

ISMA* Technical Conference

Edinburgh, United Kingdom

14-16 September 1965

**In 1982, the name of the International Superphosphate Manufacturers' Associations (ISMA) was changed to International Fertilizer Industry Association (IFA).*

THE USE OF CALCINED ROCK IN PHOSPHATE PROCESSING

By S. Stern (Chemicals & Phosphates Ltd., Israel).

1. Introduction

Phosphate Rock, being a natural material, varies in its constituents from one source to the next, and there are variations in the same field at different depths and locations. These constituents affect the value of a particular phosphate as an industrial raw material and its chemical and physical conversion and use as a fertilizer. The organic materials in natural rocks, being decomposition products of plant and animal matter, are very variable and unpredictable, and cause considerable trouble in processing, such as foaming and interference with crystallization. It is therefore common practice to calcine at comparatively low temperatures to eliminate these organic materials. (1) This makes the rock particularly suitable for the production of phosphoric acid (2) (3).

The main aim of our company in developing a calcined product was to raise the P_2O_5 content of the natural phosphate (24-26%) to obtain a high grade 35% P_2O_5 product, in order to reduce the acidulation ratio and the transportation costs. At the same time, this thermally beneficiated rock is exceptionally low in Fe_2O_3 , Al_2O_3 and other impurities and is thus particularly desirable for secondary products. This makes it equivalent or superior to other highly priced calcined phosphates, such as those produced from certain North African rocks.

It is the purpose of this paper to describe the use of the calcined phosphate for the production of phosphoric acid and superphosphate, and to give some works and laboratory observations when comparing the calcined product with other phosphates.

2. Description of the Phosphates

The rock consists of calcitic sedimentary deposits and is similar in reactivity to Moroccan phosphate. The main impurity is $CaCO_3$, and this is reduced by heating the rock to 800-950°C, which removes the free and combined moisture and most of the CO_2 . Water is added to slake the lime, which is then separated mechanically. The product, 'thermally beneficiated phosphate' TA contains approx. 35% P_2O_5 and is moderately less reactive than the natural rock (4). The

temperature of calcination is carefully controlled and kept to the minimum required to decompose CaCO_3 . Overheating is avoided, as this would cause sintering and a further reduction in reactivity.

The mechanically beneficiated rock MB 29-31% P_2O_5 , which has been used in our plants, is obtained by selective grinding and air classification.

Both phosphates are low in R_2O_3 and other impurities.

2.1 Analysis

	<u>MB 29</u>	<u>MB 31</u>	<u>TA</u>
% P_2O_5	29.5	31.3	35.1
% CaO	53.1	52.1	55.7
% MgO	0.2	0.2	0.2
% Fe_2O_3	0.4	0.2	0.1
% Al_2O_3	0.1	0.3	0.3
% Na_2O	0.7	0.7	0.4
% K_2O	0.1	0.1	0.05
% CO_2	7.7	6.2	1.2
% SO_3	3.2	2.7	2.4
% Cl	0.2	0.4	0.05
% F	3.2	3.6	4.0
% SiO_2	1.6	1.6	1.5
Organics	0.1	0.2	nil
Combined water	<u>1.5</u>	<u>1.8</u>	<u>0.7</u>
	101.6	101.4	101.7
O equivalent of Cl, F	<u>1.6</u>	<u>1.5</u>	<u>1.7</u>
	100.0	99.9	100.0

3. Use of Rock in the plant

3.1 Production of Phosphoric Acid

The mechanically beneficiated phosphate is used in our phosphoric acid plant unground, or with only moderate grinding. The filtration is then better than with finely ground rock, which is generally too reactive, forming smaller gypsum crystals. Upon changing over to the use of calcined phosphate, we were able to increase production by 30-40%, due to better filtration characteristics of the slurry formed, with reduced viscosity. With the uncalcined rock we had

occasional heavy foaming, which was reduced by using anti-foaming agents. With the calcined rock such troubles have been completely eliminated, and the process requires much less supervision, since both the gypsum and the acid are very uniform in composition. The calcined rock undergoes considerable abrasion in its production and is thus sufficiently fine for use in phosphoric acid. Additional grinding to pass 100% - 60 mesh USS screen increased the rate of attack to give 95-97% P_2O_5 recovery.

