EFFECT OF IRON OR IRON OXIDE ADDITIONS ON THE REDUCIBILITY OF TRICALCIUM PHOSPHATE BY CARBON

G.A. KOLTA, A E SABA * and A M ELROUDI

National Research Center, Dokki, Cairo (Egypt)

(Received 2 June 1981)

ABSTRACT

A study was made on the effect of adding iron or iron oxide on the reducibility of tricalcium phosphate by carbon Optimum conditions with the recovery of about 100% of their phosphorus content was achieved at about 1300°C The mechanism of reduction was presented on applying the fore-mentioned additions Activation energies of these reactions were calculated on the basis of the equation of Sharp et al The phases formed during reduction were investigated by X-ray diffraction analysis

INTRODUCTION

Carbon reduction is the conventional method for the production of elemental phosphorus from phosphate rocks. There are some admixtures which are usually present in these rocks in appreciable amounts and may affect its reducibility. A few impurities of these admixtures form phosphides [1,2], such as ferrophosphorus alloys which are formed when the phosphate rock is contaminated with iron oxide. Other compounds such as calcium ferrites and iron phosphates may be also formed [3]. However, phosphides are mainly prepared by the direct synthesis from their elements [4]. Very few attempts have been performed to prepare metal phosphides from calcium phosphate. Zergiebel and Lucas [5] succeeded in preparing iron phosphide by reducing calcium phosphates containing iron oxide with sufficient amounts of carbon.

In previous investigations, the kinetics of calcium phosphate reduction by carbon [6], and the reducibility of a local phosphate ore by carbon [7], were studied with the effect of SiO_2 and Al_2O_3 on their reducibility. The present investigation is a continuation of this study with the aim to determine the conditions governing the reduction of pure calcium phosphate with carbon in the presence of iron or iron oxide.

---

* To whom correspondence should be addressed.

EXPERIMENTAL

Materials

Chemically pure, laboratory prepared, tricalcium phosphate was used, containing 44.65% P_2O_5 and 55.35% CaO which is approximately the assay of tricalcium phosphate (45.80% P_2O_5 and 54.2% CaO). Chemically pure iron powder and iron oxide were used.

Apparatus and technique

The apparatus and experimental technique used in this investigation have been described previously [8]. Samples under treatment were weighed in a fused aluminium boat and inserted in a 100 mm fused aluminium reaction tube. The hole was heated by a horizontally moving silicon carbide tube furnace which enables rapid heating and cooling. The temperature was automatically controlled within $\pm 5°C$. Reduction extent as well as volatilized phosphorus (P_v) and phosphorus as iron phosphide (P_{Fe}) were determined from the residual phosphorus content left in the form of phosphates and phosphides. Total phosphorus was determined as magnesium ammonium phosphate applying the recommendations of the AOAC method [9]. Phosphorus attached to the metals in the form of phosphides was determined by the volumetric molybdate method, via the phosphine liberation technique [10].

The mechanism of reduction was investigated on the basis of the reduction results and X-ray analysis of the reduction products. This was performed with the aid of a Philips PW 1010 unit and applying $Cu K_\alpha$ radiation. The samples were investigated immediately after reduction.

RESULTS AND DISCUSSION

Reduction behaviour in the presence of metallic iron

Effect of iron additions

The effect of iron additions was studied for 60 min at different reduction temperatures ranging from 1000 to 1350°C using briquetted samples of pure tricalcium phosphate and carbon (C: $P_2O_5 = 5\,S$), where S is the stoichiometric carbon amount corresponding to the equation

$$Ca_3(PO_4)_2 + 5\,C \rightarrow 3\,CaO + P_2 + 5\,CO \qquad (1)$$

together with metallic iron so as to obtain Fe_{met}/P mole ratios of 0.11, 0.28, 0.56, 0.83, 1.11 and 1.67. Phase analysis of phosphorus in the residue remaining after reduction denotes that some of the phosphorus produced interacts with metallic iron added forming iron phosphide alloys. The results shown in Fig. 1 represent phosphorus recoveries as volatile phosphorus (P_v) and as iron phosphides (P_{Fe}). In these
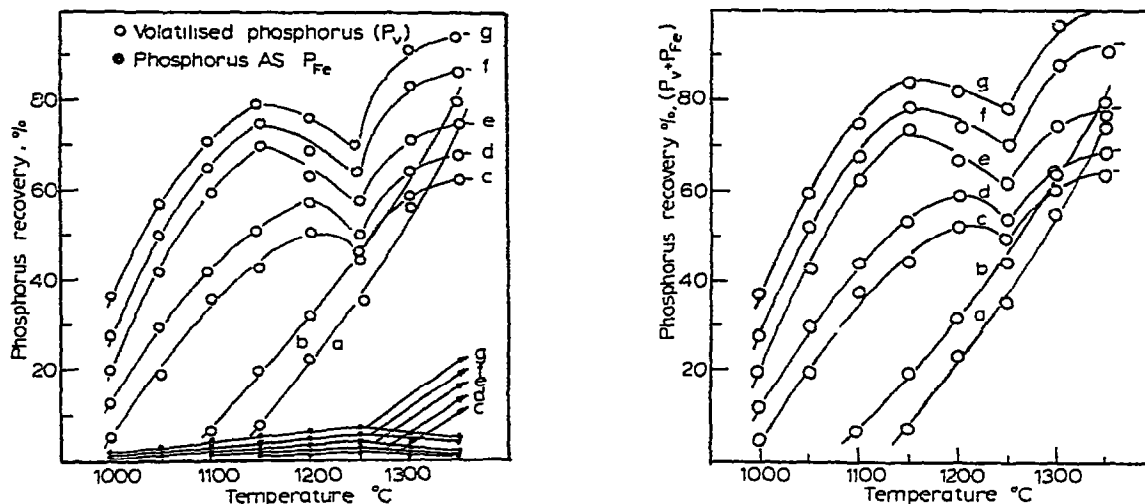
Fig 1. Effect of iron additions on phosphorus recovery from calcium phosphate reduction at different Fe/P mole ratios· a=0, b=0 11, c=0 28, d=0 56, e=0 83, f=1 11 and g=1 67 Time of reduction=60 min

