

# Developments in phosphate-rock beneficiation and the problems with Indian phosphorites

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## Introduction :

Phosphate-rock or more precisely the phosphorites form the repository of phosphate supply for the fertilizer industry for manufacture of elemental phosphorus, phosphoric acid and innumerable alkali phosphates. It has now been universally agreed that phosphorites have some kind of sedimentary marine origin, the source of phosphorous being of organic and/or inorganic origin (1). The principal phosphate mineral occurring in these deposits is referred by its generic designation as collophane (2), a carbonate bearing variety apatite, whose formula is approximately  $\text{Ca}_{10}(\text{PO}_4)_6\text{CO}_3\cdot\text{H}_2\text{O}$  with a little of F. It is porous and crypto-crystalline, occurring as compact nodules or pellets as disseminations in calcitic or quartzitic sedimentary rocks along with clay, sericite, silt, chert, free carbon and invariably associated with a little uranium (0.002 to 0.008%  $\text{U}_3\text{O}_8$  e). The typical apatite  $[\text{Ca}_5(\text{PO}_4)_3\text{F}]$  is crystalline and occurs usually in igneous and metamorphic rocks, pegmatites, granites, and schists. Its chemical composition is more defined and constant compared to the collophane of sedimentary origin. Fertilizer industry, though uses phosphate from both sources; the super phosphate manufacturers prefer phosphate-concentrates from phosphorite because of the ease with which collophane goes into solution with sulphuric acid. The physical characteristics of collophane also have bearing on its flotability.

With the growth of population there has always been increasing demand for fertilizers and therefore, for cheap phosphate sources all over the world. This situation necessitated beneficiation of phosphate-rocks; first on Florida phosphate

fields in early 1900s. The latest Figure (3) of world production of this vital raw material in 1984 is 134,321,000 tonnes to which United States' contribution alone is about 32%. Fortunately in recent years phosphate industry had made a head way in India. The latest available domestic production figure stands at around 700,000 tonnes, contributed mainly by Jhamarkotra 400,000; Mines of RSMDC 200,000 tonnes and the rest by Maton and other workings. Maton is perhaps the only phosphate beneficiation mill in the country run by Hindustan Zinc Limited with an installed capacity of 600 t.p.d. Jhamarkotra is expected to go on stream soon with 3000 t.p.d., for enriching their off grade rock, by eliminating carbonate gangue. Price of Jhamarkotra rock of  $-\frac{1}{2}$ " is Rs. 680/- per tonne ex-mines. The total estimated figure of the country's reserves as revealed from the published sources come to 246.6 million tonnes (4). Our deposits in Rajasthan viz; Kanpur, Karharbari-Ka-gurha, Birmania, Kohira, Jhamarkotra all of these are of carbonate bearing nature. The Maton deposit has quartzitic gangue plus clay. These deposits and other sources in Bihar and U.P. require to be beneficiated in order to increase their mining life.

## DEVELOPMENTS IN BENEFICIATION :

### Gravity Separation :

It may be said that phosphate beneficiation on scientific lines took birth on Florida phosphate fields. The reserves were enormous and the early practices were limited to log-washing, screening at 1 mm; and conserving only the coarse phosphates. Improved separation methods started developing, to recover the phosphate from washer's slimes. Waggman (5)

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listed 64 U.S. patents on washing, cleaning and drying methods adopted during the period 1869 to 1945. He also presented over 160 patents on the flotation of phosphate rocks, covering the period 1923-1950.

Cattermole, in early 1900s, first conceived the idea of imparting a hydrophobic coating to apatite with oleic acid, thereby giving it a buoyancy effect in water, for tabling operation. This principle was further perfected by Chapman and Littleford (6) (1934) in a gravity separation method called "agglomeration tabling" or table flotation. Separation by using Humphrey's spirals, underwater screens, and conveyor belts based on the same principle of agglomerating phosphate particles, was extended by Humbell (7). The principle is to render the collector coated apatite particles into agglomerates by the help of tiny air bubbles, so that their apparent specific gravity becomes much less than the actual specific gravity of apatite.

#### **Phosphate flotation :**

Brodbridge (8) and Sulman (9) in early 1920 developed soap flotation methods for crystalline apatite, using aliphatic carboxylic type of collectors (oleic acid, tal oil). Pamplin and Swainson (10) gave the early ore dressing practices for the pebble phosphate Florida. It was found that the crystalline apatite (igneous) could be floated with a fatty acid or its salt alone, but not the collophane of phosphorite. The important break-through in the flotation of collophane was first put forward by Crago (11). He used a mixture of fuel oil and fatty acid for selective flotation of collophane. Trotter et.al. (12) have recognised the importances of conditioning in thick pulp with reagent after desliming. Simple attrition grinding and sizing method of concentration was described by Newton and Finkelburg (13) for Idaho phosphate. In the case of leached zone (Florida) where the phosphate minerals are aluminium phosphates (wavellite and millisite) which were not amenable to fatty acid flotations; cationic collector (Armac-T) with Dowfrother was proposed by Davenport (14) to float out silica and silicate

minerals from phosphates. But lately Sun and Smith (15) made a detailed flotation study on this ore using anionic collectors, (18 — carbon fatty acids) and found that collecting power for phosphate decreased in the following order:— Linolenic acid > linoleic acid > oleic acid > stearic acid which have 3, 2, 1, 0 double bonds respectively. Using a combination of fuel oil and pamak-1 at 8.5 pH they could float a 30% phosphate concentrate.

