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

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\textbf{A R T I C L E   I N F O}

Article history:
Received 6 September 2016
Revised 15 December 2016
Accepted 16 December 2016
Available online 29 December 2016

Keywords:
Eudialyte
Rare earth elements
Silica gel
Leaching
Fuming

\textbf{A B S T R A C T}

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). 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, Si\textsubscript{9}O\textsubscript{27} and six membered calcium octahedra rings, Ca\textsubscript{6}O\textsubscript{24} which are linked together with three membered Si\textsubscript{3}O\textsubscript{9} rings and SiO\textsubscript{2} and six membered calcium octahedra rings, Ca\textsubscript{6}O\textsubscript{24} which are linked together with three membered Si\textsubscript{3}O\textsubscript{9} rings and ZrO\textsubscript{6} 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: N\textsubscript{15}[M(1)]\textsubscript{6}[M(2)]\textsubscript{3}[M(3)][M(4)]\textsubscript{12}Si\textsubscript{24}O\textsubscript{72}O'\textsubscript{4}X\textsubscript{2} where N = Na, Ca, K, Sr, REE, Ba, Mn, H\textsubscript{3}O\textsuperscript{+} M (1) = Ca, Mn, REE, Na, Sr, Fe, M (2) = Fe, Mn, Na, Zr, Ta, Ti, K, Ba, H\textsubscript{2}O\textsuperscript{+}, M (3,4) = Si, Nb, Ti, W, Na, Z = Zr, Ti, Nb; O' = O, OH\textsuperscript{−}, H\textsubscript{2}O; X = H\textsubscript{2}O, Cl\textsuperscript{−}, F\textsuperscript{−}, OH\textsuperscript{−}, CO\textsubscript{3}\textsuperscript{2−}, SO\textsubscript{4}\textsuperscript{2−}, SiO\textsubscript{4}\textsuperscript{2−}. Currently vast amounts of eudialyte mineral deposits have been reported, some of which

http://dx.doi.org/10.1016/j.mineng.2016.12.011
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located at Pajarito in New Mexico, Lovozero deposit in Kola Peninsula in Russia, Illinaussaq 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 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 fluorde 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 dilution 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:

$$\text{Na}_{11} \text{Ca}_{8} \text{Fe}_{2} \text{Zr}_{3} \text{Si}_{6} \text{O}_{27} \text{Cl}_{2} + 21 \text{H}_{2} \text{SO}_{4}$$

$$\rightarrow 7 \text{Na}_{2} \text{SO}_{4} + 6 \text{CaSO}_{4} + 2 \text{FeSO}_{4} + 3 \text{Zr} (\text{SO}_{4})_{2} + 26 \text{SiO}_{2}$$

$$+ 21 \text{H}_{2} \text{O} + 2 \text{NaCl} \quad (1)$$

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 concentrated 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.
2. Materials and methods

Norra Kärr middlings concentrate was provided by Tasman Ltd from preliminary magnetic beneficiation studies of Norra Kärr ore. The samples used were received in a powder form, without further crushing. Sulfuric and hydrochloric acid reagent grades were 95–98% w/w and 37% w/w respectively. Deionized water was used in all tests. Mineralogical characterization was made by a Bruker D8 focus X-ray diffractometer and the microstructure of the solid materials was studied in a Scanning Electron Microscope - Jeol 6380 LV. The grain size was measured with a MALVERN laser particle size analyzer. The solid samples were prepared for chemical analysis by the fusion method i.e. heating at 1000 °C the solid samples with a mixture of LiBO$_4$/KNO$_3$, followed by direct nitric acid dissolution. Metal concentrations into solution were measured by inductively coupled plasma mass spectroscopy (ICP-MS) and atomic absorption spectroscopy (AAS).

2.1. Fuming procedure and leaching

In the fuming procedure 2M of H$_2$SO$_4$ or HCl acid solution is added drop wise to an amount of heated ore concentrate, placed in an evaporating dish, at 100–110 °C. Different amount of acid (solid: liquid ratios) is applied resulting to sludge formation which progressively dries. Once the drying is completed the treated concentrate is left to cool down and subsequently leached with various leaching agents (water, 1M and 2M HCl solutions) at ambient temperature or at 30 °C in the case of HCl, under vigorous stirring in magnetic stirring plates, applying various retention time and S/L (wt/v or g/ml) ratio. After filtration, the solution obtained is chemically analyzed.

