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KINETICS OF CALCIUM PHOSPHATE REDUCTION BY CARBON

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ABSTRACT

A fundamental study was made on the reduction of calcium phosphate by carbon. The mechanism of reduction was presented on applying different additions. Both silica and alumina increased the extent of reduction but with variable rates. The activation energies were calculated on the basis of first-order reactions. The phases formed during reduction were investigated by X-ray analysis.

INTRODUCTION

For the electrothermal production of phosphorus, phosphate ores are mixed with carbon and silica and heated in electric furnaces. The role of silica in the process was investigated by many authors[1–8] who found that it increases the reduction process and decreases the reduction temperature. Some of these authors stated that below 1400 °C tricalcium phosphate was not reduced by carbon in the absence of silica. Jacob et al.[9] pointed out, however, that partial reduction of the phosphate with carbon could be achieved at 1300 °C. According to Videnova[2] the reduction extent of tricalcium phosphate was markedly influenced by the type of carbon used.

The present study aims to determine the optimum conditions for the recovery of phosphorus from tricalcium phosphate. The effect of some of the impurities usually present in phosphate rocks on the reducibility is also investigated.

EXPERIMENTAL

Materials

Chemically pure tricalcium phosphate was used. It contains 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).

Five types of carbon were applied: graphite, active charcoal (B.D.H.), locally activated charcoal, carbon black and coke. The alumina and silica added to tricalcium phosphate were of high grade purity.

Apparatus and technique

The apparatus and experimental technique used in this investigation have been described before[10]. The samples to be reduced were weighed in a fused aluminium boat and inserted inside a 100 mm fused aluminium reaction tube. The whole was heated by a horizontally moving, silicon-carbide, tube furnace, which enables rapid heating and cooling. The temperature was automatically controlled within ±5°C. The percentage of phosphorus volatilised during the reduction process was determined from the residual phosphorus content left. The amount of volatilised phosphorus was also determined by weight change of the charge.

The mechanism of reduction was investigated on the basis of the reduction results and the X-ray analysis of the reduction products. This was performed by the aid of Philips diffractometer PW1010, using K_α Cu radiation. The samples were investigated immediately after reduction.

RESULTS AND DISCUSSIONS

Effect of carbon additions

The effect of carbon additions on the extent of phosphorus recovery was studied, using charges containing charcoal amounts varying from 1–5 the stoichiometric amount (x) corresponding to the following reaction:

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

The process was conducted at 1200°C for 60 min.

Two series of experiments were performed, in the first briquets of calcium phosphate-charcoal and in the second calcium phosphate-silica-charcoal were used.

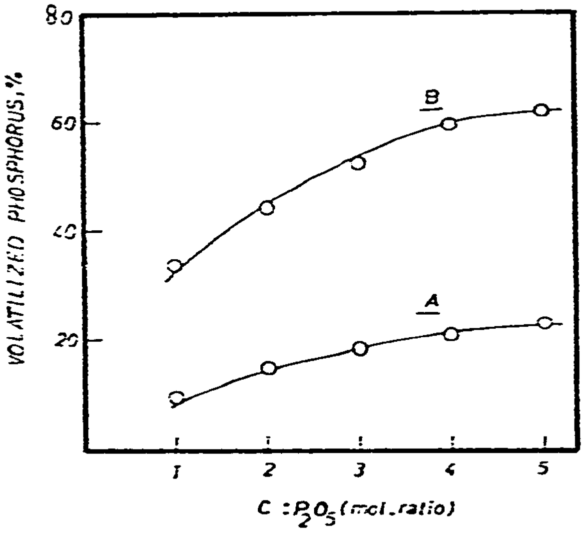

Fig. 1. Effect of carbon addition on the reduction of calcium phosphate. (A) Without silica addition; (B) with silica addition.

The results showing the volatilised phosphorus in both cases are depicted in Fig. 1. In both cases increased reduction extent is achieved with the increase of the charcoal ratio in the mixture, tending to reach a limiting value at 5*X*. Higher recoveries are obtained in presence of silica.

