New approaches for beneficiation of rare earths from low-grade sources such as phosphogypsum (REE-PG)

Jarno Mäkinen, Malin Bomberg, Justin Salminen, Mona Arnold and Pertti Koukkari

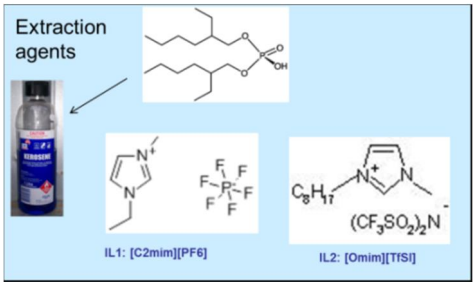
Rare earth elements (REE) are EU critical metals that have recently encountered increasing demand for their uses in many Cleantech applications. The Finnish apatite minerals, industrially utilized for producing phosphate fertilizers represent a potential secondary source of REE. In the fertilizer manufacturing process even 80 % of the RE will end up in the phosphogypsum (PG) side product, which then holds from 0.2-0.4 w-% REE.

So far economical means of recovering REE from apatite or PG have not been found. Novel active extraction or ion exchange techniques as well as innovative biochemical methods have been recently examined by VTT and its co-operation partners.

Extraction from apatite concentrate with ionic liquids

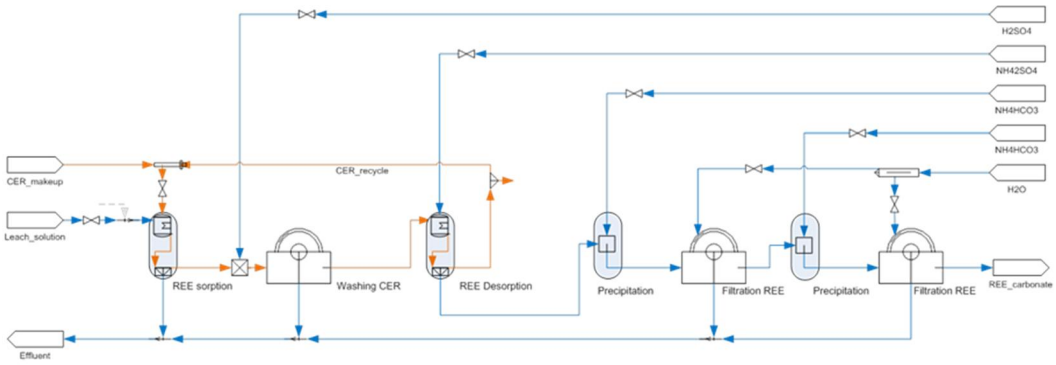
In a series of experiments nitric acid leaching of REE from the apatite fertiliser concentrate was performed. Recovery percentages varied from 80-91 % at optimal leaching pH of 0.3.

The REE content was further subjected to liquid-liquid extractants made with kerosene mixed with two ionic liquids: [EMIM][PF6] and [OMIM][TFSI]. Preliminary results, followed for seven rare earth elements have shown fair distribution coefficients of 30-99 % in single stage extraction.



Recovery from PG with solid ion exchanging adsorbents

At Ural Federal University (Jekaterinburg, Russia) REE from phophogypsum have been recovered by acidic sorption leaching as described in the model flowsheet below



With sulfuric acid leaching and commercial cationites (macroporous M-31, Dowex) as sorbents extraction efficiency of 60-65 % has been gained. Derivatives were prepared as Ce_2O_3 and as light REE and heavy REE carbonate based concentrates of 99,3-99,7% purity. A multicomponent process model has been developed at VTT (Co-op agreement RFMEFI58114X0002).

Passive treatment of PG with sulphate reducing bacteria (SRB) – REE-PG project in MISU

In the REE-PG project the sulphate extractant from PG will be subjected to microbial activity achieved by sulphate reducing bacteria (SRB). Their ability for removing heavy metals as reduced sulphides from aqueous solutions is well known. Organic acids or alcohols are typically used as electron donors. The finely divided REM sulphides will have high magnetic susceptibility and could be recovered from the bio-sludge by physical separation with a recently patented concept (FI 125550 B, 30.11.2015).

Preliminary results achieved by aqueous PG leachate amended with yeast extract and lactate donor using *Desulfovibrio desulfuricans* and mixed cultures are presented in Table 1. The result indicates substantial enrichment of rare earth metals in the formed SRB precipitate. New MISU research (REE-PG) will pursue to enhanced volumetric efficiency of the SRB based technique. SRB strains such as *Desulfovibrio, Desulfobulbus and Desulfotomaculum* will be isolated from environmental samples and cultivated, and their activity in different media containing PG sludge will be tested. The research will be conducted in co-operation with MINTEK biohydro-metallurgical division as part of the REE-PG project led by Lappeenranta University of Technology and funded by Academy of Finland (Finland-South Africa co-operation).

Table 1. REE enrichment from PG by sulphate reducing bacteria (SRB)

	PG	SRB
La [ppm]	390	30 400
Ce [ppm]	1100	66 200
Y [ppm]	23	8 800

Researchers working in VTT's REE-PG team

Material recycling and geotechnology, VTT Process Chemistry and Environmental Engineering:
- Malin Bomberg, PhD, post-doctoral researcher
- Jarno Mäkinen, M.Sc., doctoral researcher
- Pertti Koukkari, D.Sc. (Tech.), professor, subproject PI

pertti.koukkari@vtt.fi tel. +358 40 5834092