Fig 2 Effect of iron additions on the reduction extent of calcium phosphate $(P_v + P_{Fe})$ at different Fe/P mole ratios a=0, b=0 11, c=0 28, d=0 56, e=0 83; f=1 11 and g=1 67 Time of reduction=60 min

curves, the amounts of both (P_v) and (P_{Fe}) are referred to the total phosphorus originally present in the charge. The total phosphorus recoveries $(P_v + P_{Fe})$ in Fig. 2 represent the reduction extent under the various conditions. For the sake of comparison, the phosphorus recovery (P_v) achieved on reducing pure tricalcium phosphate at different temperatures without iron additions $(P_{Fe} = 0)$ [6] is also included in Figs. 1 and 2. From Fig. 1 it can be seen that with mixtures containing no iron [curve (a)] or having a Fe_{met}/P ratio = 0.11 [curve (b)], the percentage of volatile phosphorus (P_v) increases with temperature rise. This picture is also observed with mixtures up to 1200°C [curves (c) and (d)] and up to 1150°C [curves (e)–(g)]. With higher temperatures a decrease in the amount of (P_v) is observed, reaching minimum value at 1250°C, and increases once more when the temperature is raised above this value. Under the applied conditions a maximum (P_v) value of 95% is achieved at 1350°C with Fe_{met}/P ratio = 1.67. It is important to note that at one and the same temperature (P_v) values increase regularly with the increase of Fe_{met}/P ratio. The amount of phosphorus remaining as iron phosphide increases slightly with the increase of the reduction temperature up to 1250°C and Fe_{met}/P ratios. A small decrease is observed on still increasing the reduction temperature above 1250°C. It is worth noting that the amounts of iron phosphide do not exceed 7.5% of the total phosphorus present in the original charge. With iron amounts low enough to correspond to an Fe_{met}/P ratio = 0.11 no formation of iron phosphide (P_{Fe}) could be detected at all reduction temperatures applied.

The total phosphorus recoveries $(P_v + P_{Fe})$ shown in Fig. 2 reveal a similar general picture. Complete recovery of phosphorus in both forms is feasible at
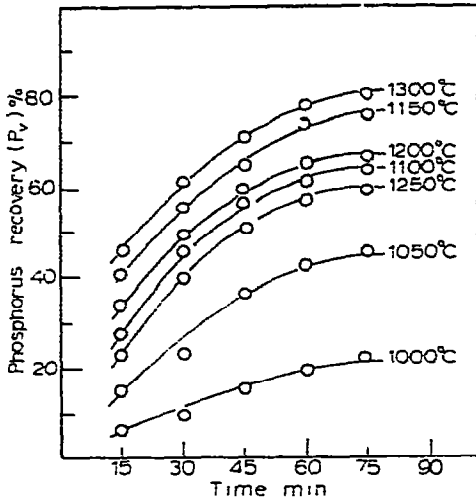
Fig 3 Effect of temperature and time on phosphorus recovery (P_v only) of calcium phosphate reduction, Fe/P=0 83
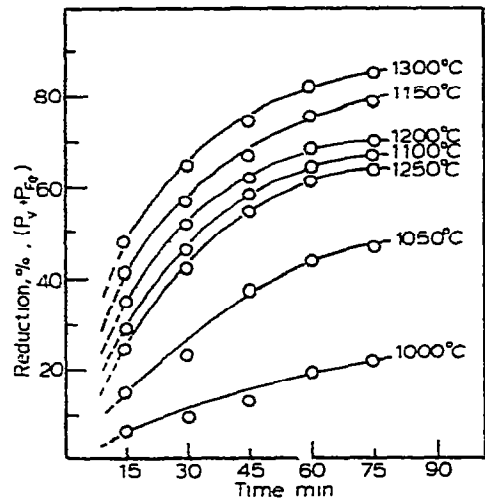
Fig 4 Effect of temperature and time on the reduction extent of calcium phosphate reduction Fe/P=0 83

1300°C with Fe_{met}/P ratio = 1.67. It is noticed that the reduction extent starts at 1000°C in the presence of metallic iron, while it takes place at 1150°C in its absence.

Effect of temperature and time

Samples containing Fe_{met}/P ratio = 0.83 were reduced for various periods up to 75 min at temperatures from 1000 to 1300°C, using carbon at the same ratio as applied before. The results obtained are given in Fig. 3. These results show increased volatilized phosphorus amounts (P_v) with the increase of reduction duration as well as temperature up to 1150°C. Above this value and up to 1250°C, the volatilized phosphorus amounts (P_v) decrease markedly. Another increase is observed at 1300°C. Steady state values seem to be approached after about 75 min. The maximum (P_v) values acquired under the applied conditions amounts to 80%.