Experiments were then conducted using five other types of reducing materials, namely carbon black, activated charcoal (B.D.H.), locally activated charcoal, coke and graphite. Simple mixtures as well as briquets were used. Working conditions and the phosphorus recoveries obtained are given in Table 1. Complete recovery is acquired when using briquets of calcium phosphate and activated charcoal (B.D.H.).

TABLE 1

EFFECT OF CARBON TYPES ON THE REDUCTION OF TRICALCIUM PHOSPHATE

Conditions: Stio. $C/P_2O_5 = 5$; $SiO_2/CaO = 1$; *temperature*, 1250 °C; *time*, 90 min.

Carbon types	*Volatilized phosphorus*	
	Mixtures	*Briquets*
Graphite	78.60	83.40
A.C. (local)	82.80	95.20
A.C. (B.D.H.)	90.60	100.00
Carbon black	97.80	not briquetted
Coke	80.30	88.00

Effect of silica additions

The effect of silica additions was studied using 0.25–1.25 the stoichiometric amounts (*x*) corresponding to the equation:

$$Ca_3(PO_4)_2+3SiO_2+5C \rightarrow 3CaSiO_3+P_2+5CO \qquad (2)$$

Experiments were conducted using 5*X* charcoal at 1200 °C for 60 min. The results obtained are represented by the curves in Fig. 2. Phosphorus recovery increases markedly with the increase of SiO_2 ratio in the mixture up to 1*X*.

Effect of temperature and time of reduction

Phosphate samples were reduced for various periods at temperatures from 1000–1300 °C using 1*X* SiO_2 and 5*X* charcoal. The results in Fig. 3 show increased phosphorus recoveries with the increase of reduction duration as well as temperatures. Complete reduction is reached after 110 and 45 min at 1250 and 1300 °C, respectively.

Effect of alumina additions

The effect of alumina additions was studied for 60 min at different reduction temperatures, using the stoichiometric amount of Al_2O_3 corresponding to the equation:

$$Ca_3(PO_4)_2+3Al_2O_3+5C \rightleftharpoons 3(CaO\cdot Al_2O_3)+P_2+5CO \qquad (3)$$

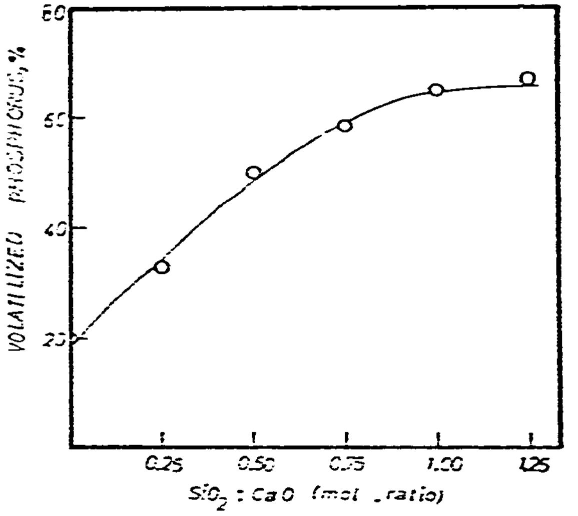

Fig. 2. Effect of silica addition on the reduction of calcium phosphate.

