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EFFECT OF COPPER ADDITIONS ON THE REDUCIBILITY OF TRICALCIUM PHOSPHATE BY CARBON

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ABSTRACT

The effect of copper additions on the reducibility of tricalcium phosphate by carbon was studied. Optimum conditions with the recovery of about 100% of their phosphorus content were achieved at temperatures ⩾1200°C. The mechanism of reduction was presented under the fore-mentioned conditions. Activation energies of these reactions were calculated on the basis of Sharp et al.'s equation. The phases formed during reduction were investigated by X-ray diffraction analysis.

INTRODUCTION

The conventional method for preparing elemental phosphorus is carbon reduction of phosphate rocks. Admixtures and gangue which are usually present in these rocks may, in most cases, affect their reducibility. A small number of these admixtures form the corresponding phosphides [1,2]. Accordingly, few attempts have been made to prepare metal phosphides from calcium phosphate. Iron phosphide was prepared by the direct reduction of calcium phosphate by carbon in the presence of iron oxide [3].

In previous studies, the kinetics of tricalcium phosphate reduction by carbon were studied with the effect of SiO_2 and Al_2O_3 [4], and Fe or Fe_2O_3 [5] on its reducibility. The present investigation is another step in these studies aimed at determining the effect of copper additions on the reducibility of tricalcium phosphate by carbon.

EXPERIMENTAL

Materials

Chemically pure, laboratory prepared, tricalcium phosphate was used [4]; it contained 44.65% P_2O_5 and 55.35% CaO which is approximately the assay of tricalcium phosphate (45.80% P_2O_5 and 54.20% CaO). Chemically pure copper powder was used.

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Apparatus and technique

The apparatus and experimental technique used in this investigation have been described previously [6]. Samples under treatment were weighed in a fused alumina boat and inserted inside a 100 mm fused alumina reaction tube. The whole was heated in a horizontally moving silicon carbide tube furnace which enabled rapid heating and cooling. The temperature was automatically controlled within ±5°C. The reduction extent as well as copper phosphide (P_{Cu}) and volatilized copper (P_v) were determined from the residual phosphorus content in the form of phosphides and phosphates. Total phosphorus was determined as magnesium ammonium phosphate applying the recommendations of the AOAC method [7]. Phosphorus attached to the metal in the form of phosphides was determined by the volumetric molybdate method, via the phosphine liberation technique.

The mechanism of reduction was investigated on the basis of the reduction results and X-ray analysis of the reduction products. This was performed using a Philips PW 1010 unit and applying CuK_α radiation. Samples were investigated immediately after reduction.

RESULTS AND DISCUSSION

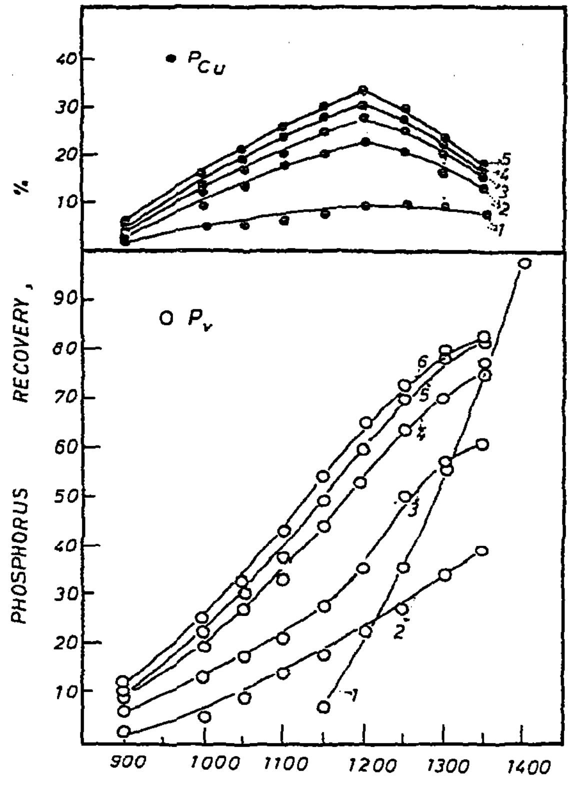
Effect of copper additions

The effect of copper additions on the reduction extent of tricalcium phosphate as well as phosphorus recovery was studied by applying a series of experiments in which various proportions of copper powder were mixed with the pure calcium phosphate so as to obtain Cu/P ratios in the range 0.13–0.78. Carbon was added in amounts to obtain C: P_2O_5 mole ratio of $5X$, where X is the stoichiometric carbon amount necessary for the reduction of calcium phosphate according to the equation

