August, 2015

HYDROMETALLURGY OF PHOSPHATE ROCK AND THE RECOVERY OF URANIUM

Fathi Habashi

Available at: https://works.bepress.com/fathi_habashi/155/
Chapter 5

HYDROMETALLURGY OF PHOSPHATE ROCK AND
THE RECOVERY OF URANIUM

Fathi Habashi*
Department of Mining, Metallurgical, and Materials Engineering
Laval University, Quebec City, Canada

ABSTRACT

Phosphate rock of sedimentary origin contains on the average 0.01 % uranium. Since large tonnage of this rock is used annually to produce fertilizers, this represented an important potential source of uranium. Before the discovery of rich uranium deposits this source was developed on industrial scale. The production of phosphoric acid by sulfuric acid process is at present facing the problem of disposal of gypsum; about 1.5 tons of gypsum is produced per ton of rock processed. This material contains all the radium originally present in the rock which results from the radioactive decay of uranium. As a result, phosphogypsum contains about 0.03 mg Ra/t or 30 pCi/g. The recovery of uranium from this source and the advantages of using nitric acid is discussed. The possibility of applying heap and vat leaching to phosphate rock is emphasized.

INTRODUCTION

After the discovery of radioactivity by Antoine Henri Becquerel (1852-1908) in 1896 and the isolation of polonium and radium from the residues of uranium plant in Joachimsthal by Marie Curie (1867-1934) in 1898, the search for uranium deposits continued. In 1908 the British physicist John William Strutt [Lord Rayleigh] (1842-1919) (Figure 1) noted that phosphate rock was radioactive due to the presence of uranium. At an annual world production of phosphate rock of 130 millions tons this represents a potential source of about 13 000 tons uranium. Because the mining and processing of phosphate rock is already

*Fathi.Habashi@arul.ulaval.ca.

Complimentary Contributor Copy
financed by the existing phosphate fertilizer industry, the cost of the uranium as a by-product should not be great.

![John William Strutt [Lord Rayleigh] (1842-1919).](image)

**Figure 1.** John William Strutt [Lord Rayleigh] (1842-1919).

**URANIUM IN PHOSPHATES**

Phosphate rock is the major source of phosphorus in nature. It exists mainly in the form of hydroxy- and fluoroapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ and $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$, respectively or a mixture of both and is used mainly for the production of fertilizers and elemental phosphorus. There are two main types of phosphate rock:

- **Sedimentary** These supply 85% of the phosphate rock for the industry, contains 100-200 ppm of uranium, 2-20 ppm thorium and about 0.5% lanthanides. Florida and North Africa phosphates are typical of this category.
- **Igneous** These supply the remaining 15%, contain < 10 ppm uranium but contain appreciable amount of thorium and lanthanides. Kola phosphate which is mined in Russia is typical of this category.

Uranium is present mainly in the tetravalent state in isomorphous substitution with calcium ion; the ionic radius of $\text{U}^{4+}$ which is 0.97Å being very near to that of $\text{Ca}^{2+}$ which is 0.99Å (Figure 2). In most cases uranium exists in radioactive equilibrium with its decay products (Figure 3).
The presence of uranium in phosphates became important only during the 1940's because of the need for uranium in the USA in connection with the Manhattan Project to produce an atomic bomb. No local uranium deposits were known at that time. The recovery of uranium as a by-product was economically feasible. Processes were therefore developed and applied to extract uranium from phosphoric acid produced by H₂SO₄ acidulation of phosphate rock. Eight plants for the recovery of uranium from phosphoric acid have been built and operated in the US since 1976.

Parallel to this activity, intensive exploration for uranium was under way which resulted in the discovery of rich uranium ores. This rendered the recovery from phosphate uneconomical, and many plants were shut down. In the early 1970's, however, the phosphate fertilizer industry became again interested in uranium as a result of development in the nuclear energy industry and shortages in uranium supplies. Consequently many fertilizer plants became again engaged in the recovery of uranium from the technical acid.

Figure 2. Illustration of the isomorphous substitution of uranium with calcium in phosphate rock of different origin. Kola phosphates is of igneous origin.

