

Hydrometallurgical Processing of Eudialyte Bearing Concentrates to Recover Rare Earth Elements Via Low-Temperature Dry Digestion to Prevent the Silica Gel Formation

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Abstract Eudialyte belongs to the group of cyclosilicate minerals and has a significant content of valuable heavy rare earth elements. In comparison to conventional ores like bastnaesite or monazite, the content of radioactive elements like thorium and uranium is quite low; thus, it is an ideal source for the sustainable extraction of rare earth elements (REE). In this way, a further processing or a disposal, direct or after using phase, of radioactive elements could be minimized. The cyclosilicate structure facilitates the easy decomposition of eudialyte by mineral acids. On one hand, this is a positive effect to lixiviate the REEs but leads to an excess liberation of silicon in the water-based system which involves the risk of silica gel formation. Within this research project, a hydrometallurgical pre-treatment is developed to decompose the eudialyte for the extraction of REEs and to stabilize the silicon in the residue during the following leaching step.

Keywords Eudialyte · Rare earth element · Silica gel · Dry digestion · Aging · Fuming · Leaching · Hydrometallurgy

Background and Theory of Eudialyte Processing

With an expected rare earth mining market share of about 85 % (2015) [1], China has a virtual monopoly in rare earth recovery. This results in a great dependence on the availability, whereby the supply of rare earth elements (REE) is considered critically. Export restrictions and resulting price fluctuations (e.g., 2011) [2] indicate the market instability. In addition, the illegal REE mining in China is estimated to be about 40 % [3] which leads to considerable environmental risks because of uncontrolled contamination with radioactive elements such as thorium and uranium, by environmentally critical gases such as HF, SO₃, and SiF₄ via acid roasting processes [4] and contamination of ground and surface water from heavy metals and ammonium [5]. Environmental legislation limits the pollution of the REE industry [6]. However, export restrictions and resulting high prices increase the lucrativeness of the uncontrollable and illegal REE mining activities. An independent supply chain could weaken the monopoly, therefore minimizing the dependency on China making illegal mining and export of REE unattractive.

Currently, REE are required for many high-tech applications like batteries, magnets, or catalysts. Future forecasts indicate an above-average increase of NdFeB magnets compared to other REE applications in particular for electric vehicles and wind power generation [2]. Thus, neodymium, praseodymium, and dysprosium are in demand in future particularly. Due to the association of REE, no corresponding deposit is known exclusively for these elements which leads to a balance problem of high- and low-demanded REE. One solution is the diversification of used deposits with various REE ratios [7]. However, there are independent recovery opportunities at Mountain Pass (USA) and Mount Weld (Australia) for the light rare

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earth elements (LREE) such as neodymium and praseodymium. Accordingly, deposits are needed rich in heavy rare earth elements (HREE) such as dysprosium.

The HREE are mined exclusively from ion adsorption clays (IAC) in Southern China. Because of their conditions of formation, they are mainly found in (sub)tropical countries. Similar types are identified in Madagascar and Laos [8]. To protect (sub)tropical landscapes, these sources should be avoided. In addition to IAC, another considered source for heavy REE is eudialyte leading ores. With occurrences particularly in Europe, they represent a potential resource [8, 9].

State of the Art of Eudialyte Processing

Eudialyte is a sodium-rich zirconium-silicate mineral with various contents of substitution elements like Ca, Fe, Mn, Sr, Nb, Ta, K, Ti, H, W, and REE [10, 11]. Globally, 199 occurrences with eudialyte mineralisation are listed at mindat.org (Nov. 2015) [12]. However, most of these occurrences are not evaluated in detail. The REE are only substitution elements in the mineral structure with various contents of < 0.5 up to 10 % REO equivalent [13]. This and the low characterization of eudialyte occurrences lead to nine deposits, four of them are located in Europe (the Ilimaussaq Complex (Greenland), Norra Kärr (Sweden), the Khibina, and Lovozero Complex (Russia)) [14]. Within these deposits, the REE content is listed at 1–3 % with a HREE ratio of partly over 50 % [15]. Additionally, due to its multielement character, eudialyte contains further valuable metals like Zr (7.5–9.7 %), Nb (0.1–1.1 %), Ta (<0.1 %), or Mn (0.9–3.2 %) [15, 16]. Consequently, eudialyte could be an economical resource for metal extraction.

Up to now, no extraction processes are known on an industrial scale. The only developed deposits with evaluated eudialyte mineralization are the adjacent Khibina and Lovozero geological complexes in Russia. However, the ore is mined from the Lovozersky Mine to obtain a loparite concentrate for Nb, Ta, and REE recovery by the Solikamsk magnesium works [17]. According to Zaitsev [18], the processing of eudialyte is just one option to increase further REE capacities. As a result, information about extraction processes is based on research and development and feasibility studies.

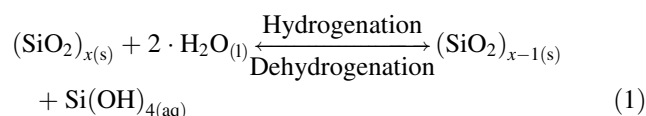
First, easy decomposition behaviors of eudialyte using mineral acids were reported in 1819 by F. Stromeyer [19]. Further publications are mainly from Russia because of its investigations after the disintegration of the Soviet Union and the resulting loss of its Zr, Nb, and Ta resources. They confirm the easy decomposition of eudialyte and resulting silica gel formation [20–22]. After the Chinese REE export restrictions and resulting price peak, various new projects

started to investigate alternative resources like eudialyte. But all developed processes are limited or do not explain the prevention of a silica gel formation.

