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THE USE OF THERMALLY BENEFICIATED (CALCINED) ROCK IN SUPERPHOSPHATE MANUFACTURE

by

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Background and problem.

Single superphosphate is made at the works of Fertilizers & Chemicals Ltd., Haifa, Israel by the continuous Kuhlmann process. Phosphate rock, mined and mechanically beneficiated to 28-29% P_2O_5 (DB) at Oron, in the south of the country, is attacked by 75% sulphuric acid. The acid enters at about 35°C, and the approximate sieve analysis of the rock is: 77% minus 200 mesh, 9% 140-200, 8% 100-140 and 6% 100 mesh. The mixture of acid and rock resides only a few seconds in the reaction vessel, in which it is vigorously stirred, and comes out, as a fairly liquid slurry, onto an endless rubber belt. When, after about 13 minutes, it reaches a squirrel cage disintegrator, it is sufficiently friable to be broken up and fall onto a second conveyor belt which takes it to the stores for curing. In the cured material some 93% of the phosphorus is water-soluble.

The mechanically beneficiated phosphate is obtained from selectively mined rock by a process of crushing, sieving and air separation developed by F. & C. Ltd. The selectively mined phosphate, which contains only about 23% P_2O_5 (DB) and more than 30% limestone, would require not less than three tons 100% sulphuric acid per ton of P_2O_5 to convert it into superphosphate, while the mechanically beneficiated material contains 28-29% P_2O_5 and consumes 2.4 tons of acid per ton P_2O_5.

A much better material is obtained by the thermal beneficiation process, investigated in the laboratories and pilot plants of F. & C. during the last years. In this process the raw phosphate is calcined at a temperature at which the limestone is decomposed into carbon dioxide and lime. The former escapes, the latter is removed and the calcined phosphate obtained includes about 35% P_2O_5 and requires two tons of sulphuric acid or less per ton phosphorus pentoxide. F. & C. will shortly begin the erection in the south of Israel of a plant for the thermal beneficiation of phosphate rock.

One of the many questions which had to be investigated was whether the calcined product, with its low CO_2 content, could be converted to good quality superphosphate in Kühlmann equipment.

This question has two aspects. In the first place the reaction to produce a dry material must be sufficiently rapid to allow disintegration at the end of the belt. Secondly, conversion efficiency after a normal curing period must be high.

The laboratory investigations described below showed that the calcined product is entirely satisfactory in both respects.

Experimental.

Two series of experiments were made. In the first one mechanically beneficiated, calcined, Moroccan and Florida phosphates were reacted with sulphuric acid. The products were analysed, after 15 minutes, 24 hours and 3 weeks, for total P_2O_5, water-soluble P_2O_5, free phosphoric acid and free sulphuric acid.

In the second series the effect was examined of acid concentration and fineness of rock on the physical state of the superphosphate 15 minutes after the beginning of the reaction and also on the conversion $\left(\frac{\text{water-soluble } P_2O_5 \times 100}{\text{total } P_2O_5}\right)$ after 2 weeks. These tests also included Kola rock but not the Florida phosphate.

In the first series the required quantity of 75% sulphuric acid, at 35°C, was weighed into a 300 ml beaker and 60 grams of ground phosphate rock added. The mixture was stirred for 30 seconds and then kept covered in an oven at 35° C. Samples were taken for analysis 15 minutes, 24 hours and 21 days after the beginning of the reaction.

In the second series the reaction vessel was a 1 litre, thermally insulated, enamelled beaker, 240 gram batches of rock of various degrees of fineness were used and various acid concentrations tried. Mixing and stirring took 20 seconds. After 15 minutes the material was disintegrated, mixed, and kept in covered bottles in an oven at 35° C. It was remixed on the following day and kept for another 13 days in the oven. The physical condition of the material was recorded after 15 minutes and the conversion determined after 14 days from start of reaction.

The quantity of acid required for each kind of rock was determined by the method described in (1).

The rocks used are listed in Table 1. The CO_2 contents of all the mechanically beneficiated samples were similar to the value given for NP7. The calcined rocks had been prepared in one of the first experiments at thermal beneficiation and still contained a considerable amount, 5%, of free lime, which increased their acid requirement.

Rocks NP3, CN1F, R7F and F1F were used in the first series of experiments and rocks NP4C, NP5F, NP6C, NP7F, CN1F, CN2M, CN2C, R7F and K1M were used in the second series.

Analytical.

Moisture was determined in 5 gram samples by drying for 4 hours at 105° C. Total P_2O_5 was determined in 5 gram samples of rock or super by the Lorenz method.

The water-soluble P_2O_5 was extracted according to A.O.A.C. and determined by the Lorenz method.

Free phosphoric acid was measured by titrating an aliquot of the above solution to pH 4.8.

