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Reaction of chlorapatite, $Ca_5(PO_4)_3(Cl,F)$ with sodium carbonate and silica

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The conversion of insoluble phosphorous minerals such as apatite, $Ca_5(PO_4)_3(F, OH, Cl)$, to phases containing phosphorous in soluble form is an essential step in the production of fertilizer grade phosphates. Developing countries lack the capital-intensive industrial base necessary to create a phosphate industry. We examine a process suitable for use in Sri Lanka which uses mainly indigenous raw materials. In this process, a chlorine-rich apatite is fused with Na_2CO_3 and SiO_2 at 900° C and 1300° C for 1 to 2 h to yield a product having $>90\%$ available phosphorous. Data necessary for the technological evaluation of the process are presented. Phase equilibria in the lime-rich portions of the system $CaO-Na_2O-P_2O_5-SiO_2$ have been studied. The section $Ca_3(PO_4)_2-Ca_2SiO_4-CaNaPO_4$ is shown to be a ternary system, and phase relations on the 1100° and 1300° C isothermal sections are presented. A reconnaisance of the system $CaO-Ca_3(PO_4)_2-Ca_2SiO_4-CaNaPO_4$ has been made. These data, combined with studies of the kinetics of the reaction, point to regions of composition and reaction conditions favouring high yields of available phosphorous.

1. Introduction

The most abundant terrestrial source of phosphorous is the mineral apatite. Common apatite has a formula close to $Ca_5(PO_4)_3(OH, F, Cl, CO_3)$: it is very stable under soil weathering conditions, and most of its P content is not available for plant nutrition. Many routes have been devised to convert apatite to more soluble phases: these are reviewed by Mellor [1] and Ullmann [2]. Typically, apatite is treated with a strong acid: H_3PO_4, H_2SO_4 or HNO_3. These processes produce a comparatively P-rich, water-soluble product but the acid requirements necessitate a capital-intensive industry. Alternative processes requiring lower investment and using indigenous raw materials are therefore attractive to developing countries.

Sri Lanka has large reserves of apatite occurring in the form of igneous masses very rich in apatite, and little beneficiation is sufficient to give a virtually pure concentrate. This apatite has an unusual chemical composition: its Cl^-/F^- ratio is close to 1.3, and it contains negligible OH^- and CO_3^{2-}. Unfortunately Sri Lanka has no acid industry, except for HCl, which is unsuited for acid-extraction processes. But it does produce NaOH, which could readily be converted to Na_2CO_3. We therefore decided to investigate reactions between Na_2CO_3 and apatite. A somewhat similar route for the production of soluble phosphates known as the Rhenania process, has been in use in central Europe for about 60 years. Its principal raw materials are apparently indigenous fine-grained hydroxy-fluor apatite ores. The apatite is mixed with Na_2CO_3 to give a molar ratio of $Na_2CO_3/P_2O_5 \simeq 1.0$, while at the same time sufficient SiO_2 is also added to combine with excess CaO. The reactants are ground together and calcined in a rotary kiln at 1000° to 1200° C for approximately 2 h. Fluorine is said to be retained in the process, although steam is sometimes admitted to the kiln in an attempt to remove at least part of the fluorine. The sintered product may be used directly as a slow-release source of P or it may be subsequently extracted with hot aqueous Na_2CO_3 solution, giving either Na_3PO_4 or $Ca_3(PO_4)_2$ depending upon the concentrations

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of reactants in solution [1]. However, the slow-release product may be applied directly to soils and it has been found to give good results when applied to the wet, slightly acid soils typically used for growing paddy rice.

A difficulty in evaluating the suitability of the Na_2CO_3 route is that the operating conditions described in the literature appear to have been chosen by empirical methods and the products obtained have been inadequately characterized. Lacking these fundamental data, it is difficult to see how the process could be optimized using Sri Lankan raw materials.

We have chosen to concentrate selectively on several aspects of the sintering process. First, we undertook to obtain basic characterization data for the phases likely to be present: while some data could be obtained from the literature, we considered that in many cases they required verification. Secondly, we have determined phase equilibria in the relevant portions of the Na_2O–CaO–P_2O_5–SiO_2 system and finally, we have correlated the kinetics and paths of reaction in sintered batches containing mineral apatite with the results of equilibrium studies and with determinations of the available P content. We have chosen to use a "materials science" approach and we therefore feel it appropriate to record the results in this journal.

2. Characterization of phases

The crystalline phases encountered in the course of this study contained Na, Ca, P, Si, O and a halide component – F and Cl. While much of the basic characterization data on phases in this system are given in well-known compilations, others are scattered and some are either unreliable or have not been reported. We made extensive use of powder X-ray patterns to characterize the fine-grained sintered products and it was thus important to have reliable crystallographic data. Table I correlates the chemical compositions of the principal phases encountered with the crystallographic data. Wherever possible, references have been given

TABLE I Composition, nomenclature and crystal data of the phases

Name	Formula	Crystal system	Cell dimensions (Å)			Crystal* data	Powder† data
Apatites	$Ca_{10}(PO_4)_6F_2$	Hexagonal	$a = 9.371$		$c = 6.885$	(3)	15–876
	$Ca_{10}(PO_4)_6Cl_2$	or	$a = 9.629$		$c = 6.776$	(3)	12–263
	$Ca_{10}(PO_4)_6(OH)_2$	Pseudohex, $P6_3/m$	$a = 9.43$		$c = 6.88$	(3)	24–33
	α-K_2SO_4	Hex. $P6_3mc$	$a = 5.78$		$c = 7.93$	(4)	(4)
Glaserite	$K_3Na(SO_4)_2$	Hex. $P\bar{3}ml$	$a = 5.66$		$c = 7.33$	(5)	(5)
Silico-glaserite	αCa_2SiO_4	Hex. $P\bar{3}ml$	$a = 5.526$		$c = 7.307$	(6)	21–1045
αRhenanite	$\alpha NaCaPO_4$	Hex. $P\bar{3}ml$	$a = 5.23$		$c = 7.04$	(5)	(5)
Phase A	$Ca_5Na_2(PO_4)_2$ ‡	Hex. P***	$a = 21.33$		$c = 21.69$	(14)	(14)
Nagelschmidtite	$Ca_7(PO_4)_2(SiO_4)_2$	Hex. P***	$a = 5.526$		$c = 7.10$	(5)	11–676
	$\bar{\alpha}Ca_3(PO_4)_2$	Hex. ?					
	β-K_2SO_4	Ortho. Pmcn	$a = 5.763$,	$b = 10.071$,	$c = 7.476$	(8)	(8)
β-Rhenanite	β-$CaNaPO_4$	Ortho. Pmcn	$a = 5.215$,	$b = 9.320$,	$c = 6.830$	(5)	(5)
Silicocarnotite§	$Ca_5(PO_4)_2(SiO_4)$	Ortho. Pnma	$a = 6.737$,	$b = 15.508$,	$c = 10.132$	(9)	21–157
	α'_L-Ca_2SiO_4	Ortho. Pcmn	$a = 18.952$,	$b = 11.184$,	$c = 6.837$	(11)	(11)
	α'_H-Ca_2SiO_4	Ortho. Pcmn	$a = 9.535$,	$b = 5.593$,	$c = 6.860$	(11)	(11)
Calcio-olivine	γ-Ca_2SiO_4	Ortho. Pbnm	$a = 5.091$,	$b = 11.371$,	$c = 6.782$	(10)	24–34
Larnite	β-Ca_2SiO_4	Monocl. P21/n	$a = 5.48$, $\beta = 94°33'$	$b = 6.76$,	$c = 9.28$	(12)	24–37
	α-$Ca_3(PO_4)_2$	Monocl. P21/n	$a = 12.887$, $\beta = 126°20'$	$b = 27.880$	$c = 15.219$	(7)	9–348
	β-$Ca_3(PO_4)_2$	Rhomb. R3c	$a = 10.439$		$c = 37.375$	(7)	9–169
	$Ca_4P_2O_9$	Monocl. $P2_1$	$a = 7.023$, $\beta = 90.90°$	$b = 11.986$,	$c = 9.473$	(13)	25–1136
	$CaNa_6P_2O_9$	Hex. P***	$a = 12.06$		$c = 18.85$	(15)	(15)

*( ) indicate reference number.