Concerning this, Motov [23] suggested the dehydration of the silica gel suspension after eudialyte decomposition and subsequent washing of the dried mass to extract the valuable metals. Such a process would need immense thermal energy for the dehydration of the entire mass. As a more applicable alternative, Lebedev [22] described a controlled dosage of eudialyte in a concentrated, hot acid solution. A similar process has been indicated for the Norra Kärr material by Tasman Metals Limited. Limitations are the permanent risk of a silica gel formation leading to a process stop and the restricted process rate of eudialyte limiting the productivity. A more stable process for eudialyte bearing minerals is the acid roasting process for monazite or bastnaesite processing. It is tested by Alkane Resources LTD for its Dubbo Zirconia Project (Australia) [24, 25]. However, for the easy eudialyte decomposition behavior such a thermal process is not needed. To investigate a suitable recovery process, a theoretical background of silica gel formation will be given.

Mechanism of Silica Gel Formation

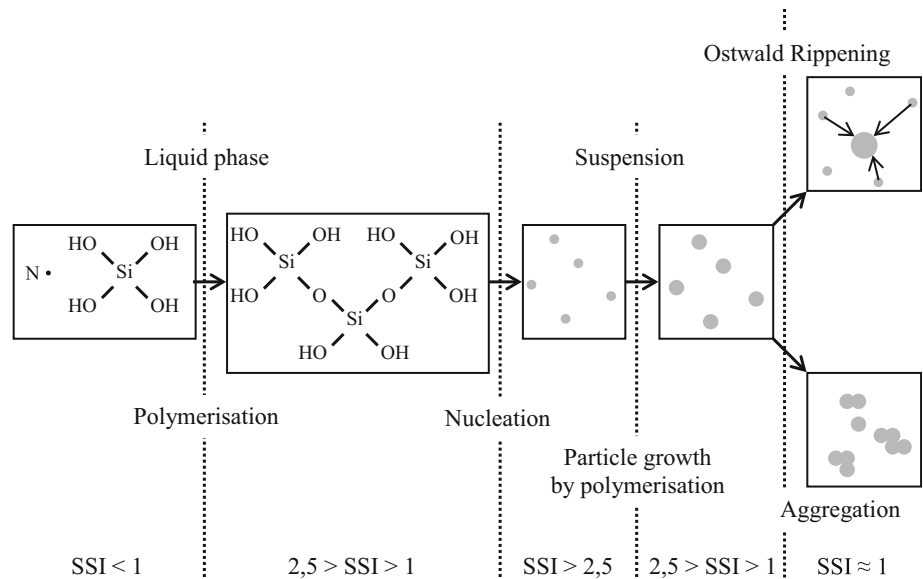
Silica has a low solubility in aqueous systems. Under standard conditions (25 °C, 1013 bar), crystalline silica (e.g., quartz) has a solubility of about 6 ppm and amorphous high porous silica only 100–120 ppm SiO₂ equivalent. In water based systems, at low concentrations, the silicon is present as silica (Formula 1) [26].



First, precipitations can be observed after a oversaturation of more than 100–300 ppm of SiO₂ equivalent in solution [26]. In this context, a silicon saturation index (SSI) can be defined to classify the different steps of silicon colloid formation (Fig. 1). The SSI defines the ratio of dissolved silicon to the maximum silicon solubility [27]. One of the main processes to form colloids are the polymerisation via condensation of Si(OH)₄ molecules forming a broad network. After the formation of a colloidal solution and at SSI of about one, the colloids are growing further via Ostwald Ripening or they start to aggregate. Especially, the aggregation process is relevant for the eudialyte because of the high ionic strength in solution [27]. Therefore, four different aggregation mechanisms are described by Iler [26]:

1. *Gelation of the suspension* Formation of a broad network of silica colloids over the whole volume without any concentration gradient.

Fig. 1 Formation mechanisms of silica colloids depending on silica saturation index (SSI) [27]



2. *Coagulation* Formation of clusters of tightly packed colloids which sediment because of gravitation.
3. *Flocculation* Formation and sedimentation of clusters using an additional flocculating agent.
4. *Coacervation* Enclosing of the colloids to minimize the hydrophilic and forming an immiscible phase.

The way of the colloid formation and precipitation is a complex process and depending on parameters like oversaturation of silicon, pH-value, temperature, and the ionic strength of the solution [26–28]. In this context, the suggested process to prevent a silica gel formation via limited eudialyte addition (Lebedev [22] and Tasman Metals [29]) describes a method to limit a silicon oversaturation. This lowers an uncontrollable nucleation over the whole solution and limits the number of colloids. Furthermore, the silicon tends to form sedimentable and filterable particles.

Innovative Approach of Silica Gel Prevention Via Dry Digestion Process

Eudialyte is an easy decomposable mineral. This leads to high silicon concentration in solution which starts to precipitate spontaneously to form a gelatinous mass of the whole suspension. A limited addition of eudialyte limits the strength of the high kinetics. Thermal decompositions of the mineral structures are not needed in terms of the easy linearization of the eudialyte mineral. In fact, the benefits of a eudialyte processing are not used properly.

In this context, the idea is to decompose the eudialyte and to liberate the value metals via a two-step process. The first step is a “dry digestion” via a mineral acid. The acid should be added to form a pasty mass to decompose the eudialyte. This leads to very high silicon liberation, at high

ionic strengths and pH-values which fastens the silicon precipitation additionally. Because of the limited available volume, the silicon precipitate should grow to bigger particles. After the precipitation took place, the valuable metals can be washed out easily while the precipitated silicon keeps in its stable residue phase [30–32].

