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In-situ and dump leaching technology: application to phosphate rock

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Abstract. The technology of in-situ and dump leaching, used widely by hydrometallurgists, can be applied with advantage to the exploitation of phosphate rock deposits especially those low in limestone. Nitric or hydrochloric acids of certain concentrations would be used instead of H_2SO_4 and the solutions obtained treated to remove radium and recover uranium and the lanthanides if desired, then evaporated to crystallize the double salt $\text{CaXH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$, where $\text{X} = \text{Cl}$ or NO_3 ; this can be decomposed at $200^\circ\text{--}250^\circ\text{C}$ to form dicalcium phosphate, CaHPO_4 , a high grade marketable product. Nearly all the acid required for leaching can be regenerated and recycled.

Introduction

Getting ores from underground is usually done by digging a hole in the deposit, big enough for the miners to descend to bring the ore to the surface. Sometimes, it is more economical to remove the waste rock (overburden) to expose the ore which is then exploited by open-pit method. A method called in-situ mining (or mining in place) was first applied at the beginning of this century to the sulfur deposits in the Gulf of Mexico region. In this method, sulfur is brought to the surface without sending the miners underground or removing the overburden, but by injecting hot water under pressure into the deposit to melt the sulfur which then comes up to the surface as a liquid together with the hot water. The process is known as the Frasch Process after its inventor.

The success of the Frasch Process suggested to engineers to apply the same principle for the exploitation of water-soluble salt deposits underground. In this case water is injected in the deposit to dissolve the salt, and the salt solution is then pumped to the surface for crystallization and recovery. Exploitation of coal seams underground was also considered and tested by a similar technology. In this case preheated air or a mixture of hot air and steam is injected in the coal bed to react forming CO or CO-H_2 mixture which is then brought to the surface for use as a fuel.

In the 1960's, this technology was adopted in metallurgy for the first time to exploit low-grade copper ores [3]. Dilute sulfuric acid was injected in the deposit underground to dissolve copper and the copper-bearing solution was brought to the surface for recovery of copper. Sulfuric acid was used because it was the cheapest acid. Later the same process was used for uranium ores. When the deposit contained much acid-soluble gangue minerals, the acid consumption could not be tolerated and therefore in the case of uranium a sodium carbonate leach solution was used. The process proved to be so very economical, that it was applied also for high grade material. Further, the ore need not be underground to be exploited in this way – it can also be above ground.

Parallel to these developments was the so-called “dump leaching” process. In this case, waste rock containing small amounts of copper already stock piled near the mine and too low to be exploited by a conventional leaching process, were sprayed with dilute sulfuric acid to dissolve the copper minerals during its passage through the dump [3]. The copper-bearing solution is then collected at the bottom for recovery. The process was further applied to dumps intentionally constructed to be treated in the same way. The technology was later extended to uranium ores and few years later to gold ores. In the case of gold ores, acid is not effective for dissolving gold but a dilute solution of sodium or potassium cyanide has to be used.

Application to phosphate rock

The technology of in-situ and dump leaching has been thus well established through the years but was never considered for the treatment of phosphate rock, either underground nor above ground. To treat phosphate rock by this technology, however, sulfuric acid cannot be used because calcium sulfate will be produced, and being insoluble, it will block the passage of acid and hence no dissolution could be effected further. To overcome this difficulty, other acids that are more expensive such as nitric and hydrochloric should be used because they form soluble calcium salts [5, 7, 8].

The application of in-situ and dump leaching to phosphate deposits would be particularly interesting because the present method of exploitation of the deposits is facing numerous problems in certain places, for example, in Florida:

- 1) A large tonnage of overburden must be removed to expose the deposit.
- 2) Once the deposit is exposed and mined by open pit methods using water hoses to break down the rock and transport it as a slurry, slimes (very finely divided minerals) are carried down with the water. These cause two problems:

- a) Difficulty in settling hence large ponds must be constructed in which a large amount of water is tied up,
- b) About one third of the phosphate value is lost in the slimes.

It is evident, therefore, that there is a material handling problem, water balance problem, phosphate value losses, expensive land is tied up unnecessarily and a danger exists in case the ponds break down. These problems were discussed extensively by experts without finding a satisfactory solution.