† Numbers under this column indicate J.C.P.D.S. File Card numbers.

‡ Ref. 15 gives the formula as $Ca_7Na(PO_4)_5$.

§ Different orientations have been selected for some members of the same family.

to readily available sources, but where conflicting data have been reported in the literature we have made a critical evaluation, selecting those which we consider to be most reliable.

Phases having basically similar crystal structures have been grouped together in Table I. Ordering of the chemical constituents may produce superstructure variants or distortions of a basic structure, but where a family resemblance exists the relevant phases have been grouped together. These structural similarities result in many of the phases having similar powder patterns. Indeed, the literature is also confused about the ocurrence of phases having the αK_2SO_4 and glaserite ($K_3Na(SO_4)_2$) structures. The two structure types differ substantially although the unit cell dimensions, symmetry and powder X-ray patterns appear very similar. For that reason we include data for both αK_2SO_4 and $K_3Na(SO_4)_2$ although only the latter is structurally glaserite-like. Several examples can be seen of families which include phases having a wide range of chemical composition. Extensive isomorphic replacement of (Na + P) by (Ca + Si), or vice versa, is frequently observed but complete solid solution does not always occur, particularly at low temperatures. Phases having similar crystal structures but differing in chemical composition may differ significantly in chemical reactivity towards aqueous solutions, hence the emphasis placed on the characterization of phases present.

3. Phase equilibria

3.1. Defininition of the problem

Preliminary experiments showed that at molar ratios of Na_2CO_3 to apatite up to 1.0, CO_2 was completely eliminated during firings made at temperatures of 900° C or above within 1 to 2 h. Furthermore, chemical analyses of representative batches showed that chlorine was almost completely evaporated in the course of reaction. Therefore batch mixtures composed initially of Na_2CO_3, apatite and SiO_2 consist of five components after firing. One of these components, fluorine, is present only as a minor component ($< 1\%$), leaving four major components: CaO, Na_2O, P_2O_5 and SiO_2. The need to deliberately include SiO_2 (if not present as a contaminant) might be questioned. Empirical experience with the Rhenania process suggests that the role of SiO_2 is to combine with free CaO, which might otherwise be liberated during the reaction between Na_2CO_3 and apatite. The literature asserts that CaO and SiO_2 combine to form Ca_2SiO_4, although phase equilibria in portions of the $CaO-Na_2O-P_2O_5-SiO_2$ system relevant to this reaction have not been studied. We accept the CaO is an undesirable constituent and should not be present but we suspected that the products of reaction between CaO and SiO_2 in the presence of Na_2O and P_2O_5 were complex. Furthermore, the presence of the tetracalcium phosphate, $Ca_4P_2O_9$, in the fired product was also believed to be undesirable. $Ca_4P_2O_9$ can readily be preserved unchanged to ambient temperatures in experiments made in the laboratory but moderately rapid cooling is essential because if $Ca_4P_2O_9$ is annealed at temperatures up to 1200° C in a moisture-containing atmosphere, it is rapidly converted to hydroxyapatite: depending upon temperature and water vapour pressure either CaO or $Ca(OH)_2$ also form. It is unlikely that $Ca_4P_2O_9$ could be preserved unaltered in the atmospheres likely to prevail in a tunnel kiln fired with a fossil fuel.

These considerations, suggesting that both free CaO and $Ca_4P_2O_9$ are undesirable constituents, prompted an investigation to determine the minimum quantities of Na_2O and SiO_2 which must be added in order to eliminate the undesirable phases. It is desirable to use the minimum quantity as an excess would result in too much dilution of the P-rich phases. We decided that the quickest method of determining these conditions unequivocally was to make a reconnaisance of the CaO- and P_2O_5-rich regions of the system $CaO-Na_2O-P_2O_5-SiO_2$. This reconnaissance disclosed that the plane of compositions lying between Ca_2SiO_4, $Ca_3(PO_4)_2$ and $CaNaPO_4$ just fulfilled the condition that CaO and $Ca_4P_2O_9$ should be absent and furthermore, that this plane of compositions constituted a true ternary system at subsolidus temperatures. Its position within the ternary system is shown in Fig. 1. It was therefore decided to concentrate the phase equilibrium studies on this ternary system and to supplement these by less-detailed studies of the CaO-rich portions of the four component system.

3.2. The system $Ca_3(PO_4)_2-Ca_2SiO_4-CaNaPO_4$

3.2.1. Previous studies

Phase equilibria in the system $Ca_2SiO_4-Ca_3(PO_4)_2$ have been investigated by Nurse, Welch and Gutt [16] and by Heymann and Heinke [17]. Both versions are similar although Nurse, *et al.* give the

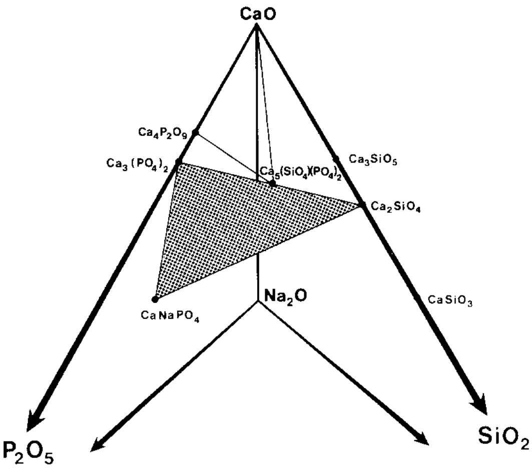

Figure 1 Subdivision of the $CaO-Na_2O-P_2O_5-SiO_2$ system. The plane $Ca_3(PO_4)_2-Ca_2SiO_4-CaNaPO_4$ has been lightly shaded.

upper stability limit of nagelschmidtite as 1125° C, considerably lower than the value reported by Heymann (1350° C). Our results are in good agreement with those of Nurse, *et al.* and therefore we prefer their phase diagram which is shown in Fig. 2. The nature of the phases obtained in this system in the range 1100 to 1450° C is very dependent on temperature. At high temperatures, αCa_2SiO_4 and $\bar{\alpha}Ca_3(PO_4)_2$ form a complete series of solid solutions. However, at somewhat lower temperatures more relevant to the apatite fusion process, solid solution is incomplete and two ordered compounds occur: silicocarnotite and nagelschmidtite. The latter has a composition lying close to $Ca_7(PO_4)_2(SiO_4)_2$, whereas above 1000° C silicocarnotite includes a more extensive range of solid solutions centred on the composition $Ca_5(PO_4)_2SiO_4$.