TABLE 1

Phosphorus present as iron phosphide in the residues remaining after reduction at different reduction temperatures and periods

Temp (°C)	Reaction period (min)				
	15	30	45	60	75
1000					
1050				1 50	2 00
1100	1 00	2 00	2 30	2 50	3 50
1150	1 50	2 70	3 00	3.50	4 50
1200	1 50	3 00	3 50	4 00	5 00
1250	1 50	3.50	4 00	4 50	6.00
1300	2 00	3 50	4 00	3.30	4.50

Chemical analysis of the residues remaining after reduction is given in Table 1 which reveals the presence of certain amounts of phosphorus in the form of iron phosphides. The total amounts of phosphorus recovery ($P_v + P_{Fe}$) values refer to the total phosphorus originally present in the charge and are given in Fig. 4.

Effect of silica additions

The effect of silica on the reduction process was performed using briquettes of calcium phosphate and iron together with silica. The silica is added so as to get SiO_2/CaO ratio = 1 and the iron corresponds to an Fe_{met}/P ratio = 0.83. Reduction experiments were performed for 60 min at various temperatures. The results obtained are graphically represented in Fig. 5. These results show a marked increase in the reduction extent with the increase of temperature up to 1200°C and then more gradual up to 1300°C. In order to elucidate the particular effect of silica addition in the absence and presence of iron, the results obtained are compared with those acquired with pure calcium phosphate alone (Fig. 6).

As may be noticed, the presence of silica and iron causes the following·

(i) At all temperatures, the reduction extents are higher than those acquired with iron addition only;

(ii) The drop observed in the phosphorus recoveries displayed along the temperature range 1150–1250°C, in the presence of iron, completely disappears when silica is added to the charge;

(iii) The extent of reduction is comparatively higher with charges containing Fe and SiO_2 than with charges containing silica alone. Also the reduction extent
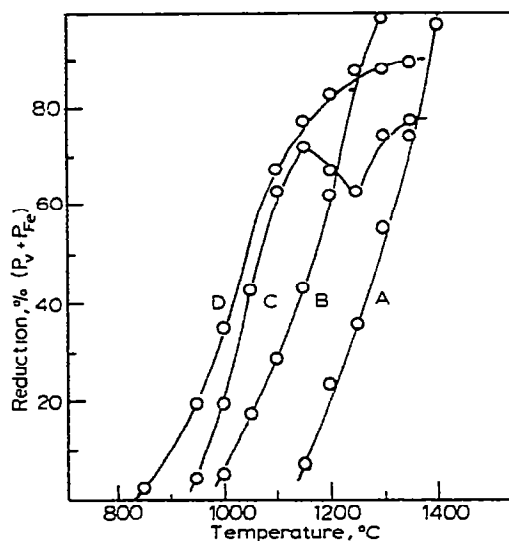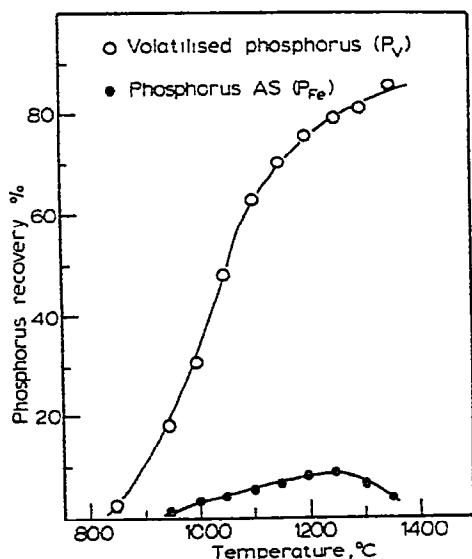

Fig. 5 Effect of temperature on the reduction of calcium phosphate in the presence of silica and iron. Fe. P = 0 83 and SiO_2/CaO = 1 Time of reduction = 60 min

Fig 6 Effect of temperature on the reduction extent of calcium phosphate· A = calcium phosphate + carbon, B = calcium phosphate + carbon + silica; C = calcium phosphate + carbon + iron, D = calcium phosphate + carbon + iron + silica. Time of reaction = 60 min.

is higher in the presence of silica than in its absence;

(iv) The amount of phosphorus combined as iron phosphide (P_{Fe}) in the presence of silica addition is higher than in its absence. The maximum (P_{Fe}) achieved at 1250°C amounts to 8.5% of the original total phosphorus in the charge with the silica additions while it is only 4.5% with silica free charges.