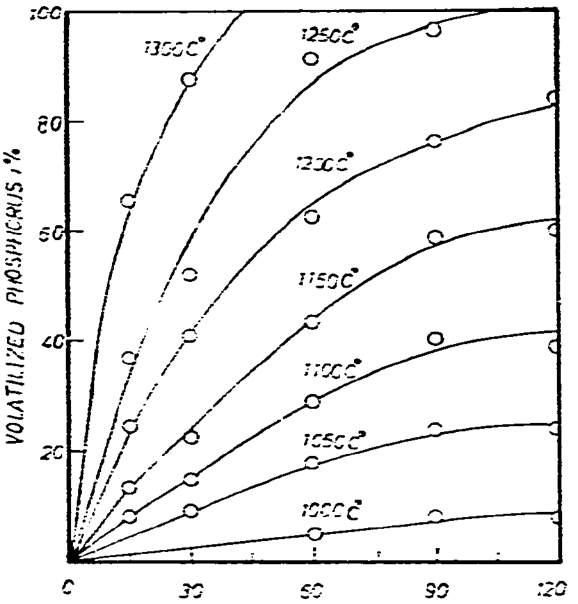

Fig. 3. Effect of temperature and time on the reduction of calcium phosphate.

The results obtained are represented by curve b in Fig. 4. It shows that the presence of alumina increases the reduction extent of calcium phosphate. The effect of alumina in that respect is lower than that of silica, curve (c) in Fig. 4. On the other hand, addition of alumina and silica in proportion equimolecular to those given in eqns (2) and (3), lead to increase the reduction extent, curve (d) in Fig. 4, becoming very close to that achieved by silica alone. It is worth noting that all four curves show the same trend along the temperature range applied.

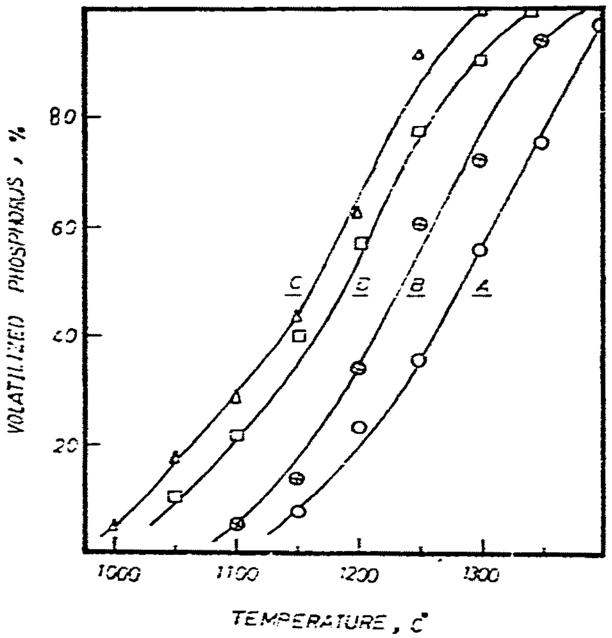

Fig. 4. Effect of temperature on the reduction of calcium phosphate. (A) = $Ca_3(PO_4)_2+C$; (B) = $Ca_3(PO_4)_2+Al_2O_3+C$; (C) = $Ca_3(PO_4)_2+SiO_2+C$; (D) = $Ca_3(PO_4)_2+SiO_2+Al_2O_3+C$.

Mechanism of reaction

The above-mentioned results may lead to investigate the mechanism of carbon reduction of calcium phosphate. One may assume that the reaction may proceed in two steps, as given in eqns (1) and (2). As the reduction of P_2O_5 by carbon is instantaneous in the applied temperature range, especially in presence of carbon contents higher than the required stoichiometric values, the dissociation of $Ca_3(PO_4)_2$ to CaO and P_2O_5 may be the rate determining step. The presence of silica may enhance the dissociation of $Ca_3(PO_4)_2$. It is found that this reaction obeys the first-order equation as given in Fig. 5, where straight lines are obtained on plotting $\log(a-x)$ vs. time. Applying Arrhenius equation, a straight line is obtained, Fig. 6. The activation energy obtained is 44.1 kcal mol^{-1}.

It is deemed desirable to mention that the CO evolved from the reduction process (eqns (2) and (3)) does not act as a reducing agent as was tested by many authors[8,9,11]. It was also investigated by X-ray analysis that no intermediate compounds (pyrophosphate or calcium phosphosilicate) are formed by the reduction.

