# Recovery of rare earth elements from nitrophosphoric acid solutions

Mahmood Alemrajabi, Åke C. Rasmuson, Kivanc Korkmaz, Kerstin Forsberg *

*Department of Chemical Engineering, KTH Royal Institute of Technology, Stockholm, Sweden*

ABSTRACT

In the present study, the recovery of rare earth elements (REEs) from an apatite concentrate in the nitrophosphate process of fertilizer production has been studied. The apatite concentrate has been recovered from iron ore tailings in Sweden by flotation. In the first step, the apatite is digested in concentrated nitric acid, after which $Ca(NO_3)_2.4H_2O$ is separated by cooling crystallization. The solution is then neutralized using ammonia whereby the REEs precipitate mainly as phosphates ($REEPO_4.nH_2O$) and together with calcium as $REE_n Ca_m (PO_4)_{(3n + 2m) / 3}$. In this work, the degree of rare earth coprecipitation during seeded cooling crystallization of $Ca(NO_3)_2.4H_2O$ has been studied. The solubility of calcium nitrate tetrahydrate ($Ca(NO_3)_2.4H_2O$) in acidic nitrophosphoric acid solutions in the temperature range of $-2$ °C to 20 °C has been determined. For the neutralization step, it is shown that the calcium concentration and the final pH play an important role in determining the concentration of REEs in the precipitate. It is found that reaching maximum recovery of REE with minimum simultaneous precipitation of calcium requires careful control of the final pH to about 1.8. It is further observed that the precipitation yield of REEs and iron is favored by a longer residence time and higher temperature. Finally, the effect of seeding with synthesized REE phosphate crystals as well as a mixture of REE and Ca phosphates on the precipitation rate and the composition of the precipitate was studied.

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## 1. Introduction

Phosphate minerals, such as apatite, are one of the main sources for the production of fertilizer and phosphoric acid. The common chemical formula for apatite is $Ca_{10}(PO_4)_6(OH, F, Cl)$. These minerals usually contain low concentrations of rare earth elements (~1 mass % REO) (Gupta and Krishnamurthy, 2005). Industrial demand for many of the rare earth elements is high and their consumption is increasing. Due to their unique spectroscopic and magnetic properties, they are needed for a wide variety of products and applications such as catalysts, rechargeable batteries, mobile phones, plasma televisions, computer disc drives, catalytic converters, components in special glasses and permanent magnets (Alonso et al., 2012; Voncken, 2016). Although the concentration of REEs in the apatite is low, the large volumes of apatite makes this material being considered as one of the secondary sources for rare earth elements extraction (Binnemans et al., 2015). The quantity of rare earth elements in phosphate sources has been estimated to be >8 million metric tons REO (Gupta and Krishnamurthy, 2005). In the present study, the recovery of REEs and phosphorus from a fluoro apatite containing 4000–5000 ppm rare earth elements was studied. The apatite is obtained as a waste product in the processing of iron ore with an annual production of ca. 43 M ton of crude ore containing 2–

11 mass % $P_2O_5$ by LKAB (Luossavaara-Kiirunavaara AB) in northern Sweden. The apatite is extracted from the tailing deposits by flotation (Pålsson and Fredriksson, 2012; Martinsson et al., 2012). A detailed composition of the apatite concentrate has been reported by Sandstöm and Fredriksson (2012).

NPK (nitrogen, phosphorous, and potassium) fertilizers can be produced by digestion of phosphate rock with concentrated nitric acid in the nitrophosphate process (Odda process); see Fig. 1 (Association European Fertilizer Manufacturers, 2000; Wiesenberger, 2002; Binnemans et al., 2015). An integrated separation of rare earth elements in the nitrophosphate process would improve the cost effectiveness of the hydrometallurgical process and would introduce a new environmentally sound source of REEs. The latter point is important since the global demand for REEs such as Nd and Dy is sketched to rise by 700% and 2600% in the coming 25 years (Alonso et al., 2012).

