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Defluorination of Wagnerite Coproduced with Magnesium Phosphate Fertilizer

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Magnesium phosphate fertilizer (MGP), produced by the reaction between molten dehydrated carnallite and rock phosphate, consists mostly of trimagnesium phosphate ($Mg_3(PO_4)_2$) and wagnerite (Mg_2PO_4F), with lesser amounts of fluorapatite, MgF_2, MgO, and $CaCO_3$. Wagnerite is insoluble in water or in citric acid and can not be used as a fertilizer. The raw MGP has been submitted to a defluorination process. The experiments consisted of passing a flow of 3 l./ min of either air, oxygen, or nitrogen carrying 0.33 g/min of water over 2 g of MGP placed in an alumina boat inside an electrically heated tube furnace. Calcination was done at temperatures between 800–1000° for 1–12 hr. Complete defluorination of wagnerite was achieved after calcination at 1000° for 4 hr. The wagnerite decomposed to trimagnesium phosphate and magnesium oxide, increasing the citric acid solubility of MGP from 66 to 90%.

The agricultural value of a phosphate fertilizer is related to the percentage of P_2O_5 which is soluble in water or in 2% citric acid. The most important source for P_2O_5 is rock phosphate, which is composed mainly of francolite. The latter is chemically stable and its P_2O_5 content is only partially available to the plants. The fluorapatite structure may be broken either by acid treatment, as used for the manufacture of superphosphates, or by thermal treatment (Sauchelli, 1963). There are two different classes of thermal treatments. One is the defluorination of sintered rock in the presence of water vapor and silica at temperatures higher than 1300° (Elmore et al., 1942; Reynolds et al., 1934). The other is fusing the rock with different materials, such as silicates or sulfates, at temperatures higher than 1400°, followed by rapid cooling. The fluorine is not completely eliminated by this kind of treatment (Boylan and Larson, 1957; Bridger and Boylan, 1953; Walthall and Bridger, 1943).

A more recent method of producing soluble phosphates is by thermally reacting the rock with magnesium chlorides. The process was developed by IMI, Israel (Baniel et

al., 1965) and tried by Israel Chemicals Limited in a pilot plant in Sodom (Helberg and Zisner, 1972). The magnesium phosphate fertilizer (MGP) thus obtained, which is a mixture of soluble trimagnesium phosphate and insoluble wagnerite, served as raw material for the defluorination experiments reported in this work.

The aim of the present work was to study the defluorination process of the wagnerite in order to increase the amount of available phosphate in the MGP fertilizer. The HF which is liberated can be recovered and utilized. In the present work, the recovery of HF was not studied.

APPARATUS

All defluorination studies were performed in an experimental setup shown in Figure 1. The raw material was placed in an alumina boat (10) in a gas flow of 3 l./min, carrying with it 0.33 g of water/min. The water temperature at (6) was kept at 50 ± 1°. The temperature in the furnace was measured with Pt–Pt 10% Rh thermocouple (9) and kept within ±5° of the experimental temperature.

PROCEDURE

MGP produced at Sodom was sieved and only the fraction between 60 and 200 mesh was used in the investigation. A charge of about 2 g of MGP was placed in a boat.