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

which is the amount necessary for maximum reduction of tricalcium phosphate [4]. Mixtures of the phosphate, copper and carbon were briquetted together and reduction was performed at different temperatures ranging from 900 to 1350°C for 60 min under purified nitrogen atmosphere. Phase analysis of phosphorus in the residues remaining after reduction shows that some of the phosphorus produced interacts with copper to form copper phosphides. The amounts of phosphorus volatilized (P_v) as well as the proportion reacted with copper to form copper phosphides are represented in Fig. 1. Both are referred to the original total phosphorus in the charge. Figure 2 shows the total phosphorus recoveries ($P_v + P_{Cu}$) which represent the reduction extent achieved under the applied conditions. For the sake of comparison, the volatile phosphorus recoveries of pure tricalcium phosphate [4] are also elucidated in the same Fig.

These results show that the percentage of volatile phosphorus increases by the



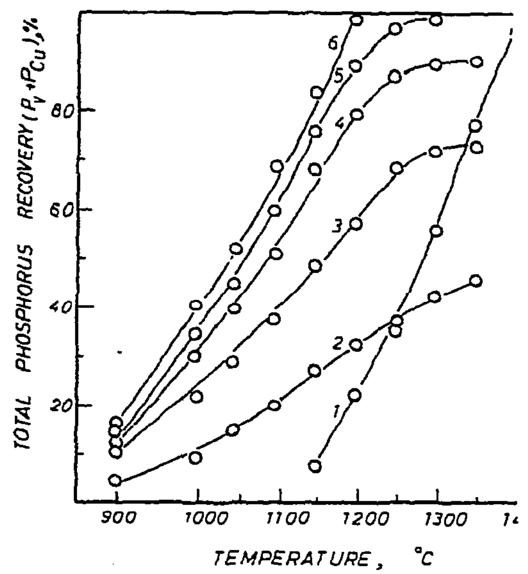


Fig. 1. Effect of copper additions on phosphorus recoveries (P_v and P_{Cu}) from calcium phosphate reduction, at different Cu/P mole ratios: 1 = 0, 2 = 0.13, 3 = 0.26, 4 = 0.39, 5 = 0.52 and 6 = 0.78. Time of reduction = 60 min.

Fig. 2. Effect of copper additions on the total phosphorus recovery from the reduction of calcium phosphate, at different Cu/P mole ratios: 1 = 0, 2 = 0.13, 3 = 0.26, 4 = 0.39, 5 = 0.52 and 6 = 0.78. Time of reduction = 60 min.

increase of reduction temperatures as well as the increase of copper additions. Such an increase is much more marked with the increase of copper ratio from 0.13 to 0.39 and from 0.39 to 0.78 mole/mole of phosphorus. Maximum volatilization of phosphorus takes place at 1350°C, reaching a recovery of 83% of the total phosphorus originally present in the charge.

With all copper proportions used, the amount of phosphorus in the form of copper phosphides present in the residues increases with rise of temperature up to 1200°C and then decreases at higher temperatures. The maximum phosphorus recovery in the form of copper phosphide achieved with the mixture containing Cu/P ratio = 0.78 amounts to 33% of the total phosphorus originally present in the charge. The value is combined in the form of Cu_3P and CuP_2. These two phosphides are in equilibrium at temperatures $>900°C$, and the formation of the latter compound from the former according to