3.11 Fluorine distribution and byproduct recovery

The distribution of fluorine in the acid, filter cake and sludge is:-

	<u>% of total F</u>
Filter cake, soluble F (Na_2SiF_6)	15-20
Filter cake, insoluble F (CaF_2)	10-30
Settled acid	40-60
Sludge from acid	10-15

15-20% of the F remains in the gypsum as Na_2SiF_6 which precipitates from solution due to reaction with the Na in the phosphate (0.3-0.4% in the rock). 40-60% of the F remains in solution and 80-90% of this may be recovered as a white Na_2SiF_6 or K_2SiF_6 by adding appropriate salts to the acid. Alternately the F may be recovered from the gas during the concentration of the acid, when most of the F is volatilized and a product particularly low in F is obtained. The gypsum by-product is converted to high strength building plaster, which, being white in colour, is particularly desirable.

3.2 Superphosphate Manufacture

The use of calcined Israeli phosphate in laboratory preparation of superphosphate and comparison with other phosphates has been reported previously (6). Our plant, which produces 25 tons of superphosphate per hour, was designed to use our reactive mechanically beneficiated rock and consists of a Kuhlmann mixer with a curing belt with a hold-up time of 8-12 minutes. The product is then disintegrated and transferred to storage. To achieve this short setting time, the uncalcined rock was ground in a Raymond roller mill to pass 90-95% - 100 mesh and 65-70% - 200 mesh screens, and this was reacted with 75-78% H_2SO_4 . The same setting time was obtained with the calcined rock by grinding some 5-10% finer and using 65-67% H_2SO_4 . 25-30% of the fluorine is volatilized as SiF_4 and is recovered as silicofluorides. The superphosphate produced is friable, and as a result of the high initial

reaction (approx. 90% conversion after 24 hrs) the superphosphate does not cake. The superphosphate produced is white and practically odourless. Due to its low R_2O_3 content, there is no reversion of P_2O_5 in the cured superphosphate.

Production of other phosphates and fertilizers

Phosphoric acid produced from these rocks is low in R_2O_3 , and ammoniation or neutralization results in comparatively little sludge formation.

Sodium tripoly- and pyrophosphate, dicalcium phosphate and other salts produced from calcined phosphate have the additional advantage of white colour, which eliminates the need for bleaching agents. Calcined phosphate is particularly suitable for the production of nitro-phosphates: it dissolves fairly readily in nitric acid, and, because of the absence of organic matter, it involves less decomposition and loss of NO_3 , particularly during the drying of the products.

4. Laboratory experiments

- 4.1 Production of Phosphoric acid-Comparison of calcined Israeli with other phosphates. The rate of P_2O_5 and F dissolution in the production of phosphoric acid and the filtration of the gypsum formed was determined by a method similar to that of Gilbert and Moreno (7).

Procedure A 5 gm sample of phosphate was introduced into 500 gm phosphoric acid (30% P_2O_5) at $70^\circ C$, the acid containing 6 gm c.p. gypsum seeds and 1.8-2.0% H_2SO_4 , i.e. sufficient to react with the phosphate and to leave 1% H_2SO_4 free acid at the end of the reaction. The reaction was carried out in a polyethylene beaker held in a constant temperature bath, and the slurry was agitated by a teflon-covered magnetic mixer. After 1, 5 & 15 minutes, $\frac{1}{3}$ of the slurry was filtered through a 70 mm diam. S/S No.595 filter paper under vacuum, and the filtration time noted. The precipitate was washed with isopropyl alcohol, to remove the freely draining adhering acid, and the residue was dried at $105^\circ C$, and used to determine the residual P_2O_5 and F.

The total soluble P_2O_5 was tested by shaking 0.2 g residue in 100 g water for a $\frac{1}{2}$ hour and determining P_2O_5 in the supernatant settled mixture. This soluble P_2O_5 includes (a) truly water soluble P_2O_5 , which gives a comparative estimation of the washability of the gypsum and (b) co-precipitated P_2O_5 ($CaHPO_4 \cdot CaSO_4 \cdot 4H_2O$), which depends mainly on the free acid of the reaction slurry. The unattacked phosphate was obtained by deducting the total soluble from the total P_2O_5 content of the gypsum and indicates the comparative rate of

H_2SO_4 . The fluorine volatilized is more variable and depends more on the temperature of reaction and the concentration of free acid in the super during the initial stages of the reaction.