Experimental Part

The aim of the experimental part is the verification of the theoretical approach of silica gel prevention via eudialyte processing with high recovery rates of valuable metals (REE, Mn, Zr, Nb, and Ta). Therefore, three different eudialyte concentrates are available.

Selected decomposition media are hydrochloric and sulfuric acid based on state of the art leaching media for REE extraction. Further process parameters are as follows:

- Amount of acid needed for an eudialyte decomposition.
- Volume of acid needed for a complete wetting of the concentrate.
- Needed reaction time for decomposition and silicon stabilization.

The decomposition temperature is expected from literature to be room temperature. The washing of the valuable metal sulfates or chlorides is expected to be water.

Material Characterization

The used concentrates are coming from the Khibina/Lovozero Complex (Russia), Norra Kärr (Sweden), and Ilimaussaq Complex (Greenland). The Khibina/Lovozero

material was a handpicked ore and used directly for this study. The material coming from Sweden was a handpicked ore as well, but first concentrated via electrostatic and magnetic separators at the Unit of Mineral Processing (AMR, RWTH Aachen University). The Ilimaussaq concentrate was delivered as a flotation concentrate. They were ground at a P100 value of $<90\text{ }\mu\text{m}$ ($P_{50} < 17\text{--}19\text{ }\mu\text{m}$) before used in experiments and differ in their chemical (Table 1) and mineralogical composition (Fig. 3). The matrix elements are analyzed via XRF at the Institute of Process Metallurgy and Metal Recycling (IME, RWTH Aachen University) and externally by ALS Minerals Division. The trace elements are analyzed via ICP-MS by ALS Minerals Division.

The mineral composition was determined by QEMSCAN (Quantitative Evaluation of Materials by SCANNing electron microscopy) [33] at the Institute of Mineralogy & Economic Geology (IML, RWTH Aachen University). This analytical method enables an X-ray-based quantitative chemical mapping of the sample material and consists of a scanning electron microscope in combination with two energy-dispersive X-ray spectrometers. The field scan mode was applied for data collection, which is an end-to-end chemical mapping of a defined area and resolution of the sample surface. More than 40 elements were chosen for measurement due to prior conducted chemical analysis. X-ray data were acquired every $5\text{ }\mu\text{m}$ (point spacing), collecting 2000-count EDX spectra on each analysis with an acceleration voltage of 25 keV and a specimen current of approximately 10 nA. Collected raw data were assigned into suitable phases by user defined “must have” and “may

have” elements with a specific concentration range for each phase using idiscover© software. During post-processing, the software verifies for every pixel, if the conditions are complied with the user definition and allocates the pixels into the appropriate phases by a “true” or “false” validation. The accuracy of phase boundaries was verified by overlapping BSE images. After this, more than 30 different mineral species could be identified. For a better overview, phases with an amount less than 2 wt% and of minor interest are subsumed to others. In the same manner, the feldspar minerals (albite ($\text{Na}[\text{AlSi}_3\text{O}_8]$), orthoclase ($\text{K}[\text{AlSi}_3\text{O}_8]$), sanidine ($(\text{K},\text{Na})[(\text{Si},\text{Al})_4\text{O}_8]$), and nepheline ($(\text{Na},\text{K})[\text{AlSiO}_4]$) are subsumed to the category “feldspars.” The accuracy of the evaluation is examined by similar structures of the complex minerals in the BSE and the false color image (Fig. 2). The rough qualitative major element composition of identified phases is presented in Table 2.

The results of the phase quantification are summarized in Fig. 3. The chemical and mineralogical composition displays the possible high heterogeneity of eudialyte. For example, the Norra Kärr concentrate comprises the lowest eudialyte content with a high REE concentration. This is based on the behavior of eudialyte to implement a high variability of substitution elements in the crystal structure already pointed out in chapter 1.1.

Fundamental Research Experiments

The fundamental research experiments are carried out in glass beaker using 25 g of one concentrate (Khibina/

Table 1 Elemental composition of used eudialyte concentrates

Locality	Concentration in mass%		
	Khibina/Lovozero complex	Norra Kärr	Ilimaussaq complex
Si	22.35	25.13	22.81
Na	10.50	7.11	10.22
Al	5.80	7.71	3.35
Ca	4.26	2.43	5.81
Fe	4.89	3.22	5.70
K	2.74	2.87	0.84
Zr	4.38	2.64	6.48
Mn	0.46	0.47	0.39
Nb	0.21	0.20	0.6550
Th	–	0.0026	0.0066
U	–	0.0032	0.0035
$\sum\text{REE}$	0.31	1.67	1.73
(LREE) ^a	66.01	48.6	73.12
(HREE) ^b	33.99	51.4	26.44

^a Ratio of light rare earth elements (Lanthanum–Gadolinium)

^b Ratio of heavy rare earth elements (Terbium–Lutetium and Yttrium)

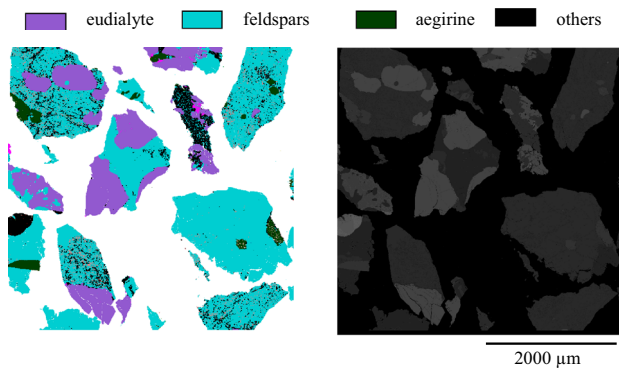






Fig. 2 QEMSCAN analysis of initial material (Ilimaussaq complex) before grinding (left: false color image after evaluation, right: initial BSE-image)