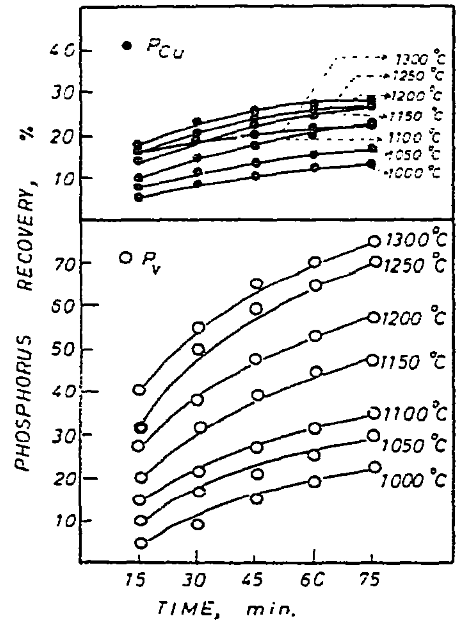
$$Cu_3P + 5\ P \rightleftharpoons 3\ CuP_2 \tag{2}$$

is greatly dependent on the phosphorus pressure in the system [8].

It is observed that in the temperature range 1150–1250°C, there is no free metal in the system and all the copper metal added is in the form of phosphides. According to many authors [9–12] the copper phosphides are unstable at temperatures higher than 1200°C, especially those containing more than 14% P (copper phosphide Cu_3P contains 14% P). It is worth noting that the total phosphorus recovery ($P_v + P_{Cu}$), representing 100% reduction was obtained after 60 min at temperatures $\geq$ 1200°C together with Cu/P ratios of 0.52 and 0.78, respectively.

Effect of temperature and time

Phosphate samples were reduced for various periods up to 75 min at temperatures ranging from 1000 to 1300°C using C: $P_2O_5 = 5X$ and Cu/P mole ratio = 0.39. The results shown in Fig. 3 reveal increased volatilized phosphorus recovery (P_v) with the increase of reduction duration as well as temperature. Maximum (P_v) values acquired under the applied conditions amount to 75% after about 75 min. Chemical analysis of the residues remaining after reduction clarify that it contains unreacted phosphate admixed with copper phosphides. The amounts of (P_{Cu}) were found to increase with increase of reduction duration and temperature up to 1200°C and then decrease with increase of temperature above 1200°C. The maximum phosphorus recovery (P_{Cu}) amounts to 28% of the original amount present in the charge and is acquired after 75



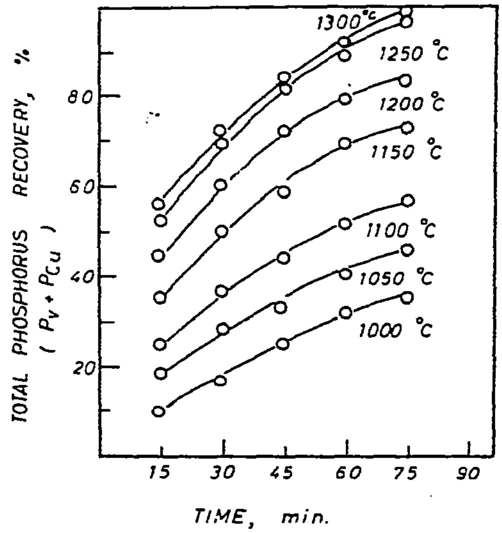


Fig. 3. Effect of temperature and time on phosphorus recoveries (P_v and P_{Cu}) from calcium phosphate reduction: Cu/P = 0.39.

Fig. 4. Effect of temperature and time on the total reduction extent of calcium phosphate; Cu/P = 0.39.

min at 1200°C. The total phosphorus recoveries ($P_v + P_{Cu}$) at different durations and temperatures are illustrated in Fig. 4.

Effect of silica additions

The effect of silica additions on the extent of reduction of tricalcium phosphate in the presence of copper was studied. This was performed for 60 min at different temperatures, using briquettes composed of C: $P_2O_5 = 5$, Cu/P ratio $= 0.39$ and $SiO_2/CaO = 1$. The results obtained are illustrated in Fig. 5. For the sake of comparison the behaviour of reducing pure phosphate by carbon in the presence of silica [4] and/or copper are also given in the same Fig. It is seen that the presence of silica and copper affects the reduction of tricalcium phosphate in the following ways.

(i) In the presence of silica and at all temperatures, the phosphorus recovery extents are higher than those acquired with copper additions only. The difference is much greater at relatively low temperatures.