Superphosphate Preparation and Fluorine Volatilization

	<u>Conversion</u>	<u>Fluorine</u>		<u>Fluorine</u>
	after 10 minutes (% of P_2O_5) (water soluble)	<u>Volatilized</u> after 10 minutes (% of F in rock)	<u>Solubilized</u>	<u>Volatilized</u> after heating cured super 2 hrs. at $105^\circ C$
			<u>Solubilized</u> & volatilized	
Mechanically Beneficiated phosphate + 76% H_2SO_4	94	10	29	28
Thermally Beneficiated Phosphate + 65% H_2SO_4	70	6	40	33
Mechanically Beneficiated Phosphate + 98% H_2SO_4	87	22	41	42
Thermally Beneficiated Phosphate + 98% H_2SO_4	74	38	58	58

This is demonstrated by the fact that practically all the solubilized fluorine is also volatilized after heating to $105^\circ C$ (temperature), and that more fluorine is volatilized with 98% acid (concentration). The soluble fluorine is held as H_2SiF_6 and is released when the vapour pressure of SiF_4 over the solution is sufficiently high. The v.p. of SiF_4 is increased by raising the temperature and concentration of the solution and by adding active silica (precipitated).

The amount of F released from calcined phosphate is similar to that from other rocks, particularly those of North African origin.

Previously it has been shown that the addition of sand, even when finely ground and with the concentrated acid, had no effect on the fluorine attacked. Very finely divided, precipitated silica in excess increased the fluorine volatilization slightly, but the increase in fluorine recovered is too small to warrant the addition of this silica.

In the factory, where the temperature is higher, and where this temperature is maintained for a longer period, with better aeration than in these laboratory

experiments, more P is volatilized.

Acknowledgement:

I wish to express my thanks to Mr. Bar-on, who performed most of the laboratory experiments, to all my colleagues for their help and advice, and to the management of Chemicals & Phosphates Ltd. for permission to publish this paper.

- References: (1) Phosphorous and Potassium No.2 pp 22-24
No.15 pp.17-21 (1965).
- (2) M. Bigot ISMA 1957/903.
- (3) S.E. Dahlgren Acta Polytechnica Scandinavia
No.16 (1962) Ch.19 (316).
- (4) A.P. Freeman J.H. Caro & M. Heinly, Agricult.
and Food Chem.12 (6) 479-86 (1964).
- (5) Tatsuhiko Noguochi et al. Kogyo Kagaku Zasshi 64
1892-1897.
- (6) E.R. Hermon J. Kosirovsky S. Stern & A. Talmi
ISMA 1957 LE 905.
- (7) R.L. Gilbert & E.C. Moreno. Dissolution of
phosphate rock by mixtures of sulphuric and
phosphoric acids. Lecture, ACS Dept. 1964.
MS.64-476 ACS Research results.
- (8) F. Fauvarque LE 901 ISMA 1957.
- (9) A. Talmi, E.R. Hermon, S. Harel & B. Peskin
Ind. Eng. Chem. 51 675-6 (1954).

attack of different phosphates under the defined conditions of reaction.

4.11 Rate of P_2O_5 and F solubility - Comparison of Phosphates of different origin

For these experiments chemically pure phosphoric acid was used to which H_2SO_4 and H_2SiF_6 were added, seeded with $CaSO_4 \cdot 2H_2O$ to contain:-

30% P_2O_5 , 1.8% H_2SO_4 , 1% F and 1.2% $CaSO_4 \cdot 2H_2O$.

The -140/+200 mesh fractions were used for each experiment.

Phosphate (140/200 mesh)	% P_2O_5 (d.b.) (in rock)	Filtration (i) 15 min.	Unattacked			
			P_2O_5 in residue (ii) (% of rock P_2O_5)		F in residue (iii) (% of rock F)	
			1 min.	15 min. (iii)	1 min.	15 min.
Israel MB	29.6		1.7	0.8	3.4	2
Israel TA	35.1	19	19	1.0	44	14
Israel Mixed MB + TA (1 : 1)	32.3	19	11	0.8	26	10
Florida	36	17	1.4	0	5	3
Kola	40	16	46	0.6	50	4
Morocco (Khourighba)	33.9	19	1.3	0.6	5	4
" (calined)	35.0	19	10	0.1	24	12
" (Safi)	32.1	16	1.0	1.0	3	3
Togo	36.6	16	2.5	0.8	5	3

Notes:

- (i) Time in seconds to filter $\frac{1}{2}$ of slurry.
- (ii) The unattacked P_2O_5 is not too accurate as it is determined by difference; values $< 1\%$ should be regarded as no significant residue.
- (iii) In evaluating these results the limitation of the analytical procedure employed must be considered. In addition, impurities normally present in technical acid (R_2O_3 and others) were practically absent and, as will be shown below, the solubility is affected by these considerably.

