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Leaching of rare earth elements from eudialyte concentrate by suppressing silica gel formation

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ABSTRACT

In this study a two stage hydrometallurgical treatment of eudialyte concentrate is presented, aiming on recovering rare earth elements and suppressing silica gel formation. The proposed treatment incorporates a preprocessing step called “Fuming”, which is the addition of an acidic solution to eudialyte concentrate heated at boiling temperatures, followed by the leaching step, where the treated concentrate is leached at ambient or low temperature. Fuming pretreatment with sulfuric or hydrochloric acid, and subsequently water leaching of the treated concentrate, resulted to >90% recovery of rare earths avoiding silica gel formation which is a major challenge to overcome during eudialyte dissolution. Scanning electron microscopy analysis, indicate that “Fuming”, transforms eudialyte into a mixture of metal salts and a siliceous secondary precipitate. Leaching of the treated concentrate dissolves soluble metal salts into solution whereas the secondary siliceous precipitate remains in the residue with the rest gangue minerals such as aegirine and feldspar. Advantages of the proposed treatment are low acid consumption, high rare earth recovery yields, avoidance of additives such as fluoride ions and avoidance of silica gel formation.

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1. Introduction

Rare-earth elements (REEs) consist of scandium, yttrium and lanthanides exhibiting similar chemical properties. Demand for rare earth elements has spiked in recent years due to their increasing usage as enablers in numerous high-technology applications, including a variety of renewable energy technologies like hybrid cars, wind turbines, solid oxide fuel cells and others (Nagaiyar Krishnamurthy, 2015). REE are essentials towards a cleaner, greener future (Binnemans et al., 2013), thus future demand of these metals is likely to increase rapidly. As such, the European Commission (ERECON, 2015; EU, 2014) and the US Department of Energy (US, 2011) labeled the REEs among the most critical raw materials in terms of supply risk and economic importance. The total REE production in 2014 estimated to be 110,000 tons with China being the dominant producer (Gambogi, 2015). Despite the great variation that exhibits in REE prices (Golev et al., 2014), the demand particularly for Nd and Dy, which are indispensable in the manufacture of high strength permanent magnets, is anticipated to increase by 700% and 2600% in the next 25 years, respectively (Alonso et al., 2012). Predominantly minerals used in

extractive metallurgy of REEs are monazite, bastnäsite and a ion-adsorption clays, processed mainly in China (Habashi, 2013; Nagaiyar Krishnamurthy, 2015). Among the several minerals that have been found to contain REEs and occur in potential economic deposits, an interesting resource of heavy rare earths (HREE), especially of Y and Dy, is the mineral group of Eudialyte. Eudialyte is a complex Na-Ca-zirconosilicate mineral containing economically attractive levels of Zr, Nb and REE whereas its geological alteration provides variable REE/Zr mineralization (Borst et al., 2016). Eudialyte chemistry has great compositional variability. Its structure involves silica-oxygen nine membered rings, Si₉O₂₇ and six membered calcium octahedra rings, Ca₆O₂₄ which are linked together with three membered Si₃O₉ rings and ZrO₆ octahedra into a zeolite like framework. In this framework vacancies are occupied by different metal ions with valences varying from +1 to +6 including rare earth elements (Johnsen et al., 2003; Rastsvetaeva, 2007; Schilling et al., 2011; Sørensen, 1992). The International Mineral Association (IMA) accepted formula for the eudialyte group (Johnsen et al., 2003) is: N₁₅[M(1)]₆[M(2)]₃[M(3)]₃[M(4)]₃[Si₂₄O₇₂]O₄X₂ where N = Na, Ca, K, Sr, REE, Ba, Mn, H₃O⁺; M (1) = Ca, Mn, REE, Na, Sr, Fe, M (2) = Fe, Mn, Na, Zr, Ta, Ti, K, Ba, H₃O⁺; M (3,4) = Si, Nb, Ti, W, Na, Z = Zr, Ti, Nb; O' = O, OH⁻, H₂O; X = H₂O, Cl⁻, F⁻, OH⁻, CO₃²⁻, SO₄²⁻, SiO₄⁴⁻. Currently vast amounts of eudialyte mineral deposits have been reported, some of which

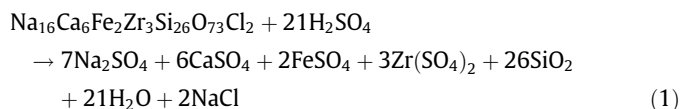
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located at Pajarito in New Mexico, Lovozero deposit in Kola Peninsula in Russia, Ilímaussaq complex in South Greenland, Mont Saint-Hilaire in Canada and Norra Kärr Alkaline Complex in Sweden. Particularly the Norra Kärr deposit, is a peralkaline intrusion hosting REE and zirconium mineralization with eudialyte being the major REE bearing mineral (Goodenough et al., 2016; Sadeghi et al., 2013; Sjöqvist et al., 2013). Due to the significant amounts of this particular mineral and its low radioactive content eudialyte mineral has the potential of becoming a primary REE resource. Therefore its metallurgical exploitation is essential towards diversifying and increasing REE supply.