Reduction behaviour in the presence of iron oxide

Effect of iron oxide additions

Briquettes of six mixtures of pure tricalcium phosphate and iron oxide were prepared so as to obtain Fe_{oxide}/P mole ratios of 0.11, 0.28, 0.56, 0.83 and 1.67. In all these mixtures carbon was added in a $C:P_2O_5$ mole ratio $= 5S$. Reduction was performed for 60 min at temperatures ranging from 950 to 1350°C. The results achieved are graphically represented by the curves in Fig. 7, which show a more or less similar feature to those obtained with metallic iron. However, the extent of reduction appears to take place at lower temperatures —1150°C compared with 1200°C with metallic iron— with slightly lower values than those acquired with metallic iron particularly along the temperature range 1100–1200°C. Under the applied conditions a maximum (P_v) recovery value of 93% is achieved at 1350°C on using Fe_{oxide}/P mole ratio 1.67. Phase analysis of phosphorus remaining in the residues after reduction shows that the amount of iron phosphide formed and remaining in the residue is comparatively higher than when metallic iron is used. It is
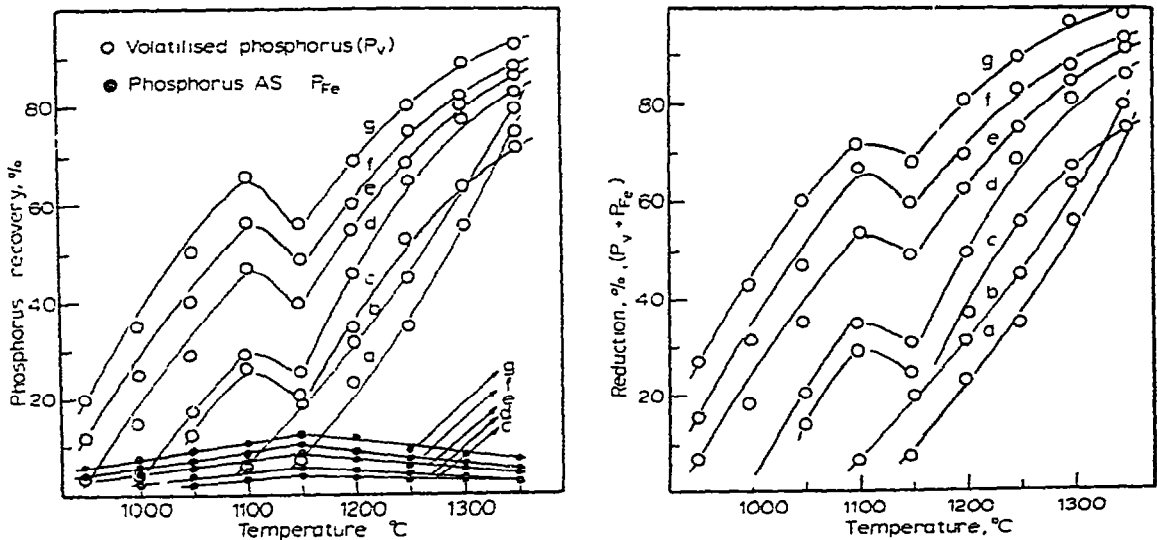

Fig 7 Effect of iron oxide additions on phosphorus recovery from calcium phosphate reduction at different Fe/P mole ratios. a=0; b=0.11, c=0 28, d=0 56, e=0 83, f=1 11 and g=1 67 Time of reduction=60 min

Fig 8 Effect of iron oxide additions on the reduction extent of calcium phosphate ($P_v + P_{Fe}$) at different Fe/P mole ratios a=0, b=0 11, c=0 28, d=0 56, e=0 83, f=1 11 and g=1 67 Time of reduction=60 min

worth noting that the amount of iron phosphide formed increases regularly and linearly with temperature up to 1150°C and decreases regularly and slightly at higher temperatures. The maximum phosphorus captured with iron, with the mixtures containing iron oxide to form iron phosphides (P_{Fe}), is about 12% at 1150°C compared with 7.5% achieved with metallic iron. No iron phosphide was detected together with Fe_{oxide}/P mole ratio $= 0.11$.

The curves in Fig. 8 representing the total recoveries of (P_v) and (P_{Fe}) reveal a similar general picture. Complete extraction of phosphorus (as P_v and P_{Fe}) is acquired at 1300°C on applying Fe_{oxide}/P mole ratio of 1.67.