Lovozero, Norra Kärr or Ilimaussaq). For the decomposition, 50 mL of acid solution (HCl or H₂SO₄) with varying concentration (2–10 mol/L) was added. The liquid to solid ratio is based on empirical experiments for wetting the whole concentrate. The pasty mass was left standing for different reaction times (0–240 min) without mixing. To wash out the valuable metals, 100 mL deionized water was added. Only for one experiment with H₂SO₄ 250 mL (leaching water factor: 2.5) was used. After 10 min of mixing, the whole suspension was filtered and the residue washed again using 150 mL of deionized water. The pregnant solutions and washing waters were analyzed on their elemental composition using ICP-MS conducted by Eurofins Umwelt West GmbH and ICP-OES conducted by IME. The residues were analyzed on matrix elements using XRF conducted by IME and on trace elements using ICP-MS conducted by ALS Minerals Division. Noted process parameters are the pH-values, oxidation potentials, masses, and volumes. Analysis and process parameters are used for the calculation of metal yields and further evaluation of the experiments, Eq. 2:

$$R_i = \frac{V_1 \cdot c_{i,l}}{m_{sA} \cdot c_{i,sA}} = 1 - \frac{m_{sR} \cdot c_{i,sR}}{m_{sA} \cdot c_{i,sA}} \quad (2)$$

where V_1 is the volume of initial leach liquor; $c_{i,l}$ is the concentration of element i in solution; m_{sA} is the mass of initial concentrate; $c_{i,sA}$ is the concentration of element i in initial concentrate/ore; $c_{i,sR}$ is the concentration of element i in leach residue; m_{sR} is the mass of leach residue 2.

Table 2 Identified phases (>2 wt%) and their elemental composition

Phase	Color	Major elements	Minor elements
Eudialyte		Si, O, Ca	Na, Fe, K, Zr, Mn, Nb, Th, U, REE
Feldspars		Al, O, Si, Na, K, Ca	Na, Fe, K, Th, U, REE
Aegirine		Si, Fe, O	Na, Th, REE
Eudialyte-residue		Si, O	Na, Al, Ca, Fe, K, Zr, Nb, Th, U, REE

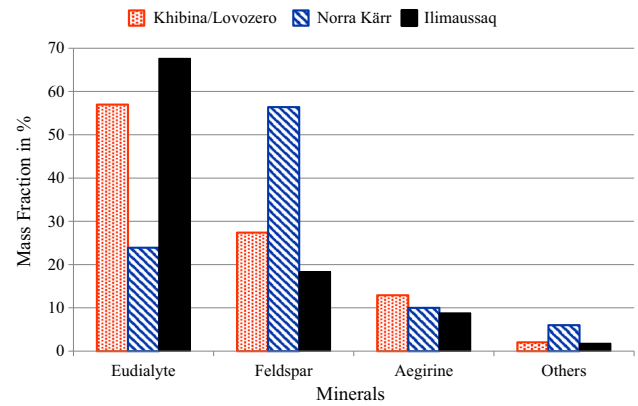


Fig. 3 Mineralogical composition of eudialyte concentrates [30]

The REE recovery of each analyze method is the average value weighted by initial REE concentration of each individual REE. Due to similar results for HCl-based experiments, the presentation of individual REE is neglected. For H₂SO₄-based systems, a different behavior only for LREE and HREE was identified and is specified below. During the experiments, an immediate exothermal reaction could be observed after adding the acidic solution to the concentrate. Depending on the acid concentration, the suspension becomes faster to get pasty with increasing acid concentration. The risk of gelling while or after washing decreases with increasing acid concentration and reaction time. At acid concentrations above 3 mol/L and reaction times above 10 min, no gelling was observed.

The different metal recoveries depending on used acid and leaching water factor are summarized in Fig. 4. The acid concentration was 10 mol/L at a constant decomposition time of 60 min. After decomposition, one experiment with H₂SO₄ was conducted with a higher leaching water amount of factor 2.5 to examine the effect on the REE sulfate solubility.

The Mn recovery (not shown) is an indicator for the eudialyte decomposition rate and is nearly the same for both acid solutions (R_{Al} : 80–82 %). In contrast, the REE recoveries are much higher for chloride-based systems. Especially, the LREE have low metal yields. It is assumed that a double sulfate precipitation took place [34], reaction (3):

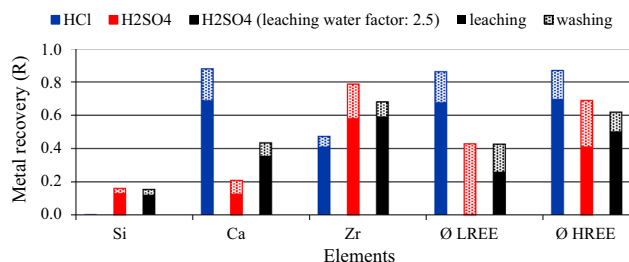
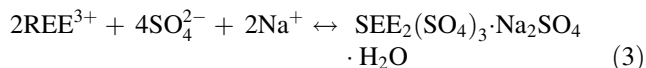


Fig. 4 Metal recovery of the Ilmaussaq concentrate depending on used acid and leaching water factor [30]



A comparison of decomposition with H_2SO_4 with varying leaching water factors indicates the possibility to increase the REE recovery during the leaching step by increased water dosages. The reason is that the low liquid volume leads to high REE, sulfate, and Na concentrations originated from the eudialyte decomposition which moves the solubility equilibrium in the direction of REE precipitation. However after washing, nearly the same over all REE leaching efficiencies, much lower as for HCl-based systems, are observed. One explanation could be the co-precipitation with Ca as gypsum. However, higher Ca recoveries while using higher water volumes do not affect an increase of REE recoveries. Consequently, more investigations are needed to understand the REE losses in eudialyte- H_2SO_4 -systems.