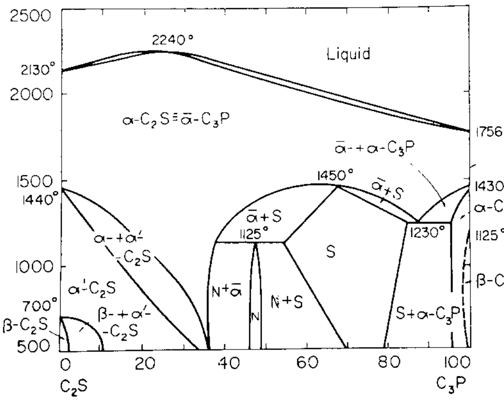

Figure 2 Phase diagram of the system $Ca_2SiO_4-Ca_3(PO_4)_2$; the data are taken from [16]. Abbreviations: C = CaO, S = SiO_2, P = P_2O_5 N = Nagelschmidtite.

The system $Ca_3(PO_4)_2-CaNaPO_4$ has been studied by Ando and Matsuno [14] and by Berak and Znamierowska [15]. The general outlines of the two phase diagrams are similar, although numerous minor differences occur. Fig. 3 shows the phase diagram of this system after Berak, amended slightly to make it agree with the phase rule. $Ca_3(PO_4)_2$ and $CaNaPO_4$ are continuously miscible only at high temperatures. At lower temperatures, between 1335° and 980° C, solid solutions rich in sodium undergo ordering to yield "phase A". The exact position of its field of single phase homogeneity is not completely agreed but below 980° C it is known to decompose readily to yield a two-phase mixture of $CaNaPO_4$ and $Ca_3(PO_4)_2$ solid solutions. Ando regards phase A as having the composition $Ca_5Na_2(PO_4)_4$, while Berak has suggested $Ca_7Na(PO_4)_5$. Both compositions certainly lie within the field of homogeneity of phase A, but in the absence of any crystal structure evidence on the nature of the sites available for ordering in phase A, it is difficult to see what evidence exists to assert that one is

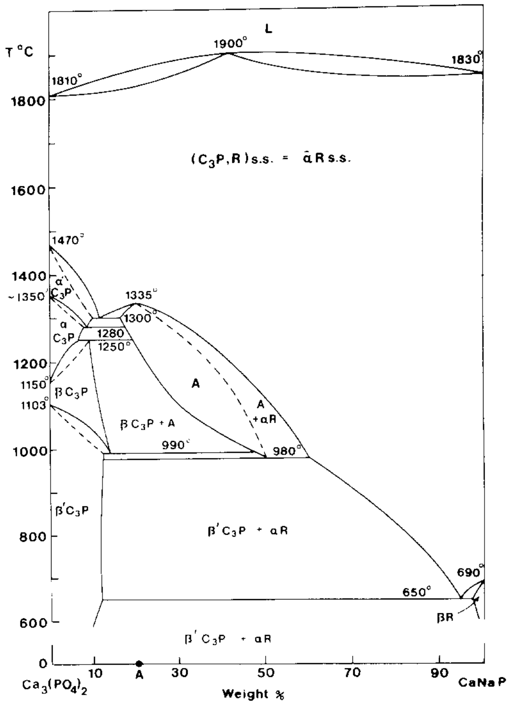

Figure 3 Phase diagram of the system $Ca_3(PO_4)_2-CaNaPO_4$. The data are taken mainly from [15] modified slightly to make it obey the phase rule. The labelling of several of the smaller two-phase regions has been omitted.

correct and the other wrong. Phase A is, however, closely related to α rhenanite in structure and chemical composition and an extensive range of rhenatite solid solutions convert readily to phase A during cooling. Phase A also appears to be structurally similar to nagelschmidtite, which has also been designated "phase A" [16]. Nagelschmidtite does not form extensive sodium-containing solid solutions and to avoid confusion about the identity of phase A we restrict its use to describe the sodium-containing phase whose compositions lie on or near the join $Ca_3(PO_4)_2$–$CaNaPO_4$.

Published data [18, 19] on the system Ca_2SiO_4–$CaNaPO_4$ are in considerable conflict. Kapralik and Hanic [18] claim the existence of a binary compound, $Ca_4Na_2(PO_4)_2(SiO_4)$, which is said to be completely miscible with both αCa_2SiO_4 and $\alpha CaNaPO_4$. This seems improbable: moreover, we cannot find any evidence in their paper to support the hypothesis that such a compound exists. Indeed, our interpretation of the evidence which they present suggests that the existence of a compound is effectively disproved. Ust'yantsev and Tretnikova [19] also report that αCa_2SiO_4 and $\alpha CaNaPO_4$ are completely miscible above 1400° C but do not find evidence of an intermediate compound. Fig. 4 shows the phase diagram for this system taken from [19]. However we have checked the extent of the two phase region of α and $\alpha' Ca_2SiO_4$ solid solutions at temperatures between 1100° C and 1300° C and find that the two phase region covers a wider range of compositions than shown in either [18] or [19]. The range of compositions lying within this region has been increased to agree with our observations. These references also conflict about the equilibrium below 900° C, but we have not obtained any data at or below 900° C.

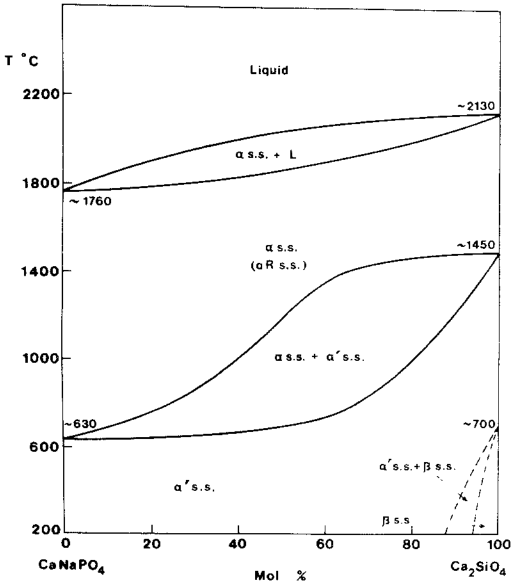

Figure 4 Phase diagram of the system Ca_2SiO_4–$CaNaPO_4$. The data are taken mainly from [19] but the extent of the two phase region of solid solutions based on α and α′ Ca_2SiO_4 has been altered to fit data obtained in the present study.