(ii) At temperatures higher than 1200°C, the reduction process changes to lower rate and reaches more or less a steady value at temperatures ⩾ 1300°C. The same behaviour is observed for both processes displayed in the presence of copper with and without silica additions.

(iii) The amounts of phosphorus as phosphides in the presence of silica range from 13.5 to 23% at 1000 and 1300°C, respectively. Lower values are obtained in the absence of SiO_2.

X-Ray analysis

The results of X-ray diffraction patterns of the residues remaining after reduction for 60 min at different temperatures are summarized in Table 1. From these results,

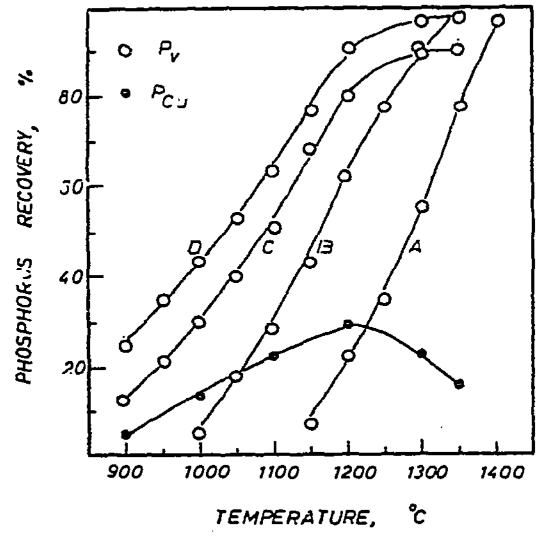


Fig. 5. Effect of temperature and time on the reduction extent of calcium phosphate. A = Calcium phosphate + carbon; B = calcium phosphate + silica + carbon; C = calcium phosphate + copper + carbon; and D = calcium phosphate + copper + silica + carbon. Time of reduction = 60 min.

TABLE 1

X-Ray diffraction analysis of the reduction products at different temperatures

Reduction temp. (°C)	Main compounds detected by X-ray
1150	$Ca_3(PO_4)_2$, CaC_2, CuP, CuP_2, $Cu_3(PO_4)_2$
1250	CaC_2, CaO, CuP, Cu_2P, CuP_2, $Cu_3(PO_4)_2$
1300	CaC_2, CaO, Cu_2P, CuP, CuP_2, Cu_3P

it is seen that the main lines of $Ca_3(PO_4)_2$, CaC_2 and copper phosphide are clearly detected at 1150°C. At 1250°C, the patterns of $Ca_3(PO_4)_2$ begin to decrease and disappear completely at 1300°C. It is worth noting that the main copper phosphide compounds detected at all temperatures are CuP and CuP_2. Lower copper phosphohides of Cu_2P and Cu_3P are also identified at 1250 and 1300°C. In addition, X-ray patterns of copper phosphates are likely to be present in the product obtained at all temperatures. Calcium carbide and calcium carbonate seem to be the end products of calcium phosphate reduction.

Mechanism of reduction

In order to investigate the mechanism of these reactions, consultation of the different kinetic equations known show that the most suitable one is that suggested

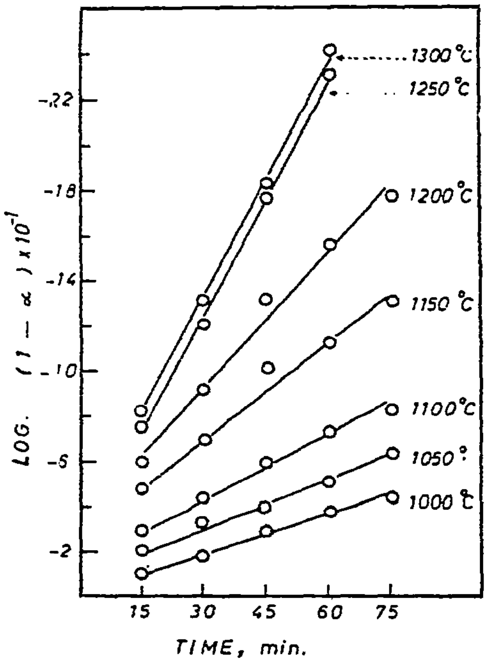


Fig. 6. Plot of log $(1-\alpha)$ vs. time for the reduction of calcium phosphate in the presence of carbon and copper.

