and gravity studies, should induce significant intraplate stresses in the crust, especially in the complex tectonic zone demarcated by domal high velocity structure and intrusive body along the Jahazpur thrust. The mechanical properties of these structures influence the stress state in the shallow part of the crust and lead to stress concentration in various parts of the profile. These results, in corroboration with measured stress data when available, can help in constraining models of the crust of this region.

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A process for making slow-release phosphate fertilizer from low-grade rock phosphate and siliceous tailings by fusion with serpentinite

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Worldwide demand of phosphate fertilizer is met essentially from phosphatic rocks. India imports most of its requirements and produces a small portion through froth flotation of Precambrian stromatolitic rock phosphate. Increasing population and consequent increase

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in demand for food production necessitated investigation to utilize the large reserves of low-grade rock phosphate to produce an alternative fertilizer. An acceptable phosphate fertilizer was obtained by fusion of low-grade dolomitic and siliceous rock phosphate from Jhamarkotra mines, effluents from beneficiation plants of Jhamarkotra and Maton Rock Phosphate Projects and serpentinite rejects from Rikhabdev décor stone industry, in an electric furnace followed by quick quenching with water. This scheme may be adopted for all low-grade ores in the world, which will help utilize the large reserves of low-grade phosphate. Useful by-products are also recovered and the process is environment-friendly.

Keywords: Fused fertilizer, phosphate, serpentinite, siliceous tailing.

TOTAL global resources of rock phosphate of all types and grades are of the order of 163,000 million tonnes (mt), out of which 55,000 mt is of recoverable resources[1]. Like most mineral resources, phosphate deposits are also distributed inequitably globally[2]. According to available data, the recoverable phosphate reserves of India[3] stand at a meagre 142 mt, to cater to the agricultural needs of one-sixth of the world's total population. The total resources of phosphate in India is estimated to be 306 mt, a greater part of which is of low grade[1]. Under these circumstances, utilization of low-grade phosphate resources with low energy inputs and in an ecofriendly way is the key to widening the base of phosphate utilization in India.

Jhamarkotra rock phosphate mine (lat. 24°29″6′–24°27″18′N; long. 73°49″30′–73°51″54′E)[4,5] of M/s Rajasthan State Mines and Minerals Ltd (RSMML), Udiapur is an economic and unique resource of rock phosphate deposit in India formed as marine chemical stromatolitic phosphorite sediment[6]. This deposit contains about 77 mt of rock phosphate ore, of which about 40 mt is low-grade ore (LGO). High-grade rock phosphate with 25–30% P_2O_5 is sold directly after crushing to fertilizer companies as chips. Annually nearly 900,000 t of LGO is subjected to double-stage, bulk and reverse flotation[5], and the concentrate is sold as beneficiated rock phosphate (BRP) having 32–34% P_2O_5, to the fertilizer plants engaged in the production of SSP, TSP, DAP, DCP and other phosphatic fertilizers in India[7]. The flotation process recovers about 80% P_2O_5 and weight recovery is about 40–45%. Thus, in the mill tailings there is a loss of 20% P_2O_5 in 55–60% of the rock slurry containing CaO, MgO and 5–10% P_2O_5.

The process generates two types of tailings: bulk circuit tail (BCT) and final carbonate tails (FCT), accounting for 5 and 50% of the material processed respectively. Both the tails are mixed and pumped into the tailing pond as waste. Some of the LGO is not amenable to flotation as it contains chert and is stacked separately at the mine site.

Fused calcium magnesium phosphate (FCMP) is a thermal fertilizer that was first produced by fusing rock phosphate with olivine[8], or other combinations[9]. It was produced by high-temperature fusion of high-grade phosphate ores (apatite), usually of igneous origin, with the addition of a suitable quantity of olivine or magnesia and silica-bearing minerals to achieve optimum fusion, followed by quick water quenching to impart citric and citrate solubility to apatite. Fusion breaks down the crystal lattice of apatite and forms alpha-tri-calcium phosphate, while silica and quick water quenching help in defluorination and retention of alpha phase of tri-calcium phosphate that is highly citric/citrate-soluble[9]. Presently, FCMP is a recognized fertilizer worldwide, and is being used successfully in developing and developed countries[10,11]. The process leaves no solid waste and retains all the nutrients available in the source rock.

