

## Low Cost Magnesium Phosphate by a Novel Process

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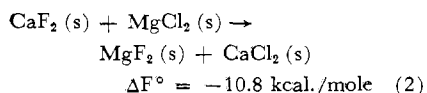
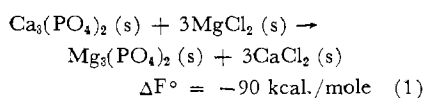
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Thermodynamically, the metathetical reaction between anhydrous magnesium chloride and tricalcium phosphate to give trimagnesium phosphate is feasible. This reaction feasibility has been translated into practice and tested on a pilot scale, using anhydrous molten electrolyte systems which contain both  $Mg^{+2}$  and  $Cl^{-1}$ . Naturally occurring carnallite, kainite, and other minerals accompanying potash are suitable. The reaction takes place around  $500^{\circ}C$ . between a liquid phase containing the magnesium and a solid phosphate rock phase, cation exchange taking place rapidly in the solid phase. In conformity with thermodynamic anticipation, the  $CaF_2$  and  $CaCO_3$  undergo conversion to the corresponding magnesium salts concurrently with the main reaction. The calcium salts formed and the unchanged potassium or sodium salts are separated from the magnesium phosphate product. The magnesium phosphate made by this process has potentialities both as a direct fertilizer and as an intermediate in fertilizer manufacture.

MAGNESIUM chloride and magnesium sulfate, primary sources of magnesium, are frequently associated with potash mining and thereby with the fertilizer industry. It was natural, therefore, to think of making these materials react in as simple a manner as possible with phosphate rock in order to obtain magnesium phosphate. A number of attempts are described in the literature (1, 2, 5, 12, 14, 15) but most of them were not successful. The present paper deals mainly with the reaction involving phosphate rock and magnesium chloride; the reaction with magnesium sulfate is referred to only briefly.

### General Considerations

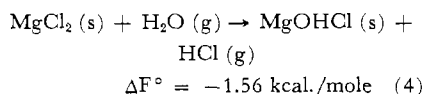
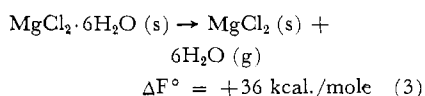
To gain an idea of the possibility of the reaction of magnesium chloride with phosphate rock, the standard free energy change in Reactions 1 and 2 (7, 17) can be considered.



A change of  $-30$  kcal. per atom of Mg reacted in Equation 1 is rather large. In view of the similarity in the molar entropies of  $MgCl_2$  and  $CaCl_2$  (21.4

and 27.2 entropy units, respectively) and presumably also in those of the two phosphates, the sign of the free energy change may be expected to remain the same at higher temperatures. By a further tentative extrapolation the same expectation may be extended to fluorapatite.

These considerations do not contradict the poor results previously obtained with magnesium chloride in experiments involving phosphate rock and the hydrated chloride (14, 15). Considering the following reactions,



it is not astonishing that extensive hydrolysis takes place before the conditions for the desired reaction are obtained. Differently put, reaction probabilities of anhydrous magnesium chloride, which has a high energy, are inherently better than those of lower energy hydrated forms.

The foregoing leaves us with two major problems:

Will the reaction actually take place at a reasonable rate and at what temperatures?

Where can a substantially anhydrous magnesium chloride be found?

Experiment proved that phosphate rock is transformed into trimagnesium phosphate under relatively moderate conditions. The second problem, that of hydration, was attacked in two ways. The first was the use of higher temperatures. In fact, magnesium chloride brines at temperatures of  $250^{\circ}C$ . or above react with phosphate rock under conditions such that HCl does not escape and complete transformation is possible (6, 9).

When dehydration of  $MgCl_2$  is performed directly, it is always accompanied by a great hydrolytic decomposition, giving rise to gaseous HCl and solid  $MgO$ . This is perhaps the reason why the previous investigators did not succeed in this reaction, as practically they did not obtain anhydrous  $MgCl_2$  by direct dehydration.

