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Direct leaching of rare earth elements and uranium from phosphate rocks

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Abstract. Phosphate rocks can contain considerable amounts of accompanying uranium and rare earth elements (REEs). Interest to extract these elements during phosphate rock processing to mineral fertilizer is given as both uranium and REEs are valuable and toxic. Recovering these elements is thus advantages from a resource conserving and environmental protection point of view. Past efforts to recover uranium and REEs focused on extracting these elements from the intermediate products (phosphoric acid and phosphogypsum) during de-hydrate wet phosphoric acid production. Another approach, that is discussed here, is direct leaching of uranium and REEs from phosphate rocks before phosphate rock processing. First successful lab scale experiments with a selected leaching reagent and phosphate rock from the Abu Tartur mine in Egypt are presented and discussed.

1. Introduction

Phosphate rocks are naturally occurring material with an elevated (5-13 %) phosphorus (P) content. Since the green revolution, the world's food production is dependent on mineral fertilizers produced from phosphate rocks mined globally. The United States Geological Survey (USGS) estimates that some 250 million tons phosphate rocks are mined annually and future mining centers will be concentrated in Northern Africa and the Middle East [1]–[4]. Phosphate rocks can contain considerable amounts of accompanying rare earth elements (REEs) and uranium [5]–[12]. Methods to extract unconventional REEs and uranium from phosphate rocks during phosphate fertilizer production exist. These methods are usually based on solvent extraction or ion exchange and recover REEs and uranium from intermediate products during phosphate fertilizer production [13]–[16]. Most (>70 %) phosphate rocks today are developed using the wet phosphoric acid process where phosphate rock is digested with sulfuric acid. Phosphoric acid (P_2O_5) and phosphogypsum are the intermediate products in the wet phosphoric acid process. There is also a relevant share of phosphate rock that is not processed but applied directly as fertilizer on agricultural soils [17]. Table 1 summarizes past pilot scale experiments conducted to recover REEs from phosphoric acid and phosphogypsum in the last century.



Table 1. Historic pilot scale rare earth elements (REEs) recovery from phosphate rocks.

Time	Activity
1890	Industrial application of Dorr Process (H_2SO_4 process)
1928	Industrial application of Odda Process (HNO_3 process)
1930s	USSR recovered REEs from phosphate rock
1960s	Industrial application of IMI process (HCl process)
1965	REEs were recovered in HCl process (Romania)
1965-1972	REEs were commercially recovered from phosphate rock in Finland
1970s	REEs were recovered in HCl process (China)
late 1970s-early 1980s	Solvay extracted REEs from wet phosphoric acid via solvent extraction
1987-1996	REEs were recovered from evaporation sludge (South Africa)
1993	REEs were recovered from hemihydrate-phosphogypsum (Poland)

In addition, to REE recovery an even greater number of countries looked into unconventional uranium extraction from phosphoric acid. Uranium concentrations in natural phosphate rock vary significantly from deposit to deposit and may exceed uranium concentrations of commercially developed uranium mines [18]. In the 1980s to the mid-1990s approximately 20 % of mined uranium in the United States was recovered from phosphoric acid in Florida and Louisiana. Kim et al. [19] estimated that at the moment 10 % of uranium required for peaceful usage in the United States could come from national phosphoric acid production and Gabriel et al. [20] further estimated that more than 15 % of uranium required for peaceful purposes worldwide could be recovered from the world's phosphoric acid production.

2. Direct uranium and rare earth elements recovery from phosphate rock

In contrast to traditional approaches to extract REEs and uranium from the intermediate products phosphoric acid and phosphogypsum, REEs and uranium can also directly be recovered from phosphate rock before wet phosphoric acid production or direct phosphate rock application on agricultural soils. The main idea of this new approach is the selection of a specific leaching reagent that has high leaching efficiencies of REEs and uranium with a minimum leaching efficiency towards the phosphate rocks P_2O_5 content. This way the majority of valuable trace elements can be recovered. If REEs and uranium are recovered from the intermediate products only the share transferring to the phosphoric acid or phosphogypsum can be extracted. Depending on the specific wet acid process and the specific process conditions approximately 60-80 % of the REEs transfer to the phosphogypsum and roughly 80-90 % of the uranium transfers to the phosphoric acid. Needless to say no trace elements are recovered if phosphate rock is applied on agricultural soils directly.

