

Calcined Phosphate Fertilizer from Jhamarkotra Secondary Phosphate Ore and Rock Phosphate Beneficiation Plant Bulk Circuit Tail

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Abstract

The secondary phosphate ore of RSMML's Jhamarkotra rock phosphate mines have high iron content that renders it unsuitable for manufacturing of phosphatic fertilizers like SSP, DAP and phosphoric acid. This paper explores the feasibility of utilizing the secondary phosphate ore by thermal treatment, which involves calcination as well as fusion. The calcined and fused products both have good citrate solubility and thus have a potential to be used as a citrate soluble phosphatic fertilizer. This paper also deals some phosphate resources which are added during thermal treatment. These additives not only assist in the fusion and calcinations but also improves soil fertility. These are more beneficial to the soil. Calcined dolomite tailing among these has a potential to be utilized as citrate soluble phosphate rich magnesium fertilizer.

INTRODUCTION

Jhamarkotra secondary phosphate ore have high iron and silicate contents. Secondary phosphate ore is basically weathered or reworked phosphorite. It has been associated with broken phosphatic columnar and laminated stromatolite fragments, which occurs as non-cohesive, but tightly packed mass. This type of phosphatic occurrence has been variously described as weathered, reworked, brecciated, fragmented or slumped. A characteristics feature of this type of weathered fragmented phosphorite is the absence of dolomite matrix. At many places the fragments are cemented by secondary silica resulting in formation of breccia. Brown colored Goethite is also found to be associated with this weathered phosphorite.

The iron and silicate minerals are mainly present as Goethite and limonite¹ and complex silicates such as amphiboles, micas and clays. High iron contents are undesirable in commercial phosphate concentrate/ore² for chemical processing into fertilizers. It has been found that when the R_2O_3 i.e., $(Fe_2O_3 + Al_2O_3)$ concentration is more than 3 to 5%, precipitating of iron and aluminum phosphate compounds take place during storage of phosphoric acid³. High R_2O_3 content also adversely affect the physical properties of super phosphate, for example, the product may difficult to dry and that may cake in storage³. Various processes have been developed for removal R_2O_3 fraction from phosphate rock. These processes are gravity separation, scrubbing, magnetic separation and flotation. Rock phosphate beneficiation plant at Jhamarkotra is not equipped to treat high iron content phosphate ores. This type of ore can also be utilized through thermal treatment i.e. by calcination and or fusion.

CALCINATION OF PHOSPHATE ORE

Calcination is rather matured and technically sound technology. The product obtained after calcining phosphate ore at a temperature of 1250-1350°C, is called calcined phosphate. Calcination of phosphate ore removes most of the organic, carbonate, fluoride and other impurities. In initial trial two low grade Indian carbonate ores were successfully upgraded using a calcination process⁴.

Calcination is usually carried out by heating phosphate rock along with silica in the presence of soda ash at 1250-1350°C, in rotary kiln. It has been found that the presence of silica promotes the disintegration of apatite lattice, which speeds up removal of fluorine⁵. Calcined phosphate have a

significant portion of phosphate in citrate soluble form. It is effective in acidic soils and is extensively used in Australia, Germany, Russia, USA, Malaysia, Indonesia, Vietnam, England, Belgium etc. Various types of calcined phosphate available in the international market are shown in the Table-1. In India, calcined phosphate could be preferably used in acidic soils of high rainfall area of Kerala, Orissa, West Bengal, North Eastern States, Tamil Nadu etc. Such area occurs to an extent of about 149 Million hectares.

Table 1: Various Calcined Phosphate Available in International Market

S.N	Trade name of calcined product	Country	Available phosphate	% of citric acid solubility
1.	Rhenania	Germany	33	100
2.	Base Phosphate	Belgium	N.A	N.A
3.	Supra Phosphate	Belgium	N.A	N.A
4.	Thermo Phosphate	Senegal	20-40	80-90
5.	Phospal	Senegal	34	80
6.	Christmas Island calcined phosphate	Christmas Island	N.A	26

INITIAL TRIALS OF CALCINED PHOSPHATE IN INDIA

Till now calcined phosphate is not used in India. Earlier, Phospal – a Senegalese calcium aluminum phosphate, containing 34% P₂O₅ (of which 80% is citrate soluble) has been tested in several field trials in India⁶.