4.12 Filtration

The filtration rate with calined rock and mixtures of this with mechanically beneficiated rock is similar to that with other rocks. The differences found are too small to be of significance. With uncalined rock variable results have been obtained, depending on origin, reactivity and organic content.

4.13 P₂O₅ dissolution

After 15 minutes reaction, all the P₂O₅ had dissolved in this acid, even with the least reactive Kola apatite. After 1 minute reaction, however, 46% of the P₂O₅ remained as unattacked rock with Kola, 19% with Israeli thermally beneficiated, 10% with Morocco rock calcined at low temperature and 1-2.5% with all the other phosphates.

4.14 Fluorine dissolution

With the Kola rock, which consists of fluoro apatite with no excess CaF₂, the F dissolved at the same rate as the P₂O₅, whereas with all the other phosphates, and particularly the calcined one, the F dissolved more slowly than did the P₂O₅.

There would thus appear to be some indication that the majority of rocks, with the notable exception of Kola, are composed of more than one constituent, the one containing more F, dissolving more slowly. Previous papers presented to ISMA, e.g. (8), have suggested that this component is CaF₂. The lower rate of solubilization of F is particularly noticeable in calcined phosphates.

4.2 The effect of impurities in the acid

Gilbert & Moreno (7) have shown that the dissolution of P₂O₅ is dependent on the free H₂SO₄ and P₂O₅ concentration in the acid. With Florida rock -170 +230 mesh, 99% of the P₂O₅ dissolved within 1 minute. This was confirmed in the above experiments. In the production of acid, however, the aqueous phase contains other ions besides P₂O₅ and H₂SO₄, and to study their effect R₂O₃ and SiO₂ (amorphous) were added to the phosphoric acid, and this was used to react with Israeli calcined and mechanically beneficiated rock.

Effect of R₂O₃ and SiO₂ on Phosphate Dissolution

Acid Composition	Mechanically beneficiated		Thermally beneficiated		u.s.		%	
	% of P ₂ O ₅ , unattacked		% of total F		% of P ₂ O ₅		% of total F	
	1 min.	15 min.	1 min.	15 min.	1 min.	15 min.	1 min.	15 min.
H ₃ PO ₄ (sp) (30% P ₂ O ₅ + 1.0% F) (H ₂ SiF ₆) + 1.8% H ₂ SO ₄	1.7	0.8	4	2	19	1.0	44	14
+ 0.6 % R ₂ O ₃	2	3	9	15	29	5	55	42
+ 1 % R ₂ O ₃	23	10	37	38	67	18	91	66
+ 0.2 % SiO ₂					111		30	60 11
Acid product from Calcined rock : TA	-----				20	0.4	28	30
Acid produced from Mech. beneficiated rock MB	6	2	48	46	-----			

- Notes: I $R_2O_3 = Al_2O_3, Fe_2O_3$ 1:1 by weight.
- II All the F was water soluble. In other experiments only 10-20% of the residual F was water soluble.
- III The residue contained excessive amounts of water soluble P_2O_5 which interfered with the determination of unattacked P_2O_5 .

These experiments show that the P_2O_5 and F dissolution is retarded with both rocks by R_2O_3 . Low concentrations of these do not affect the rate of dissolution as seen with acid produced from Israeli phosphates. However, with c.p. acid to which 0.6-1% R_2O_3 had been added, the rate of P_2O_5 and F dissolution was considerably reduced, and 1% R_2O_3 reduced this more than did the calcination of phosphate.

These results show that the method has its limitations, and to obtain a true picture of dissolution rates, the acid used should be that produced from the rock being examined. The best comparisons are obtained in a full scale production, where the acid is that produced from the same rock. The method used here is much more convenient and rapid, and uses very small samples of rock, but the results must be examined critically. Thus calcined Israeli rock is found to be considerably more reactive than e.g. Florida rock where the acid produced contains $> 1\% R_2O_3$.