In contrast to REE, the recoveries of Zr and Si are increased while using sulfuric acid. The higher Zr metal yields are positive in case of resource utilization but the higher Si recoveries increase the risk of silica gel formation and limit the high selectivity in comparison to HCl-based systems. Thus, to overcome the low REE metal yields and to keep Si in the leach residue, hydrochloric acid was used for further investigations.

In Fig. 5 the recovery rate depending on the used acid amount is plotted for the experiments with the Ilmaussaq concentrate. The decomposition time was set constant at 60 min. The corresponding pH-value was measured during the washing step. It can be seen that the recovery rates of REE and Mn are nearly the same. They are divided in two linear parts:

1. Increasing metal recovery with increasing used acid amount.
2. Nearly constant metal recovery with only slight increase with increasing acid amount.

The recovery rates of Na, Ca, and Al (not shown) are similar, which leads to the result that via the REE recovery rate the eudialyte decomposition rate can be examined.

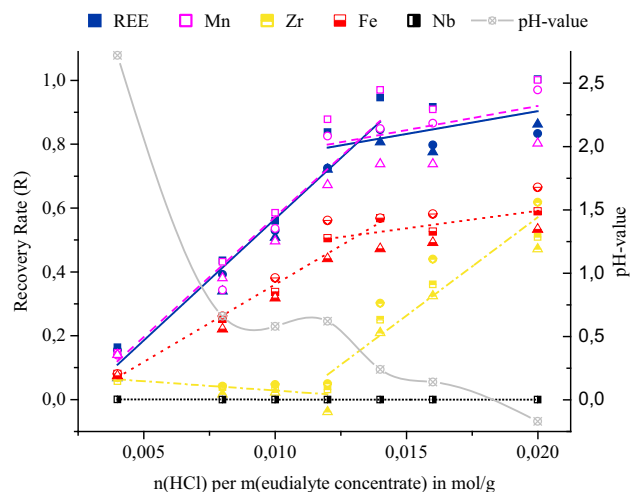


Fig. 5 Recovery rate of valuable metals of Ilmaussaq concentrate depending on acid amount at constant reaction time (60 min) [30]

This is confirmed by the drop of pH-value with increasing acid amount after the shift of the increasing to the constant recovery rate zone.

The metal recovery for Fe has the same remarkable curve shape only at lower metal recoveries. This behavior can be explained by acid-resistant aegirine [$\text{NaFe}^{3+}(\text{Si}_2\text{O}_6)$] contents. For Zr and Nb/Ta, totally, other recovery rates are Zr and Nb/Ta react differently. Nb and Ta (not shown) cannot be liberated at investigated process parameters. Therefore, more aggressive process conditions are needed. In contrast, Zr starts to dissolve in solution after the decrease of the pH-value under 0.5 and increases with further decreasing pH-value. A separate recovery of REE and Mn from Zr seems to be possible. The remarkable points are the same for the two other concentrates.

Depending on the used eudialyte concentrate, the Zr recovery is limited at 40–60 %. These results are observed by Zakharov [20] too, who explained it with the formation of acid-resistant Zr minerals and coarse eudialyte grains covered with an acid-resistant silica layer. In this case, the proposal of acid-resistant Zr minerals seems to have a higher impact because the Mn and REE recoveries are not affected at the same extent which would be caused by insufficient eudialyte decomposition.

One important parameter to evaluate the silica gel formation is the silicon concentration or silicon recovery rate in solution. In Fig. 6 the silicon recovery increases with decreasing acid amount. It can be reasoned with the characterization of different substeps and influencing parameters:

1. With higher acid amount the eudialyte decomposition rate is increased. It can be seen with the increasing REE yield. Increased eudialyte decomposition leads to higher silicon liberation. Assuming that the

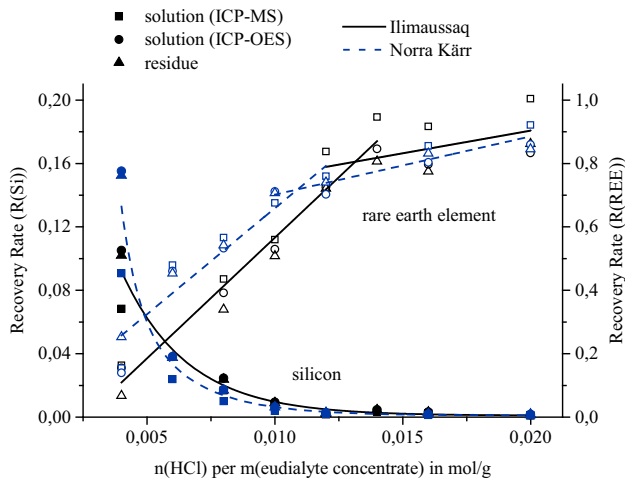


Fig. 6 Silicon recovery rate depending on acid amount [30]

decomposition rate is quite faster than the silicon precipitation, this leads to a higher silicon oversaturation in solution.

