



# Rare earth occurrences in phosphate rock processing

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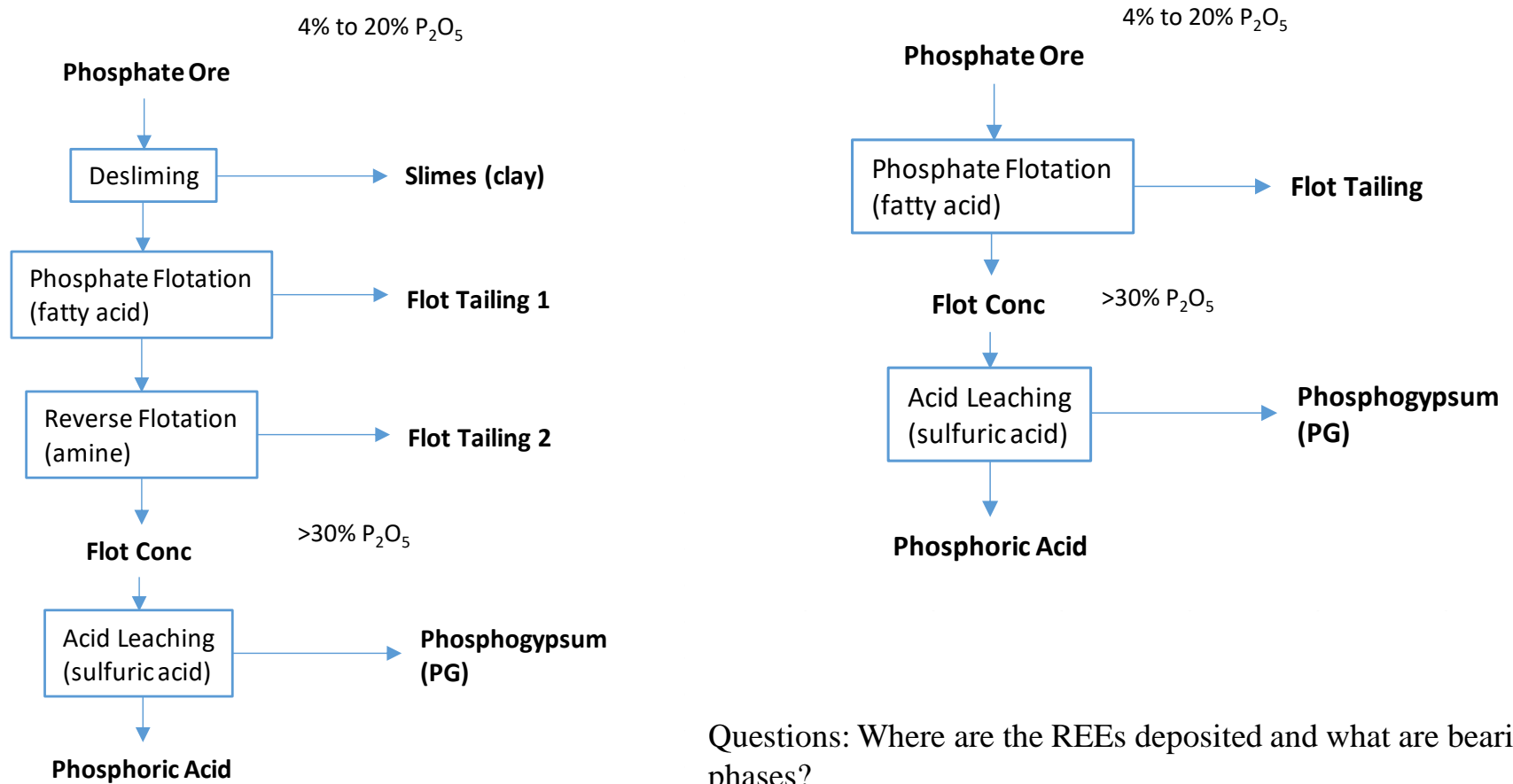
# Introduction

Apatite ores processing for REE as by-product has become more attractive recently (Stone et al., 2016; Wang et al., 2010).