The second approach consisted in removing water of hydration under conditions where no hydrolytic decomposition of the hydrated  $MgCl_2$  occurs. This refers in particular to the dehydration of magnesium and alkali metal double salts. Of the two approaches, the latter was found to be more practical from the industrial point of view and is the basis of the method described in this paper. When dry magnesium chloride is brought to the melting point ( $712^{\circ}C$ .) in contact with

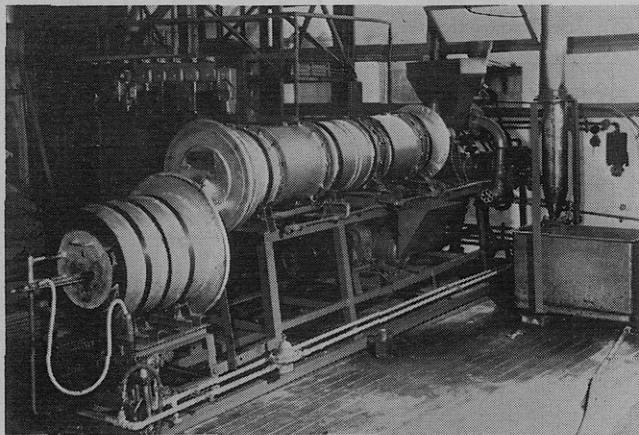


Figure 1. General view of rotary dryer and rotary melting reactor

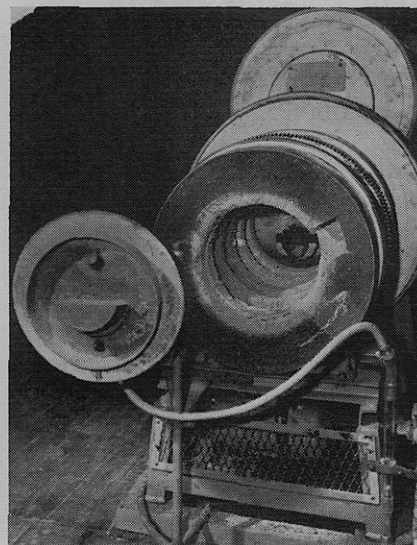


Figure 2. Rotary melting reactor

dry phosphate rock, reaction takes place instantaneously. The solid phosphate does not dissolve in the melt; on cooling and washing by water, a solution of calcium chloride is recovered and a magnesium phosphate remains. The same behavior is shown by melts containing magnesium chloride of all compositions tried thus far. All that is required is melting or incipient melting and temperatures as low as 400° to 450° C. are sufficient for reaction if the constituents used permit fusion at such a low temperature. The intimate mechanism of the interchange of Mg and Ca between the phases is not known. The rapidity of this exchange may be connected with the observed easy wetting of the solids by the molten salt phases. This wetting seems to take place even at incipient fusion.

#### Process Applicability

Phosphate rocks from various origins were examined for reactivity with dehydrated carnallite (Table I). Products from different rocks vary mainly according to their contents of fluorine, silica, calcium carbonate, etc. In general, all Ca is replaced by Mg, CaF<sub>2</sub> giving rise to MgF<sub>2</sub> and MgCO<sub>3</sub> which in turn dissociates into MgO and CO<sub>2</sub>; SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub> do not interfere. No significant changes in the product

composition were observed, when the reaction time was varied from 5 to 30 minutes after complete fusion of the salts was attained. When smaller amounts of MgCl<sub>2</sub> were used—less than that theoretically required to replace the Ca<sup>+2</sup> present in the phosphate—the percentage of Ca<sup>+2</sup> replaced by Mg<sup>+2</sup> and the relative citrate solubility (AOAC method) decreased. However, neither the reaction temperature nor reaction time had any influence on this solubility.

The reaction temperature was between 400° and 450° C. when technical grade carnallite was used; the presence of NaCl caused a lowering in the fusion point of the salts; with pure carnallite the fusion temperature was 500° to 550° C.

The recovery of phosphate was complete in all cases, since no water-soluble P<sub>2</sub>O<sub>5</sub> is produced; therefore, no P<sub>2</sub>O<sub>5</sub> is lost during the washing of the product.

The amount of carnallite required seems to depend upon the type of phosphate used; for soft sedimentary rock phosphate such as Oron, Morocco, a small excess (5 to 10%) was sufficient to obtain a good contact between the reactants and a virtually complete replacement of Ca<sup>+2</sup> by Mg<sup>+2</sup>. However, when the igneous Kola apatite is used, a larger excess seems to be required.

Anhydrous compositions containing Mg<sup>+2</sup> and Cl<sup>-1</sup>, irrespective of source, seem to be equally reactive and permit nearly stoichiometric replacement of Ca by Mg. Their detailed composition, however, is of great significance in the treatment of the reaction mixture and for the composition of the reaction product. With carnallites containing chlorides only, the only insolubles accompanying the magnesium phosphate will be those originating in the rock or their magnesium equivalents, as all other products are water-soluble. The recovery of KCl, however, may be important. When sulfates are present—e.g., from hartsalz, kainite, etc.—calcium sulfate is a major product that will accompany the magnesium phosphate unless means are adopted for its removal.