REEs and uranium are toxic or radiotoxic [21], [22] so that removing these elements at an early stage during phosphate fertilizer production can be considered advantages from an environmental point of view. Fertilizers with greatly reduced heavy metal content produced this way may also reach higher market values [23], [24]. Further, cleaner phosphogypsum can be produced. Phosphogypsum, that has the potential to be a good raw material for construction, is currently of limited use as it shows low levels of radioactivity [25]–[27].

Figure 1 shows the flow sheet of the proposed alternative process. REEs and uranium are first leached from phosphate rock. Phosphate rock with greatly reduced REE and uranium content (a recovery rate >90 % is envisaged) can further be used for traditional phosphoric acid and later fertilizer production or direct phosphate rock application. Both REEs and uranium are separated from the slurry using ion exchange resins. The valuable materials are eluted and precipitated before they can be sold.

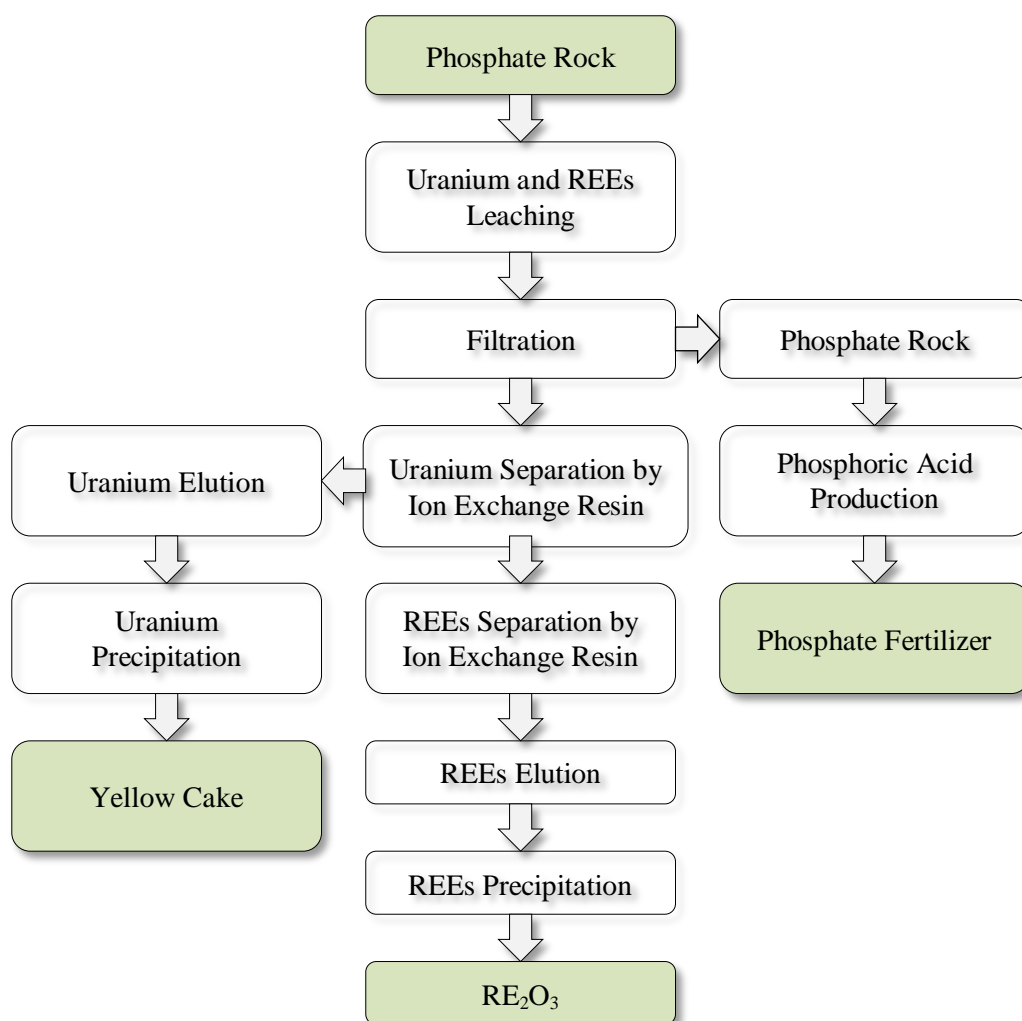


Figure 1. Proposed flow sheet for direct rare earth element (REEs) and uranium recovery from phosphate rock.