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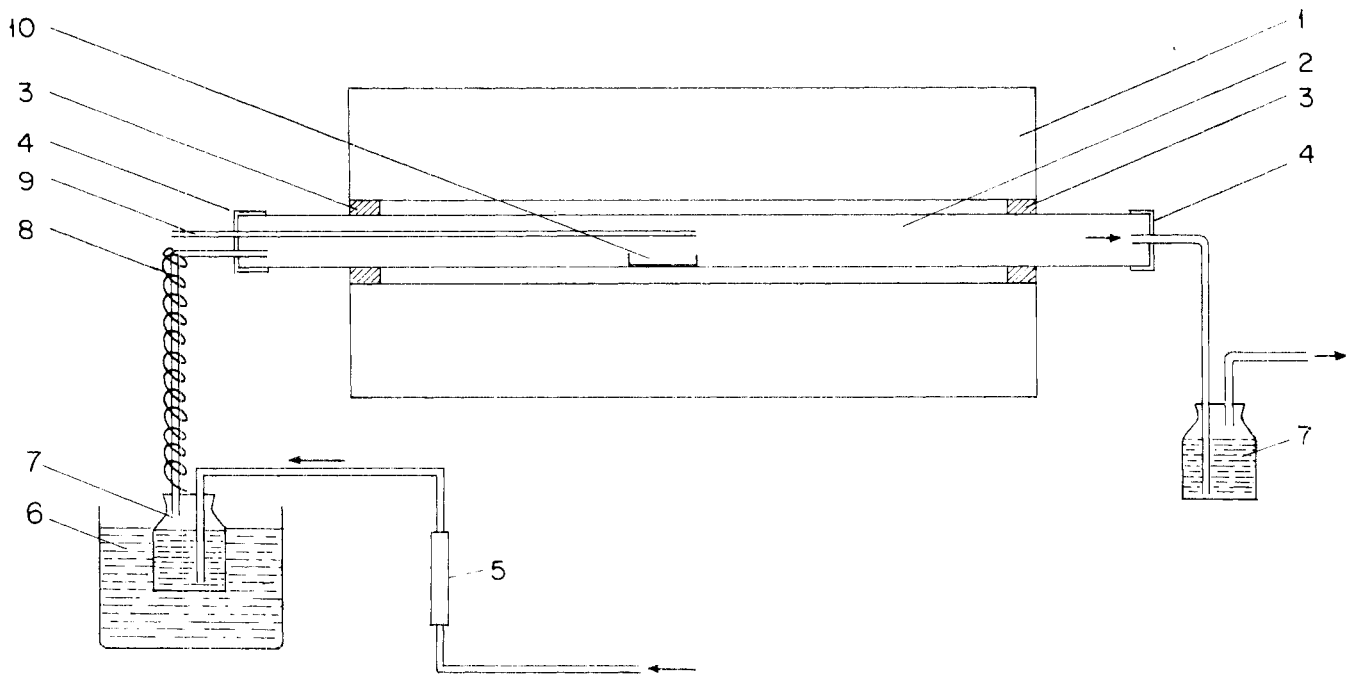
Figure 1. Vertical cross section of the furnace arrangement. (1) resistance tube furnace; (2) quartz reaction tube; (3) asbestos rings; (4) brass cover; (5) flow meter; (6) paraffin oil