Free sulphuric acid was determined after dioxane-acetone extraction according to Nunn and Dee (2).

Results and discussion.

The results obtained in the first series of experiments are given in Table 2. In addition it should be mentioned that the super obtained from Moroccan and Israeli rocks became dry and friable within 10 minutes, and contained no sulphuric acid after 15 minutes, from the onset of the reaction. On the other hand the super made from Florida rock was wet and pasty and contained traces of sulphuric acid even 30 minutes after start of reaction.

About 80% of the P_2O_5 in both kinds of Israeli rock and in the Moroccan rock became water-soluble with 15 minutes. Of this water-soluble P_2O_5 36% was in the form of monocalcium phosphate in the super from mechanically beneficiated rock, 38% in the super from calcined rock and about 48% in that from Moroccan rock. After curing the super from calcined rock no longer lagged behind that from Moroccan rock in this respect.

Good conversions and reasonable free phosphoric acid concentrations were found in the cured products from Oron and Moroccan rocks. It should be noted that in this preliminary series the rocks differed in their fineness, the calcined being the finest and the Moroccan the coarsest and that there were considerable differences in the water content of the mixtures. Not only was the calcined rock far drier than the mechanically beneficiated, but considerably less water was formed by its reaction with the acid than in the case of the mechanically beneficiated rock. For comparison less concentrated acid should have been reacted with the calcined phosphate.

Table 3 gives the conversions obtained after 14 days in the second series of experiments, in which various concentrations of acid were used. Results are included only for those products which were friable after 15 minutes. The product obtained from Kola phosphate remained wet for a week and later set to an extremely hard mass.

Attacking the rocks with an 80% acid yielded wet or even pasty products after 15 minutes.

Table 3 shows that by reacting fine or medium calcined rock with 70 or 75% acid a superphosphate of satisfactory mechanical properties and a satisfactory conversion could be obtained in the laboratory under conditions simulating those in the plant.

References

1. E. Herman, S. Harel, B. Peskin and A. Talmi, I.S.M.A. Paper LE/805, 1955.

2. R.J. Nunn and T.P. Dee, I.S.M.A. Paper LE/388, 1953.

TABLE 1.

Analysis of phosphate rocks used.

.	Moisture	P_2O_5 % D.B.	CO_2 % D.B.	Grams H_2SO_4 100% per 100 grams undried rock.	Screen analysis (U.S.S.) % minus 200	140-200	plus 140
, mechanically beneficiated Oron rock.	6.3	28.5		63.1	78	8	14
, ditto	2.5	28.4		66.0	51	20	29
, ditto	2.4	28.4		66.1	78	8	14
, ditto	2.3	28.4		66.9	51	12	37
, ditto	2.5	28.4	9.3	66.7	76	11	13
, thermally beneficiated Oron rock.	0.2	33.1	1.3	67.5	91	6	3
ditto	0.1	33.4		69.4	66	20	14
ditto	0.1	33.4		69.4	43	N.D.	N.D.
Moroccan rock	0.1	33.5	4.0	60.5	78	20	2
Florida rock	0.8	34.0	1.5	58.2	79	13	8
Kola rock	N.D.	38.1	traces	61.5	71	24	5

TABLE 2.

Superphosphate made with 75% H_2SO_4. Rate of curing.

	Time	Moisture %	Total P_2O_5 %	Water-soluble P_2O_5, %	P_2O_5 in the form of free phosphoric acid, %	Conversion %
mechani- benefici- rock	15 min.	15.2	15.6	12.9	8.2	82.7
	24 hrs.	14.2	15.8	14.3	4.6	90.5
	21 days	7.5	16.9	16.3	2.9	96.5
thermally iciated	15 min.	10.3	18.4	14.8	9.2	80.4
	24 hrs.	9.8	18.5	17.0	4.2	91.9
	21 days	6.2	19.0	18.4	2.0	96.9
Moroccan rock	15 min.	11.1	19.6	15.8	8.2	80.6
	24 hrs.	10.4	19.6		4.0	
	21 days	4.3	20.6	19.4	2.0	94.2
Florida rock	15 min.	11.7	19.7	13.6	10.8	69.0
	24 hrs.	10.9	19.7	16.3	6.1	82.8
	21 days	3.5	21.1		1.7	

TABLE 3.

Superphosphate of good mechanical properties.
Conversion after 14 days.

ntration.	Mechanically beneficiated rock fine		coarse	fine	medium	coarse	Moroccan rock fine
	NP5F	NP7F	NP6C	CN1F	CN2M	CN2C	R7F
6%	not tried		not tried	98.3	93.8	92.6	not tried
0%	96.1	97.7	--	91.9	93.5	--	91.7
5%	94.4	97.0	97.5	96.4	96.7	--	--