Routary⁷ et al prepared calcined phosphate in laboratory by heating a mixture of low grade phosphate rock containing sufficient silica with soda ash (2:1 weight ratio) at 900⁰C for two hours. These calcined phosphate unlike other silico phosphates contains both water soluble P (average 30% of total P) and citrate soluble P (average 56% of total P). Field trial has been conducted for these calcied phosphate as P source for rice in acidic soils in Orrissa, under green house conditions and have been found to be as efficient as a single super phosphate^{8,9}

APPLICATION OF CALCINED PHOSPHATE IN OTHER COUNTRIES

Several types of calcined product are available in the international market. For example Christmas Island's "C" grade rock phosphate containing about 27% P₂O₅, 10% Fe₂O₃ and 16 Al₂O₃ is an effective P fertilizer after calcination. This Calcined phosphate is also known as calciphos, was produced by calcination of C-grade Christmas Island rock phosphate by heating to approximately 500⁰C. This changes its chemical nature by making more of P₂O₅ present in available form. It is widely used in Malaysia & Indonesia¹⁰. Nuru rock phosphate fines are upgraded by high temperature calcination to remove organic carbon. This product is market as Nauru calcined rock^{11, 12}. In the USA calcined phosphate has been proved to be effective¹³ as calcium meta phosphate.

Silico phosphate or Rhenania phosphate is produced by calcination of a mixture of finely ground phosphate rock, soda ash and sand in rotary kiln at about 1250⁰C. The reaction is as follow:



This product is the mixture of Ca₂SiO₄ and CaNaPO₄. It is alkaline in nature due to the presence of calcium silicate. It is extensively used in Germany since from 1917. The first German plant has a capacity of 100,000 tons. Four kilns are available for operation. The 125' kiln had an internal diameter of 5' at the cold end and 8' at the firing end. About 150Kgs of pulverized coal is required as fuel per ton of feed. The typical chemical analysis of Rhenania phosphate along with locally produced calcined phosphate is shown in table-2. Recently Sri Lankan scientist¹⁴ have also developed and patented a similar process for manufacture of calcined phosphate fertilizer from their Eppawala apatite deposit. On similar lines Veiderma¹⁵ also suggested new thermal processing routes for phosphate rock.

Table 2: Typical Analysis of Rhenania Phosphate and RSMML's Calcined Phosphate

S.N	Description	Percentage	
		Rhenania phosphate	RSMML calcined phosphate
1.	P ₂ O ₅	28.0	23.5
2.	P ₂ O ₅ Citrate soluble	27.50	20.80
3.	CaO	42.0	37.70
4.	SiO ₂	10.50	12.35
5.	Na ₂ O	12.20	-----
6.	R ₂ O ₃	4.50	5.23
7.	F	1.5	-----

AGRONOMIC EFFECTIVENESS OF RHENANIA OR SILICO PHOSPHATE

Rhenania phosphate have been effective or even more effective than super phosphates in high P-absorbing soils in Brazil, Nigeria Ethiopia and Congo. Rhenania phosphate was also produced in Kenya in the 1950's using phosphate rock from Busumba in Uganda and soda ash from Lake Magadi.

Energy cost is usually the only important factor for determining feasibility of the calcination process for carbonate removal. Although the calcination flue gas frequently raise environment concerns. But Phosphate calcination process is quit safer environmentally than pyro-metallurgical treatment for example of sulfide ores.

Lim¹⁶, H., etal have studied the agronomic effectiveness of calcined phosphate. Bollard¹⁷ etal carried out research work on long term availability of phosphate from calcined phosphate rock compared with single super phosphate. Herbage yield decreased from first to second year in case of SSP, where as the effectiveness of calcined phosphate increased with time. Ritchey¹⁸ etal study on clover also showed that the soil properties improve after application of calcium rich products. Rhenania or silico phosphate from secondary phosphate ore of Jhamrkotra (see Table.3).Effect of soda ash on citrate solubilty was studied by addition of soda ash in various proportion.

Table 3: Chemical Composition and P₂O₅citric Solubility after Thermal Treatment

S.N	Discription of sample	Chemical composition (%)						T.T	C.S.	Remarks
		P ₂ O ₅	SiO ₂	CaO	LOI	MgO	R ₂ O ₃			
1.	Sec. Phosphate ore	27.00	11.26	42.30	7.74	0.20	7.48		----	-----
1.a	Sec. Phosphate ore + soda ash, in10:1 ratio	25.40	17.94	40.80	0.51	4.50	8.20	T.T 1hr	5.5	Moderate C.S only
2.	Sec. Phosphate ore + Dolomite, in 10:3 ratio	21.90	9.80	39.90	14.36	4.50	5.50	---	-----	-----
2.a	Calcination of above sample	23.60	-----	-----	-----	-----	-----	T.T	0.10	Very low C.S.
3.	Calcined Sec. Phosphate ore + soda ash, in 2:1 ratio	21.00	-----	-----	-----	-----	-----	T.T 1hr	19.0	W.S=2.2
4.	Sec. Phosphate ore + soda ash in 3:1 ratio	23.50	12.35	37.70	1.97	0.50	5.23	T.T 2hr	20.80	Very high C.S
5.	Sec. Phosphate ore + C.T. U/F, in a 11: 7 ratio	21.80	20.20	41.70	0.18	7.60	7.00	15 min	10.80	Moderate C.S