3.2.2. Experimental

Phase equilibria in the system $Ca_3(PO_4)_2$–Ca_2SiO_4–$CaNaPO_4$ were determined from 28 compositions. These were prepared from 'AnalaR' grades of Na_2CO_3, $CaCO_3$, precipitated $CaHPO_4 \cdot 2H_2O$, $Ca(H_2PO_4)_2 \cdot H_2O$, and a very pure crushed quartz containing 0.08% material non-volatile with HF. The phosphates were chemically analysed for their P_2O_5 content which was close to its theoretical value. It was convenient to ignite or react these chemicals to prepare stocks of γCa_2SiO_4, $\beta CaNaPO_4$, as well as $\beta Ca_3(PO_4)_2$, silicocarnotite and αCa_2SiO_4–$Ca_3(PO_4)_2$ solid solutions of known compositions. The phase equilibria were subsequently determined by preparing mechanical mixtures of the above phases in the desired proportions and annealing these for 24 to 96 h at constant temperatures. All preparations were made in Pt foil envelopes or crucibles and heated in an air atmosphere in electrically-heated muffles. Most of the data were obtained on two isothermal sections, at 1100 and 1300° C. The accuracy of temperature measurement and control are ± 10 and ± 15° C respectively on the two isotherms. Chemical analysis of selected compositions showed that their P_2O_5 content remained constant during annealing. The reaction products were cooled quickly in air or water-quenched or, when very fast quenching was required, samples were heated in a vertical tube furnace and subsequently dropped into clean mercury. The phases present in annealed samples were identified by powder X-ray diffraction using a Hägg-Guinier camera and $CuK\alpha_1$ radiation. The attainment of equilibrium was tested frequently by preparing the same chemical composition from mixtures of different sets of phases and checking that the various combinations converged on the same phase distribution after annealing. In general, the positions of phase boundaries were established from the X-ray powder diffraction patterns of annealed mixtures. The extent of single-phase regions and the positions of tie lines within two-phase regions were also determined by supplementary chemical analyses made using CORA, an analytical transmission electron microscope. These analyses were particularly useful to supplement the interpretations made from X-ray diffraction patterns.

3.2.3. *Results and discussions*

The phases present in annealed compositions are shown in Table II: Table III gives analytical results obtained from four annealed bulk compositions examined with CORA. Isothermal sections at 1100 and 1300° C have been constructed from these data as well as a knowledge of the binary phase equilibria; these sections are shown in Figs. 5 and 6 respectively. They are dominated by several fields of extensive solid solutions. The field of homogeneous α-rhenanite solid solutions reaches its maximum extent along the two binary edges but within the ternary system its extent is less. This concave limit suggests that the maximum solubility in $CaNaPO_4$ of either Ca_2SiO_4 or $Ca_3(PO_4)_2$ is depressed by the presence of the other component. The solid solutions thus have a strong negative deviation from ideality. The field of phase A has a large extent towards SiO_2-rich compositions, especially at 1300° C. Nagelschmidtite appears only on the 1100° C isotherm and its composition is essentially fixed. Silicacarnotite, $\alpha' Ca_2SiO_4$ and αCa_2SiO_4 have progressively larger fields of single-phase homogeneity. Because of the complex manner in which αCa_2SiO_4 solid solutions decompose with falling temperature, two ranges of αCa_2SiO_4 solid solutions are stable at 1300° C; one lies at low $Ca_3(PO_4)_2$ contents while the other is much richer (85–90%) in the $Ca_3(PO_4)_2$ component. The existence of this unusual situation, which can be predicted from the binary system, is actually observed in the ternary system. Contrasting the two isothermal sections, a marked increase in solid solution occurs with rising temperatures and the two phase regions of

TABLE II Results of annealing experiments

Composition (wt %)			Phases present	
Ca_2SiO_4	$Ca_3(PO_4)_2$	$CaNaPO_4$	1100°C	1300°C
52.2		47.8	$\alpha R_{ss} + \alpha' C_2 S_{ss}$	αR_{ss}
35.3		64.7	αR_{ss}	αR_{ss}
68.6		31.4	$\alpha R_{ss} + \alpha' C_2 S_{ss}$	$\alpha R_{ss} + \alpha' C_2 S_{ss}$
38.9	37.7	23.4	$A_{ss} + Sc + C_2 S_{ss}$	$A_{ss} + \alpha C_2 S_{ss}$
18.8	17.0	64.2	$\alpha R_{ss} + \alpha' C_2 S_{ss} + A_{ss}$	$A_{ss} + \alpha R_{ss}$
18.1	48.7	33.2	$A_{ss} + Sc + \alpha C_2 S_{ss}$	A_{ss}
50.0	15.0	35.0	$A_{ss} + R_{ss} + \alpha' C_2 S_{ss}$	$A_{ss} + \alpha' C_2 S_{ss}$
10.0	70.0	20.0	$A_{ss} + \beta C_3 P + Sc$	$Sc + \alpha C_3 P + A_{ss}$
24.7	37.1	38.2	$A_{ss} + \alpha R_{ss} + \alpha' C_2 S_{ss}$	A_{ss}
46.8	43.2	10.0	$\alpha C_2 S_{ss} + C_7 PS_2 + Sc$	$\alpha C_2 S_{ss} + A_{ss}$
50.0	30.0	20.0	$Sc + \alpha C_2 S_{ss} + A_{ss}$	$A_{ss} + \alpha C_2 S_{ss}$
20.0	60.0	20.0	$Sc + A_{ss}$	$Sc + A_{ss}$
10.0	40.0	50.0	$A_{ss} + \alpha R_{ss}$	A_{ss}
30.0	20.0	50.0	$A_{ss} + \alpha R_{ss} + \alpha' C_2 S_{ss}$	$A_{ss} + \alpha R_{ss}$
40.0	20.0	40.0	$A_{ss} + \alpha R_{ss} + \alpha' C_2 S_{ss}$	$A_{ss} + \alpha C_2 S_{ss} + \alpha' C_2 S_{ss}$
15.0	45.0	40.0	$A_{ss} + \alpha' C_2 S_{ss}$	A_{ss}
70.0	10.0	20.0	$\alpha' C_2 S_{ss} + A_{ss} + \alpha R_{ss}$	$A_{ss} + \alpha C_2 S_{ss} + \alpha' C_2 S_{ss}$
60.0	20.0	20.0	$\alpha C_2 S_{ss} + \alpha' C_2 S_{ss} + A_{ss}$	$A_{ss} + \alpha C_2 S_{ss}$
25.0	65.0	10.0	$Sc + \beta C_3 P$	$Sc + A_{ss}$
40.0	30.0	30.0	$A_{ss} + \alpha' C_2 S_{ss} + \alpha C_2 S_{ss}$	$A_{ss} + \alpha C_2 S_{ss}$
10.0	10.0	80.0	αR_{ss}	αR_{ss}
47.0	3.0	50.0	$\alpha R_{ss} + \alpha' C_2 S_{ss}$	$\alpha R_{ss} + \alpha' C_2 S_{ss}$
10.0	53.0	37.0	A_{ss}	A_{ss}
86.0	10.0	4.0	$\alpha' C_2 S_{ss} + \alpha C_2 S_{ss}$	$\alpha' C_2 S_{ss} + \alpha C_2 S_{ss}$
66.0	30.0	4.0	$\alpha C_2 S_{ss}$	$\alpha C_2 S_{ss}$
31.0	64.0	5.0	Sc	Sc
15.0	80.0	5.0	$Sc + \beta C_3 P$	$Sc + \alpha C_2 S$
20.0	40.0	40.0	$A_{ss} + \alpha R_{ss} + \alpha' C_2 S_{ss}$	A_{ss}

Abbreviations: R = Rhenanite, $CaNaPO_4$; Sc = Silicocarnotite, $Ca_5(PO_4)_2(SiO_4)$; ss = solid solution; A = a phase having a composition close to $5CaO \cdot Na_2O \cdot 2P_2O_5$; C = CaO; S = SiO_2; P = P_2O_5, thus $C_2S = 2CaO \cdot SiO_2$ or Ca_2SiO_4.