bath; (7) water bottles; (8) heated glass tube; (9) thermocouple; (10) alumina boat, 1.1 × 1.8 × 7.5 cm.
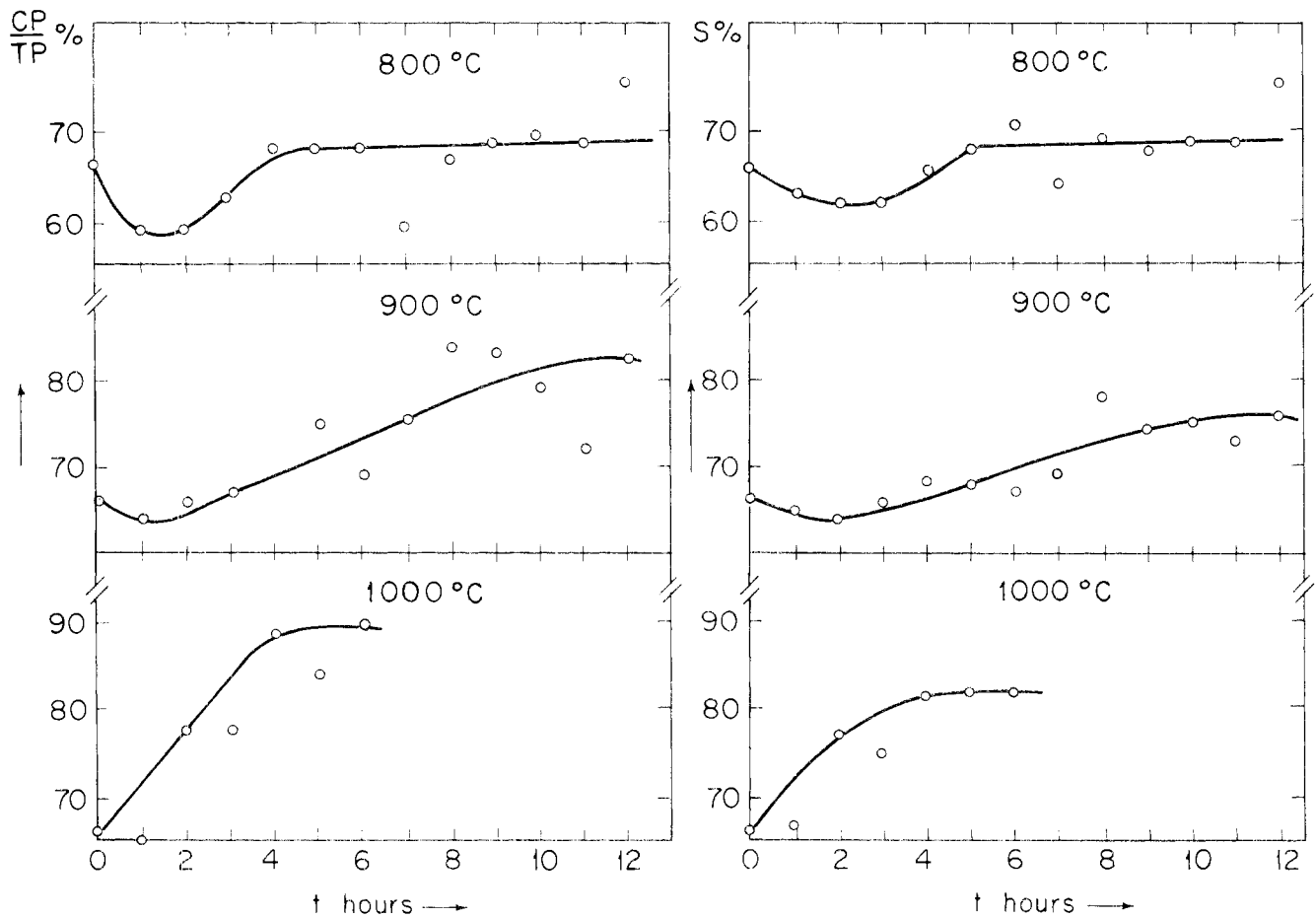
Figure 2. The P_2O_5 citric acid solubility (CP:TP) and the weight percent of soluble material(s) vs. defluorination time at 800, 900 and 1000°.