Work at Laval University [8] has shown the following:

- 1) Phosphate rock from Florida can be leached either in-situ or in dumps.
- 2) Nitric and hydrochloric acids can be used. However, their concentrations are critical: At high concentration, insoluble dicalcium phosphate forms that retards the dissolution. At low concentrations, the rate of reaction is low. Hence, the optimum concentrations were found to be as follows:
 - a) 20% HNO_3
 - b) 10% HCl
- 3) The leach solution can be treated in an original way to recover the phosphate values as a marketable product:
 - a) Evaporation, for example, in solar ponds or otherwise to crystallize the double salts:

$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ in case of HNO_3 leaching

$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ in case of HCl leaching

- b) These salts are then collected and decomposed at a moderate temperature (about 200°C) to get dicalcium phosphate (CaHPO_4) as a marketable product containing about 40% P_2O_5 and acid vapors for recovery and recycle.
- 4) Since phosphate rock contains on the average 0.015% uranium [4] and 0.5% lanthanides (rare earths) [6] it was found possible to recover these metals from the leach solution *before* evaporation by using organic solvents as follows [2]:
 - a) In the HNO_3 system, uranium is first extracted by a mixture of di-2-ethylhexyl phosphoric acid (D2EHPA) and tributyl-phosphate (TBP) in hexane. This is then followed by extracting the lanthanides with TBP.
 - b) In the HCl system, uranium is first extracted by a mixture of D2EHPA and TBP in hexane followed by lanthanides extraction with D2EHPA in toluene.
- 5) The product for the market (dicalcium phosphate) can be obtained free from radioactivity due to radium, a decay product of uranium. This can

be achieved by precipitating radium sulfate from the leach solution *before* the crystallization step, and preferably before the uranium and lanthanides extraction process. The following was observed:

- a) In the HNO_3 system $\text{Ba}(\text{NO}_3)_2$ is added followed by sulfate ion. The precipitate formed is $\text{Ba}_{0.6}\text{Ca}_{0.4}\text{SO}_4$ containing all the radium [1].
 - b) In the HCl system, BaCl_2 is added followed by sulfate ion. The precipitate formed is also $\text{Ba}_{0.6}\text{Ca}_{0.4}\text{SO}_4$ containing all the radium [8].
- 6) The leach solutions obtained when HNO_3 and HCl were used were practically free from fluorides. This may be due to the nature of the leaching process: any HF formed reacts with the bed components to form CaF_2 which is retained in the bed.

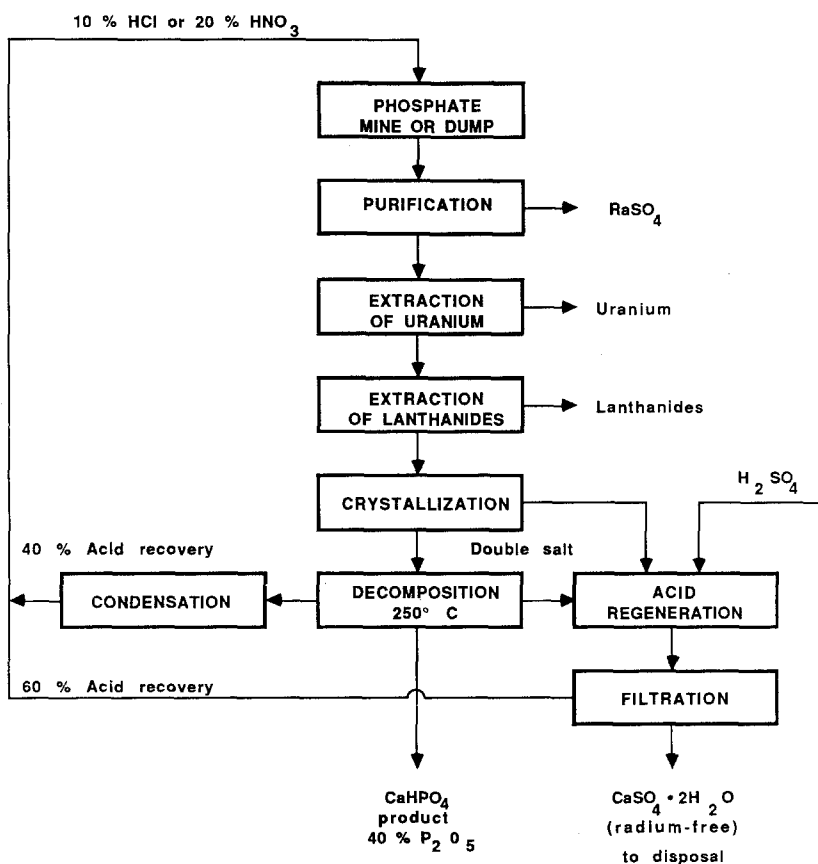
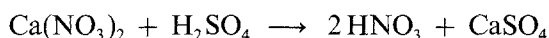
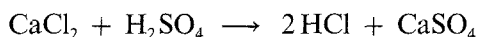


Fig. 1. In-situ and dump leaching applied to phosphate rock.

- 7) During the decomposition of the double salt, about 40% of the acid input can be recovered from the vapors.



The remaining 60% can be regenerated by reaction of the mother liquor with H_2SO_4 :



Conclusions

Material handling problems in the phosphate industry may be solved by using in-situ or dump leaching. A flowsheet of this technology is given in Fig. 1 which shows also the recovery of uranium and the lanthanides present in the rock and the production of radium-free gypsum for safe disposal.

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