Maslev et.al. (16) proposed that the residue, left over during the distillation of fatty acids, which contain higher fatty alcohol and fatty acids, as reagent, for flotation of apatite.

#### **Quartz flotation :**

Phosphate floats collected by soap flotation were not upto the mark due to entrainment of quartz. Recleaning steps did not make effective separation of collector coated apatite and quartz. Crago (17) first patented a process called double flotation or reverse flotation by introducing cationic collectors, amine-salt type. The phosphate floats collected by fatty acids were scrubbed with sulphuric acid to remove collector coating and then subjected to quartz flotation, using amine as the collector. Roberts (18) used a cyanamid reagent (Aeromine 3037) as collector for quartz. Davenport et. al. (14) have recommended primary amine acetate (Armac-T) with higher alcohol to float quartz from leached zone Florida aluminium phosphates. Terbutton et. al (19) in a number of reports have also recommended amine collectors to float quartz for the same ore. Recently authors (20) have found Rhodanine-D-acetate, a primary amine successful on Maton phosphate to remove chert and quartz.

#### **Calcite flotation :**

Flotation of calcite or dolomitic calcite from apatite did not find solution so far. The apatite and calcite both have similar flotation characteristics to anionic collector. The problem deserves serious consideration since several major world deposits are calcareous. Differential

flotation ( 21, 22 ) of calcite was first attempted by Michie on the ores of Djebloik Gafsa (N. Africa) using a collector mixture, of oleic acid, ethyl alcohol and diesel oil (R3 mix). Hoffman (23) suggested use of more selective petroleum acids. Eigeles (24) pointed out the utility of alkyl sulphate collectors for collophane. Mitzmager (25) proposed monosodium phosphate to depress apatite during calcite flotation. Zuplatec (26) patented a process of calcite flotation with fatty acids using gelatin amide as phosphate depressant. The depressant action of alkali phosphates, alkali sulphates and  $H_3PO_4$ , on apatite was recently studied by John David (27) during calcite flotation. In recent years Itshak et. al. (28) have proposed short chain saturated acids (naphthenic acid, kadimic acid) for Israeli calcareous phosphates. Fuerstenau (29) studied the role of hydrocarbon chain in anionic flotation of calcite.

#### **Slime flotation :**

The phosphate slime flotation is a tricky problem due to the presence of ultra fine clay minerals, dissolved electrolytes and different species of minerals, in all size ranges. Ralston (30) patented a process using a low carbon chain amine (cationic collector) to remove silica and clay. Haseman (31) in one patent proved the technical feasibility of recovering 40% of phosphate value by selective flocculation techniques. It was shown that selective flocculation was useful in separating minerals on size basis, for little coarser than clay particles. Mitzmager (25) proposed the use of monosodium phosphate to give a coating of di-calcium phosphate on apatite during flotation thus, depress phosphate and float the gangue from N. African phosphate slimes. Davenport et. al. in two publications (32, 33) gave an exhaustive data on size analysis of Florida slimes and suggested selective flocculation of phosphate particles using potato starch and NaOH.

Houston (34) had summarised the plant practices followed at Florida fields. It was found that after the establishment of soap flotation con-

ditions for apatite (including collophane), there was no significant contributions to the field of phosphate beneficiation during the period 1940-1960. The suggested methods if any were only the modifications to the already laid down principles of phosphate flotation. Lately electrokinetic potential studies on chlorapatite was attempted by Somasundaram (35). He pointed out that in the case of salt type mineral like chlorapatite that both lattice ions ( $PO_4^{3-}$ ,  $Ca^{2-}$ ,  $Cl^-$ ) and the  $H^+$  and  $OH^-$  ions play the role in potential determining. He also found that the equilibration takes a long time, and flotation studies done were invariably under non-equilibrium conditions. Recently Pradip et. al. (36) have made attempts to recover fine phosphate from phosphate slimes, using polyacrylamide and polyacrylic acid (anionic) type of flocculants and have found that in a dispersed mixture of clay and apatite, the Magnafloc A1 55, an anionic polymer acted as a good flocculant of clay thereby helped selective separation of clay and apatite. This could be one of the approaches in coming years for solving phosphate slime problem.

#### **Indian deposits :**

India has promising deposits in Rajasthan, Uttar Pradesh and Bihar as cited earlier. Depending on their mineralogy and from beneficiation point of view the deposits may be broadly classified into 3 types — (1) with predominant silica gangue, (2) with predominant carbonate gangue and (3) with mixed gangue.