#### Piloting

As a rule magnesium salts which can be considered as feed contain water of hydration. Phosphate rock may contain some water of hydration and will frequently contain free moisture. The reaction system was conceived therefore in two parts: drying and melting. During drying, temperatures must be

Table I. Preparation of Magnesium Phosphate by Reaction of Technical Grade Carnallite with Phosphate Rocks

Origin of Phosphate	Initial P <sub>2</sub> O <sub>5</sub> Content, %		Amount of Carnallite	Temp. during Reaction, ° C.	Time at Reaction Temp., Min.	Analysis of Washed Dry Product, %			
	P, %					P <sub>2</sub> O <sub>5</sub>	P	MgO	CaO
Oron (Israel)	25	10.9	15% above theor.	500-550	15	34.3	15	40.4	5.8
Oron (Israel)	24	10.5	20% above theor.	500-550	15	33.8	14.7	40	6.1
Oron deslimed	30.2	13.2	20% above theor.	500-550	15	37.1	16.2	43.8	0.8
Florida BPL/77	35.3	15.4	Less than theor.	450-480	10	36.1	15.8	36.6	15.5
Florida BPL/77	35.3	15.4	15% above theor.	530-580	15	37.7	16.5	44	4.2
Morocco	32.2	14.1	20% above theor.	480-510	10	37.6	16.4	45.4	3.1
Morocco	32.2	14.1	15% above theor.	500-550	15	37.2	16.2	45	3.4
Morocco	32.2	14.1	Less than theor.	500-550	15	34.8	15.2	40.8	10.9
Sukulu	40.5	17.7	25% above theor.	580	15	40.5	17.7	48	3
Sukulu	40.5	17.7	Less than theor.	480	10	40	17.5	24	26
Kola	39.6	17.3	Less than theor.	450	10	40	17.5	25	25

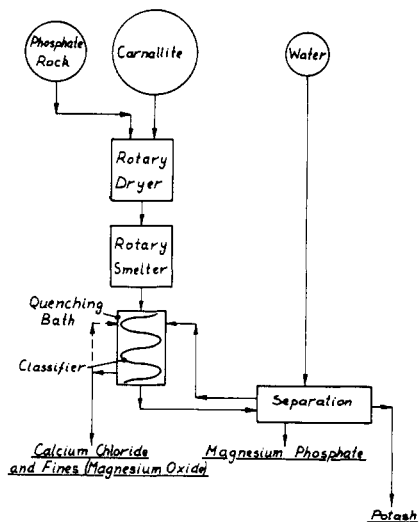


Figure 3. Flow diagram

kept below sintering. With carnallites this represents a gradient of 80° to 185° C. which is easily established in a rotary kiln. The admixture with phosphates also helps in preventing sintering. With sulfates, temperature control is less strict. The reaction proper is achieved by subjecting the dry mixture of reactants for a brief period to a temperature of 400° to 600° C.

The pilot plant consisted of a rotary dryer and a rotary melting reactor, operating continuously in conjunction with leaching (Figure 1).

The rotary dryer is a kiln of 40-cm. diameter and 200-cm. length fitted with a cage comprised of spaced louvers to help the drying process. The phosphate and the carnallite were introduced through two feeders set at the required ratio. At the discharge end a series of buckets elevated the dried material that fell through a sloped pipe into the melting furnace. The furnace was a rotating kiln lined with refractory concrete (sillimanite bricks were most suitable for the purpose). A spiral channel in the concrete conveyed the fused salts containing the phosphate in the discharge direction, allowing variation of residence time and avoiding mixing of the fresh material with the products of reaction (Figure 2). A spiral classifier of 3/4-inch diameter rotating at 3 rotations per minute immersed in a brine bath was installed after the furnace for quenching the fused reaction mixture.

In general, pilot results parallel completely those obtained in small laboratory tests and can therefore be predicted with confidence. Piloting, however, is important for the study of operations superimposed on or subsequent to the principal ones, such as classification, leaching, and filtration.

The conversion of low grade Oron rock into a concentrated Mg phosphate product, according to the flow diagram in Figure 3, is one example of pilot operation.

