

FUSION OF PHOSPHATE ROCK WITH SEA SALTS AND SODIUM CARBONATE

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(Received May 12, 1971; revised August 31, 1971)

Abstract. Phosphate fertilizer has been produced by fusing sea salt with phosphate rock at 900°C. A product of 100% available P_2O_5 is obtained which is higher than the reported values. The X-ray pattern and the reaction mechanism are also given. The feasibility of the process for commercial exploitation has been discussed.

Extensive work has been done on the production of phosphate fertilizers by fusion processes. A number of workers^{1,2} have studied the fusion of phosphate rock with different additives such as langbenite, silica, sulphides and sulphates using high temperature. Rhenania phosphate has been produced in Germany by sintering phosphate rock with sodium carbonate in the presence of silica.³ Studies have also been made in France on the production of phosphate fertilizers by heating a mixture of (i) calcium pyrophosphate and sodium carbonate, and (ii) tricalcium phosphate and sodium carbonate at 900°C.⁴⁻⁵

Production of monocalcium tetrasodium phosphate has been reported at 900°C by sintering sodium carbonate and phosphate rock.⁶ Experiments were carried out in Italy on heating a mixture of natural phosphates, coal, sand and sodium carbonate in a kiln at 1100-1150°C.⁷

All these investigations report high availability of P_2O_5 but always less than 100% at the temperatures studied. In the present investigation sea salts have been fused with phosphate rock at 900°C and a product of 100% available P_2O_5 is obtained, a small portion of which is soluble in water and the remainder soluble in 2% citric acid.

Sea salts provide a cheap source of addition agents and the presence of small quantities of magnesium cannot be overlooked as an essential plant nutrient. The product is not acidic and does not cause bag rot. Being neutral it does not necessitate liming of the soil. The fusion temperature (900°C) is not very high and hence the process can be exploited for commercial operation. The P_2O_5 content is comparable to double superphosphate.

Experimental

Phosphate rock (-200 mesh) with 33.85% P_2O_5 content was mixed with sea salts, sodium chloride (magnesium chloride, magnesium sulphate) and sodium carbonate in various proportions (Tables 1, 2 and 3). The mixture was then fused in a gas-fired refractory furnace as described by Bridger and Boylan¹ in the process of fusion of phosphate rock with langbenite. The furnace was preheated at 900°C. A porcelain crucible was used. The fusion was considered complete when the bubbles of gas stopped. The melt was kept 2-3 min longer to ensure the com-

pletion of the reaction (altogether 5-7 min). The fused product was poured into an aluminium pan, floating on cold water. It solidified immediately. The sodium chloride fused product was grey while the magnesium chloride product was white. In the fusion experiments, where the proportions of 40:60 and 50:50, i.e. where the proportion of the salts was comparatively low, the melt was liquid but could not be poured into the pan and the crucible was kept on the floating pan to cool.

The product was ground and subsequently analysed for water and citrate-solubility and total availability of P_2O_5 . The P_2O_5 content was determined by the colorimetric method⁸ (Table 1).

Discussion

The conversion of phosphate rock into the soluble form of P_2O_5 without using acids demands high temperatures so as to fuse the mixture of the rock and the flux. In the fusion processes it has been convincingly demonstrated that addition agents play an active role in this conversion. These additives react with the fluoride and thereby change the apatite structure thus increasing the solubility.

The conversion of insoluble P_2O_5 in the phosphate rock to the soluble form results in the formation of a small amount of water soluble P_2O_5 and the major portion is converted into the citrate soluble form. The optimum proportions (Fig. 1) are phosphate rock-salts(30:70). In mixtures where the amount of salts is more than the optimum proportion, it has been observed that the excess salts remain unreacted and can be leached out by water. In mixtures having the amount of salts less than the optimum proportion, the conversion from the insoluble to soluble form is not complete.

More water soluble phosphate is formed when the amount of alkali present in the reaction mixture is in excess (Table 1a, proportions, 10-90 and 20-80). As the amount of alkali decreases, the formation of water-soluble phosphate also decreases and citric acid solubility increases. This may be due to two effects which have been described by earlier workers,⁶ (i) the water-soluble sodium phosphate, formed during the process of the reaction, reverts to insoluble form by reacting with calcium also present in the product, and (ii) in the lower proportion of salts, there are fewer

TABLE 1(a). REACTION MIXTURE: PHOSPHATE ROCKS, NaCl + Na₂SO₃; TEMPERATURE 900°C.

Proportions by wt Phosphate R-salts	P ₂ O ₅ in total product (wt%)	Water sol. P ₂ O ₅ in total pro- duct (wt%)	Cit. sol. P ₂ O ₅ in total product (wt%)	Total available	
				P ₂ O ₅ (%)	conversion (%)
10:90	27.64	8.00	26.24	26.24	87.69
10:60	27.87	7.71	20.61	28.32	(100 more)
20:80	25.72	2.00	23.65	25.65	92.53
30:70	28.475	1.36	26.929	28.289	99.34
40:60	24.72	0.78	23.625	24.405	98.7
50:50	32.7	1.95	21.8	23.75	72.6

TABLE 1(b). REACTION MIXTURE: PHOSPHATE ROCK + SEA SALTS; TEMPERATURE 900°C OR 1650°F.