The process starts with digestion of the phosphate rock in concentrated nitric acid. The overall reaction, which takes place at a temperature of about 70 °C is given in reaction (1). The kinetics of this reaction has been studied extensively by Olanipekun (2001).

$$Ca_5PO_{43}Fs + 10HNO_3aq \rightarrow 5CaNO_{32}aq + 3H_3PO_4aq + HFg \qquad (1)$$
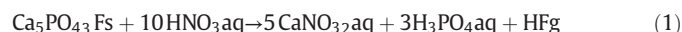
Calcium is a non-nutrient in NPK fertilizer and seen as a diluent. Calcium nitrate tetrahydrate is removed from the digestion solution in order to increase the nutrient content as well as to reach the appropriate $CaO:P_2O_5$ ratio. This is achieved by cooling crystallization down to
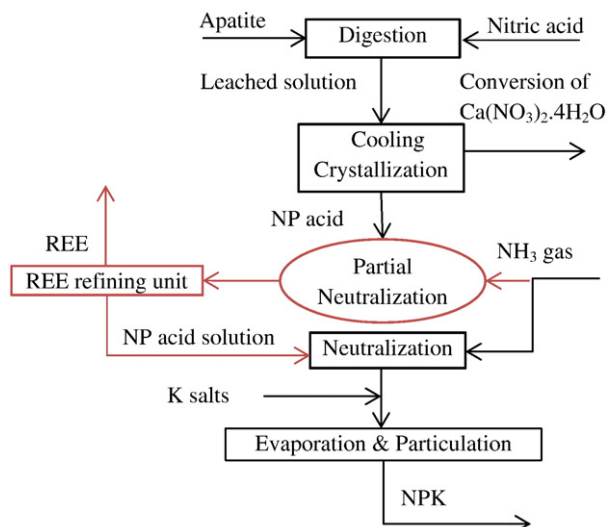
**Fig. 1.** Nitrophosphate process with integrated rare earth recovery. (The red lines show the integration of the REE isolation unit to the nitrophosphate process).

$-5$ °C – 0 °C (Wiesenberger, 2002) at which $Ca(NO_3)_2 \cdot 4H_2O$ is the most stable hydrated form of $Ca(NO_3)_2$ (Paulik et al., 1983). This separation of calcium nitrate and the phase equilibria in the system of $CaO - P_2O_5 - N_2O_5 - H_2O$ over a wide temperature range from 0 °C to 100 °C has been studied by Akimov (1975). The overall nutrient concentration and the $N:P_2O_5$ molar ratio of the final NPK are the main factors that determine the minimum amount of $Ca(NO_3)_2 \cdot 4H_2O$ which has to be removed. The best range for $CaO:P_2O_5$ ratio is 0.3–1 (Kongshaug, 2000). After cooling crystallization of $Ca(NO_3)_2 \cdot 4H_2O$, by considering the initial concentration of fluoride and cadmium in the nitrophosphoric acid solution, defluorination and decadmiation processes may be needed to increase the quality of the produced fertilizer (Wang et al., 2015; Syers, 2001; Haraldsen, 1991).

A review of literature shows that, although numerous researchers have reported details of the process (Wiesenberger, 2002; Kongshaug, 2000), there are only few reports on the recovery of REE within the nitrophosphate process. The rare earth elements are dissolved in the nitrophosphoric acid solution in the digestion of the apatite and they are mainly present as: $REE^{3+}, CeNO_3^{2+}$ and $CeH_2PO_4^{2+}$ (Puigdomenech, 2013). The REEs leaching efficiency has been investigated (Bandara and Senanayake, 2015; Sandstöm and Fredriksson, 2012; Forsberg et al., 2014; Monir and Nabawia, 1999). The highest recovery of REEs is reported in 5 mol/L nitric acid, at 60 °C, solid liquid ratio of 1:6 g/mL and after 120 min of leaching. The digestion of apatite in the nitrophosphate process is performed in more concentrated acid in order to reduce the amount of water in the processing.