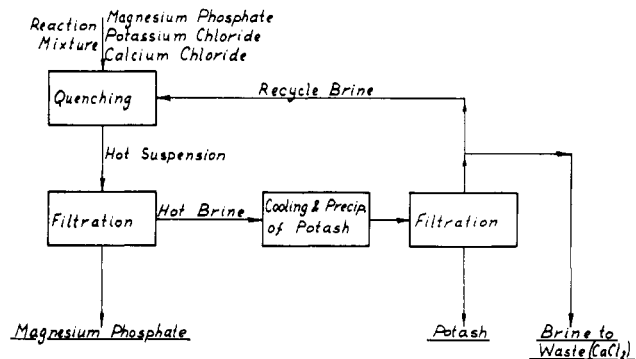


Figure 4. Scheme for KCl recovery

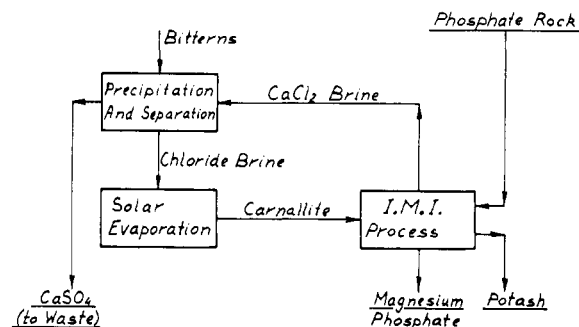


Figure 5. Integration of KCl recovery from bitterns with magnesium phosphate production

Oron rock phosphate (crushed to +65 mesh) containing 24.8%  $P_2O_5$ , 50.4% CaO, and 13.5%  $CO_2$  was introduced through a screw conveyor into the rotary dryer at a rate of 2.9 kg. per hour. At the same time 10.25 kg. per hour of Sodom carnallite (technical grade) containing 27.8%  $MgCl_2$ , 18.1% KCl, and 18.3% NaCl were introduced through a second screw feeder. The mixture of carnallite and phosphate from the rotary dryer entered the rotary melting furnace through a sloped pipe. After 12 minutes in this furnace the molten salt containing the solid phosphate was quenched in a brine solution, and the solid phosphate was separated by a classifier and washed by water. The concentration of the brine allowed the solubilization of the  $CaCl_2$ ; the magnesium oxide fines were separated along with the brine, and the KCl was recovered by a separate hot leach.

The dry product obtained at a rate of 1.70 kg. per hour contained 36.9%  $P_2O_5$ , 6.1% CaO, and 40.7% MgO. An upgrading of phosphate from 25 to 37%  $P_2O_5$  was thus achieved. The yield of  $P_2O_5$  recovered in the magnesium phosphate was more than 85%. About 66% of the total  $P_2O_5$  was citrate-soluble (AOAC method).

The fines removed along with the  $CaCl_2$  brine from the classifier were more than 80% magnesium oxides and hydroxides.

#### Industrial Applicability

Magnesium salts and phosphate rock are both low value products. Their transportation in large tonnages should be avoided as much as possible. Areas

where both feed materials are available in proximity, such as the Oron and Dead Sea areas in Israel, or, alternatively, areas in which magnesium salts are available and into which phosphate rock is being transported for fertilizer manufacture, will be particularly suitable for the process.

Magnesium phosphate as obtained by this new process is a very concentrated product when considered as a carrier of both MgO and  $P_2O_5$ , since these total 80% or more.

When the available magnesium salts contain potassium values, their recovery is an important consideration. Fortunately, in all cases studied, this recovery after reaction with phosphate rock was similar to direct recovery or even simpler. Let us consider several cases:

**Potassium Carnallite.** The system  $CaCl_2$ -KCl- $H_2O$  (8) admits no double salts, the solid phase being KCl up to very high  $CaCl_2$  concentrations in the aqueous phase. Quenching the reaction mixture in a recycle brine, filtration, cooling, and filtration permit better than 80% KCl recovery. A typical scheme of operation is given in Figure 4. If desired, the flowsheet can be modified to leach only the  $CaCl_2$  and leave the KCl with the magnesium phosphate.

**NaCl-Containing Potassium Carnallite.** The procedure is similar to the former, only here a NaCl-KCl mixture is recovered with a KCl yield of 75%. This mixture can be processed by any of the current procedures.