Effect of temperature and time

Briquettes of phosphate–iron oxide–carbon samples containing Fe_{oxide}/P mole ratio $= 0.83$ and $C:P_2O_5 = 5S$ were reduced at different temperatures and periods. No silica addition was made. Samples were reduced for various periods up to 75 min at temperatures ranging from 1000 to 1300°C. The results are illustrated by the curves in Fig. 9. It is clear that the amounts of volatile phosphorus recovered (P_v) increase with the increase of reduction periods as well as temperature up to 1100°C. On increasing the temperature to 1150°C the values (P_v) decrease markedly. Another increase appears at 1200°C and higher temperatures. Under the applied conditions, the maximum phosphorus recovery (P_v) amounts to 82%. Analysis of phosphorus as iron phosphide in the residues is given in Table 2. Total phosphorus recoveries (P_v) and (P_{Fe}) values were computed from both values and are given in Fig. 10.
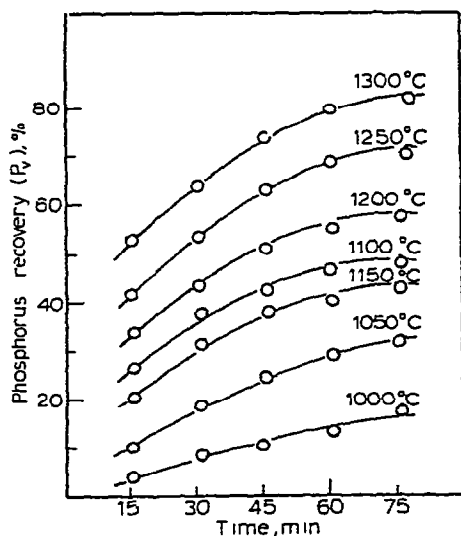
Fig 9 Effect of temperature and time on phosphorus recovery (P_v only) on calcium phosphate reduction, Fe/P=0 83, using iron oxide.
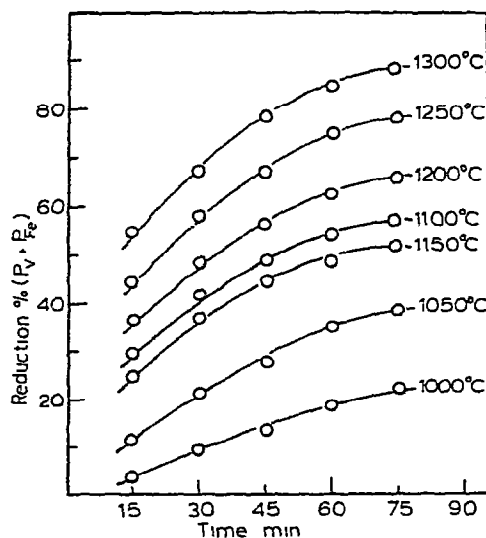
Fig 10 Effect of temperature and time on the reduction extent of calcium phosphate ($P_v + P_{Fe}$), Fe/P=0 83, using iron oxide.

TABLE 2

Phosphorus as iron phosphides at different reduction temperatures and periods

Temp (°C)	Reaction periods (min.)				
	15	30	45	60	75
950			1.20	2 30	2 30
1000		1 80	3 00	4 50	5 00
1050	1 50	3 30	4 50	6 00	6 70
1100	2 70	4 80	6 00	7 00	8 80
1150	4 60	6 00	7 20	8 50	9 40
1200	3 20	5 10	6 00	7 50	8 50
1250	2 70	4 00	4 80	6 00	6 70
1300	2 00	3 00	4 00	5 30	6 00

X-Ray analysis

The results showing the X-ray diffraction patterns of the residues obtained after reduction for 60 min at different reaction temperatures (1150–1350°C) are summarized in Table 3. It is noticed that the main components present are $Ca_3(PO_4)_2$, CaC_2, $Ca_2Fe_2O_5$ and iron phosphides at 1150°C, whereas the patterns obtained at 1250°C reveal the decrease of line intensities of $Ca_3(PO_4)_2$. At 1350°C, no patterns corresponding to $Ca_3(PO_4)_2$ can be traced. Regarding iron phosphides and based on the line intensities acquired, FeP and FeP_2 are first formed and constitute the basis for the formation of Fe_2P and Fe_3P which are mainly formed through the thermal decomposition of the other two phosphides. Only a few lines indicating the presence of calcium carbonate are detected. This compound is most probably formed as a result of the interaction between calcium oxide and atmospheric carbon dioxide when the residue is removed from the reacting tube.

Mechanism of reaction

To obtain evidence concerning the mechanism of calcium phosphate reduction under the previous applied conditions, consulation of the different kinetic equations known is of marked importance, from which the three-dimensional spherical symme-

TABLE 3

Results of X-ray analysis of the reduction products at different reduction temperatures

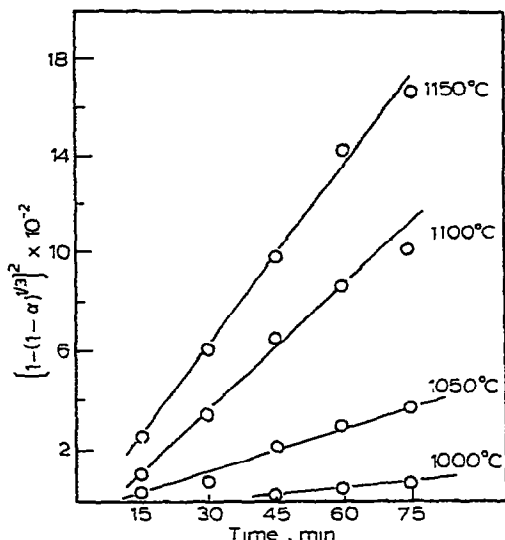| Reduction temp (°C)	Main compounds investigated by X-ray
1150	$Ca_3(PO_4)_2$, CaC_2, $Ca_2Fe_2O_5$ FeP, FeP_2, $Fe_{20}C_9$, $FePO_4$
1250	CaC_2, CaO, Fe_3P, $Ca_3(PO_4)_2$ Fe_2P, FeP, FeP_2, $Fe_{20}C_9$
1350	CaC_2, CaO, Fe_3P, Fe_2P, FeP, FeP_2 and $Fe_{20}C_9$