- According to the formation mechanism of silica colloids (Fig. 1), the nucleation seems to be the dominant process step. Because of the high decomposition rate and low used liquid volume a SSI much higher than 2.5 is expected.
- Studies on silica precipitation behavior by Gorrepati [35] point out a strong increase of silica monomer disappearance and flocculation rate with decreasing pH-values (higher used acid amounts) at pH 0 and below.
- Higher ionic strengths (e.g., achieved by higher eudialyte decomposition) increase the nucleation rate [27]. Studies by Gorrepati [35] on the influence of salt solutions indicate a disappearance of monosilic acid and flocculation of primary particles in the following order: $\text{AlCl}_3 > \text{CaCl}_2 > \text{MgCl}_2 > \text{NaCl} > \text{CsCl} > \text{no salt}$.

Summarizing, high acid concentrations increase the silicon precipitation via nucleation. Additionally, the silicon precipitation is increased at high salt concentrations resulting from higher eudialyte decomposition rates and low pH-values. Higher silicon concentrations are assumed with low acid concentrations because of lower precipitation kinetics based on lower silicon oversaturation and lower ionic strengths. This evaluation meets the observation during the decomposition experiments that an increased acid concentration speeds up the solidification of the pasty mass.

Because the silicon precipitation seems to be a kinetic process, decomposition experiments varying the time (0–240 min) were performed (Fig. 7). The acid amount ($n(\text{HCl})/m(\text{eudialyte}) = 0.012 \text{ mol/g}$) was kept constant.

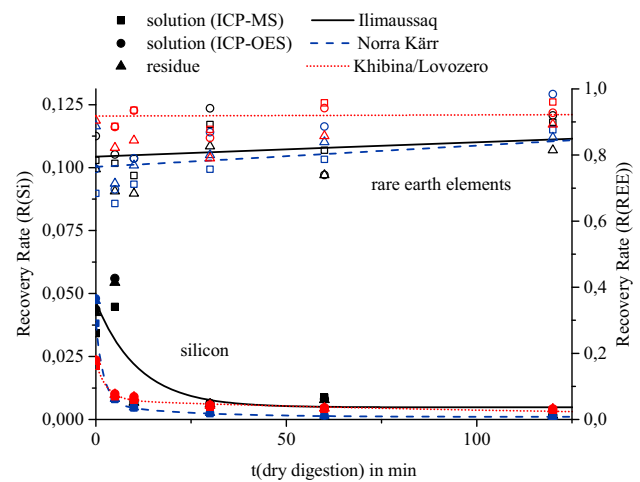


Fig. 7 Silicon recovery rate depending on reaction time at constant acid amount (0.012 mol/g) [30]

According to the high REE recovery rates, after short dry digestion times the eudialyte decomposition is quite fast. Further reaction times do not increase the metal yield which leads to the assumption that the reaction is completed. By comparison, the silicon recovery rate decreases during the first ten to fifteen minutes. The assumed hypothesis of a faster eudialyte decomposition rate in contrast to the silicon precipitation kinetic is established.

First Upscaling Stage

The aim of the upscaling experiments is the verification of a processability of eudialyte concentrates via the dry digestion process. Therefore, the experiments are carried out using 1.5 kg of Norra Kärr or Ilimaussaq concentrate. The process is presented in Fig. 8. In contrast to the fundamental research experiments, two minor adoptions are made. To overcome that the material becomes incrustated, a wetting step was implemented before the dry digestion. To increase the metal recovery, a three-stage leaching and washing process is arranged in countercurrent.

During the upscaling experiments, no gel formation was observed at any time. With maximum silicon content of 50 mg/L in the pregnant liquor solution, it is approved that the silicon stays in the residue. XRD analyses of the leach residue detect a new amorphous phase. Phase analyses via QEMSCAN [33] indicate a total digestion of eudialyte and a new scavenger phase with a Si–O-ratio similar to quartz (Fig. 9). The comparison of the initial eudialyte concentration and the eudialyte residue phase using the concentrates with varying eudialyte content at same process parameters leads to a constant factor of initial eudialyte to the eudialyte residue phase of 0.77 ± 0.03 . This leads to the assumption that the silicon-rich eudialyte residue phase

