Phase Diagrams of $Ca_3(PO_4)_2$–$Mg_3(PO_4)_2$ and $Ca_3(PO_4)_2$–$CaNaPO_4$ Systems

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$Ca_3(PO_4)_2$–$Mg_3(PO_4)_2$ system is important for a fundamental study of fused phosphate fertilizers such as calcium magnesium phosphate (serpentine fused) or defluorinated tricalcium phosphate with magnesia. However little information is found in literature on phases of this system except in the case of tricalcium phosphate.

On the other hand, $Ca_3(PO_4)_2$—$CaNaPO_4$ system is important for the study on calcined phosphate fertilizer, especially on low-alkali phosphate as was produced in England under the name of silicophosphate or as has been produced in Japan for these several years. Among the phases of this system, $CaNaPO_4$ is well known as rhenanite which is a principal constituent of Rhenania phosphate in Germany, and the structure of a phosphate with a composition $Ca_4Na(PO_4)_3$ was stated by Klement[1].

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[1] R. Klement and F. Steckenreiter, *Z. anorg. allg. Chem.*, **245**, 236-253 (1940).

In the present work, phase systems were investigated systematically by means of differential thermal analysis, X-ray diffraction, microscopy and chemical analysis.

Experimental and Results

(I) $Ca_3(PO_4)_2$-$Mg_3(PO_4)_2$ System Samples were prepared by calcining or fusing the mixture of refined calcium oxalate, magnesium hydroxide and phosphoric acid, and were tested by thermal analysis in a small platinum vessel during fusion and cooling at a rate of 5°C/min.

Fig. 1 illustrates the results of thermal analysis. Within the range from 3 CaO·P_2O_5 to 1.5 CaO·1.5 MgO·P_2O_5 tricalcium phosphate first crystallizes from the melt. In this range the liquidus temperature was not detected clearly by thermal analysis and was determined by quenching the melt from various temperatures and examining it with microscope and X-rays.

It was found that the phase diagram of this system was of peritectic type and that a new compound $Ca_3Mg_3(PO_4)_4$ was formed below 1175°C (Fig. 1, 2 and 4).

Samples with more than 1.5 mol. MgO to 1 mol. P_2O_5 consist of trimagnesium phosphate and $Ca_3Mg_3(PO_4)_4$. Even in samples with more than 1.5 mol. CaO to 1 mol. P_2O_5, formation of trimagnesium phosphate was detected by thermal analysis. This shows that the reaction of tricalcium phosphate and the melt to form $Ca_3Mg_3(PO_4)_4$ is not accomplished under such a cooling condition.

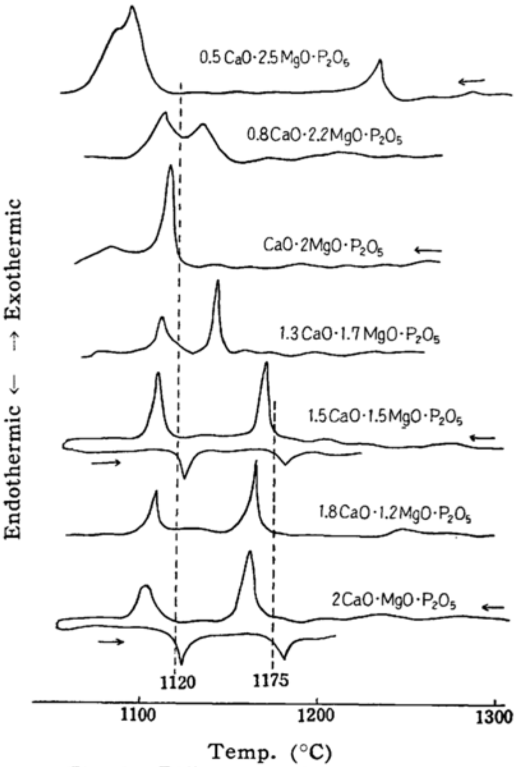

Fig. 1. Differential thermal analysis of samples.