Fig 11 Plot of $[1-(1-\alpha)^{1/3}]^2$ vs time. for reduction of calcium phosphate with carbon in the presence of metallic iron
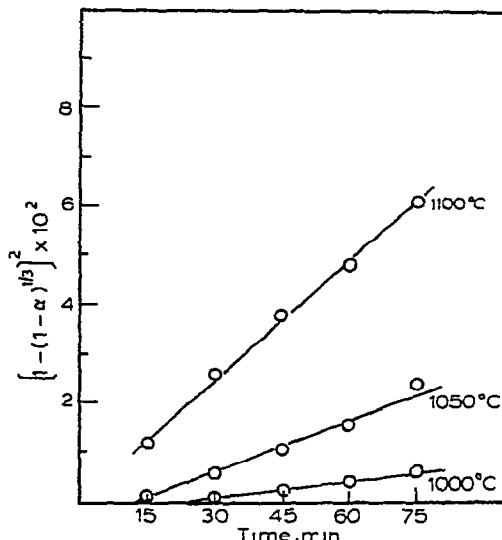
Fig 12 Plot of $[1(1-\alpha)^{1/3}]^2$ vs time, for reduction of calcium phosphate with carbon in the presence of iron oxide

try diffusion process, introduced by Stava and Skvara [11] for solid state reactions was found to be the most suitable. The following equation was used

$$\left[1 - (1 - \alpha)^{1/3}\right]^2 = Kt \tag{2}$$

where α is the fraction reacted at time t. This equation was applied to the results illustrated in Figs. 4 and 10. Straight lines are obtained on plotting $[1 - (1 - \alpha)^{1/3}]^2$ vs. time t in the temperature ranges 1000–1150°C and 1000–1100°C on using iron and iron oxide additions, respectively (Figs. 11 and 12). Applying the Arrhenius equation for obtaining the activation energies, straight lines are obtained (Fig. 13). The calculated activation energies are found to be 58.5 and 57.6 kcal mole^{-1} with iron and iron oxide, respectively. It is worth noting that the temperature range along which the equation is not found to be applicable corresponds to the range along which drops in reduction extents appear. Here the reaction rate seems to obey another diffusion equation.

With silica additions, the experiments performed were conducted for fixed periods at various temperatures (Fig. 6, curve D). Here, Sharp et al.'s equation [12] was applied.

$$E = R \ln \frac{t_{0.5}(T_1)}{T_{0.5}(T_2)} \Big/ \frac{1}{T_1} - \frac{1}{T_2} \tag{3}$$

where $t_{0.5}$ values were derived from the curve F_1 in Fig. 14 [6]. Plotting log $t_{0.5}$ vs. $1/T$ gives a straight line as shown in Fig. 15. The activation energy could be derived from eqn. (3), and amounts to 36.4 kcal mole^{-1} at temperatures up to 1100°C, at
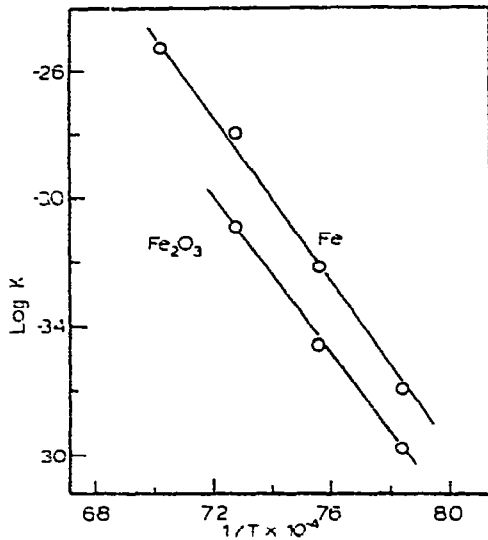
62

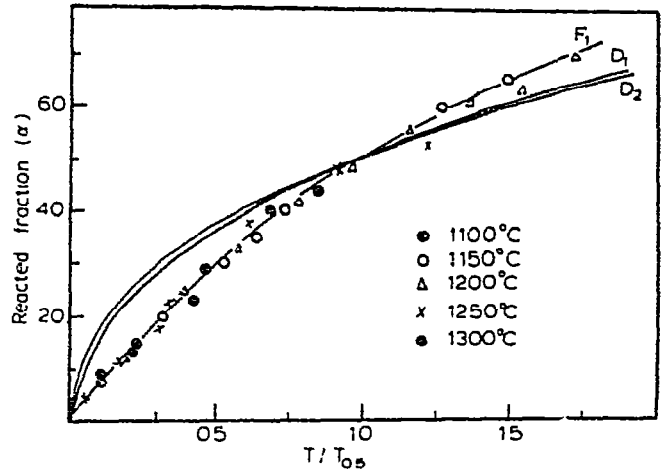Fig 13 Arrhenius plot Fe=with metallic iron addition. Fe_2O_3 =with iron oxide addition

Fig 14 Bnndly equation of first order and diffusion reaction [6]

which temperature deviation appears ($E = 16.6$ kcal mole^{-1}). In the presence of silica, the reaction rate seems to obey a pseudo-first order equation. The calculated activation energies are given in Table 4.

The above-mentioned results may lead to an insight regarding the mechanism of phosphate reduction by carbon and the influence of the presence of iron and iron oxide on the process. In this respect, the following aspects may be considered.

