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Production of epsom, gypsum and other industrial products from the mill tailings of Jhamarkotra rock phosphate project, India

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At the Jhamarkotra rock phosphate mines, the low-grade Proterozoic rock phosphate containing 14–19% P₂O₅ is beneficiated by froth flotation process to produce beneficiated rock phosphate having 32–34% P₂O₅, to provide raw material for fertilizer plants. The process generates considerable quantity of dolomitic tailings which contain 5–6% P₂O₅, 16–18% MgO and 32–34% CaO, that are potentially useful in agriculture. It is therefore necessary to utilize these products to conserve the diminishing, meagre and non-renewable phosphate resources of India. About 1500–1800 tonnes per day (TPD) of dolomitic tailings is produced through the processing of ~3000 TPD of the ore, which is collected in the tailing ponds. Investigation carried out on final carbonate tails (FCT) of Jhamarkotra rock phosphate froth flotation beneficiation plant revealed that good quality epsom (MgSO₄·7H₂O)/fertilizer-grade magnesium sulphate, gypsum (CaSO₄·2H₂O) and magnesium ammonium phosphate (MAP) can be produced by leaching FCT with dilute sulphuric acid (30%) at 60–80°C and subsequent crystallization through evaporation and cooling. MAP also can be produced, which has citrate solubility of about 96%. MAP has proved to be beneficial for rice crop on acid as well as alkaline soils. Additionally, ammonium carbonate/carbon dioxide, hydrogen fluoride/calcium fluoride can also be produced. This scheme will certainly help reduce the wastage of these resources, mitigation of pollution and will generate additional revenue to the company.

Keywords: Epsom, fertilizer, gypsum, magnesium ammonium phosphate, mill tailing.

IN the present global scenario of ever-increasing pollution, any effort or investigation to mitigate pollution needs to be encouraged. Utilization of waste tailings is the best way to deal with the problem, but till now the tailing utilization is restricted to brick making and as construction material¹. This aspect was unsuccessfully tried for the Jhamarkotra mill tailings too; therefore, a different and better approach was necessary. With this objective, a chemical utilization approach was carried out for the tailings of Jhamarkotra rock phosphate beneficiation plant of

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the Rajasthan State Mines & Minerals Limited (RSMML), Udaipur, India. Jhamarkotra ore has 16–18% P₂O₅, 10–12% MgO and 4–6% SiO₂. The major minerals are sedimentary cryptocrystalline apatite (cellophane), dolomite and quartz minerals along with minor quantities of oligoclase, sillimanite, etc. Jhamarkotra deposit contains about 40 million tonnes (mt) of such low-grade ores. As desired by RSMML, the Indian Bureau of Mines (IBM) has tested the ore lumps through crushing and grinding to 90% passing through 74 μm followed by bulk flotation of apatite and carbonate minerals, leaving siliceous gangue into the tailing. The bulk concentrate is thickened and taken to the second stage flotation, where acidic pH (5.0–5.5) is maintained using sulphuric acid and phosphoric acid is used to depress apatite minerals while floating dolomite with oleate. This process was also tested by IBM and the phosphate concentrate was found² to range from 32 to 36%. Beneficiation of low-grade phosphate ore generates large quantities of solid waste, that in turn create land pollution and affect groundwater due to the associated water disposed along with the waste slurry. Several countries, notably Australia, have banned beneficiation of low-grade (phosphatic) ores due to this reason. But countries which have limited resources of high-grade ore cannot do without beneficiation, as they have to provide P-fertilizer for their agriculture. India is a fitting example of this situation, as it has a meagre resource of rock phosphate, i.e. only 159 mt compared to the world reserve of 33 billion tonnes^{3,4}. Of the recoverable reserve, Rajasthan⁵ has 79 mt. High-grade rock phosphate ore containing >30% P₂O₅ is crushed and supplied to the chemical and fertilizer industry, while the low-grade rock containing 14–20% P₂O₅ is beneficiated by the flotation process to produce a concentrate of 32–34% P₂O₅, to make it suitable for the fertilizer and other industries. RSMML has captive rock phosphate mines at Jhamarkotra (lat. 24°29'6"N–24°27'18"N; long. 73°49'30"E–73°51'54"E)⁶. The company also has a beneficiation plant. The plant has an installed capacity to process 3000 tonnes per day (TPD) of low-grade ore. During the beneficiation process two types of tailings are generated: final carbonate tail (FCT) and bulk circuit tail (BCT). The carbonate tailings