Reaction mixture P	Proportion by wt	Water sol. P ₂ O ₅ (%)	Cit. sol. P ₂ O ₅ (%)	Total available	
				P ₂ O ₅ (%)	Conversion (%)
*Phosphate rock + MgSO ₄ + NaCl	1:3:3	Nil	21.75	21.75	64.2
Phosphate rock + MgCl ₂ + Na ₂ CO ₃	1:3:3	13.5	15.7	29.2	80.35
Phosphate rock + NaCl + MgCl ₂	1:3:3	0.19	9.52	9.71	28.68

*Temperature 1000°C

TABLE 2. RESULTS OF FUSION OF PHOSPHATE ROCK WITH MgCl₂ AND Na₂CO₃; TEMPERATURE 900°C OR 1650°F.

Proportion by wt phosphate rock-salts	Water sol. P ₂ O ₅ (%)	Cit. sol. P ₂ O ₅ (%)	Total available	
			P ₂ O ₅ * (%)	Conversion (%)
10:90	3.16	20.25	23.41	69.57
10:60	1.88	20.25	22.13	65.37
20:80	2.04	17.62	19.66	59.3
30:70	0.84	12.56	13.40	39.64
40:60	0.53	11.962	12.492	36.9

*P₂O₅ has been made soluble by the addition agents over the amount of 33.85% present in the phosphate rock.TABLE 3. RESULTS OF FUSION OF PHOSPHATE ROCK WITH MgCl₂ AND NaCl; TEMPERATURE 900°C OR 1650°F.

Proportion by wt phosphate rock-salts	Water sol. P ₂ O ₅ (%)	Cit. sol. P ₂ O ₅ (%)	Total available	
			P ₂ O ₅ * (%)	Conversion (%)
10:90	0.76	8.3	9.06	26.7
20:80	—	7.100	7.1	20.9
10:60	—	16.05	16.05	47.9
30:70	—	2.8	2.8	8.26
40:60	—	0.802	0.802	2.36

*P₂O₅ has been made soluble by the addition agents over the amount of 33.85% present in the phosphate rock.

molecules of sodium oxide, which do not permit the formation of water soluble phosphate and the tendency of the reaction is towards the formation of citrate

soluble phosphate. This is further substantiated by Table 2, showing results using magnesium chloride, the P₂O₅ availability is less. This would be expected since the amount of magnesium on a weight by weight basis is lower because of the presence of water of crystallization in magnesium chloride, magnesium being much more compact and closed packed than sodium.

In the mixtures in which sodium carbonate is used, the observed yields are higher because it decomposes easily at the temperature at which the experiment is carried out. In other mixtures where sodium carbonate is not used the yields are low (Table 3). Sodium chloride also melts at the temperature used in the experiment and facilitates the reaction, but does not decompose and remains in the fluid state over a wide range of temperature. The conversion into citrate soluble form is, therefore, not complete, in spite of the evidences which suggest the occurrence of reactions.

The product has been exposed to X-rays to find the chemical composition (Fig. 1). The fusion product has a glassy structure with incipient crystallinity which does not correspond to any known compound showing that the composition of the product is of complex nature. The presence of NaCl in the fused product indicates that the NaCl itself does not take part in the reaction nor does it decompose at the fusion temperature but helps that mixture acquire liquid consistency which interacts with the apatite structure forming different compounds of ortho, meta or pyrophosphates depending upon the position of Na₂O molecules around the apatite structure. The presence of magnesium chloride further complicates the matter probably because molecules of magnesium chloride are larger than the molecules of sodium chloride and thus a thick molten mass which affects the overall availability of P₂O₅. The excess salts separate out