(1) During reduction of pure tricalcium phosphate with carbon, the following reaction is liable to take place
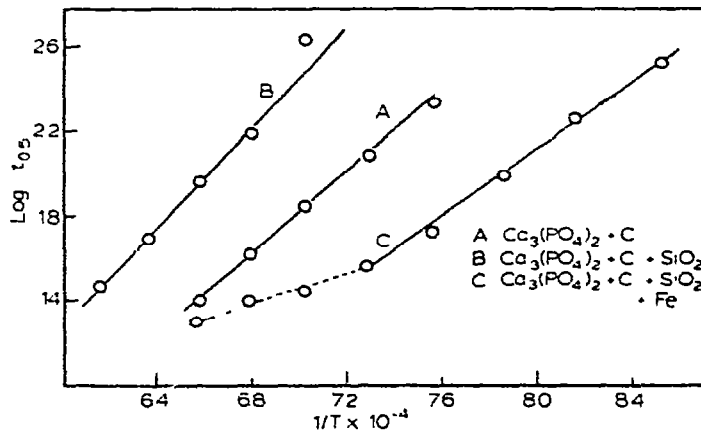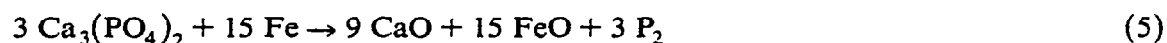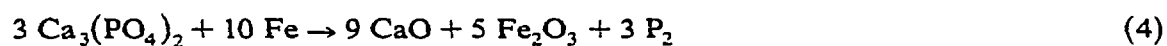
$$Ca_3(PO_4)_2 + 5\,C \rightarrow 3\,CaO + P_2 + 5\,CO \tag{1}$$

Fig 15 Plot of log t_{05} vs $1/T$ according to eqn (3)

TABLE 4

Calculated activation energies "in the presence of silica"

Reaction	Temp range (°C)	Activation energy (kcal mole^{-1})
$Ca(PO_4)_2 + 5\,C$	1100–1400	54 30
$Ca_3(PO_4)_2 + 3\,SiO_2 + 5\,C$	1050–1300	44 10
$Ca_3(PO_4)_2 + C + Fe$	1000–1150	58 50
$Ca_3(PO_4)_2 + C + Fe_2O_3$	900–1100	57 60
$Ca_3(PO_4)_2 + C + SiO_2 + Fe$	900–1100	36 40
$Ca_3(PO_4)_2 + C + SiO_2 + Fe$	1100–1250	16 60

In the presence of iron, one may consider the probability of an additional reaction to take place between the phosphate and iron according to

$$3\,Ca_3(PO_4)_2 + 10\,Fe \rightarrow 9\,CaO + 5\,Fe_2O_3 + 3\,P_2 \qquad (4)$$

$$3\,Ca_3(PO_4)_2 + 15\,Fe \rightarrow 9\,CaO + 15\,FeO + 3\,P_2 \qquad (5)$$

These reactions are thermodynamically feasible.

Accordingly, the increase in phosphorus recovery (P_v) as well as reduction extent ($P_v + P_{Fe}$) in the presence of iron may be related to such an additional reduction effect. In the presence of carbon, most of the iron oxides formed will be reduced to the metallic state by CO formed in the reaction atmosphere. Any iron oxide escaping reduction may react with CaO leading to the formation of ferrites and/or ferrates according to the reactions

$$Fe_2O_3 + CaO \rightarrow CaFe_2O_4 \qquad (6)$$

$$Fe_2O_3 + 2\,CaO \rightarrow Ca_2Fe_2O_5 \qquad (7)$$

Such reactions lead to the shift of the reactions in eqns. (4) and (5) towards the right-hand side, i.e towards more release of phosphorus. Ferrite and ferrate formation is only detected in the X-ray diffraction patterns of the products obtained at 1150°C. The effect of iron on the reduction process is partially masked as it forms iron phosphides.

(2) The observed drop in the volatile phosphorus (P_v) as well as the reduction extent ($P_v + P_{Fe}$) displayed in the temperatures ranges 1150–1250°C and 1100–1150°C in the presence of iron and iron oxide, respectively, may be tentatively explained as being due to the low melting points of the formed iron phosphides, e.g. Fe_3P melts at 1166°C, a temperature which decreases more as the iron ratio in the phosphide increases [13–16]. Such a phenomenon is elucidated from the P–Fe phase diagram [17] as well as from the higher calculated values for the activation energy along that temperature range as compared with those obtained in the absence of iron and iron oxide. Therefore, one may plausibly assume the drop in phosphorus recovery observed along the temperature ranges given above to be due to the sintering and melting of part of the reacting mass; this results in some decrease of the surface contact between calcium phosphate and carbon.

Such an effect is mainly dependent upon the reduction temperature and iron content in the charge. In the absence of iron or in its presence in small amounts, no change in the increasing trend of the phosphorus recovery with the increase of temperature can be noticed.
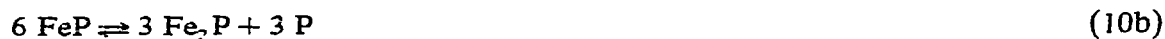
According to the X-ray diffraction patterns which show the presence of faint lines corresponding to iron phosphate in the reaction products, one may tentatively state that part of the iron phosphide is formed through the intermediate formation of iron phosphate according to

$$Ca_3(PO_4)_2 + Fe_2O_3 \rightarrow 2\ FePO_4 + 3\ CaO \tag{8}$$

Iron phosphate is then further reduced by carbon as follows

$$FePO_4 + 4\ C \rightarrow FeP + 4\ CO \tag{9}$$

(3) The re-increase in phosphorus recovery as well as reduction extent achieved at temperatures > 1250 and 1150°C in the presence of iron and iron oxide, respectively, may be attributed to the decomposition of the formed iron phosphides and the liberation of phosphorus as follows

$$6\ FeP_2 \rightleftharpoons 6\ FeP + 6\ P \tag{10a}$$

$$6\ FeP \rightleftharpoons 3\ Fe_2P + 3\ P \tag{10b}$$

$$3\ Fe_2P \rightleftharpoons 2\ Fe_3P + P \tag{10c}$$

Such a process is known to be enhanced at relatively high temperatures [17–20]. Due to the decrease in iron proportions in the phosphides, the melting points of the formed compounds increase. Such an effect also results in the presence of some untreated metallic iron, which plays a role in increasing the reduction extent of the phosphates [eqns. (4) and (5)].