The layer depth in the boat was 0.5 cm. The furnace was brought to a temperature of about 10° higher than the experimental one and then the flow of gas through the reaction tube (2) was started. Four boats containing the
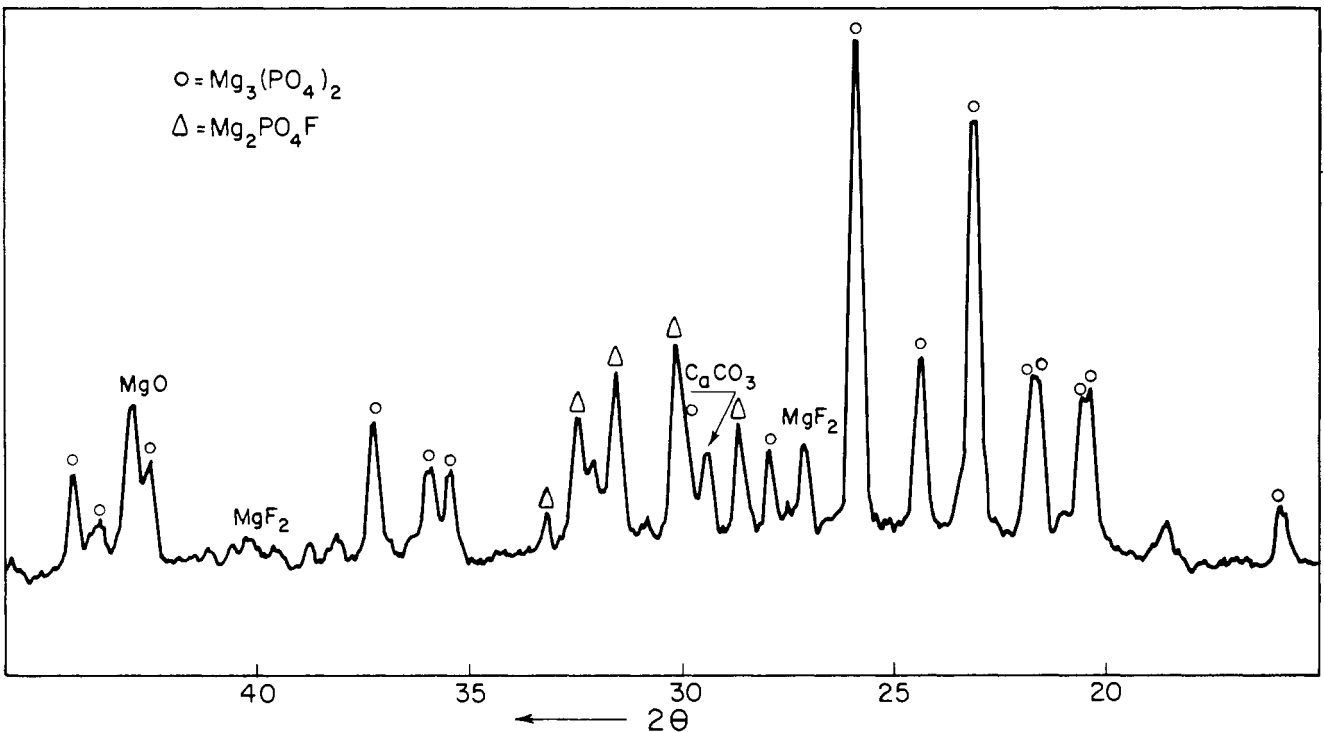
Figure 3. X-Ray diffraction of raw MGP, containing $Mg_3(PO_4)_2$, Mg_2PO_4F, and small amounts of MgO, MgF_2, and $CaCO_3$.
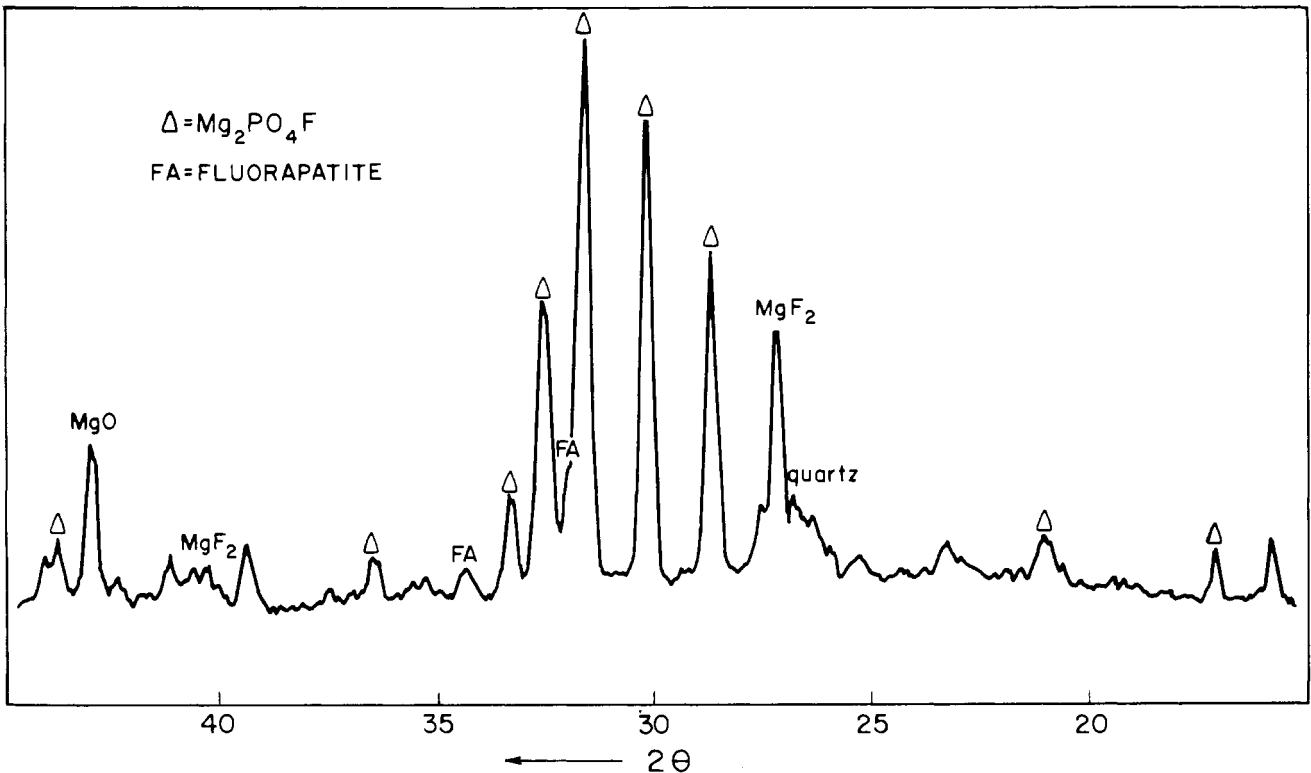