generated amount to about 50% by weight of the ore processed and contain 5–8% P₂O₅, 15–17% MgO and 33–35% CaO. At present, both FCT and BCT are being pumped to the tailing ponds as waste.

The general flow-sheet of the process is given in Figure 1. FCT contains substantial amount of dolomite, which can be utilized to produce useful products like gypsum (CaSO₄·2H₂O) and epsom (MgSO₄·7H₂O) salts by way of value addition to the tailing⁷. Epsom salt has varied industrial applications and is in great demand in industries related to health, beauty, garden etc.⁸. Likewise, dolomite wastage can also be used as a raw material, which is the main objective of the present investigation.

Presently, epsom salt is produced in India in two ways: (i) By treating magnesium carbonate or hydroxide with sulphuric acid and (ii) from 'Sels' mixture obtained during the manufacture of common salt from sea water. At present, 9000 t of magnesium sulphate is produced in India annually; 6000 t based on sulphuric acid and 3500 t from sea bitterns⁹.

About 50 kg of FCT sample was collected from the Jhamarkotra rock phosphate beneficiation plant of RSMML to find out the technical feasibility to produce magnesium sulphate. The collected FCT was thoroughly mixed and a representative sample of 10 kg was obtained after coning and quartering.

Sieve analysis was carried out on 100 g of the sample using Standard BS Testing Sieves (Table 1). From the representative sample, 10 g of the sample was taken and subjected to chemical analysis. The assay is given in Table 2.

Investigation was carried out to study and optimize parameters to leach all the available values, i.e. MgO, CaO and P₂O₅ of FCT by sulphuric acid.

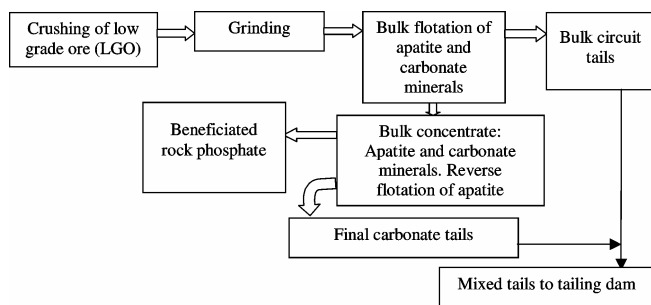


Figure 1. Flow sheet of the beneficiation process.

Table 1. Size analysis

Size in mesh no.	Weight % retained
+ 60	0.03
-60 + 100	0.91
-100 + 150	0.51
-150 + 200	4.76
-200	93.78
Total	99.99

Table 2. Chemical analysis of FCT

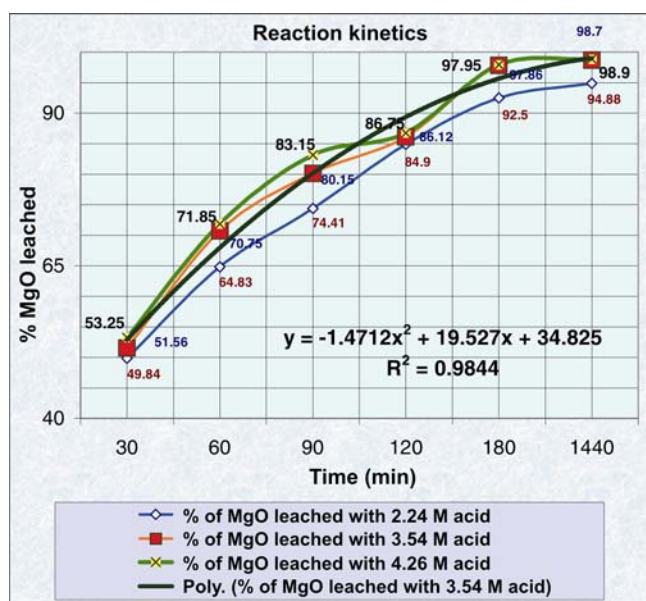
Element	Weight (%)
P ₂ O ₅	07.85
CaO	33.80
MgO	16.25
SiO ₂	01.80
R ₂ O ₃	00.45
LOI	38.50