(4) On the addition of iron in the form of Fe_2O_3, the decrease in the phosphorus recovery temperature by 50°C compared with those obtained with metallic iron additions may be attributed to the more active metallic iron formed from the reduction of Fe_2O_3. In the same time and for the same reason, the amounts of iron phosphides are increased on using Fe_2O_3. The increase in the volatile phosphorus recovery which is displayed at 100°C lower than these obtained with metallic iron additions, may be explained by the high affinity of the newly formed iron together with carbon to form iron carbides. Iron carbides may act as strong reducing agents co-acting with carbon to reduce calcium phosphate. This may explain the disappearance of iron carbide in the X-ray patterns of the residues obtained at high reduction temperatures.

(5) In the presence of silica no drop in reduction extent of phosphate iron mixtures was observed along the whole temperature range. Silica acts as a slagging material according to eqn. (11).

$$Ca_3(PO_4)_2 + 3\ SiO_2 + 5\ C \rightarrow 3\ CaSiO_3 + P_2 + 5\ CO \tag{11}$$
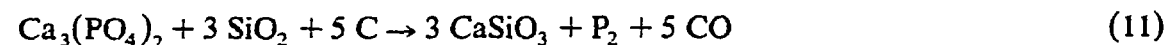
There is also the probability of interaction between silica and iron oxide formed according to eqn. (5) to form iron silicates, e.g. fayalite ($2\ FeO \cdot SiO_2$). This

assumption is substantiated by X-ray diffraction patterns. Both silicates may float on the surface of the reacting materials. This process increases the surface of the reacting mass. The general behaviour of iron phosphide formation and decomposition is more or less the same whether in the presence or absence of silica.

The mechanism of reduction of tricalcium phosphate by carbon in the presence of both silica and iron seems to obey a pseudo-first order equation. The activation energy amounts to 36.10 kcal mole^{-1} in the temperature range 900–1100°C. It is also noticed that deviation starts at temperatures > 1100°C, as represented by the dashed lines in Fig. 15. Such a mechanism is explained on the premise that in the temperature range 900–1100°C, where iron and silica were added, the role of metallic iron or formed iron on using Fe_2O_3 is to accelerate the reaction [as given in eqns. (4) and (5)] to the right-hand side, as it combines with the produced phosphorus. However, at temperatures > 1100°C, the formed iron phosphide melts and retards the reduction rate.

REFERENCES

1 V V Mikhail, R D Simbinov, S V Mikhailov and A N Potanina, Proiz Sily Yuzh Kaza, 3 (1966) 23
   Chem Abstr, 67 (1967) 880815
2 S B Kápilevich, U S S R Pat 193,458, 13 March 1967
3 D A Patrushev, Tr Ural Nauchno-Issled. Khim Inst, 19 (1970) 82
4 G V Samsnov and L L Vereikina, Khim. Fosfidov Poluprov Svoistvami, 5–10 (1970) Chem Abstr 74 (1971) 18831j
5 C P Zergiebel and J W. Lucas, Trans Electrochem Soc, 81 (1942) 8 pp
6 M K Hussein, G A Kolta, A E. Saba and A M El Roudi, Thermochim Acta, 10 (1974) 177
7 M K Hussein, G A Kolta, A E. Saba and A M El Roudi, Chem Erde, 35 (1976) 271
8 M K Hussein, G A Kolta, I F Hewaidy and A El Roudi, J Chem U A R, 14 (1971) 289
9 O Samvelson, Ion Exchange in Analytical Chemistry, Wiley New York, 1956
10 L Moser and A Z Brukl, Z Anorg Allg Chem, 121 (1921) 73
11 V Stava and F Skvara, J Am Ceram Soc, 52 (1969) 591
12 J H Sharp, G W Brindly and B N N Achar, Brindley and Ray Sci Rep No AFCRL-65-606, 1965, 94–104
13 E Gercke, Metallurgie, 5 (1908) 604
14 R Vogel, Arch. Eisenhuttenwes, 3 (1930) 369
15 R Roquet and G Jegaden, Rev Metall, 48 (1951) 712
16 R Vogel and H Klose, Arch Eisenhuttenwes, 27 (1956) 75
17 M I. Hansen and K Anderko, Constitution of Binary Alloys, McGraw-Hill, New York, 2nd edn, 1958, pp. 607, 692
18 W Franke, K Meisel and R Juza, Z Anorg Allg Chem, 218 (1934) 346
19 F Weibke and G Schrag, Z Elektrochem, 47 (1941) 222
20 G. Lewis and C E Myers, J Phys Chem, 67 (1963) 1289