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A Short Review on REE Recovery from Ion-Adsorption Clays

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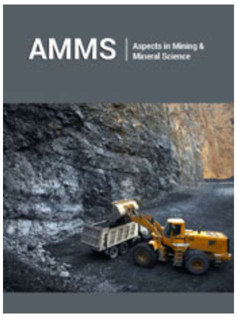

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Abstract

In temperature and tropical regions, Rare Earth Elements (REE)s-bearing minerals abundant in particular igneous rocks normally decompose to REE3+ throughout chemical weathering then absorbs on the surface of weathered rock forming minerals and form ion-adsorption clay REE deposits. Due to obtainability of REEs in ion-exchangeable phases in such deposits, simple diluted electrolyte solution such as Ammonium Sulphate can extract significant amount of REEs at ambient temperature. Through different types of leaching methods can be utilized which are heap, tank/pool, and in-situ leaching methods, in-situ leach mining is the dominating technology now cause of more efficiency and less environmental impacts. Later on, more pured REE solutions can be achieved by using advanced techniques such as solvent extraction.

Introduction

Rare Earth Elements (REEs: La-Lu Plus Y and Sc [1]) are known to be enriched in the melt mantle during magmatic differentiation. They can also be enriched in the granitoids through the accumulation of REE-bearing minerals such as apatite, allanite, monazite, titanite and xenotime, since they tend to remain in the melt until the late stages of magmatic differentiation [2]. Rare earth deposits are formed by different geological processes in deep-seated intrusive environment, magmatic–hydrothermal environment, and surface weathering environment. REE resources can be divided into two categories: primary deposits associated with igneous and hydrothermal processes and secondary deposits concentrated by sedimentary processes and weathering. Within these two groups, REE deposits can be further subdivided depending on their genetic, mineralogy and form of occurrence [3]. Two significant types of secondary deposits are the placer and ion-adsorption clays deposits. REEs ion-adsorption type deposits are formed by weathering of igneous rocks (typically granites) that contain particular REE-bearing minerals. Due to surface weathering, REE minerals are decomposed, and ionized REEs (REE^{3+}) are absorbed on clay minerals (normally kaolin and smectite groups). Ion-adsorption ores generally contain higher amount of HREEs and lower amounts of Th and U than other REE ores [4].

Promoting of intensive chemical weathering and breakdown of REE-bearing minerals by temperate and tropical climates (based on Koppen-Geiger climate classification [5]) suggest that those regions -with igneous bedrock- are potential zones for ion-adsorption clay REE resources. Southern China has the most developed ion-adsorption type deposits currently [6], however, several projects have been also known in the countries outside China in the recent years [7] such as: The Tantalus REE project in northern Madagascar, The Malawi REE project, The Serra Verde REE project in Brazil [8] as well as some other projects in Myanmar, Vietnam [9] and western Thailand [10].

Processing

Mineralogy is a key variable in determining the ease or difficulty, the cost of processing and extraction of REEs. Primary, hard rock deposits with the most abundant REE minerals such as bastnäsite, monazite, xenotime, loparite, parasite, and perhaps apatite is more likely to be economical compared with those deposits with eudialyte, allanite, or zircon [11,12]. Cause the latter group are more refractory and economic processing of REE from these minerals is not currently possible. In ion-adsorption ores, REEs are mostly present in ion-exchangeable phase of weathered granites, therefor, blasting, crushing, grinding, or mineral processing are not needed. REEs are easily extracted by ion exchange using diluted electrolyte solutions such as ammonium sulfate solution at ambient temperature [13-17].

There are different types of leaching methods have been utilized to extract REEs from ion-adsorption clays, such as heap, tank/pool, and in-situ leaching methods [18]. Previously, heap leaching was a commonly operated method which involves excavating minerals, placing them in a mound, and spraying them with solutions [17]. Tank/pool leaching involves placing the minerals into a tank/pool and immersed with solutions [18]. In-situ leach mining is now the dominating technology, given that there is less topsoil removed, the process can be performed on site, and the environmental impacts are reduced [19,20].

The schematic monovalent salt leaching extraction of REE^{3+} (Figure 1) suggested by recent studies [21] is:

$$[Al_2Si_2O_5(OH)_4]_m.nREE_{(s)}{}^{3+}+3nN_{H4}{}^{+}(aq) \leftrightarrow [Al_2Si_2O_5(OH)_4]_m.(NH_4{}^{+})_{3n(s)}{}^{3+}+nREE_{(aq)}{}^{3+}$$

In most cases, the rare earth leach liquor contains a significant amount of some impurities such as $(NH_4)_2SO_4$, Al^{3+}, Fe^{3+} and Ca^{2+}, accompanied by a small amount of Fe^{2+}, Pb^{2+} and Mn^{2+} [22]. The traditional process of extracting rare earth from such leach liquor is usually treated with chemical precipitation with oxalic acid or ammonium carbonate as precipitant, forming rare earth oxalate or carbonate, followed by washing and filtering and calcining into rare earth oxides [23,24]. However, the rare earth oxides need to be dissolved with hydrochloric acid before being separated by solvent extraction or used as materials for many rare earth users [25]. Although, they have been applied to industry practice, these precipitation technologies are complicated, time-and reagent-consuming, and the serious disadvantage is that these impurity ions cannot be removed, and the product purity is low, in addition, the rare earth yield is also low [26]. Recently, efficient non-precipitation techniques such as solvent extraction, ion exchange, and liquid membranes has been developed and applied in some mining sites [27].

Conclusion

Simple divalent electrolyte solution such as $(NH_4)_2SO_4$ are capable to extract the significant amounts of REEs absorbed on clay minerals such as kaolinite, halloysite and montmorillonite at room temperature cause of REEs accumulation in ion-exchangeable phase of ion-adsorption REE deposits. The leachate was then precipitate using oxalic acid or ammonium carbonate followed by a roasting stage. Obtained mixed REEs oxide contains a significant amount of impurities which purify by means of hydrochloric acid dissolution technique before applying further fine separation techniques. New researches are investigating on non-precipitation methods such as solvent extraction, ion-exchange and liquid membranes due to low product purity of precipitation methods.

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