Table 3. Details of leaching studies

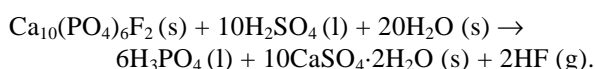
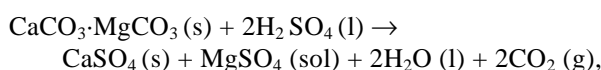
Molarity of H ₂ SO ₄ (M)	Time of leaching (min)					
	30	60	90	120	180	1440
2.24	49.84	64.83	74.41	84.9	92.5	94.88
3.54	51.56	70.75	80.15	88.21	97.86	98.7
4.26	53.25	71.85	83.15	86.75	97.95	98.9

Table 4. Specifications of magnesium sulphate as FCO

Details	FCO specifications	Epsom produced in the laboratory
Form	Free-flowing crystals	Free-flowing crystals
Water-insoluble matter	1.0% max	1.0% max
Magnesium as (mg) by wt	9.6% min	>9.6%
pH of 5% solution	5.0–8.0	+5.5
Lead	0.003	Nil

**Figure 2.** Reaction kinetics of leaching.

The following reactions occur when sulphuric acid is added to the material:



The above two reactions are exothermic and so heat is released during the reaction, therefore, some water evapo-

rates. This heat helps in increasing the solubility of magnesium sulphate while decreasing that of gypsum in the water (refer to solubility data of epsom and gypsum¹⁰). Details of optimization of acid concentration and leaching time are given in Table 3 and Figure 2.

During the study it was observed that the best leaching is obtained at around 60–70°C, i.e. below 80°C, to get dihydrate crystals of gypsum and a high concentration of MgSO₄ solution. It can be observed from the solubility data that the solubility of MgSO₄ increases with temperature and that of CaSO₄ decreases with temperature. However, above 80°C the hemi-hydrate of gypsum forms a hard mass resulting in the entrapment of carbonates and apatite particles, which reduces conversion of these particles into sulphate. Filtration of hemi-hydrate is also difficult.

Thus the optimum conditions for leaching FCT are: temperature, 60–70°C; solid-to-liquid ratio, 20–25 g/100 ml of solution; stirrer speed 400–500 rpm; acid concentration, 3–4 M, and time of leaching, about 3 h.

Thus leaching with 30% acid below 80°C with vigorous agitation is suggested to get 95–98% conversion of MgCO₃ to MgSO₄ and CaCO₃ to CaSO₄. The quantity of acid added was about 20% excess of the stoichiometric requirement, considering all the acid-reactive compounds of the carbonate tails. Reaction time of 3 h is required to get 95–98% conversion. Filtration of the material produced 16–18% solution of MgSO₄. The gypsum needs to be washed thoroughly with hot water (60–70°C) to remove all the absorbed solution of MgSO₄ from gypsum.

Crystallization of epsom was carried out in two stages at 25–30°C and subsequently at 10°C. After evaporation concentration of the wash a strong filtrate of 1.35 specific gravity was obtained. Purification and recrystallization yielded epsom conforming to FCO specifications¹¹ (Table 4). The product is shown in Figure 3.