Applying Brindley equations[12] in investigating the mechanism of solid-state reactions, a curve (D_1, D_2 and F_1 in Fig. 7) can be plotted for each of the three types of kinetic reaction equations:

$$D_1(\alpha):\ \alpha^2 = (k/x^2)\,t = 0.25\,(t/t_{0.5}) \tag{4}$$

$$D_2(\alpha):\ (1-\alpha)\ln(1-\alpha)+ = (k/r^2)\,t = 0.15343\,(t/t_{0.5}) \tag{5}$$

$$F_1(\alpha):\ \ln(1-\alpha) = -kt = 0.6931\,(t/t_{0.5}) \tag{6}$$

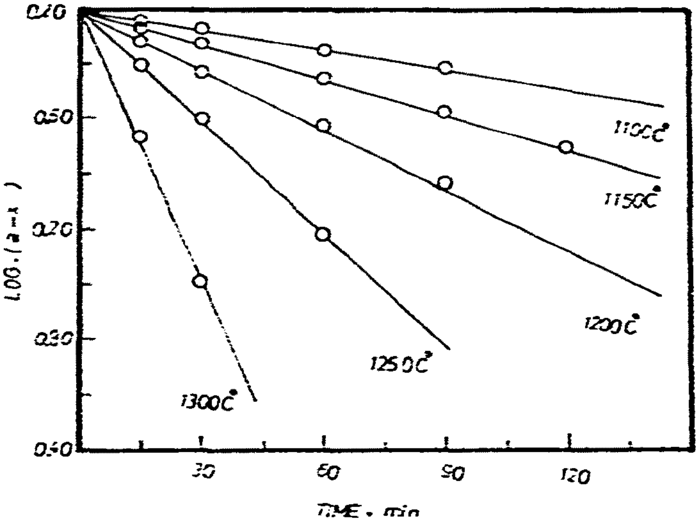

Fig. 5. Plot of log $(a-x)$ against time.

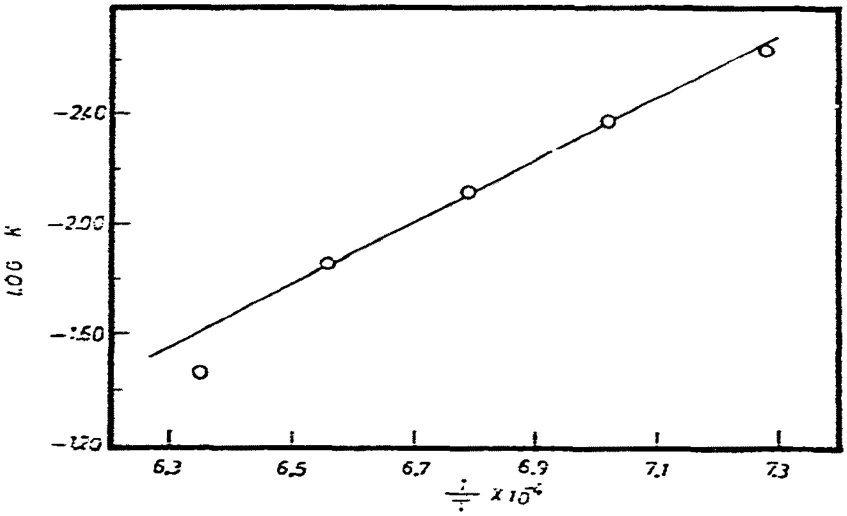

Fig. 6. Arrhenius plot.

The values of x of volatilized phosphorus for variable $t/t_{0.5}$ at different reaction temperatures are also illustrated in Fig. 7. The fact that most of these values fall exactly on curve F_1, confirms that the process of $Ca_3(PO_4)_2$ reduction by carbon obeys the first-order kinetic equation.