TABLE III Chemical composition of phases in sintered products

Bulk composition (wt %) and firing conditions			Phases present by X-ray	Number of crystals analysed	Chemical composition of phases					
					Atomic ratios (Si = 1.0)			Composition (wt %)		
C_3P	C_2S	$CaNaPO_4$			Na/Si	P/Si	Ca/Si	C_3P	C_2S	$CaNaPO_4$
0.0 (1300° C, 43 h)	35.3	64.7	$\alpha CaNaPO_4$ ss	9	1.97	1.97	4.28	0.0	37.5	62.5
60.0 (1100° C, 120 h)	20.0	20.0	silicocarnotite ss	8	0.18	2.67	5.64	63.0	30.0	7.0
			+ phase A ss	12	3.70	8.40	13.90	48.0	13.0	39.0
37.1 (1300° C, 48 h)	24.7	38.2	phase A ss	8	1.20	2.38	5.09	32.0	31.5	36.5
20.0 (1300° C, 71 h)	60.0	20.0	phase A ss	10	1.72	5.27	2.76	24.0	28.0	48.0
			+ αCa_2SiO_4 ss	8	0.07	0.43	2.61	22.0	73.0	5.0

(phase A and α rhenanite) and of (phase A and αCa_2SiO_4 solid solutions) both expand rapidly over this temperature interval. On both isothermal sections, phase A solid solutions are in equilibrium with all the other phases, the only exception being nagelschmidtite which of course occurs on the 1100° C isothermal but not at 1300° C.

The X-ray analysis of the phase composition presents some potential difficulties on account of similarities between the powder patterns of phases having chemically dissimilar compositions. Table III shows results obtained from the analysis of sinters whose X-ray powder patterns were interpreted as consisting either of a single phase or a mixture of two phases. The chemical compositions of the individual phase(s) were determined with a transmission analytical microscope, CORA, which is very well suited to the analysis of fine-grained sinters because a satisfactory analysis can be obtained from grains as small as 10^{-3} to 10^{-4} mm equivalent diameter. The energy-dispersive system of analysis gives reasonable count rates and counting statistics for Si, P, Ca and Na, although its accuracy for Na is notably less than for the other elements: oxygen and fluorine lie outside its detection limits. The number of grains analysed from each preparation is included in Table III. The analyses supported the interpretation of the X-ray diffraction patterns with respect to the number of phases present and the limits of chemical substitution in individual phases.

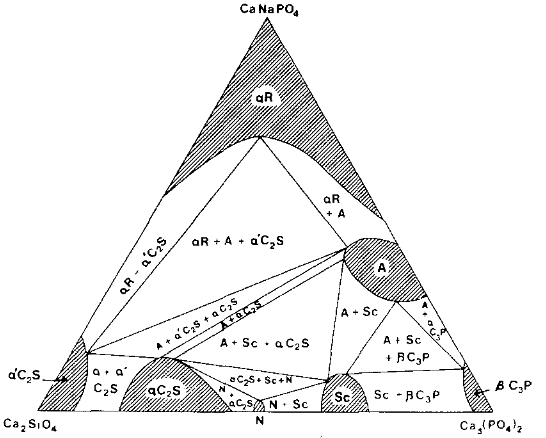

Figure 5 1100° C isothermal section of the system $Ca_3(PO_4)_2$–Ca_2SiO_4–$CaNaPO_4$ (in wt.%). The extent of single-phase solid solution fields are indicated by shading. Abbreviations used for the solid solution fields are as follows: α, $\alpha' C_2S = \alpha$ and α' phases of Ca_2SiO_4, N = nagelschmidtite, Sc = silicocarnotite, $\beta C_3P = \beta Ca_3(PO_4)_2$, $\alpha R = \alpha$ rhenanite or $CaNaPO_4$, A = a phase first described in [14, 15].

3.2.4. Quenching of high-temperature phases

During the course of the phase equilibrium studies, some insight was gained into the ability to quench phases stable at higher temperatures to ambient. These observations on the kinetics of phase transformation in the direction of decreasing temperatures are helpful in anticipating the behaviour of larger batches, which cannot readily be quenched on account of their large thermal inertia. Although α rhenanite close to the ideal $CaNaPO_4$ composition inverts to the β phase and cannot be quenched to ambient, the presence of either Ca_2SiO_4 or $Ca_3(PO_4)_2$ (or both) in solid solution has a marked stabilizing effect on the α phase. Phase A solid solutions close to the Na- and Ca-rich limits of saturation are readily preserved to ambient temperatures even during slow cooling. Phase A is reported to be unstable below 980° C [14]. We confirm that phase A which is free from Si^{4+} decomposes rapidly below ~ 980° C. However, "Ca_2SiO_4" in solid solution has a marked stabilizing effect on phase A which greatly retards its rate of decomposition below 980° C. Likewise, the α and α' polymorphs of pure Ca_2SiO_4 cannot be quenched to ambient but the presence of P_2O_5 in solid solution greatly retards their conversion to either of the low-temperature polymorphs (β and γ). Moreover, the conversion of appropriate αCa_2SiO_4 solid solutions to either silicocarnotite or especially, nagelschmidtite, is slow. Of the phases stable at high temperatures in this system, only solid solutions based on the α and $\beta CaNaPO_4$, α and $\alpha' Ca_2SiO_4$ and phase A structures are likely to be obtained at ambient temperatures in preparations which have been annealed and then slowly cooled.

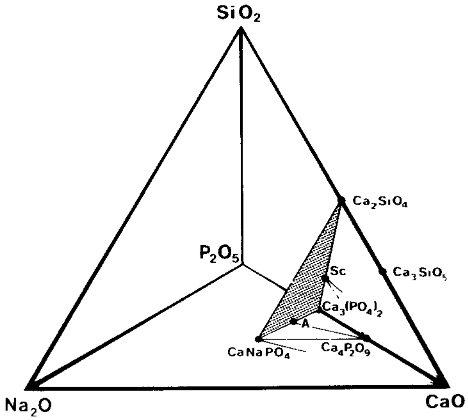

Figure 7 Part of the system $Ca_3(PO_4)_2$–Ca_2SiO_4–$CaNaPO_4$–CaO. The diagram has been considerably simplified to show the general phase relations.