#### **Type—1 Maton deposit :**

Its mineralogy is simple consisting of silica gangue and clay minerals. Compact pellets or nodules of collophane are enmeshed in this matrix. The problem here was two-fold (1) the presence of clay and (2) polynucleated texture of phosphate pellets which enclosed lot of silt sized ( $15-40\mu$ ) quartz or chert grains. Straight grinding and flotation without desliming does not give good separation of phosphate and gangue due to interference by clay particles which use up collector excessively. An

investigation report by the authors (20) gives in detail the discussion of this problem and a feasible process method together with flow-sheet.

The process in brief, the feed (23.4%  $P_2O_5$ ) after secondary crushing i.e. at around 18 mm size was first deslimed thoroughly to remove clay minerals, prior to flotation steps. After fine grinding to required size, the grind was classified into fines and sand. They were separately subjected to soap flotation. For sands an emulsion of amyl alcohol L. D. oil and linoleic acid was used and for the fines a mixture of sodium oleate and diesel oil was used as collector. Sodium silicate was used for gangue depression. The fines form bulk of the grind, and after three cleanings, yield a fairly clean high grade concentrate in large scale batch tests. The results were reproducible. An overall recovery of 75% was obtained at composite grade of 37%  $P_2O_5$  containing around 7%  $SiO_2$ . This product meets all the specifications given by H. Z. L.

#### **Type—2 Kanpur Deposit :**

The Kanpur west block sample assays 16.4%  $P_2O_5$  and has predominant calcite dolomite gangue. The problem of calcite-apatite separation by flotation has already been dealt with earlier. Comparatively calcite surface is more responsive to oleic acid adsorption than that of collophane. Therefore, hitherto researchers have attempted creating differential flotation conditions to float out carbonate gangue depressing phosphate with alkali phosphate (25), phosphoric acid, soda ash, NaOH, starch, gelatine, gum etc.

The problem was solved ultimately by resorting to a thermal beneficiation. A French scientist first proposed a method (37) of enriching phosphate rocks by calcination. A successful method of calcination suitable to Kanpur rock was developed by the authors (38) whereby a

good acid grade (34.3%  $P_2O_5$ ) concentrate was obtained at 76% recovery. The rock was crushed to -6 mm and subjected to static bed calcination at constant temperature ( $950^\circ \pm 10^\circ C$ ) in a muffle furnace. At this temperature the calcite decomposed to calcium oxide and carbon dioxide, while the apatite remained unaffected. Only at high temperature above  $1316^\circ C$  defluorination (5) takes place in apatite. After calcining the charge for required duration of time (here 2 hours for this size), it was quenched hot in fresh water. The idea was to prevent recarbonation of calcium oxide to calcium carbonate. The lime forms a milky white suspensoid in water which could be eliminated by any method of gravity separation like tabling or desliming. The deslimed sands got enriched remarkably from 16.4%  $P_2O_5$  to above 33%  $P_2O_5$  by elimination of carbonate gangue. The concentrate thus obtained met with specifications of fertilizer industry.

#### **Type—3 Maldeota :**

This rock (17%  $P_2O_5$ ) contained a mixture of silica and carbonate gangue. Others are iron oxide, pyrite, clay minerals and free carbon. The mineralogy is rather complicated and so was the separation problem. The reserves are quite extensive in this deposit, but unfortunately so far no satisfactory process method has been developed. Presence of pyrite and free-carbon gives trouble during calcination and flotation process. This rock could perhaps be enriched by calcination to furnace grade  $>24\%$   $P_2O_5$ . Elemental phosphorus can be directly obtained by furnace process.

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## DISCUSSION :

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*Question 1 : If reverse flotation is used for beneficiation of phosphate ore, will 2 cycles be required i. e. (i) flotation with sleric acid etc. and then (ii) reverse flotation with Amines ? If yes, will present plants have to invest in additional capital expenditure ?*

*Author :* Yes. If there is no alternative solution to make the product, the reverse flotation had to be adopted. At Florida, even today it is the practice. Amine collector consumption extremely low.

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*Question 2 : What are the latest developments in the use of chemicals (collectors) in the flotation process ? Is any work being done in India on development of more effective collectors for flotation process like fatty amines and their derivatives ? Which laboratories are doing this work ?*

*Author :* Use of fatty amines in India I have no knowledge; do not know if any one is manufacturing. Perhaps M/s. Hoechst may be able to reply. Dr. Arjun Raja is making flotation chemicals like xanthates and amine collectors.

*Question 3 : Is there any plant in India using cationic collector ?*

*Author :* To my knowledge there is no plant in India using cationic collector.

*Question 4 : What are the various problems associated with beneficiation of rock phosphate ore ? What is the role of chemicals like cationic surface active agent in making the process more efficient w. r. t. silica reduction ?*

*Author :* Elimination of silica content, elimination of carbonate gangue and slime are problems. Answer to all the above 3 problems have been dealt within the paper.

*Question 5 : How do you view the future of cationic surface active agents in upgrading phosphate ore ?*

*Author :* Not yet tried. It may be useful in flocculating clay and quartz particles.

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