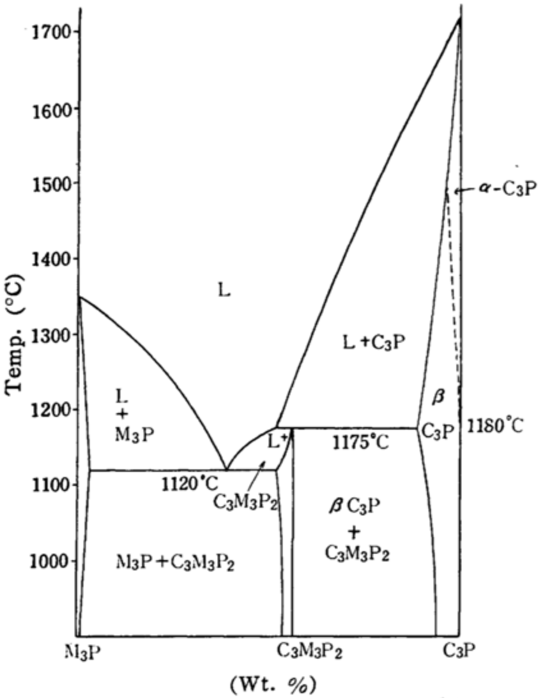

Fig. 2. Phase diagram [$C_3P=Ca_3(PO_4)_2$, $M_3P=Mg_3(PO_4)_2$, $C_3M_3P_2=Ca_3Mg_3(PO)_4)_4$].

Fig. 3 illustrates the solubility of samples treated in various ways. Samples with the mark A were prepared by calcining at 1100°C. Samples with the mark B

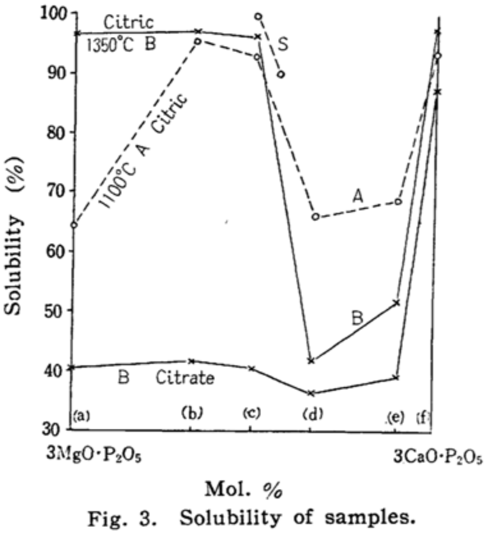

Fig. 3. Solubility of samples.

were heated in a platinum crucible at 1350°C and then cooled quickly in air. 'Citric' means the solubility tested by the Japanese official method, (150 ml. of 2% citric acid to 1 g. of sample pulverized to pass 100 meshes per inch sieve; shaking for an hour). 'Citrate' means the solubility tested by the American official method with neutral ammonium citrate solution.

Samples with less than 1 mol. MgO to 1 mol P_2O_5 consist mainly of tricalcium phosphate. By substitution of magnesia for lime β modification of tricalcium phosphate is stabilized. The distance between the crystal planes becomes smaller and the solubility of the phosphate is reduced remarkably.

The fused product with the composition of $1.5CaO \cdot 1.5MgO \cdot P_2O_5$ consists mostly of the compound $Ca_3Mg_3(PO_4)_4$; however as mentioned above, small amounts of unchanged β-tricalcium phosphate and trimagnesium phosphate are mixed. The melt of this sample was quenched, powdered and then sintered at 1140°C for 5 hours; thus pure $Ca_3Mg_3(PO_4)_4$ was obtained. Samples prepared by such a procedure are indicated in Fig. 3 by the mark S.

The compound $Ca_3Mg_3(PO_4)_4$ is completely soluble in citric acid by the Japanese official method. Citric solubility of the compound, tested by the method with 100 ml. of 2% citric acid for 1 g. of sample (shaking for half an hour), was 91%. However the compound is less soluble in citrate by the American official method. Also the sample with more magnesia is soluble in citric acid but less soluble in citrate.