The activation energy of this reaction changes with the addition of different compounds (SiO_2 and/or Al_2O_3). This behaviour can be deduced from the results illustrated in Fig. 8 for four series of reactions performed at different temperatures for 60 min. The activation energies of these processes can be calculated as follows:

The addition of silica, alumina or a mixture of both compounds to the system accelerates the reaction rate to different extents depending on its reactivity with one of the products, CaO. Such reactions do not affect the order of the reaction. Accordingly, these reduction reactions obey the first-order kinetic equation as soon as the amount of carbon is higher than the stoichiometric value for reducing P_2O_5. Such

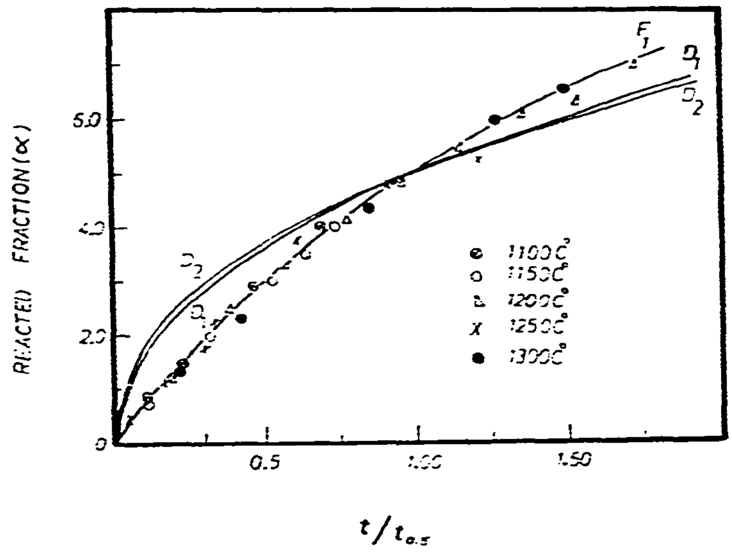

Fig. 7. Brindley equations of first-order and diffusion reactions.

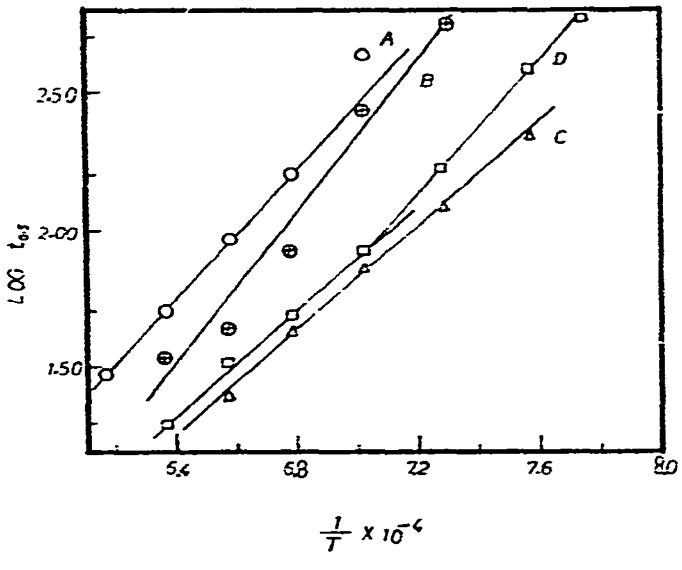

Fig. 8. Plot of log $t_{0.5}$ against $1/T$ according to modified eqn (10).

assumption will establish that at $t_{0.5}$,

$$K_T = \ln 2/t_{0.5} \tag{7}$$

i.e., at all experimental temperatures $t_{0.5}$ is inversely proportional to K. Applying Arrhenius equation:

$$K = Z_1 \cdot e^{-E/RT} \tag{8}$$

one may conclude from eqns (7) and (8) that:

$$t_{0.5} = Z_2 \cdot e^{-E/RT} \tag{9}$$

and

$$E = R \ln \frac{t_{0.5}(T_1)}{t_{0.5}(T_2)} \Big/ \frac{1}{T_1} - \frac{1}{T_2} \tag{10}$$

where Z_1 and Z_2 are constants.