Figure 4. X-Ray diffraction of the insoluble citric acid residue of the raw MGP, containing Mg_2PO_4F and small amounts of MgO, MgF_2, $Ca_5(PO_4)_3F$, and quartz.

charge were introduced into the tube simultaneously, causing a slight decrease of the temperature, which soon reached the desired value. After being heated for a given length of time (1-12 hr), the boats were withdrawn. The material was ground to pass a screen of 200 mesh, 1 g of the sample was added to 100 cm³ of 2% citric acid, and, after shaking it for ½ hr and filtering, its solubility was determined by the gravimetric AOAC method (Horwitz, 1960). The results are expressed in terms of the ratio CP:TP, where TP is the total P_2O_5 content, CP is the P_2O_5 content soluble in 2% citric acid, and the CP:TP ratio is the solubility, *i.e.*, the percent of P_2O_5 soluble in 2% citric acid. The defluorinated charge and the insoluble residue were analyzed by X-ray diffraction.
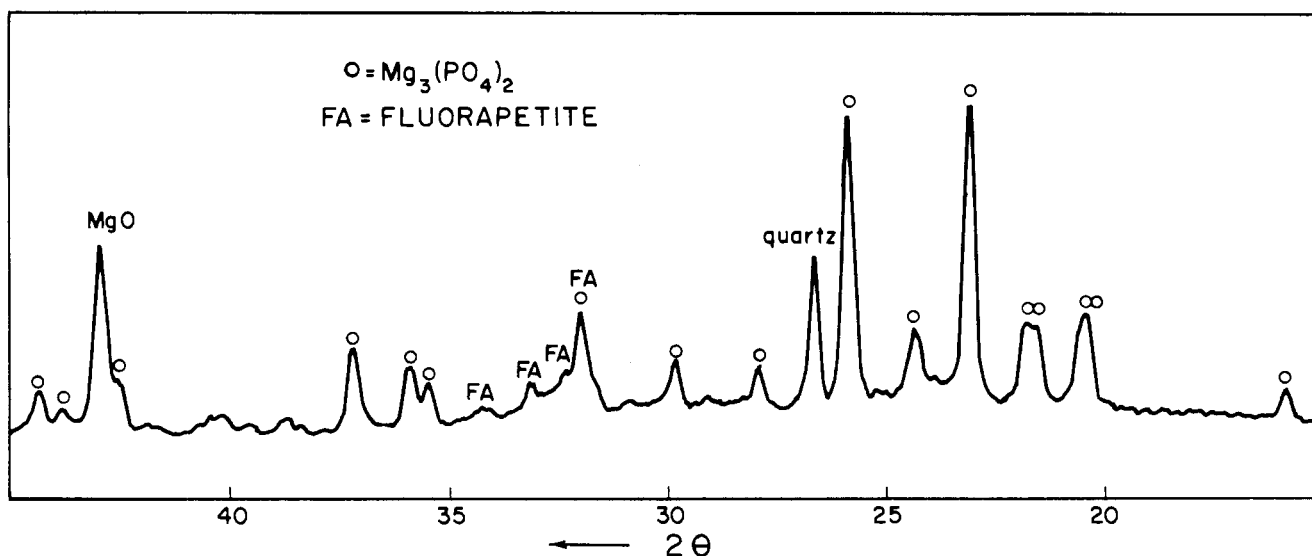
Figure 5. X-Ray diffraction of defluorinated MGP at 1000° for 4 hr, containing $Mg_3(PO_4)_2$, MgO, unreacted $Ca_5(PO_4)_3F$, and quartz.
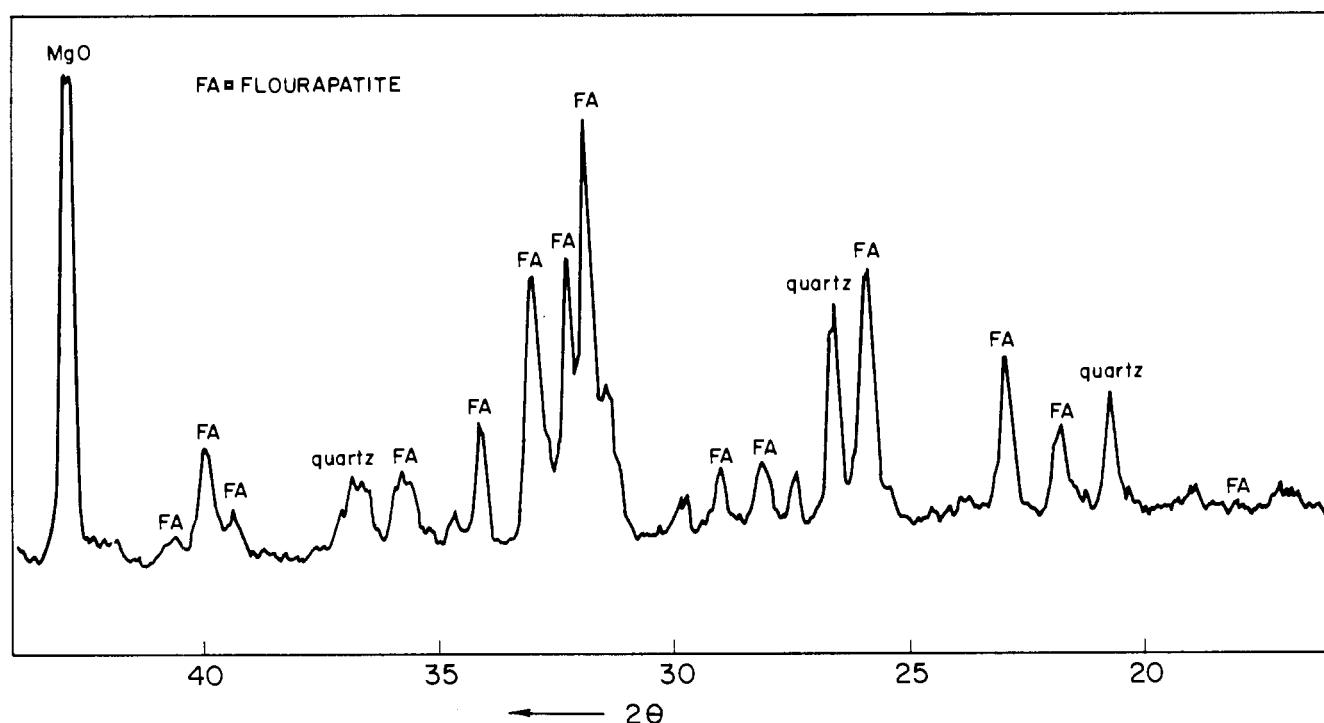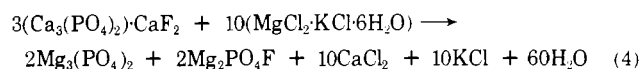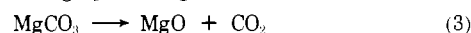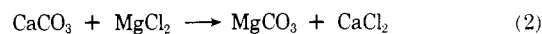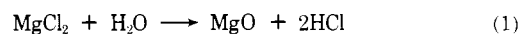