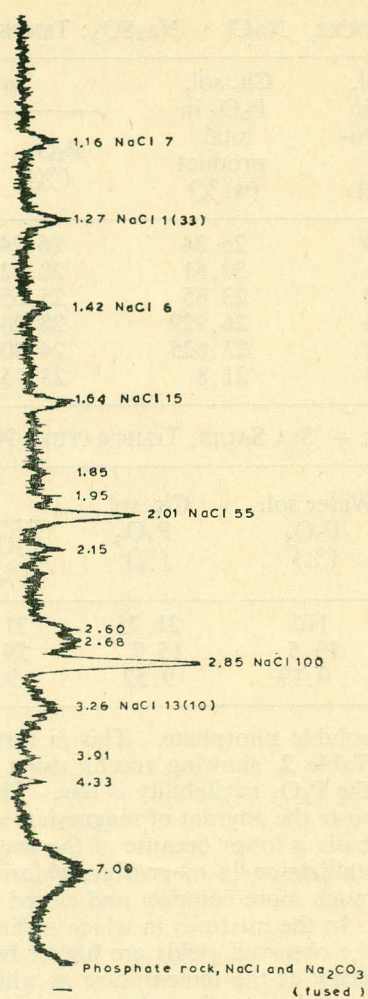


Fig. 1

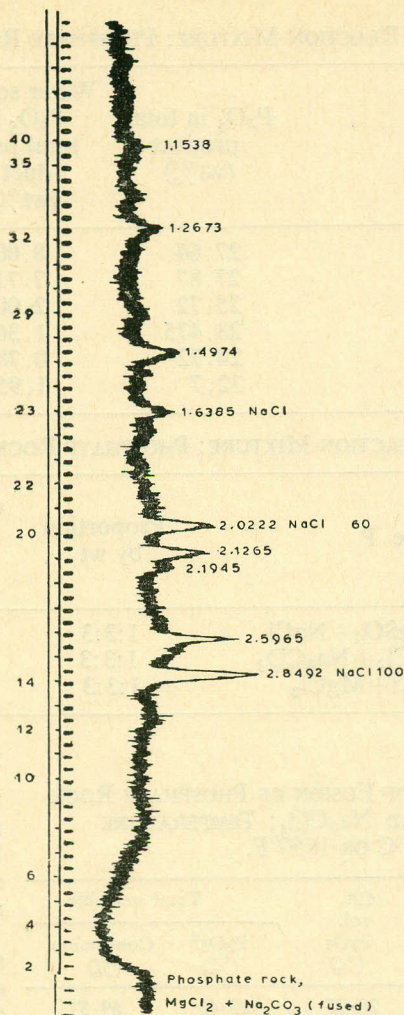
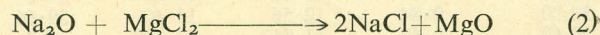
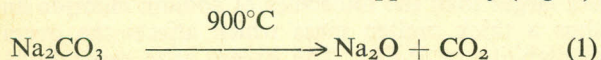


Fig. 2

from the product on keeping the citrate-soluble extract for a long time.

In the mixture in which magnesium and sodium chlorides are used the availability is not much (Table 3). It is because sodium chloride is an inert substance in these reactions. Magnesium chloride being more dense reacts in a different manner, therefore, the reaction between the three components of the mixture is just 50%.

The three strongest lines in the X-ray pattern (Figs. 1 and 2) and their relative intensities indicate that there is interaction between apatite structure and Na_2O molecules, which are formed by the decomposition of Na_2CO_3 . It has been suggested in the previous publication⁶ that the formation of a compound, corresponding to the formula $\text{CaNa}_4(\text{PO}_4)_2$ takes place by penetration of Na_2O molecules into the apatite structure of the phosphate rock. In the process of fusion of the rock with magnesium chloride and sodium carbonate, Na_2O molecules react with MgCl_2 with the formation of NaCl . This is supported by (Fig. 2).



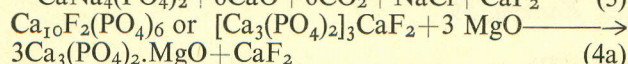
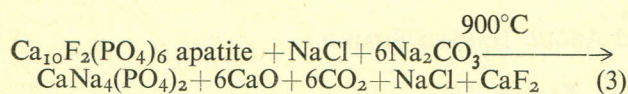
under these conditions MgO molecules may penetrate into the apatite lattice and may displace CaF_2 , thereby increasing citric acid solubility.

It has been reported with definite proof² that removal of fluorine increases citrate solubility, therefore, the mechanism which explains the possible mode of reaction is that CaF_2 is displaced by MgO in the first instance. This is followed by the removal of the second calcium of tricalcium phosphate (phosphate rock is mostly tricalcium phosphate) with the formation of the compound $\text{CaMg}_2(\text{PO}_4)_2$ which corresponds to the monocalcium phosphate, $\text{CaH}_4(\text{PO}_4)_2$. The former is citric-soluble, while the latter is water-soluble. In the third stage of reaction, water-soluble sodium phosphate is produced.

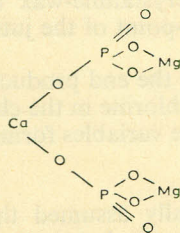
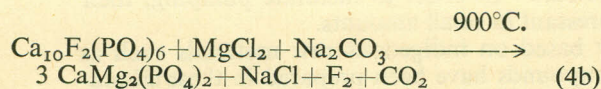
It may be further noted that when the products are leached with water, the unreacted salts and water-soluble sodium phosphate are not hydrolysed. The X-ray pattern does not correspond to a known compound. This X-ray pattern and the relative intensities of the lines strongly indicate the formation of the new

compound proposed above.

The overall process may be represented by the following equations:



When the compound $\text{Ca}_3(\text{PO}_4)_2 \cdot \text{MgO}$ is leached with citric acid, it is converted to $\text{Ca Mg}_2(\text{PO}_4)_2$



The structure of the compound may therefore be represented as follows.

Acknowledgement. The author is thankful to the U.S. Government for award of Fulbright Research Fellowship under Technical Assistance Programme, to Department of Chemical Engineering, Iowa State University, Ames, for providing facilities for the above work and Dr. D.R. Boylan for his valuable advice.

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