamics, rare-earth processing,