The phosphate rock production in the world was 255 Mt in 2016 and 263 Mt in 2017 according to the USGS report (2018). Most (over 80%) of apatite ores are used for fertilizer production. Assuming average REE content of 460 ppm in phosphorite, the world's phosphate production (>170 Mt) would represent over 7.8 Mt of contained REE (Simandl et. al., 2011).



# Phosphate rock processing streams



Questions: Where are the REEs deposited and what are bearing phases?

# Incorporation and occurrence modes (phases) of REE in wet-process of phosphoric acid production

- The incorporation of REE in PG has been investigated for different REE grade phosphate rocks and concluded that about 60-70% of the initial REE content reported to the PG (Ogawa and Shikazono, 2006; Ogawa et al., 2007; Playà et al., 2007; Wang et al., 2010; Dutrizac, J.E., 2017; Koopman and Witkampetc, 2000; Harbi et al., 2011; Sandström and Fredrikssonm,2012).
- The occurrence modes or the precipitated phases of REE in the PG are concerned but conclusions are still disputable.

Jin et al. (2011): REE present as tiny crystals of rare earth sulphates;

Santos, A.J.G. et al. (2006): REE enriched in PG but not associated with CaSO<sub>4</sub> itself;

Borges et al. (2016): REE occur as sulphates, carbonates, fluorides and phosphates;

Schmidt et al. (2009): Eu<sup>3+</sup> (Europium ion) adsorbed as an inner-sphere species on PG;

Alhassanieh et al. (2012): Eu<sup>3+</sup> was incorporated in the structure of PG as opposed to being adsorbed on the surface;

Dutrizac, J.E. (2017): REE ions are structurally incorporated in gypsum (CaSO<sub>4</sub>), three Ca<sup>2+</sup> ions replaced by two REE<sup>3+</sup> ions and a vacant Ca<sup>2+</sup> lattice site.

## **Incorporation and occurrence modes (phases) of REE in the beneficiation process**

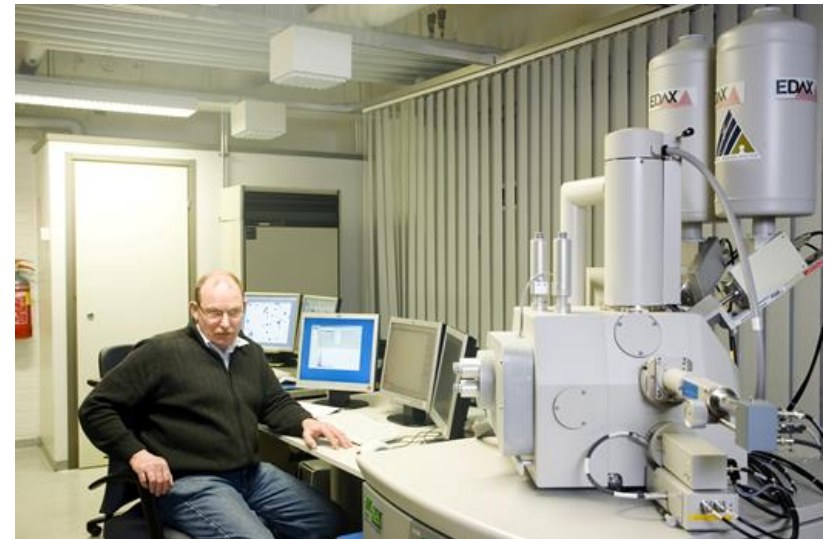
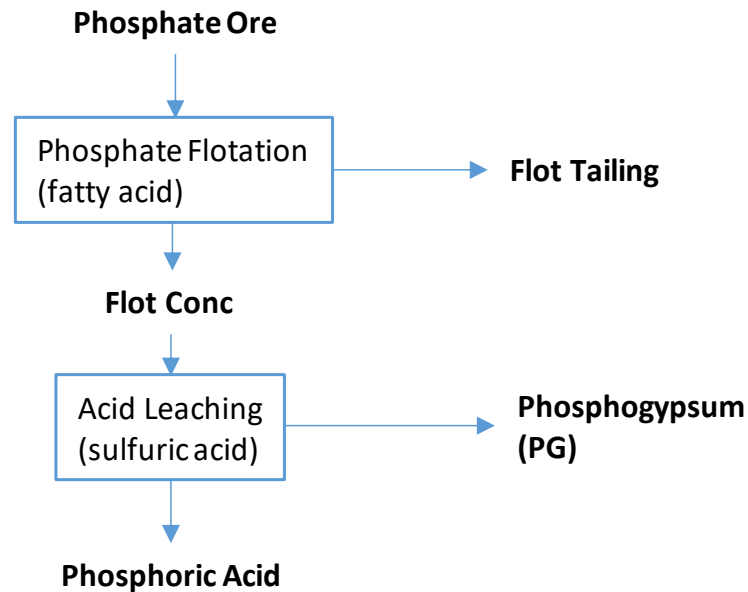
Comparing to the studies on the incorporation and the occurrence modes of REE in the PG during the wet-process of phosphoric acid production studies about REE transferring and their occurrences in the beneficiation process are very limited.

