Leaching of Eudialyte concentrate and REE-precipitation

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Abstract

The work deals with continuous rare earth leaching and precipitation from Eudialyte concentrate, which belongs to the group a cyclosilicate minerals. It has a significant content of rare earth elements and the content of uranium and thorium is very slow. Within this study a hydrometallurgical treatment was used to decompose the eudialyte for the extraction of rare earth elements in a subsequent leaching step. The precipitation with sodium carbonate is a final step for the formation of sodium carbonate, which is required for the solvent extraction. Results of this study show possibility to recover valuable product containing rare earth elements [1].

1 Introduction

Rare earth elements (REE) are called the industrial vitamins and believed can improve the quality of various industrial products even only with a small addition. The application of REE ranges from the traditional metallurgy, glass to the modern phosphors and magnets production. Moreover, REE are now more involved into the green energy field. They play a critical role in the turbine of wind power, in the generator of hybrid or full electrical vehicles and in the hydrogen storage material. However, above 90% of the REE in the market of the world is supplied only by China, who has abundant rare earth mine and advanced rare earth production technology. For a long time Europe has to import REE from China, which has already attracted attention of the public on the stability supply of this critical material. Maintaining the balance between the demand by the economic markets and the natural abundance of the rare earth elements in ores constitutes of the challenge for production of these elements [1].

Eudialyte, whose name means “well decomposable” in Greek, is kind of raw material mainly for the production of zirconium. The chemical formula of eudialyte is $Na_4(Ca, Ce, Fe)_2ZrSi_6O_{17}(OH, Cl)_2$.

But the component of the mineral may sometimes differ because of the zeolite crystal structure that possesses ion-exchange properties of eudialyte. Thus it is met in the nature a large number of its mineral forms differ by the chemical composition. Though eudialyte is normally used as the raw material for recovery of zirconium, it contains 1.5-2% REE of which is enriched with yttrium and heavy elements, making it a potential REE production raw material [2-4].

Eudialyte has been used as the raw material of zirconium production for a long time, though also regarded as potential tantalum, niobium and REE resources, and studied a lot but mainly in Russia. From the reported news technological strategies like decomposition with sulfuric, hydrochloric and nitric acids have already been suggested and partly researched in the laboratory and used in industryIn the treatment of eudialyte concentrate fluoride ions are usually introduced to promote the decomposition degree. It is pointed out fluoride ions can facilitate the distraction of the complex crystal structure of eudialyte as well as reduce possibility the formation of slurry silicate gel that hinders filtration C

Friedrich et al. [6] studied hydrometallurgical processing of eudialyte bearing concentrates to recover rare earth elements via low-temperature dry digestion to prevent silica gel formation Within this research project, a hydrometallurgical pre-treatment is developed to decompose the eudialyte for the extraction of rare earths and to stabilize the silicon in the residue during the subsequent leaching step. Friedrich et al. [7] presented new eudialyte process route showing reduced environmental burdens, although the total REE content in eudialyte is much smaller than in the Bayan Obo deposit.
The main aim of this study is to present Continuous REE Leaching and Precipitation from Eudialyte concentrate.

2 Experimental

2.1 Material and methods

The main aim of the this work was to develop a processing route in order to recover valuable rare earth elements from the eudialyte concentrate with following content in weight. % (52 % SiO_2, 15.2 Fe_2O_3, 11.2 Na_2O, 8.6 Al_2O_3, 2.9 ZrO_2, 2.1 CaO, 0.94 TREE). As it has been noticed earlier, eudialyte is an easily decomposable mineral and the main difficulty in its processing is a formation of colloidal bad filterable slurry during leaching. The first aim of this experimental work was to study at which process conditions gelatinisation occurs and to learn the ways to avoid or to reduce that process. Second aim of this work was to determine the most efficient process conditions at which the highest recovery of valuable elements might be reached. The work is mainly concentrated on rare earth elements including lanthanide group (primary products), while zirconium is considered as a by-product.

The general strategy for the extraction of rare earth oxides is shown at the Fig. 1.