3. Results and discussion

3.1. Norra Kärr middlings concentrate characterization

Chemical analysis of the middlings concentrate can be seen in Table 1, particularly REE concentration can be seen in Fig. 1:

Table 1
Chemical analysis of Norra Kärr middlings concentrate.

<table>
<thead>
<tr>
<th>Elements</th>
<th>SiO$_2$</th>
<th>Fe$_2$O$_3$</th>
<th>Na$_2$O</th>
<th>Al$_2$O$_3$</th>
<th>CaO</th>
<th>K$_2$O</th>
<th>TREO</th>
<th>ZrO$_2$</th>
<th>LOI</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration wt.%</td>
<td>50%</td>
<td>14%</td>
<td>12%</td>
<td>9%</td>
<td>2%</td>
<td>1%</td>
<td>1.65%</td>
<td>3%</td>
<td>1.8%</td>
<td>5.5%</td>
</tr>
</tbody>
</table>

REE account for 1.65% of the middlings concentrate and among them, 49% are heavy REE (Y, Eu-Lu) constituting the Norra Kärr middlings concentrate a significant HREE resource.

Mineralogical analysis identified minerals such as aegirine (acmite) [NaFeSi$_2$O$_6$], albite[NaAlSi$_3$O$_8$], microcline[KAlSi$_3$O$_8$], eudialyte [(Na,K)$_{16}$(Fe,Mn)$_2$Ca$_6$(Si,Al)$_2$Zr$_2$Si$_4$O$_7$(OH,Cl)$_2$]$\cdot$H$_2$O] and natrolite [Na$_2$Al$_2$Si$_3$O$_10$$\cdot$2(H$_2$O)]. SEM images of the middlings concentrate indicate the minerals identified by XRD (Fig. 2). Individual grains of eudialyte were observed together with minerals of aegirine and feldspars. Particle size distribution indicate that 90% of particles are smaller than 150 μm having a mean size of $d_{50}$:63 μm.

3.2. Sulfuric acid fuming

Preliminary results on leaching eudialyte concentrate with 2M H$_2$SO$_4$ at ambient temperature, resulted to an unfilterable sludge due to gel formation (Fig. 3) whereas leaching with concentrated H$_2$SO$_4$ at 110 °C resulted to REE recovery <14%.

Fuming pretreatment was conducted by adding 2M sulfuric acid solution dropwise to the heated ore concentrate at 110 °C (Fig. 4). Initially a sludge is formed which progressively dries out due to water vaporization. The resulting treated concentrate is subsequently leached with water at ambient temperature under vigorous stirring using different S/L ratios and retention time. Total REE recoveries (average recoveries of La through Lu) and silica concentration into solution through the two stage process are shown in Table 2. No distinction between light and heavy REE recoveries were observed at the studied conditions.

On a two stage treatment of eudialyte using H$_2$SO$_4$ fuming, almost 90% of REE recovery achieved at 24 h retention time, whereas Si concentration of the final solution measured to be 100–130 mg/L which is the threshold of metastable Si precipitation (Iler, 1979). However, by reducing significantly retention time during water leaching resulted to similar REE recoveries, providing lower concentration of Si into solution. It was observed that REE dissolution after H$_2$SO$_4$ fuming pretreatment occurs almost instantaneously, as 1 min retention time during water leaching resulted...
to 65% REE recovery, whereas 30 min are needed to reach 90% REE recoveries (Fig. 5).

The effect of the S/L ratio during fuming pretreatment, indicate that increasing S/L ratio resulted in decreased REE recoveries, whereas decreasing S/L ratio at 1/4 is sufficient to achieve >90% of REE recovery having in all cases Si concentration <30 mg/L (Table 2). Moreover, studying the effect of the S/L ratio during water leaching of the treated concentrate, it was found that for S/L ratios within the range of 1/20–1/3 no appreciable differences in the dissolution behavior of LREE and HREE was observed while at the highest studied S/L ratio 1/2, LREE recovery was substantially lower in comparison to the HREE (Fig. 6). This is attributed to the different solubility of REE sulfate salts.