Figure 6. X-Ray diffraction of the insoluble citric acid residue of the MGP defluorinated at 1000° for 4 hr, containing unreacted $Ca_5(PO_4)_3$, MgO, and quartz.

The defluorination experiments were performed at three temperatures, 800, 900, and 1000°. Defluorination at higher temperatures was not tried since the charge started to melt at 1100°. At each temperature, defluorination was studied as a function of both the time (1-12 hr) and the type of carrier gas (air, oxygen, and nitrogen).

RAW MATERIALS

The raw material used in the present investigation was magnesium phosphate fertilizers (MGP) produced at Sodom by the reaction between molten carnallite and rock phosphate (Helberg and Zisner, 1972). The original process is described by Baniel *et al.* (1965), who did not call attention to the occurrence of wagnerite obtained in Sodom according to the following reactions (Ando, 1972; Baniel *et al.*, 1965; Slawski, 1970).

$$MgCl_2 + H_2O \longrightarrow MgO + 2HCl \qquad (1)$$

$$CaCO_3 + MgCl_2 \longrightarrow MgCO_3 + CaCl_2 \qquad (2)$$

$$MgCO_3 \longrightarrow MgO + CO_2 \qquad (3)$$

$$3(Ca_3(PO_4)_2)\cdot CaF_2 + 10(MgCl_2\cdot KCl\cdot 6H_2O) \longrightarrow$$

$$2Mg_3(PO_4)_2 + 2Mg_2PO_4F + 10CaCl_2 + 10KCl + 60H_2O \qquad (4)$$

According to reaction 4, in the ideal case the original P_2O_5 transforms in the proportion of 2:3 as soluble $Mg_3(PO_4)_2$ and 1:3 as insoluble Mg_2PO_4F (wagnerite). The content of citric acid soluble P_2O_5 in the MGP can not exceed 67%.