Figure 3. Illustration of the radioactive equilibrium of uranium with its decay products in phosphate rock.
**RECOVERY FROM PHOSPHORIC ACID**

Uranium was recovered from phosphoric acid by precipitation methods but mainly by extraction with organic solvents without interfering with the manufacture of fertilizers (Figure 4). At least three extraction processes were used commercially (Table 1).

The OPPA process was the first solvent used industrially in the 1950's by the International Minerals & Chemical Corporation in Bartlow, Florida. OPPA was prepared by dissolving $\text{P}_2\text{O}_5$ in octyl alcohol in absence of moisture and below $15^\circ\text{C}$. It is a complex mixture of organic phosphorus compounds, and its effectiveness as an extractant is due to a synergic effect between its components. It extracts uranium in the tetravalent state; therefore, a reducing agent, usually metallic iron is added to the acid to reduce its uranium content. It is unstable and hydrolyzes slowly to octyl orthophoric acid which is a much less effective solvent. The hydrolysis is accelerated by strong acids and by increased temperature. Uranium is stripped from the solvent by concentrated hydrofluoric acid yielding $\text{UF}_4$. Other extractants were later developed (Table 1).

**Table 1. Extractants for uranium from phosphoric acid**

<table>
<thead>
<tr>
<th>Process</th>
<th>Formula</th>
</tr>
</thead>
</table>
| **OPPA process** | Octyl pyrophosphoric acid where R is $\text{CH}_3(\text{CH}_2)_6\text{CH}_2$- |}
TREATMENT OF PHOSPHATE ROCK WITH SULFURIC ACID

The phosphate fertilizer industry is at present based mainly on the use of sulfuric acid. The problems of this technology are the following:

- Generation of large amounts of radioactive gypsum that represents storage and environmental problems (Figure 5).
- The use of expensive reactors for acidification that necessitates the frequent replacing the damaged agitators (Figure 6).
- Extensive material handling problems, and in the case of Florida, there are large losses of P$_2$O$_5$ values in the circuit (Figure 7).

Figure 5. Gypsum stacks in Florida.

Figure 6. A typical reactor for phosphoric acid production by the sulfuric acid rout [Lurgi].
Nitric acid is used to a minor extent for treating phosphate rock. It represents about 15% of the total fertilizer produced. In this process phosphate rock is dissolved in 50%-60% HNO$_3$ to form phosphoric acid and calcium nitrate:

$$\text{Ca}_{10} (\text{PO}_4)_6 \text{F}_2 + 20\text{HNO}_3 \rightarrow 6\text{H}_3\text{PO}_4 + 10\text{Ca} (\text{NO}_3)_2 + 2\text{HF}$$

Calcium nitrate is then removed because of its hygroscopic character. This is done by crystallization as tetrahydrate, Ca$(\text{NO}_3)_2$·4H$_2$O, by cooling to -5°C. Calcium nitrate crystals obtained are converted to carbonate as indicated by the reaction:

$$\text{Ca}(\text{NO}_3)_2 + 2\text{NH}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow 2\text{NH}_4\text{NO}_3 + \text{CaCO}_3$$

A flowsheet of the process is shown in Figure 8. The advantage of this route is that there is no disposal problem due to gypsum. In addition it permits the use of heap and vat leaching of the phosphate rock. Work conducted at Laval University showed that adopting this technology which is widely used for recovering copper, uranium, gold, potash, and other salts has great advantages. It will not be possible to use H$_2$SO$_4$ in such technology because gypsum formed during leaching will block the flow of the solution in the bed.
Applying hydrometallurgical techniques such as heap leaching (Figures 9-13) to phosphate processing could solve the problems faced in sulfuric acid route, i.e., the disposal problem of gypsum and the erosion of the agitators in the reaction vessel. Leaching in vats like leaching copper ores in Chile can also be used (Figure 14).

**HYDROMETALLURGY AND THE PHOSPHATE INDUSTRY**

Figure 8. Nitric acid process for treating phosphate rock.

Complimentary Contributor Copy
Figure 9. Hydrometallurgical techniques: preparation of terrain.