In the present study the thermal phosphate was successfully produced from LGO by adding serpentinite[12] that is locally available as waste product of the décor stone industry (erroneously known as green marble in the industry). A made-to-order, three-phase, high-temperature furnace (1500°C; Figure 1 *a*), controlled by a temperature regulatory console (Figure 1 *b*) was used for fusion. Quartz crucibles (250 cc, 10 cm dia, 10 cm high) with graphite coating were used to fuse the hand-mixed raw material (Figure 1 *c*). After retaining the constituents at ~1450°C for about 30 min, the fused substance was quenched as shown in Figure 1 *d*. Various proportions of different additives, i.e. serpentinite, quartz, magnesium oxide, tailings containing magnesia and silica were tried to study fusion and citrate solubility of the products. Details of raw materials are given in Table 1 and Figure 1 *e*.

LGO, BCT and FCT were obtained from Jhamarkotra beneficiation plant directly from the process streams. These materials are 80–90%, 74 μm (200-mesh) in size. Other additives such as serpentinite and quartz were ground to 80% 100 μm (150 mesh) before addition. After fusion, the material was quickly quenched in a steel tank with flowing water facility (Figure 1 *d*). A granular, glassy but porous FCMP was obtained.

Samples of low-cost El-nasr ore imported by RSMML were also fused along with serpentinite to investigate the feasibility of the ore for production of FCMP (Figure 1 *f*). The low cost of this ore may offset the transportation cost. It was found that this ore is amenable for fusion and citric/citrate-soluble phosphate improved to 48% in the fused product. It may improve further by changing the composition of the recipe. Details of feed mix, temperature and times of retention at fusion temperature are given in Tables 2 and 3.

The product FCMP was ground to 80% 100 μm (150 mesh) size to analyse citrate solubility of its phosphate content. Neutral ammonium citrate was used to determine the solubility. Effect of temperature and additives was studied to obtain good fusion and maximum cit-