Addition of SiO_2 tended to increase the rate of dissolution and particularly that of the F. However, due to its large volume and amorphous nature, it reduced the filtration rate and interfered with the washing of the precipitate, retaining excessive amounts of water-soluble P_2O_5 and F in the precipitate. During the calcination of the phosphate most of the unreactive SiO_2 present in the rock is converted to the reactive calcium silicate by reaction with the CaO. This silicate is readily decomposed by the acid and contributes to the P_2O_5 and F solubilization. However, the total amount of silica present in the Israeli

calcined rock is limited, and there is no excess to interfere with filtration.

In the evaluation of a rock, all factors contributing to its dissolution must be considered, including :

- a) The physical state of the rock. Thus the rate of solution is in the following order: sedimentary \succ calcined \succ igneous.
- b) The concentration of acid. Excess P_2O_5 retards rock dissolution, due to reduced solubility, and H_2SO_4 forms impervious coatings which block the reaction.
- c) Fe_2O_3 and Al_2O_3 . These probably reduce the solubility by forming insoluble salts and are liable to interfere with gypsum crystallization.

The P_2O_5 and H_2SO_4 concentration, the temperature of reaction, and agitation which are all contributory to the reaction, can be adjusted in the operation and design of the process. Impurities in the acid depend on the phosphate and can only be modified by proper choice and blending of the rock used. This affects not only the rate of dissolution but also the filtration properties of the slurry.

Thus rocks which are high in R_2O_3 would be expected to be much less reactive than Israeli phosphates after calcination and this is borne out in fact. This is also supported by the work of Tatsuhiko Noguchi et al (5), who have shown that the reactivity of a phosphate is reduced by its R_2O_3 content and increased by the Ca/P ratio.

The somewhat slower dissolution of the calcined phosphate when compared with the uncalcined rock, and the absence of organic matter, ensures better conditions for gypsum crystallization and a more rapid filtration of the slurry.

4.3 Particle size of phosphate.

The rate of P_2O_5 dissolution was determined for different size fractions of calcined phosphate and the approximate time of 95% attack was estimated.

<u>Mesh fraction</u> <u>US sieve</u>	<u>% of P_2O_5</u> <u>unreacted</u>	<u>Reaction time</u> <u>for 95% attack</u>
	1 min. 15 min.	(mins.)
+ 20	nd 65	60

Mesh fraction USS sieve	% of P_2O_5 unreacted		Reaction time for 95% attack (mins.)
	1 min.	15 min.	
20/70	40	25	40
70/140	38	8	20
140/200	19	1	8
- 200	10	0	4

The reaction with even the coarse fractions is fairly rapid and compares favourably with results reported for Florida rock of the same mesh fraction (7), i.e. with the -80 + 100 mesh Florida Pebble, 42% remained unattacked after 1 minute, and 32% after 15 minutes.

After grinding the phosphate to pass a 60 mesh screen, 95% of the P_2O_5 is dissolved within $\frac{1}{2}$ hour, which is considered generally adequate.

5.1 Superphosphate - Laboratory Experiments

Superphosphate was prepared in a stainless steel insulated beaker preheated to $110^\circ C$ by mixing 200 gm phosphate with the theoretical quantity of acid as determined by the analytical procedure of S. Harel and E. Hermon (9). The concentrations used were 76% H_2SO_4 for mechanically beneficiated and 65% H_2SO_4 for thermally beneficiated rocks, which were found to be optimum. The rate of conversion to water sol. P_2O_5 was determined after 25 minutes, 24 hours and after 10 days for rocks of different fineness and the results are shown in Figure 1, where the mean particle diameter of the rock is plotted against the conversion to water-soluble P_2O_5 . This shows that the calcined phosphate is less reactive than m.b. rock, if not sufficiently finely ground. If, however, the thermally beneficiated rock is ground so as to pass 95-100% -100 mesh sieve and 70-80% -200 mesh it reacts as fast and even faster with sulphuric acid (65%) than the uncalcined phosphate with 76% H_2SO_4 .

5.2 F evolution

Superphosphate was prepared in the laboratory mixer where both calcined and uncalcined rocks were reacted with 65-76% and 98% H_2SO_4 and the residual total and sol. F determined in the super.

The phosphates used were relatively coarse, only 75% passing a 100 mesh screen.

With calcined rock more of the fluorine was attacked (solubilized and volatilized) than with the uncalcined rock, both with the more dilute and with 98%

FIGURE 1 : SUPERPHOSPHATE FROM THERMALLY & MECHANICALLY BENEFICIATED ISRAELI ROCK