X-ray diffraction pattern of $Ca_3Mg_3(PO_4)_4$ resembles that of α-tricalcium phosphate (Fig. 4 and Table I). Possibly these two compounds are isomorphous but can hardly form a crystalline solution with each other because of the difference of axial ratio.

Formation of trimagnesium phosphate was not accomplished by calcining the sample with the composition of $3MgO \cdot P_2O_5$ at 1100°C but a considerable amount of insoluble magnesium pyrophosphate was mixed. By fusing the sample at 1350°C pure trimagnesium phosphate was obtained. Also trimagnesium phosphate is soluble in citric acid but less soluble in citrate.

Fused trimagnesium phosphate with an excess of P_2O_5 is mixed with magnesium pyrophosphate, and the fused product with excessive magnesia is mixed with crystals of MgO.

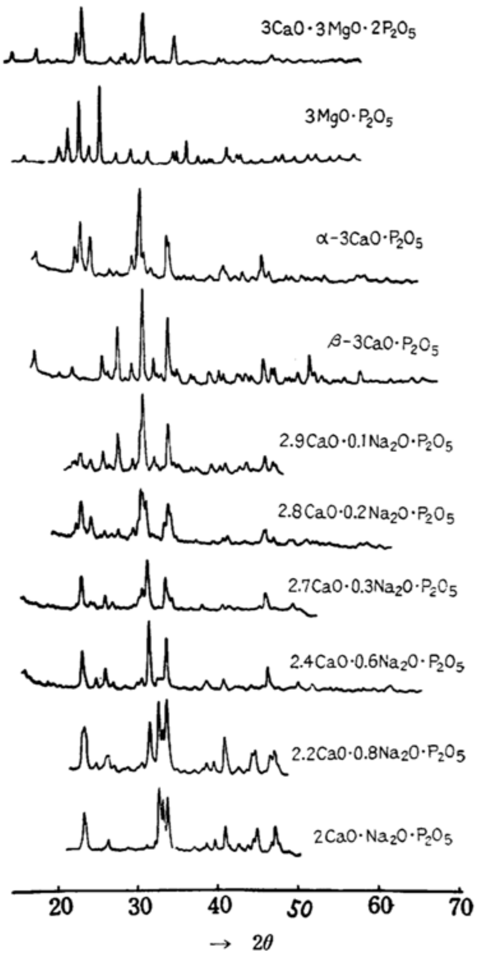

Fig. 4. X-ray diffraction patterns by Geiger-counter spectrometer. (Cu, Kα, Ni Filter)

(II) $Ca_3(PO_4)_2$-$CaNaPO_4$ Systems Samples of this system were prepared by calcining the mixture of refined calcium oxalate, sodium carbonate and phosphoric acid for half an hour at 1300°C. X-ray diffraction patterns of samples, cooled quickly in air after calcination, are shown in Fig. 4 and Table I.

$CaNaPO_4$ has β-rhenanite structure, low-temperature modification of rhenanite $CaNaPO_4$. Inversion of this compound from α (high temperature) to β modification occurs so quickly that α modification can not be obtained at room temperature even if the phosphate is cooled quickly from a high temperature as was described by Bredig[2]. Reversible $\alpha \rightleftarrows \beta$ inversion was observed at 660°C by thermal analysis. X-ray diffraction patterns of the sample $2.4CaO \cdot 0.6Na_2O \cdot P_2O_5$ coincides with that

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[2] M. A. Bredig, *J. Phys. Chem.*, **46**, 478 (1942).