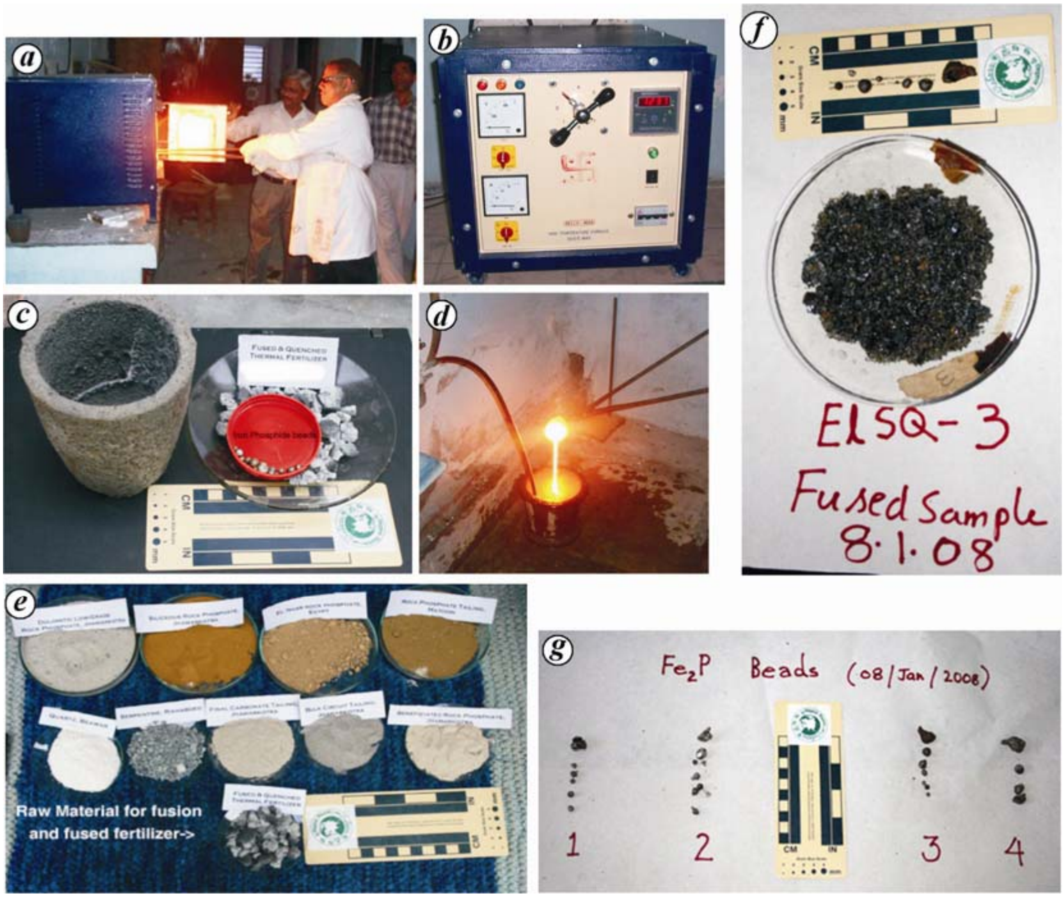

Figure 1. ***a***, Fused material being removed from the furnace. ***b***, Furnace control panel. ***c***, Crucible used for fusion with fused Fe_2P beads. ***d***, Quenching of melt in running water. ***e***, Various raw materials. ***f***, Product FCMP obtained from fusion of El-nasr ore. ***g***, Beads of ferro-phosphorus recovered from the fused material.

Table 1. Details of raw materials

Material	Details of elements in wt%				
	P_2O_5	CaO	MgO	SiO_2	R_2O_3
Beneficiated rock phosphate of Jhamarkotra	32.40	45.92	0.80	8.35	
Dolomitic low grade ore (LGO) of Jhamarkotra	14.7	39.76	12.20	4.90	2.70
Siliceous LGO of Jhamarkotra	9.60	15.50	1.4	60.34	
El-nasr ore of Egypt	13.5	23.20	0.80	29.8	1.60
Final carbonate tail of Jhamarkotra	7.9	33.9	16.3	1.83	0.45
Bulk circuit tail of Jhamarkotra	9.60	25.20	10.00	34.60	3.60
Serpentinite from Rikhabdev area	0.00	0.00	24.50	45.20	16.00
Quartz from Beawar				95.00	

rate-soluble P_2O_5 in the product. Metallic beads obtained with FCMP were identified by XRD study as ferro-phosphide (Fe_2P, interested readers can obtain XRD data from the authors). Beads recovered from fusion are displayed in Figure 1*g*. Carbon dioxide liberated during fusion can be collected for the production of ammonium carbonate/dry ice. Fluorine liberated as hydrogen fluoride during fusion needs to be washed with water from the gases and precipitated with lime as calcium fluoride. Details of product analysis are given in Table 4.

Specification for the fused magnesium phosphate fertilizer popular in China and Southeast Asian countries is given below[13–15]. It compares well with the described fused phosphate fertilizer.

P_2O_5: 18–20%, SiO_2 : 20–27%, CaO: +30%, MgO: +12%.

The P_2O_5 analysis of raw materials and products was carried out using quinolinmolybdate (gravimetry), ammonium molybdate (volumetry) and ammonium venedo

Table 2. Fusibility of LGO with different additives

	Weight of materials mixed (g)							
Run code	LGO	Serpentinite	Quartz	MgO	Total weight (g)	Temperature (°C)	Retention time (min)	% CS P_2O_5 of FCMP
FCMP-12	200	0	60	0	260	1450	30	46.81
FCMP-13	200	40	60	0	300	1450	30	63.80
LS-1	50	50	0	0	100	1450	30	45.79
L S-2	50	40	0	0	90	1450	30	52.23
LS-3	50	30	0	0	80	1450	30	75.25
LS-4	50	20	0	0	70	1450	30	75.22
RLS-1	50	20	0	0	70	1450	30	81.05
RLS-2	50	15	0	0	65	1450	30	75.50
LSMg	50	20	0	10	80	1450	30	86.73
LBSMg	50	25	BCT 25	2	102	1450	30	70.06

%CS P_2O_5 = (Citrate-soluble P_2O_5 content in the sample/total content of P_2O_5 in the sample) × 100.