by Sharp et al. [13,14] and Stava and Skvara [15] which is applied for random nucleation with one nucleus on each particle and usually for solid state reactions, and is expressed by

$$-\ln(1-\alpha)=Kt \qquad (3)$$

where α is the fraction of phosphorus volatilized after time t. On plotting $\ln(1-\alpha)$ vs. time, for the results obtained in the temperature range 1000–1250°C (Fig. 4), straight lines are obtained (Fig. 6). Applying the Arrhenius equation, a straight line is obtained (Fig. 7). The activation energy was calculated and found to amount to 28.3 kcal mole^{-1}. It was found that the reaction rate follows eqn. (3) only up to 1250°C. At temperatures higher than 1250°C, the reaction rate becomes independent of the temperature, where parallel straight lines are obtained representing the plots of $\ln(1-\alpha)$ vs. time. The same eqn. (3) was used to determine the reaction rate in the presence of SiO_2 together with copper additions (Fig. 5, curve D). As has been found before [4], the reaction rate appears to follow a pseudo-first order equation [14]. From such equation, values of $t_{0.5}$ can be simply calculated as

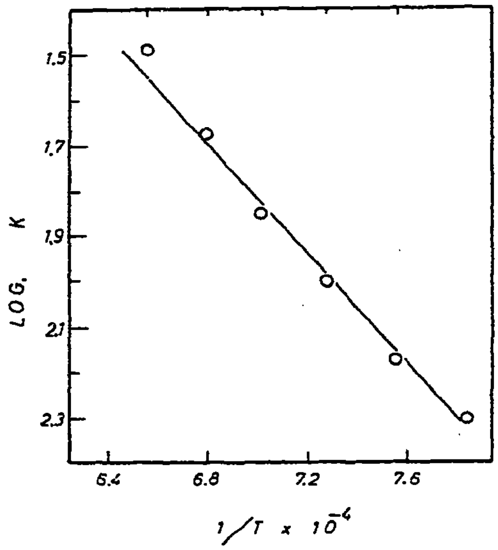


Fig. 7. Arrhenius plot for the results of Fig. 6.

$$F(\alpha)=K/t_{0.5} \qquad (4)$$

Accordingly, when applying this equation with the results illustrated by Fig. 5 (curve D), and on plotting $\log t_{0.5}$ vs. $1/T$, a straight line was obtained (Fig. 8). The activation energies were calculated and compared with those obtained in Fig. 5 (curves A, B and C). The results are given in Table 2.

Also, on plotting $\log t_{0.5}$ against $1/T$ for mixtures containing different copper additions, the straight lines illustrated in Fig. 9 were obtained. The calculated activation energies are in the order of 20 ± 0.8 kcal mole^{-1}.

From the above results the following conclusions can be made.

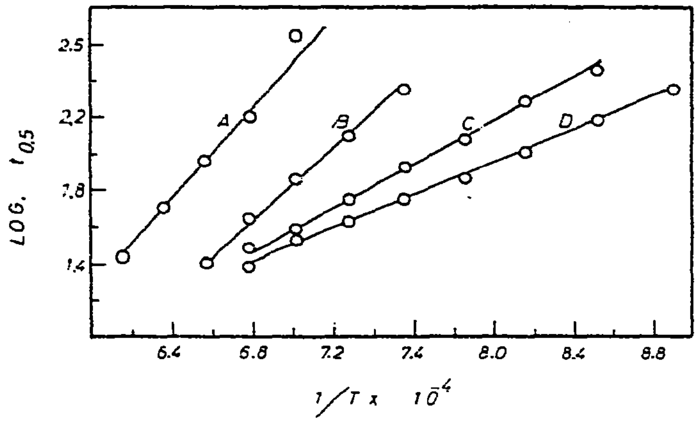


Fig. 8. Plot of log $t_{0.5}$ vs. $1/T$. A = Calcium phosphate + carbon; B = calcium phospate + carbon + silica; C = calcium phosphate + carbon + copper; and D = calcium phospate + carbon + silica + copper.