TABLE I
RESULTS OF X-RAY ANALYSIS OF SAMPLES

$Ca_3Mg_3(PO_4)_4$		$Mg_3(PO_4)_2$		α-$Ca_3(PO_4)_2$		2.4 $CaO \cdot 0.6\ Na_2O \cdot P_2O_5$	
d	*I*	*d*	*I*	*d*	*I*	*d*	*I*
8.42	ww	5.61	ww	7.31	ww		
6.11	ww	4.35	w	5.18	ww	4.79	ww
5.01	w	4.12	m	4.02	m		
3.87	m	3.85	s	3.90	ms	3.90	ms
3.75	s	3.66	w	3.69	m	3.60	w
3.25	ww	3.45	s			3.44	mw
3.11	ww	3.20	w			3.31	ww
3.05	w	3.00	w	2.91	s	2.93	w
2.82	s	2.79	w	2.87	w	2.85	s
2.75	ww	2.54	w	2.63	ms	2.67	s
2.71	ww	2.50	w	2.60	ms		
2.51	ms	2.42	m	2.25	ww	2.32	w
2.17	ww	2.13	mw	2.17	mw	2.20	mw
2.14	ww	2.07	w	2.405	w	2.03	ww
2.02	ww	2.045	w	1.943	m	1.94	m
1.877	w	1.831	w	1.907	w	1.80	w
1.807	ww	1.725	w	1.821	ww		
1.629	ww	1.692	w	1.800	ww		
1.605	ww	1.563	w	1.759	ww	1.743	w
				1.670	w	1.490	w

of α modification of rhenanite tested by a high-temperature X-ray camera. Also the sample 2.6 $CaO \cdot 0.4\ Na_2O \cdot P_2O_5$ shows the same pattern. Samples with 0.3 or 0.2 mol. Na_2O consist of α-rhenanite and α-tricalcium phosphate. The sample with 0.8 mol. Na_2O consists of both α and β modification of rhenanite.

Thermal analysis of samples with 0.5~0.8 mol. Na_2O shows endothermic reaction on heating and exothermic reaction on cooling between 615~620°C, corresponding to the $\alpha \rightleftarrows \beta$ inversion of rhenanite. This illustrates the fact that by partial substitution of lime for Na_2O of rhenanite, high-temperature modification of rhenanite is stabilized and can easily be obtained at room temperature. The α-rhenanite type crystalline solution is most stable when nearly half of Na_2O is replaced by CaO. Inversion of these crystalline solutions is not reversible. By repeated cooling and heating of the sample, the inversion temperature detected by thermal analysis gradually approaches that of $CaNaPO_4$, the crystalline solution being decomposed to β-rhenanit and β-tricalcium phosphate. Samples with 0.2 or 0.3 mol. Na_2O do not show any distinct peak of reaction between 600~700°C. These samples are easily decomposed to β-tricalcium phosphate and β-rhenanite by slow cooling.

Thermal analysis of the sample with 0.1 mol. Na_2O gives distinct peaks of endothermic reaction on heating and exothermic reaction on cooling between 1130~1180°C. $\alpha \rightarrow \beta$ inversion of tricalcium phosphate is so much quickened by substituting a small amount of Na_2O for CaO that the phosphate almost inverts to β modification even if cooled quickly from high temperature.

Solubility of these samples is illustrated in Fig. 5. The sample with 0.1 mol. Na_2O is less soluble because this consists mainly of β-tricalcium phosphate. α-Rhenanite type crystalline solution is highly soluble in both citric acid and neutral ammonium citrate. The solubility is reduced when the crystalline solution is cooled slowly and decomposed to β-tricalcium phosphate and β-rhenanite.

The α-rhenanite type crystalline solution is furthermore stabilized by the addition of calcium orthosilicate. A sample with a composition of 2.9 $CaO \cdot 0.1\ Na_2O \cdot P_2O_5 + 0.35\ (2\ CaO \cdot SiO_2)$, calcined at 1350°C and cooled quickly, consists of a mixture of α-rhenanite, α-tricalcium phosphate and β-tricalcium phospate. A sample with a composition of 2.8 $CaO \cdot 0.2\ Na_2O \cdot P_2O_5 + 0.35\ (2CaO \cdot SiO_2)$ treated in the same way consists of α-rhenanite type crystalline solution and a small amount of α-tricalcium phosphate.