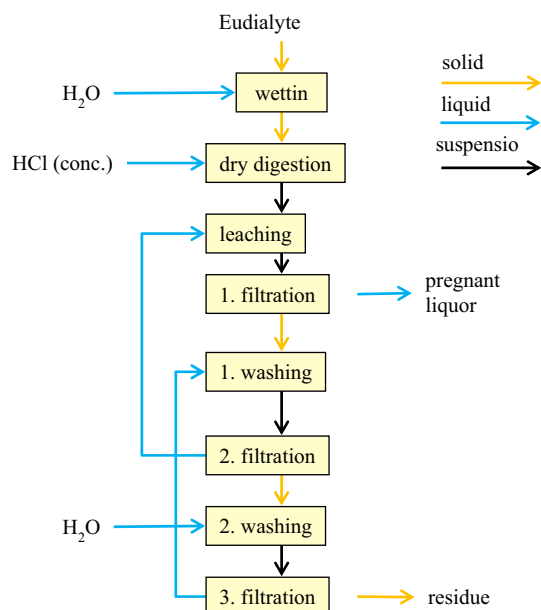
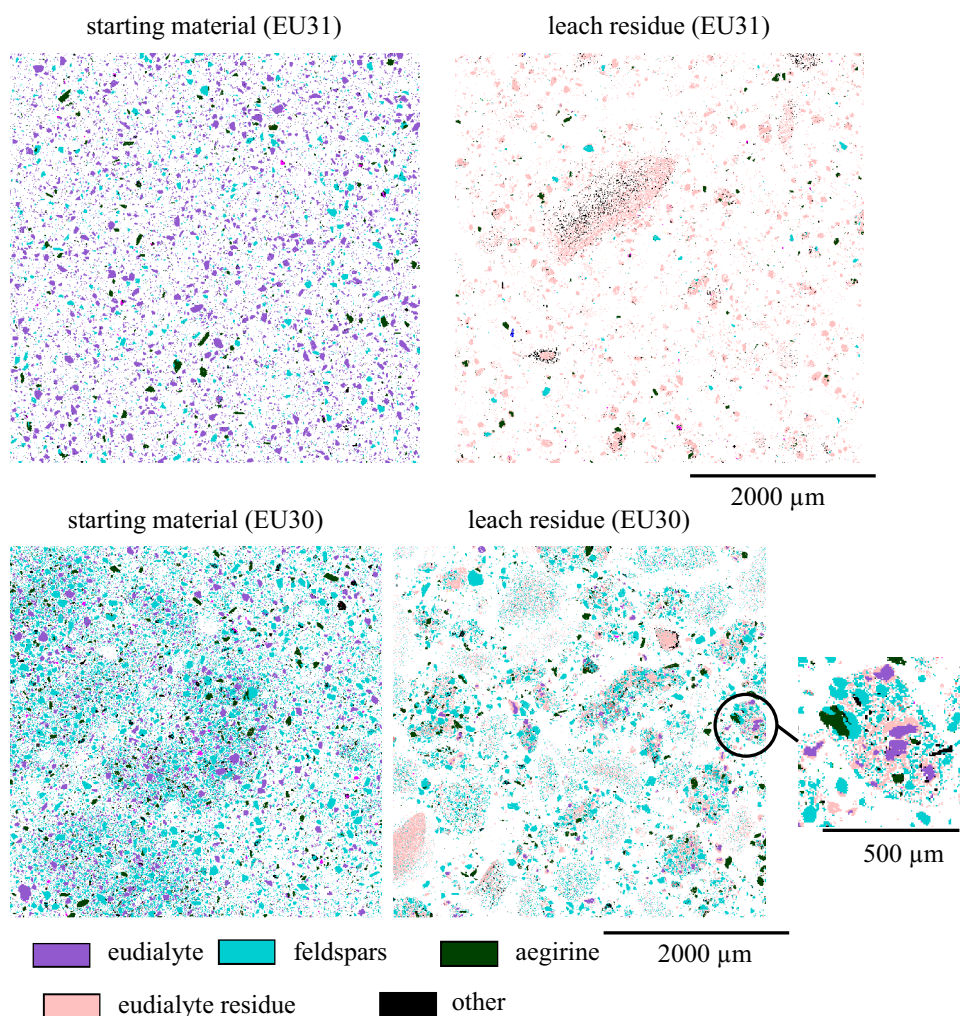


Fig. 8 Process flow sheet of the eudialyte decomposition and metal recovery

Fig. 9 QEMSCAN of the starting materials and the leach residues [30]



originates from the eudialyte digestion. Additionally, the silicon stabilization mechanism seems to be similar to the gel formation which is described in the literature as an amorphous Si-O-phase after drying.

The lab-scale experiments indicated Zr, Mn, and REE as main extractable, valuable metals. This result is confirmed by Fig. 10. The leaching stage liberates about 65–75 % of REE and Mn, whereas the Zr recovery is about 40–50 %. Within the washing stages, the metal yield of REE and Mn can be increased further 13–16 % points in the first and further 4–6 % points in the second washing step. The further increase is only half for Zr. In conclusion, the reachable metal recoveries are 87–93 % for REE, 79–87 % for Mn, and 49–59 % for Zr.

The metal recovery of valuable metals is increased for the Ilmaussaq concentrate. This behavior corresponds with the results of the QEMSCAN. The Ilmaussaq concentrate (Fig. 9) indicates a nearly total eudialyte digestion with only 0.03 % eudialyte found in the residue. In contrast about 3 % of eudialyte remained in the Norra Kärr residue (Fig. 9). Enlargements of the false color image indicate the