T.T*-thermally treated at 950⁰C & t-soaking time.

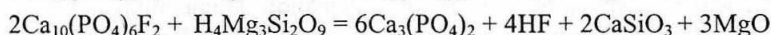
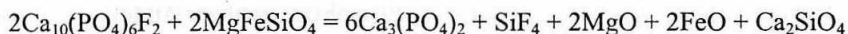
C.S- Citrate solubility of P₂O₅.

W.S- Water solubility of P₂O₅

FUSED CALCIUM MAGNESIUM PHOSPHATE

Fused Calcium Magnesium Phosphate (FCMP) is manufactured either by fusing phosphate rock with lime stone and quartzite at 1400-1450°C in an open hearth or shaft furnace¹⁹. Phosphate rock can also be fused at lower temperature of 1250-1350°C in presence of magnesium minerals like serpentine i.e., hydrated magnesium silicate (H₄Mg₃Si₂O₉) or olivine (Mg,Fe²⁺)₂SiO₄. These additives form eutectics, which assists in reducing the fusion temperature. The melt leaving the furnace is quenched with water so as to disintegrate into fine granules and also assists in preserving high percentage of citrate soluble P₂O₅ in the product. Fused phosphates contain about 80-90% P₂O₅ in citric acid soluble form. FCMP is widely used in China, South Korea, Japan, Vietnam, Russia, Brazil, and USA²⁰.

The chemical reactions are as follows:



The product contains 22% P₂O₅ of which about 88% is in citrate soluble form. This material has not been produced in India.

FCMP FROM SECONDARY PHOSPHATE ORE OF JHAMARKOTRA

FCMP was earlier produced at lab scale at Phosphate Research & Development centre, Jhamarkotra from Bulk circuit tail. The secondary phosphate ore of Jhamarkotra contains about 25-27%P₂O₅, 10-12% SiO₂, 40-42% CaO, <1% MgO, 6-8% R₂O₃ and around 8 % loss on ignition. The major minerals are apatite, quartz, goethite, calcite and other silicate minerals. The composition and the mineralogy of ore suggests that the ore can be fused with any magnesium mineral in appropriate proportion so that the product contains a total P₂O₅ at + 20% and most of it present in 2% citrate soluble form. 27%

Table 4: Chemical Composition Bulk Circuit Tail and C.S after Thermal Treatment

S.N	Discription of sample	Chemical composition						T.T	C.S.	Remarks
		P ₂ O ₅	SiO ₂	CaO	LOI	MgO	R ₂ O ₃			
1.a	Bulk circuit tail	12.60	24.58	30.80	20.66	9.20	0.55	---	---	-----
1.b	Bulk circuit tail mixed with soda ash in 2:1 ratio	11.80	-----	-----	-----	-----	-----	(Cal) 950 ⁰ c t-1hr	11.00	Very high C.S.
2.	Bulk circuit tail (190gm) mixed soda ash(10gms)	13.70	31.79	37.00	0.25	10.0	1.68	(Fus) 1450 ⁰ c	12.60	Excellent citric solubility
3.	Bulk circuit tail	15.7	-----	-----	-----	-----	-----	(Cal) 1250 ⁰ c	1.00	Very low c.s
4.	Bulk circuit tail	13.7	-----	-----	-----	-----	-----	(Fus) 1450 ⁰ c	6.6	Medium C.S
5.	Carbonate Thickener Under flow	7.8	5.03	33.70	35.18	15.4	0.55	-----	-----	-----
6.a	Dolomite Tail	4.60	0.50	32.90	41.12	18.20	0.58	-----	1.00	low
6.b	Calcined dolomite tail	8.80	5.92	52.10	0.79	27.20	1.25	(Cal) 950 ⁰ C 1 hr	3.80	
7.a	Fault Gauge Ore	10.30	35.23	25.00	17.86	7.20	2.25	-----	-----	----
7.b	Fused Fault Gauge ore	12.40	38.76	32.80	0.11	9.50	4.90	(Fus) 1350-1400 ⁰ C	10.30	High citrate solubility

P₂O₅ secondary phosphate ore was mixed with beneficiation plant tailings having a composition of 4-6% P₂O₅, 16-18 MgO, 25-30 CaO, 3-5% SiO₂ and 35-38% loss on ignition. This charge was melted in a graphite crucible at fusion time of 15 minutes. The temperature was expected to be at 1400-1450 deg.C. Some preliminary results are shown table-4 .