However, the sample 2.8 $CaO \cdot 0.2\ Na_2O \cdot$

P_2O_5+0.7 (CaO·SiO) treated in the same way consists mainly of α-tricalcium phosphate, illustrating that Na_2O is combined with excess of silica and does not react with calcium phosphate, so that in the manufacture of low-alkali calcined phosphate, addition of excessive silica must be avoided.

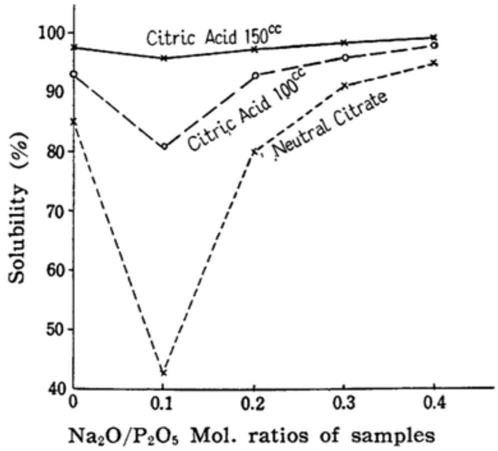

Fig. 5. Solubility of samples cooled quickly from 1300°C.

Discussion

Magnesia in fused phosphate fertilizers affects seriously the constitution and the solubility of the phosphate. In order to render the phosphate soluble, magnesia content in the phosphate which usually contains 20—30% of silica must be kept less than 5% so that the formation of α-tricalcium phosphate is not prevented; otherwise it must be kept around more than 12% so that the melting point of the phosphate is lowered and the phosphate can easily be rendered to a glass state by quenching with water[3].

In a usual fused phosphate fertilizer, the compound $Ca_3Mg_3(PO_4)_4$ is not easily formed because magnesia combines with silica to form Mg_2SiO_4, $MgSiO_3$ and $CaMg(SiO_3)_2$[4].

The compound $Ca_3Mg_3(PO_4)_4$ as well as the serpentine fused phosphate fertilizer is less soluble in neutral citrate or in Petermann's citrate, though these are highly soluble in citric acid. It seems that the low solubility of these phosphates in these citrate solutions is attributable to the low solubility of magnesium phosphate in neutral or alkaline solution with much ammonia. For testing the solubility of phosphate fertilizer with much magnesia neither the neutral nor the alkaline ammonium citrate method is suitable, but citric acid or acidic citrate method is preferable. On the other hand, calcium sodium phosphate is soluble in both citric acid and citrate. On the calcination of low-alkali phosphate fertilizer with 0.2—0.6 mol. Na_2O to 1 mol. P_2O_5, Na_2O reacts with phosphate rock to promote decomposition and defluorination of apatite, to depress the effect of alumina and iron oxide which stabilize β-tricalcium phosphate and to form a soluble crystalline solution of α-rhenanite structure.

Summary

The small amount of magnesia contained in tricalcium phosphate replacing lime stabilizes β modification of the phosphate. However, a new compound $Ca_3Mg_3(PO_4)_4$ is formed below 1175°C when more than 0.6 mol. of MgO to 1 mol. of P_2O_5 is introduced into the phosphate. This compound is soluble in citric acid but less soluble in neutral ammonium citrate similarly as is serpentine-fused phosphate fertilizer.

In $Ca_3(PO_4)_2$-$CaNaPO_4$ system, a crystalline solution with α-rhenanite structure is easily formed within the range of 2.6 CaO·0.4 Na_2O·P_2O_5—2.4 CaO·0.6 Na_2O·P_2O_5, and is furthermore stabilized by the admixture of calcium orthosilicate. This crystalline solution is highly soluble in both citric acid and citrate, composing a principal part of low-alkali calcined phosphate fertilizers.

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[3] J. Ando, *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zassi*) **59**, 1112 (1956).

[4] J. Ando, ibid, **60**, 1101 (1957).