(1) The increase of phosphorus recovery by the increase of copper additions may be attributed to the reduction of P_2O_5 by metallic copper according to

$Ca_3(PO_4)_2 + 5\ Cu \rightarrow 5\ CuO + 3\ CaO + P_2$ (5)

The CuO so formed is instantaneously reduced by carbon to metallic copper, which again plays a role in the reduction process. In addition, the produced phosphorus vapour is liable to react with metallic copper to form copper phosphide. Such a reaction is looked upon to accelerate the reduction process as it shifts reaction (5) to the right-hand side.

(2) One can assume that the reaction between metallic copper and phosphorus takes place in two steps

$3\ Cu + P \rightarrow Cu_3P$ (6)

$Cu_3P + 5\ P \rightarrow 3\ CuP_2$ (7)

The melting point of Cu_3P was reported [8,9] to be 1022°C and that Cu_3P and metallic copper form compounds with lower melting points (the eutictic melts at 714°C with a composition of 8.38% P). Based on these considerations, the liquid phase formed from Cu–Cu_3P mixtures around the phosphate grains may hinder

TABLE 2

Activation energies calculated

Reaction	Temp. range (°C)	Activation energy (kcal mole^{-1})
(A) $Ca_3(PO_4)_2 + 5\ C$	1100–1400	54.3
(B) $Ca_3(PO_4)_2 + 3\ SiO_2 + 5\ C$	1050–1300	44.1
(C) $Ca_3(PO_4)_2 + Cu + C$	900–1200	26.4
(D) $Ca_3(PO_4)_2 + SiO_2 + Cu + C$	850–1200	19.4

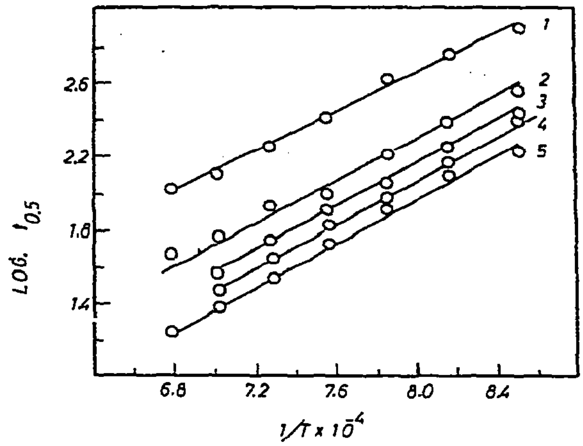


Fig. 9. Plot of log $t_{0.5}$ vs. $1/T$ in the presence of Cu/P mole ratios: 1 = 0.13, 2 = 0.26, 3 = 0.39, 4 = 0.52 and 5 = 0.78.

further reduction of calcium phosphate by carbon. Such a process may lead to a complete stop of the reduction process at temperatures $\geqslant$ 1022°C. The instability of Cu_3P is well detected at temperatures > 1200°C, which is manifested by the decrease in the proportions of this compound in the residues, as illustrated in Fig. 3. The results given in Fig. 4 show increased total phosphorus recovery with rise in temperature above 1200°C. It seems possible to assume that copper phosphide decomposes at these high temperatures according to

$$Cu_3P \rightarrow 3\ Cu + P \qquad (8)$$

where phosphorus is volatilized and the released copper metal acts as a reducing agent for calcium phosphate.

(3) The mechanism of reduction of tricalcium phosphate by carbon in the presence of both silica and copper is identical to that mentioned above. Curve D in Fig. 5 acquired together with SiO_2 in the presence of copper additions, follows the same trend as curve C (obtained with Cu addition only), and resembles curves A and B without any copper additions. It can be observed that on applying the results of isothermal experiments, the activation energy for reaction C as achieved from Fig. 7 amounts to 28.3 kcal $mole^{-1}$ which is similar to the value obtained from Fig. 8 (26.4 kcal $mole^{-1}$). On the other hand, the addition of silica to the system containing copper in a Cu/P ratio of 0.39 leads to acceleration of the reaction rate, and the activation energy obtained is only 19.4 kcal $mole^{-1}$.

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