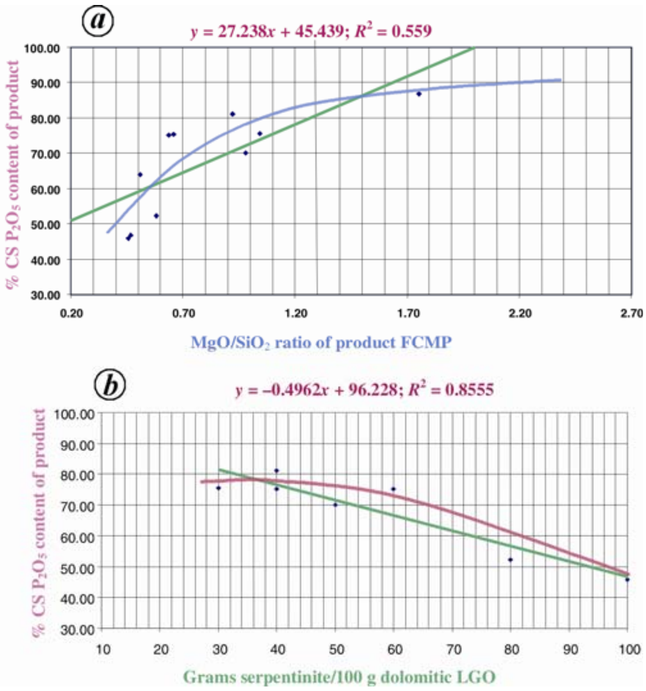

Figure 2. ***a***, Effect of $MgO : SiO_2$ ratio on %citrate-soluble P_2O_5 of the product with its trendline equation. ***b***, Effect of serpentinite addition to dolomitic LGO on %CS P_2O_5 content of product with trendline equation.

molybdate (spectrophotometry) methods. CaO and MgO were analysed by standard EDTA (complexometry) method. SiO_2 and R_2O_3 were analysed by standard gravimetric methods[16–18].

For the fusion of BCT and FCT, different additives in varying quantity with variable temperature and time were tried. Silica-poor FCT was not amenable to fusion, while BCT fused without any additive but had poor citrate solubility. The effect of the $MgO : SiO_2$ ratio of FCMP on %citrate-soluble (CS) P_2O_5 is presented in Figure 2 *a*. The effect of serpentinite addition to dolomitic LGO on %CS P_2O_5 content of FCMP is given in Figure 2 *b*. Water solubility of FCMP is nil.

FCT alone was not fusible, but it can be used as a source of magnesia in the fusion of siliceous ores. Silicate tails (BCT) and LGO responded well to fusion with quartz and serpentinite. Details of fusion experiments of LGO and BCT with different additives are given in Tables 2 and 3.

Low-grade ore and BCT of Jhamarkotra rock phosphate beneficiation plant have responded favourably to fusion. This thermal fertilizer is used widely for acidic soils and a variety of crops[9,19]. It contains essential primary nutrient phosphorus as well as the secondary nutrients, Ca and Mg. Its silica content is useful for plants and it also imparts porosity to the soil. Phosphate of water-soluble phosphatic fertilizers SSP, DAP and TSP is quickly fixed by iron and aluminum oxides of the soil and is thus made unavailable for plants. As such only about 15% of the water-soluble phosphates is utilized by the plants and is available only for a short period. But FCMP is water-insoluble, and so it will not get drained along with water when the crop fields are watered or heavy rains flood the fields[8,9]. Other advantages of FCMP are as follows. It is long-lasting and releases P to the plants in a sustained manner. It is a fertilizer similar to those that are soluble in 2% citric acid or in neutral ammonium citrate, such as di-calcium phosphate. No chemicals are required for its production. No solid waste is generated. It will not deteriorate during storage. The only input is power. To achieve melting of the material a considerable quantity of power is required. Its cost can be reduced if the charge is pre-heated in a high-temperature solar tunnel that can achieve temperatures[20,21] of up to 450°C (up to 600°C, pers. commun., RSMML). Alkalinity of a tonne of FCMP is equal to that of about 0.6–0.8 t of limestone when applied to the soil. It is non-hygroscopic and does not cake when bagged and will not corrode the bags. It requires no curing period unlike SSP. It also contains small amounts of micronutrients like Zn, Cu and Fe (if required micronutrients like Mn and B can also be incorporated). It can be used in combination with other fertilizers. This process should be of interest to countries that are defi-