Addition of sulfuric acid solution to a heated amount of eudialyte concentrate results to a simultaneous rapid dissolution of eudialyte and evaporation of water, leading to the formation of a mixture of metal sulfate salts and a secondary siliceous precipitate. Temperature of 110 °C is suitable for water evaporation while is significantly lower from the concentrated sulfuric acid baking processing temperature (200–500 °C) used in REE extractive metallurgy. SEM Images on the treated concentrate after fuming with sulfuric acid can be seen in Fig. 7.

The grains examined (Fig. 7) consist of small needle-like crystals referring mostly to aluminum and sodium sulfate salts whereas also calcium sulfate and cerium sulfate salts were detected. The sulfate salts form a thin layer on the surface of mineral particles like feldspars and aegirine, which remain intact from this process. Moreover, SEM image of the residue obtained after water leaching of the treated concentrate can be seen in Fig. 8. Grains with high Si content (Fig. 8) were found in the residue after water leaching indicating that the siliceous precipitate formed during fuming, remains as an easily filtrarable form. SEM analysis indicate that during the two stage treatment eudialyte mineral dissolves forming soluble REE sulfate salts and a filtrarable secondary siliceous precipitate. The final residue from the two stage treatment, consist mainly of aegirine and feldspars whereas minerals like natrolite and eudialyte are highly affected during acid treatment.

### 3.3. Hydrochloric acid fuming

During leaching of the eudialyte middlings concentrate with HCl at ambient temperature, it is very difficult to distinguish if there have been changes in the solution. The easiest way to notice that solution has converted into a colloid is by filtration. When gel or colloid is formed, filterability of the slurry ranges from very slow to non filtrarable. Solid liquid separation even of a small amount of slurry (sampling of around 20 ml) cannot be completed (using gravity filtration or vacuum pump). The slurry has creamy gel-like homogeneous consistency. Another opportunity to detect changes is to stop mixing of the slurry through stirring. After several minutes solid settles on the bottom of the beaker and, in case of gelatinization, a cloudy layer between precipitated solid and leaching solution can be observed (Fig. 9).

Once mixing has been stopped, formed gel hinders further mixing of the slurry. When electro stirrer is started again it cannot rotate properly, the shaft of the stirrer vibrates while blades are trying to destroy the formed network. However, in case of short pauses during mixing it is possible to continue mixing. Filterability of other samples without formation of colloid was good, especially when warm solution was filtrated. Yet when solid residue was washed with deionized water filtration was slower, probably due to the hydration of the silica in the residue and formation of silicic acid which causes gelatinization.

Fuming pretreatment of Norra Kärr middlings concentrate with HCl followed by leaching (Fig. 10) can result to REE recoveries >95% with negligible dissolution of Si. Summary of results from the 2 stage treatment of Norra Kärr middlings concentrate with HCl can be seen in Table 3.

It can be seen from Table 3, that the best leaching efficiency of REE (97%) for minimal silica concentration into solution (19 mg/l),
was obtained at conditions of 2M HCl fuming at S/L ratio 1/5 followed by water leaching of the treated ore at S/L ratio 1/10 at 30°C. It was found that the 1st stage of HCl fuming pretreatment has major effect on REE recovery, whereas the subsequent HCl leaching of the treated ore after fuming had no effect on REE recovery compared to water leaching. The results showed that

Table 2
Summary of the experimental results for the two stages leaching of the Nora Kärr middlings concentrate. 1st stage is H₂SO₄ fuming and 2nd stage is water leaching of the treated concentrate.