The lanthanides can be recovered from the authentic leach solution after crystallization of $Ca(NO_3)_2 \cdot 4H_2O$ and defluorination then adjusting the pH to between 0.3 and 1.4 by $NH_4OH$ at 70 °C–90 °C; the recovery of REEs and their concentration in the obtained precipitate as phosphates is a function of pH and calcium concentration (Habashi, 1985). Al-shawi and Engdal (2002) studied the separation of REEs from nitrophosphoric acid solutions in Norsk Hydro's rare earth recovery plant by precipitation with ammonia at a pH of 1.8. It was reported by Al-shawi et al. that the coprecipitation of REEs with separated $Ca(NO_3)_2 \cdot 4H_2O$ is negligible but no attempt was made to report the degree of REEs coprecipitation and loss of phosphorous. Beltrami et al. (2015) studied the influence of temperature, pH, stoichiometric excess of phosphate, aluminum contamination and residence time on the precipitation of REEs as phosphates at different temperatures between 40 °C and 100 °C in synthetic solution; for a fixed quantity of phosphates added

to the stock solution prepared by dissolving different REE oxides in sulfuric acid in order to optimize the REE recovery and to minimize the precipitation of iron.

In the present study, the key industry-relevant parameters that affect the recovery of REEs from an apatite concentrate have been investigated. These include $CaO/P_2O_5$ ratio, pH and residence time as well as the influence of temperature and seeding on the composition of the REE precipitate. The experimental results have been evaluated against speciation calculations by the MEDUSA speciation software (Puigdomenech, 2013).

## 2. Materials and methods

### 2.1. Characterization of the apatite concentrate

The apatite concentrate was dried and dissolved completely in a mixture of nitric acid, hydrochloric acid and perchloric acid at elevated temperature. Acids of PA grade and deionized water were used. The concentration of REEs, Fe, Ca, P and a number of heavy metals were measured by ICP-OES (Thermo Fisher iCAP 7400). The solid material was also analyzed by powder XRD (Forsberg et al., 2014). The particle size was measured by means of a microscope fitted with a digital camera and analyzing the images with the Image – Pro Plus software. The specific surface area of the apatite concentrate was measured by the BET method in a Micromeritics ASAP 2000/2010 unit. The apatite particles were dried at 100 °C overnight prior to analysis. The BET area was estimated by $N_2$ adsorption at $-196$ °C and relative pressures between 0.06 and 0.2.

### 2.2. Leaching and cooling crystallization

The apatite concentrate was leached in 10 mol/L nitric acid with specific solid to liquid ratio of 2.4 mL/g (20% excess of nitric acid). The leaching was done in a 2 L open batch reactor made of glass, with an overhead stirrer (400 rpm) to make sure that the solid materials were well dispersed. The reactor was immersed in a water bath at 70 °C for 120 min and the leach solution water loss due to evaporation was 1.3% of the total volume. The leaching residue was filtered off by suction filtration using filter paper (0.2 μm), washed with cold water, dried and then dissolved completely in a mixture of acids and analyzed by ICP-OES.

The leach solution was cooled in a FP50 JULABO chiller bath filled with ethylene glycol 50% (v/v) as a cooling medium. 250 mL of leach liquor in a 500 mL glass beaker was immersed in the cooling bath for each experiment. The solution was stirred with a magnetic stirrer. In the following cooling crystallization, seeding was done at 20 °C with $Ca(NO_3)_2 \cdot 4H_2O$ crystals (99 mass %, Alfa Aesar), specific density of 1.820 and average crystal size of 1500 μm. The seed crystals were added in a quantity of 25 mg per kg of digestion liquor (Utrecht, Netherlands, Patent No. 4.569.677, 1986). Samples of about 0.5 mL digestion liquor were taken at different temperatures from 25 °C down to $-2$ °C. For sampling, the crystals were let to settle down for a couple of minutes and the sampling was done by means of pre-cooled cellulose acetate syringe filters (0.2 μm) after 20 min, 2 h, 4 h and 24 h at each temperature, to study the time to reach equilibrium. A quick cooling crystallization was performed by cooling down the leach solution with an average cooling rate of 3 °C/min from 20 °C to $-2$ °C and the sampling was done after 2 h of retention time at $-2$ °C. The samples were diluted 100 times with 5% (v/v) nitric acid and the concentration of calcium was determined by ICP-OES. For the ICP-OES analysis the wavelength were carefully selected and hafnium with concentration of 15 ppm was used as an internal standard in order to avoid overlapping and to reduce the background effect. All samples were stored in HDPE sample tubes before the analysis. All solution concentrations in the aqueous phase were recalculated in order to compensate for the loss