A typical chemical analysis of raw MGP used in the present investigation contained 36.1% P_2O_5, 3.1% F, 3% SiO_2, and 7.2% loss on ignition.

RESULTS AND DISCUSSIONS

The defluorination of wagnerite obtained by reacting the charge with the vapor of H_2O carried with a carrier gas proved to be independent of the nature of the carrier. The same amount of available P_2O_5 was obtained in air, oxygen, and nitrogen carriers, provided that the amount of H_2O was kept constant. The kinetics of defluorination at 800, 900, and 1000° in air are shown in Figure 2.

It can be seen that there is a negligible increase in soluble P_2O_5 at 800°, a greater one at 900°, and a maximum value is reached at 1000° after 4 hr. At the start of the defluorination process at 800 and 900°, there is a decrease in the solubility, the cause of which could not be determined. We assumed that in the first stage of the reaction, some of the free MgF_2 reacted with $Mg_3(PO_4)_2$ (a reaction which takes place at temperatures higher than 600°) and produced insoluble wagnerite before it had a chance to defluorinate, but this hypothesis was not confirmed by X-ray diffraction, nor did we find in the residue undissolved $Mg_3(PO_4)_2$.

The raw materials, the defluorinated ones and their insoluble residues, have been studied by X-ray diffraction. It can be seen that the main component of the raw MGP (Figure 3) which did not dissolve in the citric acid solution is wagnerite (Figure 4), which disappears completely after defluorination at 1000° for 4 hr (Figure 5). Fluorapatite, which can not be defluorinated at this temperature, is the main insoluble compound of the defluorinated MGP (Figure 6). The fluorapatite is not seen in Figure 3 due to the fact that it is present only in relatively small amounts which are masked by the other major components of the MGP. MgO is partially soluble in citric acid, as indicated in Figures 4 and 6.

CONCLUSIONS

Magnesium phosphate fertilizer, produced by the reaction between phosphate rock and molten carnallite, contains a large amount of wagnerite which is not soluble in

2% citric acid solution. The wagnerite can be completely defluorinated at 1000° for 4 hr in the atmosphere of a wet carrier gas. It decomposes according to the following reaction. The HF can be recovered and utilized.

$$2Mg_2PO_4F_{(s)} + H_2O_{(v)} \longrightarrow Mg_3(PO_4)_{2(s)} + MgO_{(s)} + 2HF_{(v)} \quad (5)$$
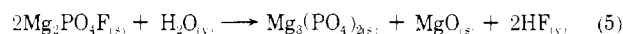
Some unreacted phosphate rock, mainly fluorapatite, makes up to 10% of the total amount of the fertilizer and is not defluorinated at 1000°. Therefore, the citric acid solubility of the calcined fertilizer is only about 90%.

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Distribution of [14C]Ethylene and the Incorporation of Radiocarbon in "Valencia" Oranges after Exposure to [14C]Ethylene

James F. Fisher

Externally applied [14C]ethylene was found to distribute throughout the internal environment of the orange. Radiocarbon was incorporated into the ether-soluble material and fractions containing amino acids, organic acids, and the 80% ethyl alcohol-soluble carbohydrates. The greatest activity was in the ether-soluble and organic acid fractions. Citric acid was isolated and found to be radioactive.

Ethylene has been reported to incorporate in plant material such as avocado and pear tissue by Buhler et al. (1957) and Jansen (1963, 1964), in cotton and coleus

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plants by Hall et al. (1961), and in Japanese morning glory seedlings by Shimokawa et al. (1969). Burg and Burg (1962) reported that the internal content of ethylene in oranges increased when they were in the presence of external ethylene. Stewart and Wheaton (1972) have shown that ethylene enhances the synthesis of carotenoids in oranges. Recently, Maier et al. (1973) showed the specific effect of ethylene in accelerating limonoid metabolism in