3.3. The CaO-rich portions of the system CaO–Na_2O–P_2O_5–SiO_2

Our studies have not been sufficient to disclose more than the general nature of the phase relations in this region of the quaternary system. Fig. 7 shows an overall view. The plane $Ca_3(PO_4)_2$–Ca_2SiO_4–$CaNaPO_4$, shown in more detail in Figs. 5 and 6, is shaded lightly: ranges of solid solution on this plane have been omitted. The quaternary phase relations are based on studies of the reactions of CaO and $Ca_4P_2O_9$ with phases whose compositions lie on the ternary plane. The results show that $CaNaPO_4$ is in equilibrium with both CaO and $Ca_4P_4O_9$: silicocarnotite may also be in equilibrium with either or both the latter two phases. $Ca_3(PO_4)_2$ and phase A, on the other hand, exist in equilibrium with $Ca_4P_2O_9$. These data provide the experimental justification for the conclusion stated previously – that compositions to the CaO-rich side of the ternary plane $Ca_3(PO_4)_2$–Ca_2SiO_4–$CaNaPO_4$ develop one or more undesirable phases. Phase relations in the quaternary system are shown in somewhat more detail in Fig. 8. Most of the experimental evidence on the extent of the one- and two-phase regions has been obtained by studying compositions lying on one of the faces of the quaternary system: Fig. 8 depicts these regions at ~ 1200° C. CaO and

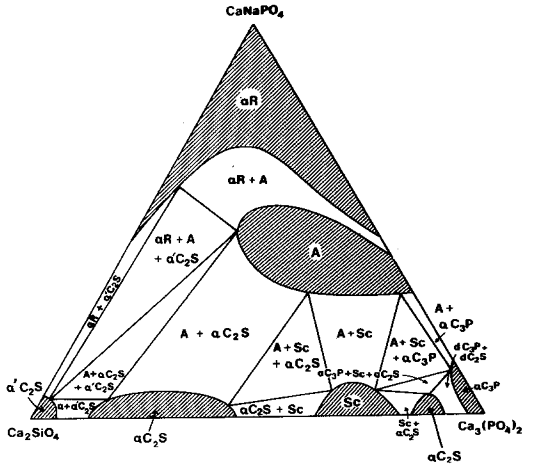

Figure 6 1300° C isothermal section of the system $Ca_3(PO_4)_2$–Ca_2SiO_4–$CaNaPO_4$ (in wt.%). Other symbols and abbreviations are explained in the legend to Fig. 5.

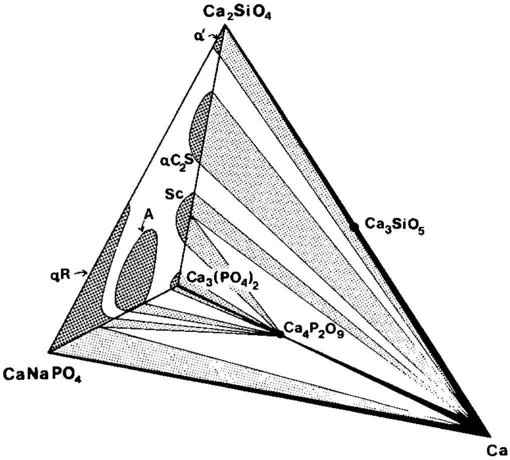

Figure 8 Part of the system $Ca_3(PO_4)_2$–Ca_2SiO_4–$CaNaPO_4$–CaO, showing the phase relations at ~1200° C in more detail. The Ca_3SiO_5 composition is shown for reference only, inasmuch as Ca_3SiO_5 is unstable with respect to CaO and Ca_2SiO_4 below ~1250° C.

$Ca_4P_2O_9$ are phases having essentially constant compositions. Different shadings have been used to distinguish the single-phase regions on the $Ca_3(PO_4)_2$–Ca_2SiO_4–$CaNaPO_4$ face from the two-phase regions on the CaO–$Ca_3(PO_4)_2$–Ca_2SiO_4 and CaO–$Ca_3(PO_4)_2$–$CaNaPO_4$ faces. We do not know the details of the subdivision of the interior space of the composition tetrahedron, although a solid model showing more details of the $Ca_3(PO_4)_2$–Ca_2SiO_4–$CaNaPO_4$ face would undoubtedly help to disclose some of the more important subdivisions.

Several experiments were also made to determine phase equilibria in the Na_2O-rich portions of the system. These disclosed the existence of a three-phase assemblage containing $Na_6CaP_2O_9$, $CaNaPO_4$ and CaO.

4. Solubility studies

The laboratory evaluation of the available phosphorous content of fertilizer is generally made by determining either water-soluble or citrate-soluble P_2O_5 [20]. Field trials correlate well with results obtained by these methods. Slow-release phosphorous fertilizers are often comparatively insoluble in H_2O, but are soluble in citrate solutions. Amongst the recommended citrate solutions, both 2% citric acid and either neutral or alkaline ammonium citrate solutions have been used. We used 2% citric acid as an extractant, a method first employed by Wagner [20].

4.1. Experimental procedure

The samples were ground to pass 100 mesh B. S. sieve. Approximately 1.0 g samples were extracted with 100 ml of 2% citric acid in a mechanical shaker operating at ~260 oscillations min^{-1} for 30 min at 18° C. The extract was subsequently analyzed for its P_2O_5 content by the vanadomolybdate method [21], using a Unicam SP 600 colorimeter at a wave length of 460 nm. The total P present in apatite and other phosphates was also determined by the same technique following extraction with a more powerful solvent system as recommended in [21].

4.2. Results and discussion.

Table IV records the results of solubility determinations made on pure single-phase preparations. For present purposes availability is defined by the relation:

$$\%\ \text{available}\ P_2O_5 = 100 \times \frac{\text{citric acid soluble}\ P_2O_5}{\text{total}\ P_2O_5}$$

Ground mineral apatite is poorly soluble: only 17–18% of its P_2O_5 content is "available".

Amongst the phases having 100% available P_2O_5 are $Ca_4P_2O_9$, nagelschmidtite, silico-

TABLE IV Results of solubility studies

Sample	P_2O_5 Soluble in 2% citric acid (wt%)	Solubility as percentage of total P_2O_5
$\beta Ca_3(PO_4)_2$	34.0	74
$\alpha Ca_3(PO_4)_2$	36.6	80
$Ca_4P_2O_9$	38.9	100
$Ca_4P_2O_9$ heated at 1000° C in air	7.8	20
$Ca_5(SiO_4)(PO_4)_2$	30.1	100
$Ca_7(SiO_4)_2(PO_4)_2$	21.9	100
α-Ca_2SiO_4 ss containing $Ca_3(PO_4)_2$ [Composition = 70.0 wt% Ca_2SiO_4]	14.0	100
A phase – $Ca_5Na_2(PO_4)_4$	40.1	90
A ss containing SiO_2 [Composition = 20 wt% Ca_2SiO_4, 40% $Ca_3(PO_4)_2$, 40% $CaNaPO_4$]	36.4	100
$\beta CaNaPO_4$	45.0	100
α-$CaNaPO_4$ ss containing SiO_2 [Composition = 10 wt% Ca_2SiO_4, 10% $Ca_3(PO_4)_2$, 80% $CaNaPO_4$]	40.5	100
$CaNa_6P_2O_9$	36.9	100
Sri Lanka Apatite Sample (1)	6.3	17
Sri Lanka Apatite Sample (2)	6.2	18

Note: ss = solid solution; Sri Lanka apatite sample (1) is a sample of pure apatite from the "leached zone" in the deposit at Eppawela, Sri Lanka. Sample (2) is a commercially beneficiated sample of apatite from Eppawela, Sri Lanka.

carnotite, $CaNaPO_4$ and its solid solutions, and an αCa_2SiO_4 solid solution containing 30 wt% $Ca_3(PO_4)_2$. Phase A is not completely soluble unless it contains Ca_2SiO_4 in solid solution. Both α and $\beta Ca_3(PO_4)_2$ give less than 100% available P_2O_5. Moreover, while $Ca_4P_2O_9$ has 100% availability, it is readily converted to hydroxyapatite by annealing in air and this treatment greatly reduces the available P_2O_5 content: it decreases from 100 to 20%. The composition of the compound $CaNa_6P_2O_9$ lies outside the range of composition which was studied in detail. A preparation was made and found to be 100% extractable. On account of its hygroscopic nature, however, this phase is judged to be an undesirable constituent of sintered products.