<table>
<thead>
<tr>
<th>Exp. no.</th>
<th>Leaching solution</th>
<th>Concentration of acid</th>
<th>T/°C</th>
<th>Time</th>
<th>S:L</th>
<th>REE% recovery</th>
<th>Si mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp 1:</td>
<td>H₂SO₄ fuming</td>
<td>2M</td>
<td>110</td>
<td>1 h</td>
<td>1:4</td>
<td>87.5</td>
<td>128</td>
</tr>
<tr>
<td>1</td>
<td>H₂O leaching</td>
<td></td>
<td></td>
<td>24 h</td>
<td>1:20</td>
<td>91.8</td>
<td>115</td>
</tr>
<tr>
<td>2</td>
<td>H₂O leaching</td>
<td></td>
<td></td>
<td>24 h</td>
<td>1:10</td>
<td>87.8</td>
<td>112</td>
</tr>
<tr>
<td>3</td>
<td>H₂O leaching</td>
<td></td>
<td></td>
<td>24 h</td>
<td>1:5</td>
<td>87.8</td>
<td>112</td>
</tr>
<tr>
<td>Exp 2:</td>
<td>H₂SO₄ fuming</td>
<td>2M</td>
<td>110</td>
<td>1 h</td>
<td>1:4</td>
<td>64.3</td>
<td>6</td>
</tr>
<tr>
<td>1</td>
<td>H₂O leaching</td>
<td></td>
<td></td>
<td>1 min</td>
<td>1:20</td>
<td>79</td>
<td>13</td>
</tr>
<tr>
<td>2</td>
<td>H₂O leaching</td>
<td></td>
<td></td>
<td>15 min</td>
<td>1:20</td>
<td>91.2</td>
<td>28</td>
</tr>
<tr>
<td>3</td>
<td>H₂O leaching</td>
<td></td>
<td></td>
<td>30 min</td>
<td>1:20</td>
<td>87</td>
<td>15</td>
</tr>
<tr>
<td>Exp 3:</td>
<td>H₂SO₄ fuming</td>
<td>2M</td>
<td>110</td>
<td>1 h</td>
<td>1:4</td>
<td>84.03</td>
<td>43</td>
</tr>
<tr>
<td>1</td>
<td>H₂O leaching</td>
<td></td>
<td></td>
<td>30 min</td>
<td>1:10</td>
<td>77.85</td>
<td>70</td>
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<tr>
<td>2</td>
<td>H₂O leaching</td>
<td></td>
<td></td>
<td>30 min</td>
<td>1:3</td>
<td>74.92</td>
<td>86</td>
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<tr>
<td>3</td>
<td>H₂O leaching</td>
<td></td>
<td></td>
<td>30 min</td>
<td>1:2</td>
<td>59.97</td>
<td>156</td>
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<tr>
<td>4</td>
<td>H₂O leaching</td>
<td></td>
<td></td>
<td>30 min</td>
<td>1:2</td>
<td>59.97</td>
<td>156</td>
</tr>
<tr>
<td>Exp 4:</td>
<td>H₂O fuming</td>
<td></td>
<td></td>
<td>30 min</td>
<td>1:20</td>
<td>22.9</td>
<td>24</td>
</tr>
<tr>
<td>1</td>
<td>H₂SO₄ fuming</td>
<td>2M</td>
<td>110</td>
<td>1 h</td>
<td>2:1</td>
<td>52.6</td>
<td>19</td>
</tr>
<tr>
<td>2</td>
<td>H₂SO₄ fuming</td>
<td>2M</td>
<td>110</td>
<td>1 h</td>
<td>1:1</td>
<td>82.9</td>
<td>18</td>
</tr>
<tr>
<td>3</td>
<td>H₂SO₄ fuming</td>
<td>2M</td>
<td>110</td>
<td>1 h</td>
<td>1:3</td>
<td>78.8</td>
<td>21</td>
</tr>
<tr>
<td>4</td>
<td>H₂SO₄ fuming</td>
<td>2M</td>
<td>110</td>
<td>1 h</td>
<td>1:4</td>
<td>91.2</td>
<td>28</td>
</tr>
</tbody>
</table>

Fig. 5. REE recoveries and Si concentration. Kinetics of water leaching on the treated concentrate at S/L 1:20. Retention time used, 1, 15, 30 min and 24 h.

Fig. 6. LREE/HREE/Zr recoveries during water leaching of the fumed concentrate (H₂SO₄ 2M, 110°C, 1 h, S/L = 1:4) at S/L ratio range from 1:20 to 1:2 retention time 30 min at ambient temperature.

Fig. 7. SEM images of treated concentrate after fuming pretreatment with H₂SO₄. Needle like grains of sulfate salts appears on the surface of a feldspar.
the process is more efficient, in terms of higher REE recovery and decreasing Si concentration, when fuming is performed under low S/L ratios and more concentrated HCl acid solutions. Under the exactly opposite conditions (fuming with less concentrated HCl at high S/L ratios and dissolution with HCl acid solutions) Si concentration into solution exceeds substantially the threshold of 100 mg/L for metastable Si gel formation, reaching values as high as 657 mg/L.