Figure 10. Hydrometallurgical techniques: preparation of heap.

Figure 11. Another method for preparation of heap.
Nitric acid concentration, however, must be only 20% so that the leach solution is monocalcium phosphate and calcium nitrate:
Ca_{10}(PO_4)_6F_2 + 14HNO_3 → 3Ca(H_2PO_4)_2 + 7Ca(NO_3)_2 + 2HF

Higher concentration will produce phosphoric acid at the top of the bed which reacts further with apatite on its descent to form insoluble dicalcium phosphate and the flow of solution will be blocked (Figure 15).

Figure 15. Optimal leaching conditions for phosphate rock in a static bed is at 20% HNO_3.

Figure 16. Proposed process for the treatment of phosphate rock in-situ, dump, or vat leaching.

When this technology is used calcium nitrate cannot be crystallized and a double salt is obtained: Ca(NO_3)_2·Ca(H_2PO_4)_2·2H_2O [or Ca(NO_3)_2·H_3PO_4·H_2O] known as calcium nitrate phosphate. This can be crystallized and decomposed at low temperature (200°-250°C) to form dicalcium phosphate and acid vapours:

\[ \text{CaNO}_3\text{H}_3\text{PO}_4\text{H}_2\text{O} \rightarrow \text{CaHPO}_4 + \text{HNO}_3 + \text{H}_2\text{O} \]
The acid vapours can be condensed or washed with water for recycle. The residue which typically analyzes 40% $P_2O_5$ is insoluble in water but soluble in citric acid and can be marketed as a fertilizer or as a high grade phosphate product (Figure 16).

**Uranium, Rare Earths, Radium, and Fluorine**

Methods were devised to recover uranium and rare earths by extraction with organic solvents while radium can be co-precipitated with barium sulfate. From nitrate system, uranium is first extracted by a mixture of bis(2-ethylhexyl)phosphoric acid (D2EHPA) and tributyl phosphate (TBP) in hexane followed by the extraction of the lanthanides with TBP. The loaded organic phase was scrubbed with the least amount of distilled water at the aqueous/organic phase ratio 1/10 in three stages to remove all the co-extracted impurities. The organic phase was then stripped with 10% ammonium carbonate solution to form ammonium uranate precipitate. The organic solvent was then recycled to the extraction stage.

The extraction of lanthanides was possible by TBP alone at the natural pH of the leach solution ($pH = 0.3$), and at the organic/aqueous phase ratio 1/1 in one stage, it was found that 100% of lanthanides was transferred into the organic phase. The lanthanides were stripped from the organic phase by dilute $HNO_3$ acid in two stages at the aqueous/organic ratio 1/1 and then selectively precipitated by 12% oxalic acid solution. The oxalate precipitate was then calcined at 1200°C for 1 h to yield a concentrate analyzed as 12% $Ln_2O_3$ and 88% $CaO$.

Under the mild leaching conditions used in this process, HF in solution reacts with silica to form fluorosilicic acid:

$$6HF + SiO_2 \rightarrow H_2SiF_6 + 2H_2O$$

which can be precipitated with sodium nitrate to form sodium hexafluorosilicate:

$$H_2SiF_6 + 2Na^+ \rightarrow Na_2SiF_6 + 2H^+$$

**CONCLUSION**

Dilute nitric acid [20%] can be used to advantage for leaching phosphate rock. This permits the use of standard hydrometallurgical processes such as vat and heap leaching. Uranium can be recovered from such solution by solvent extraction. There will be no disposal problem and the final product is dicalcium phosphate containing 40% $P_2O_5$.

**REFERENCES**

Awadalla F. T., F. Habashi, “Extraction of Uranium and the Lanthanides from Ca($H_2PO_4$)$_2$–Ca(NO$_3$)$_2$–H$_2$O and Ca($H_2PO_4$)$_2$–CaCl$_2$–H$_2$O Systems,” *I & EC Research* 28, 1101–1103 (1989)


Habashi F., “Chemical Beneficiation of Phosphate Rock”, *Engineering & Mining Journal* 64-67 (October 2014)