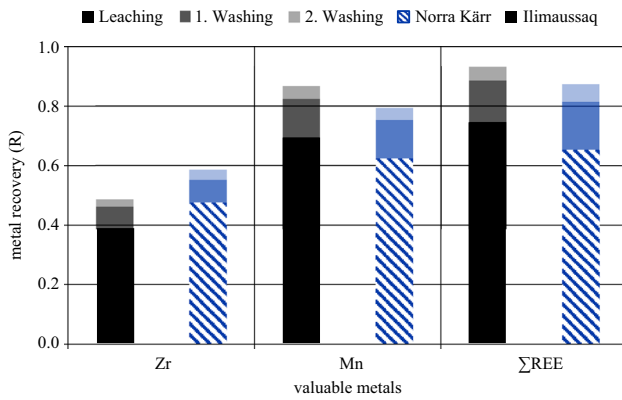


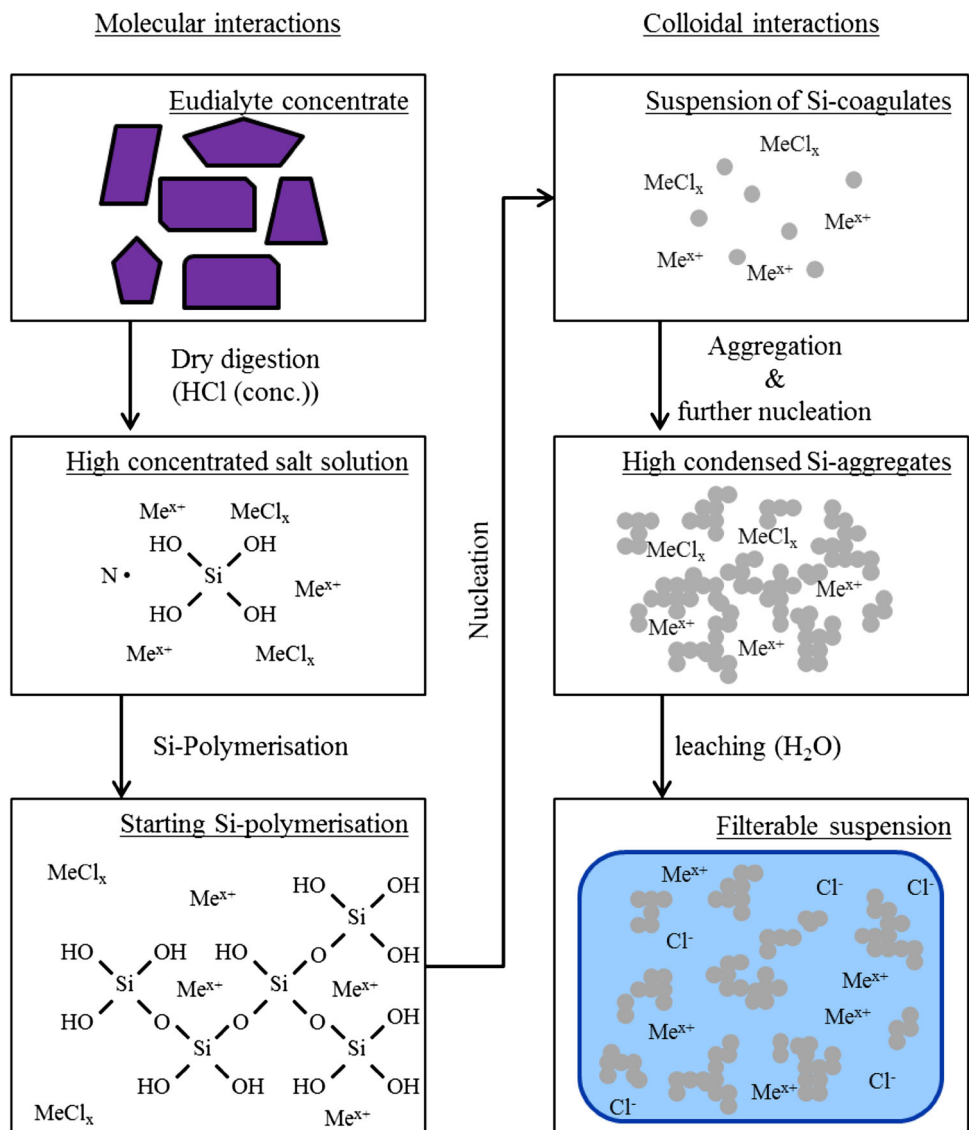
Fig. 10 Metal recovery of extractable, valuable metals depending on process stage calculated via residues [30]

embedding of eudialyte by the eudialyte residue and the aggregation with feldspars. Similar results are already discussed above related to an insufficient Zr recovery investigated visually by Zakharov [20]. Within this research project, this result is approved analytically and could be extended in general to an insufficient valuable metal recovery.

Results and Outlook

The two stages processing of eudialyte via a dry digestion and subsequent leaching establishes a suitable prevention of silica gel formation with high recoveries of REE, Mn and Zr. The main parameters are the type of acid (HCl is favored than

Fig. 11 Proposed dry digestion mechanism [30]



H₂SO₄ in case of REE recoveries), the concentration of acid (> 4 mol/L) and the digestion time (> 10 min). With the optimal choice of parameters (main parameters for dry digestion: s:l-ratio: 1:1.8, HCl-concentration: 10 mol/L, reaction time: 2 h) maximum metal yields of 93 % REE, 87 % Mn and 59 % Zr are achieved. Phase analysis via QEMSCAN and XRD indicate an amorphous, Si–O-rich residue phase coming from eudialyte digestion. The theory of silica gel formation and the findings of this investigation indicate a similar precipitation mechanism (Fig. 11). The first step is the eudialyte digestion which leads to silicon in solution (Si(OH)₄) and metals (Me^{x+}) in solution or precipitated as chlorides (MeCl_x) because of an oversaturation. Immediately, the silicon starts to polymerize to form nuclei. Because of the low volume and the high ionic strengths, it is assumed that many nuclei are formed and start to aggregate forming clusters. These clusters are insoluble and filterable, so that the metals and metal chlorides can be washed out easily.

In the future, the achieved pregnant liquor has to be subjected to further processing to obtain marketable REE, Mn, and Zr products. First, experiments indicate a suitable two-stage pH-adjustment using lime or magnesia to precipitate Zr, Fe, and Al. After that, the REE can be precipitated selectively as carbonates. Further, the leach residue contains valuable metals like Nb, Ta, and residual contents of Zr which should be recovered too.

This investigation points out a solution to prevent the silica gel formation for the hydrometallurgical eudialyte processing. However, other silicon rich-materials with the risk of a silica gel formation should be tested in the same way. First experiments using red mud or a silicon-rich slag indicate a successful adoption of the dry digestion.

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