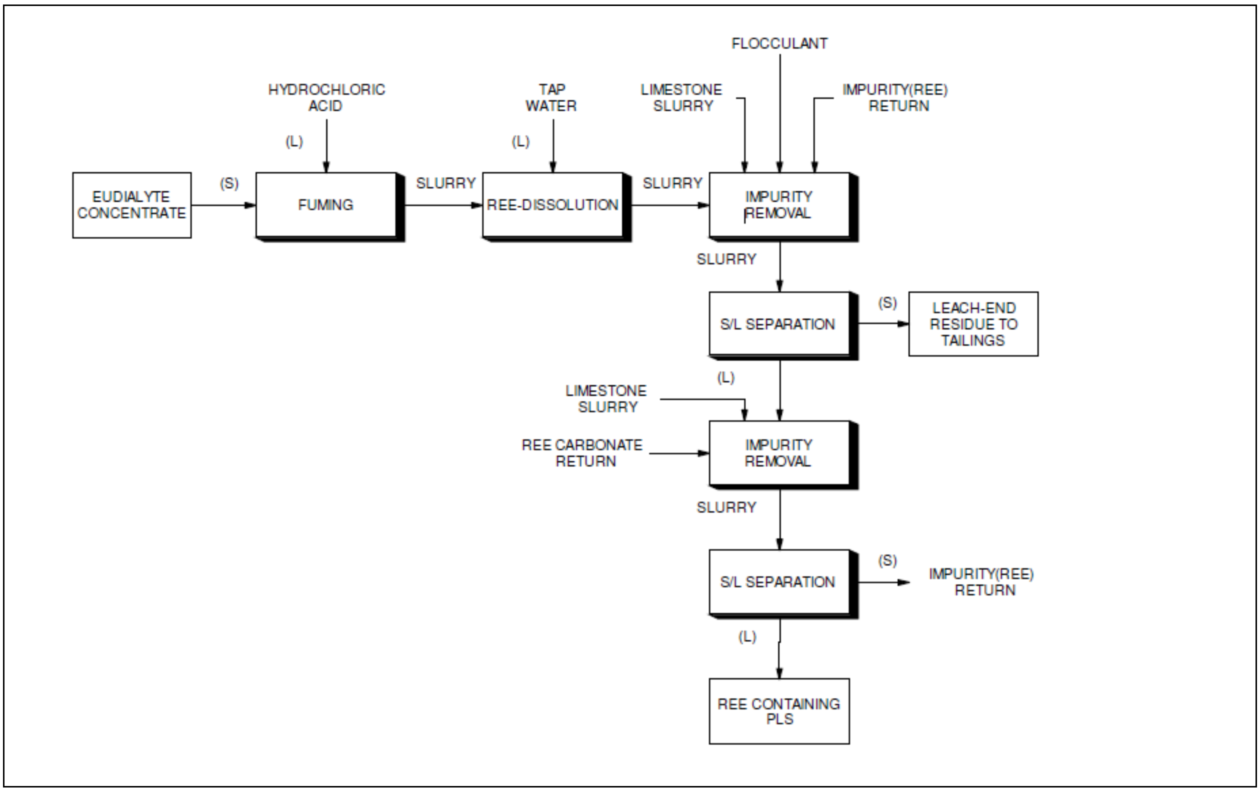

Figure 1: Block flow diagram – Eudialyte Leaching and Impurity Removal Process

The testing of laboratory obtained results regarding to treatment of Eudialyte concentrate will be performed at new MEAB/IME, RWTH demonstration plant:

- Pre-treatment units for fuming process (2 glass vessels, 40 L active volume)
- Leach preparation unit (2 vessels in PVDF, 100 l active volume, incl. agitator, heater, and slurry pump),
- Leaching cascade (4 vessels in glass, active volume in glass, incl. agitator, pH sensors, PT 100),
- Neutralisation slurry discharge (1 tank in PVDF, 250 l active volume, incl. agitator and pump),
- Membrane filter press, incl. pumps, piping and auxiliary equipment.
- Precipitation slurry discharge (1 tank in PVDF, 250 l active volume, incl. agitator and pump),

Figure 2: Demonstration plant in Aachen without a pre-treatment unit

3 Result and discussion

The influence of different experimental parameters such us the leaching time, the leaching temperature and the concentration of hydrochloric acid on rare earth dissolution from eudialyte concentrate Norra Kärr, Sweden were firstly investigated in laboratory conditions. Parameters for the processing of eudialyte concentrate are tested in scale up equipment As shown at Figure 2, and listed in table 3.

Table 1: Experiment conditions for the processing of eudialyte concentrate

Weight of Norra Kärr eudialyte concentrate	40 kg
Eudialyte Concentrate/30 % concentrated HCl (kg/L)	1Kg /1L
Fuming Time	60 min
Fuming Temperature	20°C
Leaching time	60 min
Leaching temperature	45°C
pH during neutralization process with $CaCO_3$	0-4.1.
pH during precipitation process with Na_2CO_3	5.19 to 6.50

** Flocculants were injected in small amounts in order to accelerate the separation process*

The fuming process starts with addition of eudialyte concentrate and hydrochloric acid in appropriate ratio to avoid silica gel formation (max. 5kg per charging in one reactor). After fuming process the leaching was performed with an addition of water in order to dilute of obtained suspension. After one Continuous REE Leaching and Precipitation from Eudialyte concentrate the formed rare earth carbonate is dryed and shown at Figure 3. Besides the testing of the developed processing strategy in laboratory conditions the most important aim was to successfully transport the suspension after fuming to leaching tanks in order to dilute it with water. Because of some agglomoeration This eudialyte concentrate is not suitable for this transport and requires an using of very strong pump for this work in order to finish it as soon as possible faster.

Figure 3: Filter cake after fuming, leaching, neutralisation, filtration (Left) and produced REE-carbonate (right)

Table 5: Chemical composition of REE-cabonate using our strategy

Element	Al	Ca	Fe	Hf	Mn	Na	Nb
REE-Carbonate (%)	2.62	21.3	1.04	0.003	0.57	2.40	0.007
Element	Zr	Ce	Dy	Gd	La	Nd	Pr
REE-Carbonate (%)	0.15	3.55	0.75	0.58	1.49	1.84	0.50
Element	Yb	Tb	Si	Zn	Sm	Y	residue
REE-Carbonate (%)	0.42	0.11	0.042	0.039	0.55	5.36	CO_2

4 Summary

The work deals with Continuous REE Leaching and Precipitation from Eudialyte concentrate. The produced rare earth concentrate contains 15.1 % of rare earth elements. Based on the results obtained from the small scale experiments, the large scale experiments were carried out successfully. The fuming process should start with addition of concentrate first and then the acid in appropriate ratio to avoid silica gel formation. During neutralization with $CaCO_3$ (pH = 4), more than 95% of Zr, Al and Si go into the residue which can be used as a potential source of zirconium recovery. During precipitation with Na_2CO_3 (pH ~ 5.5-6), more than 95% of REEs are precipitated for both the concentrates, thus increasing the amount of REEs in the REE-carbonate produced

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