3. Material and methods

First lab scale leaching experiments of the proposed approach have been conducted using phosphate rock from the Abu-Tartur phosphate mine in Egypt. Specifically the phosphate rock samples were collected at the Abu Tartur plateau located in the Western Desert of Egypt. All samples were pretreated crushed, washed with water, dried overnight at 105 °C, cooled and then concentrated using gravity separation. The chemical composition of the samples was determined using x-ray powder diffraction (XRD) and is provided in Table 2.

Table 2. Chemical composition of the concentrated Abu-Tartur phosphate rock samples used.

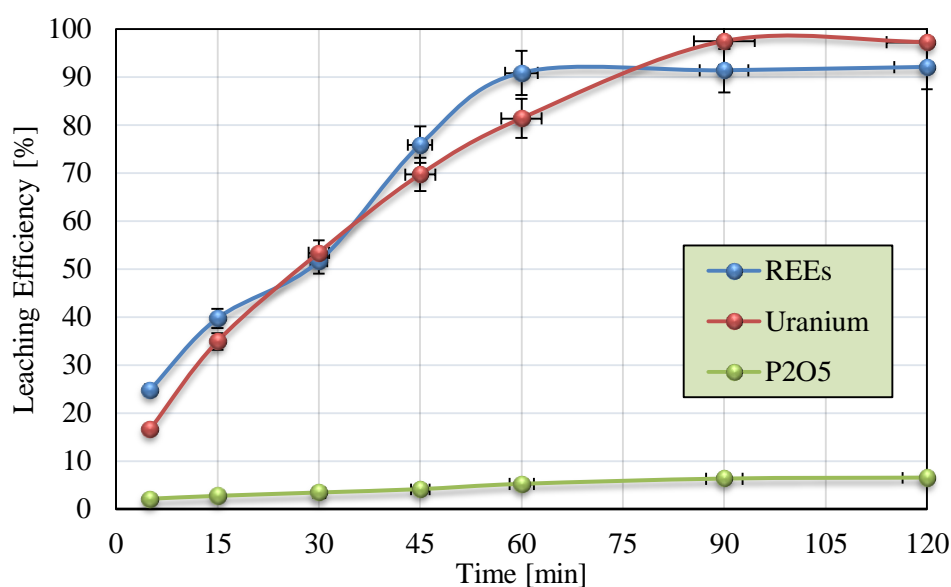
Constituent	CaO	P ₂ O ₅	Fe ₂ O ₃	F	SiO ₂	SO ₃	MgO	Al ₂ O ₃	Na ₂ O	LOI*
Content [wt%]	46.67	30.84	3.80	2.80	2.30	1.50	0.90	0.46	0.28	5.1

*LOI=Loss of Ignition

The XRD-analysis suggests that the phosphate rock consists mainly of Francolite together with minor amounts of Dolomite and Calcite. Abu Tartur phosphate rock contains relevant amounts of REEs in the order of 0.100 wt% and a relatively low content of uranium in the order of 0.003 wt% [28]–[31]. These values could also be confirmed as part of this study.

4. Results and discussion

The leaching kinetics of REEs, uranium and P₂O₅ have been investigated and are depicted over time in Figure 2. More than 90 % of the REEs can be recovered after 60 min. In the same time a bit more than 80 % of the uranium but also 5 % of the P₂O₅ is removed from the phosphate rock. After 60 min the percentage of REEs leached stays fairly constant while the percentage of uranium and P₂O₅ continues to rise to 97 % and 6 % respectively at 90 min. The leaching efficiency is not considerably changed when the experiment is continued for another 30 min to a total time of 120 min.

**Figure 2.** Leaching efficiency of rare earth elements (REEs), uranium and P₂O₅ of Abu-Tartur phosphate rock over time.

5. Conclusions

The first results presented here are promising in a way that a leaching reagent was found that can extract the majority of REEs and uranium in a manageable time frame without removing too much of the ores P₂O₅ content. Further lab scale experiments with different phosphate rocks as well as larger scale pilot plant experiments will, however, be necessary to understand how this approach can best be integrated in existing phosphate rock processing plants. Besides technical considerations, economic considerations will ultimately determine the acceptance of direct leaching versus traditional wet-acid phosphate rock processing with or without REE and uranium recovery.

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