SEM observation of the treated concentrate with HCl revealed the formation of a mixture of chloride crystals and a siliceous precipitate surrounding crystals of aegirine that remain intact from the HCl fuming treatment (Fig. 11). Siliceous precipitate appears in a form of clusters of silica mixed with metal chloride salts akin to sulfuric acid treatment. It appears that feldspars and aegirine remain intact during HCl two stage process.

3.4. Overall metal recoveries at most efficient process parameters

The most efficient process parameters during thermal pretreatment were found to be 2M HCl solution at 100 °C, S/L ratio of 1/5 followed by subsequent water leaching at S/L 1/10 at 30 °C, and 2M H₂SO₄ solution at 110 °C, S/L ratio 1/4, followed by water leaching at ambient temperature, S/L ratio 1/20. Fig. 12 represents the individual REE metal recoveries and the rest of the metals recoveries for both acidic treatments at leaching conditions described above.
Si recovery was found to be negligible whereas moderate recoveries obtained for the rest of the metals (Fig. 12). The two-stage treatment can be applied using either sulfuric or hydrochloric acid resulting in almost similar metal recoveries. Particularly, Zr found to have higher recovery yield in H₂SO₄ treatment compared to HCl. Most of the metal impurities originate from eudialyte and natrolite minerals dissolution that are present in the middlings ore concentrate. The resulting final leachate obtained after water leaching of the treated concentrate had a pH value of 0.8–1 and can be further treated for REE purification. Acid addition on leaching conditions that provide the highest REE recovery found to be 0.98 g HCl (37% w/w) or 0.81 g H₂SO₄ (95–98% w/w) per g of middlings ore concentrate.

Compared to direct leaching, advantages of fuming with acid are high REE recovery rate, no silica gel formation and no additional additives for suppressing silica gel. Moreover, in contrast to sulfuric acid, hydrochloric acid can be easily recovered, especially during the fuming treatment, where it can be collected directly after evaporation. On the other hand, such a two-stage process is complicated and more sophisticated, acid corrosion resistant equipment is required. According to the proposed two-stage treatment, the following conceptual flowsheet on Eudialyte hydrometallurgical processing is developed (Fig. 13).

### 4. Conclusion

Leaching REE from eudialyte mineral by suppressing silica gel formation is crucial for its effective hydrometallurgical treatment.

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**Table 3**

Summary of the experiments and factors studied on two-stage leaching of Nora Kärr middlings concentrate with HCl. 1st stage is HCl fuming and 2nd stage is water/acid leaching of the treated concentrate.

<table>
<thead>
<tr>
<th>Exp. no.</th>
<th>Leaching solution</th>
<th>Concentration of acid</th>
<th>T/C</th>
<th>Time (h)</th>
<th>S:L</th>
<th>REE% recovery</th>
<th>Si mg/L</th>
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At this study a two stage treatment of Norra Kärr middlings concentrate resulted to >90% REE recovery providing a pregnant solution with low Si concentration. The proposed treatment dissolves eudialyte structure forming soluble metal salts and a secondary siliceous precipitate, leaving the remaining gangue minerals such as aegirine and feldspars intact during the two stage treatment. Upon fuming pretreatment silica precipitates in an insoluble form generating a filtrable sludge in the subsequent water leaching step. The most efficient process parameters during the proposed two stage treatment were found to be:

- 2M HCl solution addition to a heated concentrate at 100 °C S/L ratio of 1/5 followed by water leaching of the treated concentrate at 30 °C, S/L 1/10 for 1 hour, resulting to 97% REE recovery.
- 2M H2SO4 solution addition to a heated concentrate at 110 °C, S/L ratio of 1/4 followed by water leaching of the treated concentrate at ambient temperature, S/L ratio 1/20 for 30 min, resulting to 91% REE recovery.

The resulting solution can be further treated for REE purification and separation by known methods. The proposed process flow-sheet is capable of achieving high REE recovery yields with negligible Si dissolution avoiding silica gel formation and minimizing the reagents input in the process. Successful hydrometallurgical treatment of this REE bearing silicate mineral, can have major impact for its future exploitation as a primary REE resource.

Acknowledgments

“This research has received funding from the European Community’s Seventh Framework Programme ([FP7/2007–2013]) under grant agreement n°309373. This publication reflects only the author’s view, exemepting the Community from any liability". Project web site: www.eurare.eu.

References