It therefore appears that, of the phases which are present in the CaO-rich portions of the system silicocarnotite, nagelschmidtite, αCa_2SiO_4, phase A solid solutions which contain SiO_2, and α or $\beta CaNaPO_4$ solid solutions can be classified as potentially desirable constituents. $\alpha' Ca_2SiO_4$ was not tested: on account of its low P content, it would simply act as a diluent for other P-containing phases.

5. Reaction of apatite with Na_2CO_3 and SiO_2

The reaction of mineral apatite (minus 100 mesh) with Na_2CO_3 and SiO_2 (quartz, minus 120 mesh) were studied. The apatite was taken from the "leached zone" of the deposit: Table V gives a complete analysis typical of the concentrate as well as a partial analysis of the particular batch of apatite concentrate used in this study. Microscopically, the apatite occurs as anhedral grains. Reaction batches were prepared by blending these raw materials and firing at a constant temperature for 2h. Table VI records the results of the annealing treatments. The phases present were determined by X-ray powder diffraction but the sensitivity of detection varies from one phase to another. For example, at least 5% unreacted apatite was required for detection, whereas as little as 0.5–1.0% free lime or 1.0% quartz could be detected. The other phases were present as major phases and it was unnecessary to determine their detection limits.

TABLE V Chemical composition of Sri Lanka apatite

Wt%	Sample EP/N/J from the leached zone*	Sample 1 of this study
CaO	55.30	–
SrO	1.18	–
MgO	0.01	–
MnO	0.01	–
Fe_2O_3	0.08	–
SiO_2	0.40	–
P_2O_5	40.75	38.10
F	1.78	1.70
Cl	2.29	2.20

*Analysis reported by the Geological Survey Department, Colombo 2, Sri Lanka (1973). The two samples were believed to be essentially identical.

5.1. Essential role of SiO_2

In the absence of SiO_2, mixtures of apatite and Na_2CO_3 react to produce large amounts of free CaO. Therefore, if free CaO is deemed to be an undesirable constituent, it is essential to add something to combine with it: SiO_2 fulfils this role.

5.2. Attainment of equilibrium in fired batches

Much of the reaction is completed swiftly. During the first stage of reaction, a molten phase develops which must be rich in Na_2CO_3. The liquid phase subsequently disappeared upon isothermal annealing: this was demonstrated by following the progressive elimination of CO_2 from batches. For example, at 900° C, a batch having the molar ratio Na_2CO_3 : apatite : SiO_2 = 4 : 8 : 3 lost ~80% of its CO_2 content within the first 20 min of reaction. Thus the liquid phase has only a transient existence and once it has gone, reaction can only continue by solid state sintering. Moreover, free quartz had disappeared and only a small quantity of unconsumed apatite remained after the first 20 min of reaction. Dicalcium silicate was not observed as a reaction product except in batches having very low sodium contents.

The bulk compositions of batches containing apatite were recalculated in terms of their potential content of $Ca_3(PO_4)_2$, $CaNaPO_4$ and Ca_2SiO_4: only a few compositions did not lie reasonably close (± 10%) to this section. A close correspondence exists between the phases actually observed and those predicted with the aid of the phase equilibrium data. However, those sodium-rich compositions which are capable of yielding substantial quantities of rhenanite and phase A reacted more completely and at a lower temperature than compositions likely to yield sodium-poor phases, e.g. silicocarnotite, $\alpha' Ca_2SiO_4$, and $Ca_3(PO_4)_2$ solid solutions. As a rough guide, batches having a molar ratio of apatite to Na_2CO_3 ranging between 1:1.5

TABLE VI Available P_2O_5 content of sinters made with apatite

Composition				Temp. (°C)	2% Citric acid solubility		Phases present
Molar ratio apatite : Na_2CO_3 : SiO_2	Wt%						
	Apatite	Na_2CO_3	SiO_2		Wt% P_2O_5	% of total P_2O_5	
1:1:0	82.9	17.1	0.0	1100	20.5	55	βR + CaO + F ap
				1300	28.5	76	βR + αR + CaO + F ap
2:3:0	76.3	23.7	0.0	900	23.0	67	βR + αR + CaO + F ap
				1100	27.8	81	βR + αR + CaO + F ap
				1300	29.5	86	βR + αR + CaO + F ap
1:2:0	71.0	29.0	0.0	900	31.4	90	βR + $CaNa_6P_2O_9$ + CaO + tr. F ap
				1100	35.0	100	βR + CaO
				1300	34.7	100	βR + CaO
1:10:0	32.9	67.1	0.0	900	16.6	100	CaO + $CaNa_6P_2O_9$
5:2:8	78.6	6.5	14.9	1100	8.0	23	F ap + αR + βR
				1300	14.4	42	F ap + A
4:2:3	85.1	8.1	6.8	1100	9.8	27	F ap + αR + βR
				1300	15.8	43	F ap + A
10:8:3	82.9	14.2	2.9	1100	18.1	49	βR + F ap + CaO
				1300	18.8	51	βR + F ap + CaO
13:10:11	79.4	12.7	7.9	900	10.0	36	F ap + βR
				1100	16.5	59	βR + F ap
				1300	20.4	73	A + βC_3P + F ap
1:1:1	75.5	15.6	8.9	1100	18.8	55	βR + F ap
				1300	25.1	74	A + βR + F ap
4:6:3	71.5	22.2	6.3	900	21.7	67	βR + αR + F ap
				1100	29.7	91	βR + αR + F ap
				1300	30.0	92	βR + αR + F ap
2:3:3	67.3	20.9	11.8	1100	21.8	70	βR + F ap
				1300	24.9	80	βR + F ap
4:8:3	66.6	27.5	5.9	900	27.0	92	αR + βR + CaO + tr. F ap
				1100	30.4	100	βR + αR + CaO
				1300	31.1	100	βR + αR + CaO
1:2:1	65.3	27.0	7.7	900	25.5	91	αR + βR + tr. F ap
				1100	28.1	100	αR
				1300	28.6	100	αR
*Silicophosphate, P617	?	?	?	1300	33.6	100	A + αR

Note: Sri Lanka apatite sample 1 was used in this study.

*This sample was provided by the Rothamstead Experimental Station, Harpenden, Herts.

Abbreviations: R = Rhenanite, $CaNaPO_4$; F ap = Fluorapatite, $Ca_5(PO_4)_3F$; tr. = trace. The composition of A phase is probably $Ca_5Na_2(PO_4)_4$; α and β are the high and low temperature forms respectively.

and 1:2.0 gave the most rapid reaction at low temperatures. These batch proportions correspond to a weight percentage of Na_2CO_3 between 20 and 27%. If the optimum proportions of all three components are considered, molar ratios of apatite : Na_2CO_3 : SiO_2 close to 1:2:1 are favourable for reaction. If the SiO_2 content is reduced slightly below this optimum, for example to 4:8:3 (which is equal to 1:2:0.75), a high yield of available phosphorous is obtained, but free CaO is also developed. Similarly, reduction of the soda content leads to incomplete reaction and the appearance of unreacted apatite which can only be removed by sintering at 1100 to 1300° C. In general, the phase compositions of the wide range of mixtures shown in Table VI corresponds closely with the phase distribution which would be predicted on the basis of the phase equilibria studies.