ROLE OF ADDITIVES

Jhamarkotra Mines is endowed with wide variety of phosphate resources as shown in Table.5. These could be utilized, although in small amount, during thermal treatment. These include natural phosphate resources and also tailings from beneficiation plant. One of typical resource is nicked name as fault gauge ore. It usually occur as an interface between ore bodies and ore burden. It is rich in iron oxide and silica. A glassy material is obtained when fused. This fused material has good citrate solubility and is equivalent to fused Calcium Magnesium Phosphate fertilizer. Additions of such resources during fusion or calcinations assist in reducing fusion/calcinations temperature and increase the fluidity of the melt due to presence of silica and iron. These additives are listed in Table. -5

Table 5: Role of Additives in, Thermal Treatment and Agriculture Field

S. N	Name of the additive	Description of Additive	Minerals in order of abundance	Role of Additives	
				Thermal treatment	Agriculture
1.	Bulk circuit tail	Predominantly a silica gangue material. It is I stage bulk floatation tail.	quartz, apatite, dolomite, calcite.	Quartz assists in fusion.	Silicates boost the immune system
2.	Carbonate Thickener under flow	Carbonate thickener under flow predominately consists of dolomite gangue from cleaner II froth, of 2 nd stage floatation.	dolomite, apatite, quartz, calcite.	quartz make fusion easier .	Presently finds no application
3.	Fault gauge material	Basically a ferruginous ,highly siliceous low grade phosphate ore usually found in the intermediate zone between ore bodies and ore burden'.	quartz, goethite, apatite, dolomite	Presence of Fe, assists in fusion.	A low grade FCMP
4.	Calcined dolomite tail	dolomite gangue from cleaner II froth, calcined at 950 ^o C for 1 hr.	dolomite, apatite, quartz, goethite	easily calcined at 950 ^o C.	Phosphate rich magnesium fertilizer

AVANTAGES OF THERMAL PHOSPHATE

- a) Utilizes secondary phosphate ores which are not suitable for beneficiation.
- b) Low cost as well as long lasting fertilizer.
- c) No adverse effect on soil fertility.
- d) Viable alternative to either SSP or DAP.
- e) Calcination removes impurities and increases P concentration.
- f) Do not fixed or revert to soil.
- g) Not readily leached.
- h) Free running and will not cake.
- i) Provide a opportunity to utilize the tailing material which is being disposed off. Utilization of tailing in long run help in reducing degradation of land besides this increases the revenue.

EXPERIMENTAL SET UP

The thermal treatment involved both calcination and fusion. The thermal treatment was imparted to secondary phosphate ore and other phosphate resources with keeping in view producing silico phosphate and fused calcium magnesium phosphate.

CALCINATION OF SECONDARY PHOSPHATE ORE

Secondary phosphate rock was crushed to -100# and mixed with soda ash in appropriate ratio (by weight). Laboratory scale Calcination of this mixture was carried out in silicon carbide furnace at a temperature of 950°C for one hour (see Table.3). Similar calcination was also carried out on Bulk Circuit tail. The detail chemical composition prior to and after calcination is shown in Table-4 .

FUSION OF SECONDARY PHOSPHATE ORE.

Secondary phosphate ore was mixed with carbonate thickener under flow i.e., gangue material from the flotation circuit which consists of 6-8% P₂O₅, 4-6% SiO₂, 15-18% MgO, 32-34% CaO, 35-38% loss on ignition and 0.5-1.0 % R₂O₃ in appropriate proportion and fused with acetylene flame in a graphite crucible. The fusion was carried out for 15 minutes .The melt was immediately quenched with water. This is shown in Table.3 at serial no.3 .

