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Hydrometallurgy to Solve Phosphate Processing

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CuO 0.05
NiO 0.05
Cr₂O₃ 0.04
ZnO 0.05
Cl 0.15
LOI 0.4
Moisture 0.2

Average particle size: 0.5-0.9 µm
BET 3.5 m²/g

The chlorine value should be as low as possible in order to avoid chemical attacks and other unwanted side reactions in other applications. The chlorine value depends on plant production parameters, and stringent control on this value in the resulting iron oxide is necessary.

The resulting spray roast oxide is packed into big-bags, sometimes in silos. From there it is transferred to producers of pigments, magnets, ferrites, or the concrete industry.

Spray roasting technology, which has been mainly developed to regenerate acids from steel pickling lines, has found an attractive economic by-product market. The iron oxide produced in the heat converter system, the spray roaster, can be upgraded by appropriate means into high quality iron oxide pigment. The routes proven are, chemical control, stringent process control, after treatments, like calcining, milling, and co-milling with other oxides, to achieve certain pigment colour shades and effects. Co-milling together with MnO, Al₂O₃, ZnO, TiO₂, Cr₂O₃, V₂O₅, SnO₂ will produce different shades and complex chemical structures of different crystallo-graphic structures.

Though iron oxide is a frequently used material, derived from different processes, such as the process routes by the Bayer or BASF chemical companies, spray roasted iron oxide amounts to only a small part, 1-2%, among them. Considering a modest value of spray roasted iron oxide of some US$50-100/tonne, pigment upgraded material can be valued to around $500/tonne.

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**Hydrometallurgy to solve phosphate processing**

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

- Generation of large amounts of radioactive gypsum that represents a storage and environmental problems.
- The use of expensive reactors for acidification that necessitates the frequent replacing the damaged agitators.
- Extensive material handling problems, and in the case of Florida, large losses of P₂O₅ values in the circuit.

Applying hydrometallurgical techniques to phosphate processing could solve these problems. For example, using in situ, heap, or vat leaching solves the problem of the reactor, but nitric acid must be used in this case instead of sulphuric. It is more expensive but this solves the disposal problem due to gypsum. The acid concentration must be 20% HNO₃ so that the leach solution is monocalcium phosphate and calcium nitrate [4]:

\[
Ca_{10}(PO_4)_6F_2 + 14 HNO_3 \rightarrow 3 Ca(H_2PO_4)_2 + 7 Ca(NO_3)_2 + 2HF
\]

Instead of evaporating the leach solution of monocalcium phosphate, limestone is added to precipitate finely divided dicalcium phosphate:

\[
Ca(H_2PO_4)_2 + CaCO_3 \rightarrow 2 CaHPO_4 + CO_2 + H_2O
\]

The product (40% P₂O₅) is insoluble in water but soluble in citric acid and is an excellent fertiliser. Because it is neutral it can be mixed with other nitrogen containing fertilisers. An option also exists: instead of filtering off the dicalcium phosphate, the slurry is evaporated under vacuum to produce dicalcium phosphate - calcium nitrate fertiliser mixture.

In this technology, less nitric acid is used as compared with the nitrophosphate process which is based on the following reactions:

\[
Ca_{10}(PO_4)_6F_2 + 20 HNO_3 \rightarrow 6 H_3PO_4 + 10 Ca(NO_3)_2 + 2 HF
\]

After crystallising a portion of calcium nitrate, the solution is then treated with ammonia:

\[
Ca(NO_3)_2 + 2 H_3PO_4 + 3 NH_3 \rightarrow 2 NH_4NO_3 + CaHPO_4 + NH_4.H_2PO_4
\]

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

\[
6HF + SiO_2 \rightarrow H_2SiF_6 + 2H_2O
\]

which can be recovered from the leach solution by precipitation with sodium nitrate to form sodium hexafluorosilicate:

\[
H_2SiF_6 + 2Na^+ \rightarrow Na_2 SiF_6 + 2H^+
\]

Dicalcium phosphate produced by this process can be used also as animal feed.

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