TABLE VII Halogen analysis of the products

Composition Molar ratio of apatite: $Na_2CO_3:SiO_2$ and firing conditions	Wt % F in the product	Amount of F retained as % of total F	Wt % Cl in the product	Amount of Cl retained as % of total Cl	Wt % F extractable in water	Wt % F extractable in 2% citric acid	Wt % Cl extractable in water	Wt % Cl extractable in 2% citric acid
1:2:0 (1100° C, 2 h)	1.16	84.6	0.00	0.00	0.051	0.300	0.000	0.000
1:2:0 (1300° C, 2 h)	0.93	67.9	0.00	0.00	–	–	–	–
2:3:0 (1300° C, 2 h)	0.75	52.1	0.00	0.00	0.010	0.187	0.000	0.000
4:6:3 (1300° C, 2 h)	0.56	41.8	0.00	0.00	0.037	0.200	0.000	0.000
2:3:3 (1100° C, 2 h)	0.89	71.0	0.20	12.3	0.002	0.065	0.032	0.030
2:3:3 (1300° C, 2 h)	0.61	48.7	0.13	8.0	–	–	–	–

Note: Extractions were carried out using 1 g material in 100 ml of water or 2% citric acid solution for 30 min in a mechanical shaker (≈260 oscillations per min.) at 18° C. The apatite sample used in this study contained 1.70 wt % F and 2.20 wt % Cl.

5.3. Role of halides in the reaction

During the course of reaction between apatite and molten Na_2CO_3, the apatite probably undergoes ion exchange. In all samples containing residual unreacted apatite, the *d*-values obtained were characteristic of pure fluorapatite. It is probable, therefore, that before apatite can be converted to other phases it will exchange its Cl^- for F^-.

Table VII shows some data on the retention of halogens in the sintered charges. Analyses for fluorine were made using a fluorine ion electrode against a calomel reference [22]; the method is useful for F in the presence of P and Cl. Chlorine analyses were made on 25–50 mg samples dissolved in 1 ml of 1:1 HNO_3. These were diluted with ethanol and titrated to a potentiometric end point against standard 0.05 M $AgNO_3$. The data show that while Cl is virtually eliminated during firing F is retained, especially at 900–1100° C. However, the amount of F retained is too great to be accounted for by the relatively small quantity of unreacted apatite which remains, even if it is fluorapatite. We have attempted to determine the fate of the F by supplementing X-ray diffraction with chemical extraction studies. Water extracts were found to contain negligible F, which excludes the presence of F in water-soluble phases, e.g., NaF. Citric acid extracts, which dissolved everything except residual fluorapatite, were also analysed. Little F^- was found, which apparently leaves much of the known total of F unaccounted for. The likeliest explanation is that the electrode used in the analysis is sensitive only to F^- ions and will not detect F in the form of complex ions e.g., SiF_6^{2-}, or fluorophosphate species. Fluorine is believed to be present in rhenanite and phase A, but subsequently goes into solution as a complex species rather than as simple F^- ions. Upon standing these solutions eventually precipitate a F^- containing phase of unknown composition.

It should, however, be recalled that the data on halogen retention are for *c.* 10 g batches heated in an open system, and will not necessarily reflect losses which might be expected to occur in larger-scale preparations.

6. Reaction between apatite and sodium silicate

The Si and Na necessary to convert apatite to phases containing available P can be supplied in various forms. Sodium silicate is relatively cheap and presents an obvious possibility. To test its reactivity, reaction batches were made by mixing apatite with commercially-available "sodium metasilicate" ($Na_2SiO_3 \cdot 5H_2O$). These were mixed in a 2:1 ratio: the bulk composition recalculated in terms of $Ca_3(PO_4)_2$, Ca_2SiO_4 and $CaNaPO_4$, was 40.0%. 20.0% and 40.0% respectively (in mol %): this composition expressed in weight % is 56.0, 15.5 and 28.5%, respectively. Virtually no reaction was obtained after heating for 2 h at either 900 or 1100° C, although the sodium silicate had melted in the preparation made at 1100° C. At 1300° C. some reaction, resulting in formation of phase A, was observed in 2 h; however even when the reaction time was increased to 19 h much unreacted apatite remained. The performance of sodium silicate is thus markedly inferior to Na_2CO_3, even though the latter must also assimilate SiO_2 present as comparatively inert quartz particles. Moreover, preparations made using $Na_2SiO_3 \cdot 5H_2O$ have halogen contents comparable to those made using Na_2CO_3, suggesting that the halogens play a far less important role in promoting reaction than molten carbonate.

7. Conclusions

Apatite can be converted to more soluble phosphorous-containing phases by heating it with Na_2CO_3 and SiO_2 in the temperature range 900–1300° C. Na_2CO_3 melts during the initial stages of firing. Although the molten carbonate liquid has a comparatively transient existence this is sufficient to decompose apatite and cause it to combine with SiO_2 and Na_2O derived from the carbonate. Once the melt phase has disappeared, subsequent reaction must occur by solid-state sintering.

Phase equilibrium studies have been made of the CaO-rich portions of the system $CaO-Na_2O-P_2O_5-SiO_2$ and the section $Ca_3(PO_4)_2-Ca_2SiO_4-CaNaPO_4$ has been shown to be a ternary system. Bulk compositions made from mixtures of apatite, Na_2CO_3 and SiO_2 lie on or close to this plane after firing and the phases developed in fired compositions made using Sri Lankan apatite are similar to those which would be predicted from the phase diagram studies. The presence of ~1 wt % fluorine does not greatly alter the phase relationships. Compositions close to the molar ratio of 1 part apatite to 2 parts Na_2CO_3 and 1 part SiO_2 are well suited for the process. After firing these yield mainly α or β rhenanite solid solutions, or mixtures of rhenanite with phase A.

They have a typical content of 25–30% P_2O_5 which is all soluble in 2% citric acid. Reaction is essentially completed at 900° C and the product is obtained as a friable sinter cake free of CaO and $Ca_4P_2O_9$. The use of compositions comparatively rich in Na_2O promotes reaction at temperatures as low as 900° C. If the batch composition is formulated to have a lower Na_2O content a product having 100% available P can be obtained but this requires a final solid-state sintering at temperatures above 1100° C.

Much of the SiO_2 component is present in solid solution in either phase A or in α and β $CaNaPO_4$ phases or in both. The presence of SiO_2 in solid solution in phase A not only stabilizes it against decomposition during cooling but also enhances its reactivity using 2% citric acid as an extractant.

Chlorine is almost entirely eliminated during the firing of apatite-containing batches, although most of the fluorine is retained. The fluorine is believed to be present in solid solution in phases which are soluble in citric acid. When these phases are dissolved in citric acid, fluorine is probably present in the solution in the form of fluorosilicate complexes.

The efficiency of sodium metasilicate as a flux compares unfavourably with mixtures of Na_2CO_3 and with SiO_2. With sodium silicate, the reaction with apatite is incomplete after 2h at 1300° C, and it is generally much less effective as a flux than Na_2CO_3.

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