1.1. Hydrometallurgical studies on eudialyte mineral

Despite being easily dissolved with acids, eudialyte processing can be very challenging as co-dissolved silica forms a gelatinous phase that is literally unfilterable. Hydrometallurgical treatment of eudialyte has been extensively studied from Russian teams by using strong mineral acids especially sulfuric acid directly or in a two stage decomposition process for recovery of rare earths and zirconium (Lebedev, 2003; Lebedev et al., 2003; Zakharov et al., 2011). Processing eudialyte ore concentrate involves high temperature leaching with concentrated sulfuric acid followed by dilution of the pulp with a sodium sulfate solution. In this process zirconium, aluminum, iron, and manganese are gained into solution whereas REE remain in the insoluble residue as double sulfate salts. The double sulfate salts are subsequently washed with water and recovered by converting their sulfates into nitrates or chlorides by calcium nitrate or chloride respectively, followed by neutralization to obtain rare earth hydroxides (Lebedev, 2003). The same team stated that direct sulfuric acid leaching of eudialyte under stoichiometry, leads to gel formation but under 100% excess, silica concentration in the pregnant solution found to be 5.5 g/L, whereas under 200% excess silica concentration reduced to 0.17 g/L. Moreover eudialyte decomposition with mineral acids has been studied indicating that sulfuric acids perform better in comparison to nitric and hydrochloric acid (Lebedev et al., 2003). Total decomposition using mineral acids could not be achieved due to the chemical variability and the presence of metals such as Ti and Nb found within eudialyte structure. Furthermore investigations on zirconium extraction from eudialyte indicated that a yield of more than 82% recovery cannot be exceeded due to the formation of acid resistant minerals covered with dense silica layers, which are impenetrable by acids (Zakharov et al., 2011). Additionally another study has shown that silica gel formation can be avoided by applying a combination of mechanochemical treatment and extraction with nitric acid/tri-n-butylphosphate (Chizhevskaya et al., 1994). Introduction of F⁻ ions during leaching, increase the efficiency of eudialyte decomposition (Dibrov et al., 2002; Litvinova and Chirkist, 2013). One of the advantages is an increase of zirconium recovery up to 98% due to the formation of zirconium strong complexes with fluoride ions. Another important influence of fluoride ion is a catalyzing effect on coagulation of silicic acid in the solution, which leads to reduction of silica content in the solution and provides a good filterable slurry. The processing route includes, leaching with 30 wt.% sulfuric acid at 90 °C and addition of fluoride ions in a form of NaF. The amount of fluoride ions is determined by the molar ratio of F:Zr = 6. The leaching products are a solution enriched with zirconium and heavy rare earths and a precipitate containing up to 95 wt.% of SiO₂ and light rare earths. The dissolution of eudialyte using sulfuric acid has been described in the following equation:



The main drawback of this process is that the total REE dissolution is much lower in comparison to the one in the pure sulfuric acid treatment due to precipitation of double sulfate salts of REE and Na (coming from the NaF addition). The solubility of REE sulfate salts in water decreases with the decrease of the atomic number of the REE except for Ce and Pr which have relatively higher solubility than the neighboring REE (Kul et al., 2008; Lokshin et al., 2005; Pietrelli et al., 2002). Therefore most of the light rare earths are precipitated whereas heavier rare earths remain in the solution. This leads to the scattering of the REE between the process products, especially in case of intermediate rare earths, such as Eu, Gd, Tb and Dy, which are partly precipitated and partly dissolved in the solution. Although in case of the HREE (such as Yb and Lu), the recovery rate is high, LREE recovery rate is low resulting to additional processing steps for their extraction from the formed precipitates. Another major drawback of this process is that the introduction of NaF requires additional control and safety measures as HF is formed.

Furthermore, in a patented process (Friedrich et al., 2016), silica was stabilized either by using concentrate HCl under dense pulp followed by dilution of the pulp with water or by a heating pretreatment of the eudialyte feeding material at 1000–1400 °C followed by quenching at concentrated HCl. From this patent, a two stage treatment of eudialyte was developed by applying dry digestion with concentrated HCl followed by dilution of the pulp with water (Voßenkaul et al., 2016). This treatment resulted to silica precipitation in a filterable form and transformed the REE values into soluble chlorite salts for further leaching. Insights on the mechanism of silica precipitation, where silica particles agglomerate under intense acidic HCl conditions have been provided (Gorrepati et al., 2010; Iler, 1979; Voßenkaul et al., 2016).

Silica sols stability depends on pH and ionic strength of the solution. (Iler, 1979). Maximum temporary stability with long gel time formation obtained at low pH around 1.5–3, and a minimum stability with rapid gel formation at pH 5–6. Also the presence of salts such as Na₂SO₄ lowers the ionic charge of particles leading to better stability on gel formation (Iler, 1979). Additionally the effect of pH and added salts in concentrated HCl solutions has shown that monomeric silica species consumed to form silica nanoparticles (Gorrepati et al., 2010). Therefore, during hydrometallurgical treatment of eudialyte, intense acidic conditions must be applied in order to avoid silica gel formation. It should be noted that a solution having Si concentration above 0.1 g/L is adequate on forming a metastable gel precipitate (Iler, 1979). The dry digestion process developed took advantage of the silica behavior in concentrate HCl to overcome silica gel formation (Voßenkaul et al., 2016).

In the present study a variation of the dry digestion process under a two stage treatment of eudialyte is described using 1–2 M solutions of sulfuric or hydrochloric acid added at a heated sample of Eudialyte concentrate at 100–110 °C, forming a sludge which progressively dries through water evaporation. The dried material is subsequently water leached at ambient temperature achieving high REE recoveries and allowing only a very small portion of Si to dissolve into the pregnant solution. Using the same chemistry but substituting high acid consumption with higher temperature processing, similar results can be achieved. The aim of the first process step is to suppress silica dissolution by forming a precipitate and metal salts which are easily leached out in the second step, resulting to a final low silica concentration solution. Final products obtained, are a solid residue of gangue material and an enriched REE solution for further purification.

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