RESULTS AND DISCUSSION

1. Table-1.Shows various calcined products available in international market. So far these products are not manufactured in India.
2. Table-2-shows a typical chemical analysis of Rhenania phosphate produced in lab scale at PRDC, Jhamarkotra. This compare well with the Rhenania phosphate produced in Germany.
3. Table-3-effect of soda ash on phosphate citrate solubility .The secondary phosphate ore was mixed with soda ash in different ratio like 10:1,10:3,2:1and 3:1.The calcination time of all the samples except the last one was kept for one hour.
 - a) Table-3 (s.no.1.a to s.no.4).Depicts that the phosphate citrate solubility increases with the increase in amount of soda ash.Table 3. (sn.5). The phosphate citrate solubility also increases in case of increase in soaking time i.e.,2hours instead of one. This hold good even in case where the amount of soda ash is reduced.
 - b) Table3. (s.no.1.a & 2.). Indicates that even a small fraction of soda ash i.e., in a ration of (10:1) increases citrate solubility. This calcined material has a C.S of 6 and it have a potential to be used as a low cost citrate soluble fertilizer. It is equivalent to "Christmas Island" calcined phosphate which is quit popular in Indonesia and Malaysia.
 - c) Table.3-(s.no.5.). shows that when PR:Soda ash ratio is 3:1,the calcined material is similar to Rhenania phosphate fertilizer. In this some fraction of phosphates are water-soluble also.
 - d) Table.3-(S.no.6).-Shows that when secondary phosphate ore is mixed with beneficiation plant tailings in a ratio of 11:7,the fused mass have 21.80% available P₂O₅ along with 10.80% phosphate citrate soluble. This is quite similar to Fused Calcium magnesium Phosphate.
4. Table.4-Shows chemical composition of various additives. This table also depicts the thermal treatments imparted to these phosphates resources. The observation are as under:
 - a) Table.4 (S.no.1a). Citrate solubility increases in the presence of soda ash from 1 to 11.00. Soda ash also decreases the fusion or calcination temperature.
 - b) Table.4. (S.no.3). Show that the Bulk circuit tail citrate solubility is very less in absence of soda ash.
 - c) Table.4 (s.no.2).Shows that in case when bulk circuit & soda ash is mixed in the ratio of 19:1 and fused, the fused product has good citrate solubility. This product is similar to low-grade FCMP.

- d) Table.4 (s.no. 6a.& 6.b). Shows that when dolomitic tail when calcined at about 950°C have a chemical composition of 8% P₂O₅,6% SiO₂,52% CaO,27% Mgo and 3.8 citrate solubility. This calcined mass is alkaline in nature and CaO, Mgo, and SiO₂ are in highly active state. This calcined dolomite tailing from rock phosphate beneficiation plant can contribute as calcined dolomite fertilizer. Calcined dolomite fertilizer is widely used in acidic soils of Spain and New Zealand.
- e) Table.4.(s.no.7.a). Shows that when the fault gauge ore is fused,the fused mass has very high citrate solubility.It is similar to a low grade fused calcium magnesium phosphate.
- f) Table.5-Role of Additives in, thermal treatment and agriculture.
- g) Table.6-Thermal phosphates envisaged from RSMML phosphate resources.

Table 6: Thermal Phosphates Envisaged From RSMML Phosphate Resources

Sn.	Description of phosphate resources	Thermal Treatment	Product formed
1.	Secondary phosphate ore + soda ash in appropriate ratio	Calcination	Silico phosphate
2.	Bulk Circuit Tail	Fusion	FCMP
3.	Bulk Circuit Tail + soda ash in 3:1 ratio	Calcination	Product hach high C.S and high silicate content.
4.	Dolomitic Tail or C.T under flow	Calcination	A phosphate rich magnesium fertilizewr
5.	Fault Gauge ore	Fusion	A glassy material equivalent to FCMP.

CONCLUSION

- a) Rhenania or silico phosphate type of citrate soluble fertilizer can be obtained from secondary phosphate of Jhamarkotra mines.
- b) It is feasible to produce fused calcium magnesium phosphate fertilizer by carrying out fusion of a mixture containing secondary phosphate ore and rock phosphate beneficiation plant tailing.
- c) Calcined dolomite tailing can contribute as a finished value added product since it has a potential to be utilized as a phosphate rich magnesium fertilizer.
- d) Fault gauge ore, after fusion converts into a glassy material .It has all essential ingredients for potential application as a low-grade fused calcium magnesium phosphate.

ACKNOWLEDGMENTS

The authors are grateful to shri R. Mishra,MD RSMML, for encouraging the authors to take this work.Authors are also thankful to shri J.Shantaram ,GGM(Phosphate Division) RSMML.

The authors are indebted to Shri I.J.Sonker and Shri S.N Garg for their help and assistance during the work.

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