The study by Zhang et al. (2018) indicated that the REE in the phosphate ore are distributed approximately 40% in waste clay, 10 % in amine tails, 38% in phosphogypsum, and 12% in phosphoric acid. But how they occur in what REE-bearing phases in these products were not investigated.

# Rare earth occurrences and distributions in phosphate rock processing\*

Material: apatite ore, flotation concentrate and PG

Methods: XRF, ICP-MS technique; Mineral Liberation Analyzer (MLA); Electron Microprobe Analyses (EMPA)



## Extraction of the REE from beneficiation tailings

In the tailing the REE occur in the phases of apatite, monazite, allanite and pyrochlore. Flotation could be used to concentrate apatite and monazite using fatty acids or hydroxamates as the collectors. But allanite and pyrochlore are normally poor in floatability using conventional reagents. Wet high intensity or gradient magnetic separation could improve their recoveries (Yang et al., 2015).

Fine grain sizes of the REE-bearing phases, low liberation degrees of them and low grade of the REE would cause the recovery of REE very challenging by physical techniques (flotation and magnetic separation).

Limited studies have been conducted on REE recovery from the beneficiation tailings. In a study (Zhang et al., 2018) gravity separation using a shaking table followed by flotation was applied to concentrate the REE-bearing minerals, monazite and xenotime. Then sulfuric acid leaching was used to recover the REE from the concentrate. But the REE recovery of the physical process was about 30% and the final recovery of the REE was less than 20%.

## Extraction of the REE from PG

In the PG the REE mainly occur in the phases of gypsum and monazite. Physical methods such as screening, flotation and magnetic separation could be applied to concentrate monazite but the recovery of REE will be very low because only 20% of the REE are carried by monazite.

In the PG gypsum takes up over 95% in the weight chemical leaching is the only approach to extract the REE. REE recovery from PG by acid leaching using HCl, HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub> has been investigated extensively (Hammas-Nasri et al., 2016; Jarosinski et al., 1993; Walawalkar et al., 2016; Azimi et al., 2007, 2008; Z.H. Ismail et al., 2015; Todorovsky et al., 1997; Reid, 2017). Because in the PG gypsum is the dominant component and the REE<sup>3+</sup> ions are structurally incorporated in the lattice (Alhassanieh et al., 2012; Dutrizac, 2017) high acid concentration (>2.0 M) and high temperature (>60° C) are normally needed to release the REE. Addition of Ca(NO<sub>3</sub>)<sub>2</sub>, the pre-treatment of PG by microwaving and mechanoactivation by grinding were found to improve the REE leaching efficiencies. In addition, resin-in-leach process was indicated feasible for recovery of REE from PG (Padayachee et al., 1996) using diluted sulphuric acid as lixiviant.

Meanwhile, if REE<sup>3+</sup> ions adsorb on the PG surface as detected by Walawalkar et al. (2016) they could be dissolved in the electrolytes solutions such as NaCl, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and NH<sub>4</sub>Cl by ion-exchange as used for extraction of REE from the ion adsorption rare earth ore (Chi and Tian 2007, 2008).



# Acknowledgement

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**Thank You for your Attention!**