Table 3. Fusibility of BCT, FCT and LGO with different additives

Run code	Details of feed mix Weight of individual materials (g) LGO	SBT	FCT	Serpentine	Quartz	Total weight mix (g)	Temperature (°C)	Total (min)	Remarks
FCMP-I	0	100	100	0	10	210	1360	15	No fusion
FCMP-2	0	200	0	0	0	200	1450	2	No fusion
FCMP-5	0	125	0	75	0	200	1450	30	Fusion achieved
FCMP-6	0	150	0	50	0	200	1450	30	Fusion achieved
FCMP-7	0	0	200	0	0	200	1450	30	Only calcination
FCMP-8	0	200	0	0	0	200	1450	30	Fusion achieved
FCMP-11	300	0	0	0	0	300	1450	30	No fusion
FCMP-12	200	0	0	0	60	260	1450	30	Fusion achieved
FCMP-13	200	0	0	40	60	300	1450	30	Fusion achieved

Table 4. Analysis of the FCMP produced

Run code	Analysis of product FCMP %P_2O_5	%CaO	%MgO	%SiO_2	%CS P_2O_5 of product
FCMP-1	12.92	42.91	15.53	27.44	51.50
FCMP-2	13.06	34.29	13.61	37.07	42.51
FCMP-5	6.53	30.60	18.17	33.85	52.00
FCMP-6	9.98	30.12	16.12	32.75	51.86
FCMP-7	10.41	51.70	25.24	3.10	22.04
FCMP-8	13.23	36.65	15.40	31.81	41.04
FCMP-12	14.10	37.10	14.00	30.00	46.81
FCMP-13	10.50	36.56	16.40	32.20	63.80
LS-1	7.38	19.20	12.80	28.00	45.79
LS-2	8.96	19.80	14.40	24.80	52.23
LS-3	10.22	20.40	15.00	22.80	75.25
LS-4	11.20	20.36	13.70	21.56	75.22
RLS-1	11.68	32.76	21.60	23.45	81.05
RLS-2	13.18	39.20	20.00	19.18	75.50
LBSMg	12.69	38.64	21.20	21.60	70.06
LSMg	11.90	36.40	28.40	16.20	86.73

%CS P_2O_5 = (Citrate-soluble P_2O_5 content in the sample/total content of P_2O_5 in the sample) × 100.

cient in high-grade phosphate ore, but possess low-grade phosphate. Silica content of FCMP is useful for rice and sugarcane crops. Therefore, citrate solubility cannot be the sole criterion for evaluating its agronomic value. This process has been patented[22].

In conclusion, for the dolomitic LGO, silica content of 15–22% is required in the mixture to achieve fusion that should be carried out at around 1450°C for about 30 min. Serpentinite improves fluidity, fusion and citrate solubility of apatite. $MgO : SiO_2$ ratio is important for obtaining optimum fusion and CS P_2O_5 in the product, which should be around 1.2–1.5. About 75–80% of the total P_2O_5 of the FCMP can be made CS P_2O_5 by fusion of dolomitic LGO with serpentinite. About 35–45 g of serpentinite per 100 g of dolomitic LGO gives approvable FCMP. FCT is a useful additive for high-silica LGO. High-silica ores can be used as additives for silica. Beneficiated rock phosphate and magnesite can be used as sweeteners to improve P_2O_5 and MgO contents. Through this process we can also obtain valuable by-products, viz. ferro-phosphide, ammonium carbonate/dry ice, and hydro-fluosilicic acid/calcium fluoride.

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MEETINGS/SYMPOSIA/SEMINARS

Workshop on Electrophoresis Techniques

Date: 21–30 May 2009
Place: Yercaud

Topics include: Basic theory and practical of various electrophoresis techniques. Paper, agarose, immunoelectrophoresis techniques, submarine agarose gel, isoelectric focusing, polyacrylamide gel, 2D PAGE, preparative electrophoresis, silver staining, gel documentation and electrophoresis in PCR, RAPD, RFLP analysis.

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Seminar on Biotech Institute–Industry Interaction (BIII-09)

Date: 3–4 April 2009
Place: Sathyamangalam

Areas covered: Approaches for enhancing interaction between academia and industry for fostering collaborative research, and internships and training for biotech graduates.

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