Gypsum was dried at 100°C to remove free water (Figure 4). Anhydrous gypsum analysis is given in Table 5. Standard methods have been followed for analysing the products^{12,13}.

The remaining mother liquor containing MgSO₄, excess H₂SO₄ and P₂O₅ can be recovered as a mixed salt by neutralization with ammonium hydroxide to a pH of 8–9. The mixed salt will be a good fertilizer containing ammonium sulphate, magnesium ammonium phosphate, and magne-

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sium hydroxide and minor quantities of metallic sulphates.

Carbon dioxide liberated during the process can be used for producing ammonium carbonate or could be collected for other industrial uses. Hydrogen fluoride liberated is scrubbed with water and removed. Wastewater containing hydrogen fluoride is precipitated with lime to get industrial calcium fluoride¹⁴.

Thus a near-complete utilization of the final carbonate tails has been achieved. The process has been patented¹⁵ in June 2007. Figure 5 shows a flow sheet of the leaching process of FCT.

Table 5. Assay of anhydrous gypsum

Ingredients	% Weight	Ingredients	% Weight
CaSO ₄	94.90	CO ₂	1.04
CaO	39.98	SiO ₂	1.66
MgO	0.46	P ₂ O ₅	0.14



Figure 3. Epsom crystals developed from FCT.



Figure 4. Cakes of fine grained gypsum dried in solar dryers.

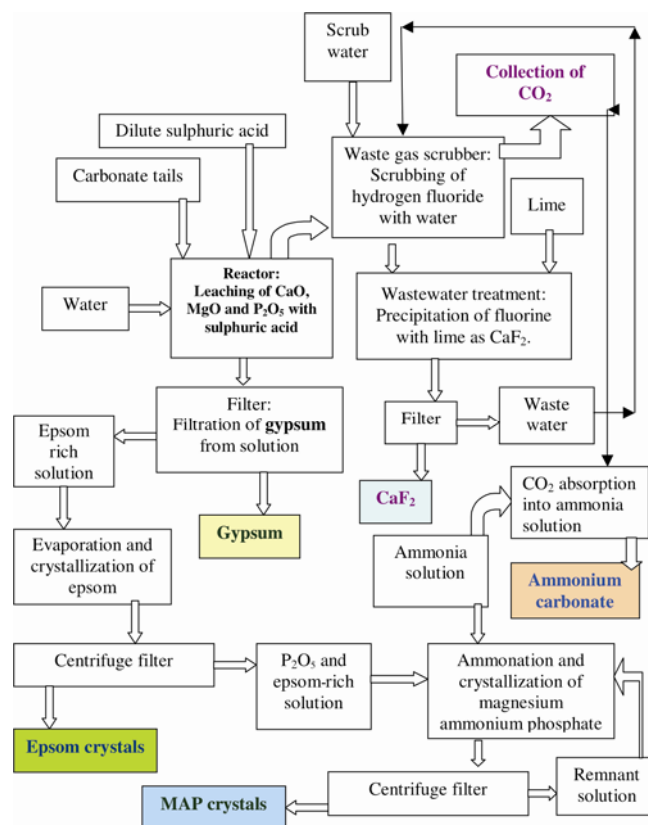


Figure 5. Flow sheet of the leaching process of FCT.

In conclusion, both gypsum and epsom were successfully produced at bench scale in the laboratory with AR-grade chemicals and FCT obtained from RSMML beneficiation plant at Jhamarkotra, Udaipur. Recovery of values, i.e. CaO, MgO are about 95–98% and yield of MgSO₄ with respect to that present in the leach solution is about +70%. The quality of epsom conforming to the specifications of the Fertilizer Control Order has been produced. Gypsum obtained can be used for producing ammonium sulphate, plaster of Paris and other calcium products. As the results achieved are encouraging, the technical viability of the project is positive. Similar utilization studies could be taken up for the other beneficiation mills. Integrated flow sheet for complete utilization of ores and tails will become the order of the day to achieve near-zero waste.

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