**$MgSO_4$ -Containing Salts.** The difficulties of recovering  $K_2O$  values from such salts are well known. In the reac-

tion with phosphate rock the sulfate can be completely converted to insoluble calcium sulfate, with the result that KCl is obtained in a SO<sub>4</sub>-free system, lending itself to easy separation.

By-product CaCl<sub>2</sub> is obtained as a highly concentrated brine. Where markets exist in proximity, anhydrous CaCl<sub>2</sub> can be easily prepared. Otherwise the CaCl<sub>2</sub> brine may present a disposal problem. Particular interest attaches to potash recovery from bitterns, which requires tedious operations. Fractional crystallization by solar evaporation can be greatly simplified if SO<sub>4</sub><sup>-2</sup> ions are removed first from solution. This may be achieved simply by CaCl<sub>2</sub> obtainable in the magnesium phosphate process, as represented in Figure 5.

When the phosphate rock is high in calcium carbonate, an equivalent amount of magnesium oxide will be produced. This can be separated readily from the phosphate and recovered as a good quality MgO.

#### Uses of Magnesium Phosphate

Magnesium phosphate may be applied to soil as such or used as an intermediate in the manufacture of complex fertilizers or for chemicals. Pot tests indicate phosphorus availability in most acid and alkaline soils which is as complete and as rapid as that of monocalcium phosphate, and a positive response in Mg-deficient soils (10).

The soils used in these pot tests and their relevant properties were:

Texture	pH	% CaCO <sub>3</sub>
Sandy loam	8.05	7.2
Clay	6.50	0.0
	7.75	2.3

The experiments were performed in pots each containing 8 kg. of soil. From the yield figures, graphs were plotted and it was found that in two of the soils, one acidic and the other limy and basic, the magnesium phosphate was comparable to or even better than the standard monocalcium phosphate. Field tests are now under way in various parts of the world.

Magnesium phosphate presents advantages in the manufacture of Mg-containing highly concentrated mixed fertilizers. Being accompanied by P<sub>2</sub>O<sub>5</sub>,

its use enhances over-all nutrient concentration. Furthermore it can be added as such in granulation or, if preferred, in acidulation with HNO<sub>3</sub> or H<sub>2</sub>SO<sub>4</sub>. Uses of magnesium phosphate as intermediate may be best seen by considering its reactions with the major mineral acids (4).

**Phosphoric Acid.** Trimagnesium phosphate is easily attacked and forms the expected products. Mg(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> appears to be hygroscopic. MgHPO<sub>4</sub> forms an anhydrous nonhygroscopic powder. Both of these may be converted to magnesium ammonium phosphate. In this case magnesium values are utilized and phosphate values are made fully equivalent to those of wet process acid if compared to existing processes which utilize phosphoric acid directly (3).

**Sulfuric Acid.** MgSO<sub>4</sub> and phosphoric acid suitable for rock acidulation or ammonium phosphate are easily obtained. Thus magnesium phosphate may be used as a source of MgSO<sub>4</sub> wherever this happens to be a customary soil additive.

**Nitric Acid.** Under proper acidulation conditions a considerable proportion of the magnesium may be recovered as Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O. The H<sub>3</sub>PO<sub>4</sub> concurrently obtained contains some Mg<sup>+2</sup> and NO<sub>3</sub><sup>-</sup>, which on neutralization by ammonia are converted to MgNH<sub>4</sub>PO<sub>4</sub> and NH<sub>4</sub>NO<sub>3</sub>. Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O may serve as starting material for high-grade magnesium chemicals.

#### Conclusions

Magnesium phosphate has potentialities as a fertilizer (7,3) and as an intermediate in fertilizer manufacture. A quotation from a recent paper (16) seems appropriate: "In today's intensive agriculture, magnesium has to be regarded as a major plant nutrient. An inadequate supply in the soil of this nutrient will lead to lower yields. Therefore all Mg-deficient soils, whether they are widespread as in Germany or only sporadic as in Britain, should be dressed with adequate amounts of Mg-containing fertilizers. There will then be no more danger in regard to an induced Mg deficiency by any antagonistic cation."

The new process for magnesium phosphate upgrades the P<sub>2</sub>O<sub>5</sub> values and

provides new outlets for magnesium salts associated with the potash industry.

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#### Correction The Carotenoids of *Diospyros Kaki* (Japanese Persimmons)

In this article by J. Brossard and G. Mackinney [*J. Agr. Food Chem.* **11**, 501 (1963)], footnote a in Table IV, on page 503, does not actually apply to the data in that table and, therefore, should be deleted.