The respective values of $t_{0.5}$ can be simply calculated from the equation:

$$f(\alpha) = Kt/t_{0.5} \tag{11}$$

where α is the fraction of phosphorus volatilized after time t (60 min). The α values for all temperatures are given in Fig. 4. The $t/t_{0.5}$ respective to different values of α are predicted from Fig. 7. Plotting log $t_{0.5}$ against $1/T$ for all experiments carried out at different additions, straight lines are obtained (Fig. 8). From these lines, the activation energies are calculated and tabulated in Table 2.

TABLE 2

ACTIVATION ENERGIES CALCULATED FROM THE PLOT log $t_{0.5}$ vs. $1/T$

Reaction	*Temp. range (°C)*	*Activation energy*
(A) $Ca_3(PO_4)_2 + 5C$	1100–1400	54.3 k cal mol^{-1}
(B) $Ca_3(PO_4)_2 + 3Al_2O_3 + 5C$	1100–1400	63.5 k cal mol^{-1}
(C) $Ca_3(PO_4)_2 + 3SiO_2 + 5C$	1050–1300	44.1 k cal mol^{-1}
(D) $Ca_3(PO_4)_2 + \tfrac{3}{2}SiO_2 + \tfrac{3}{2}Al_2O_3 + 5C$	1050–1150	55.0 k cal mol^{-1}
	1150–1300	44.0 k cal mol^{-1}

It is noticed that the activation energies calculated by this method and that deduced before from Fig. 6 for reaction (c) are exactly the same. A higher value of the activation energy is obtained for a reduction process without silica addition. However, addition of alumina instead of silica is accompanied by the highest value of the activation energy. Addition of both silica and alumina in equimolecular amounts (reaction d) does not pertain a direct straight line but a break is displayed at 1150 °C, whereby two values of activation energies are obtained.

The above results may throw light on the mechanism of the reduction reaction of calcium triphosphate with carbon. The reaction proceeds with a relatively high rate on adding silica to form calcium silicate. Addition of alumina instead of silica made it necessary to proceed the reaction at markedly higher temperatures. Meanwhile, the reduction in presence of Al_2O_3 proceeds with higher activation energy than that given by reactions (a) and (c). On the other hand, addition of SiO_2 and Al_2O_3 in equimolecular amounts, proceeds in a similar fashion as that of reaction (c) only at temperatures higher than 1150 °C, whereby the same activation energy is obtained. Under these conditions, alumina does not play any role in the reduction process. It may react further with the calcium silicate formed to give calcium aluminium silicate according to the following equation:

$$2CaSiO_3 + Al_2O_3 \rightarrow Ca_2Al_2SiO_7 + SiO_2 \qquad (12)$$

Silica which is formed according to eqn (12) may react again with calcium phosphate according to eqn (2). This assumption is substantiated by the results of X-ray analysis which are summarised in Table 3.

TABLE 3

THE RESULTS OF X-RAY ANALYSIS OF THE REACTION PRODUCTS AT DIFFERENT ADDITIONS

Reaction	*Reduction temp. (°C)*	*Compounds investigated by X-ray*
$Ca_3(PO_4)_2 + 3Al_2O_3 + 5C$	1300	Mainly $CaAl_2O_4$
$Ca_3(PO_4)_2 + 3SiO_2 + 5C$	1300	Mainly $Ca_3Si_2O_7$ and $CaSiO_3$
$Ca_3(PO_4)_2 + \frac{3}{2}SiO_2 + \frac{3}{2}Al_2O_3 + 5C$	1300	Mainly $Ca_2Al_2SiO_7 + CaSiO_3$
	1100	Mainly $Ca_3(PO_4)_2 + Al_2SiO_5$

On the other hand, the relatively high activation energy obtained at temperatures below 1150 °C, may also be explained on the premise of the results of X-ray analysis, where the product investigated is mainly aluminium silicate. This result may also explain the break obtained in Fig. 8, as Al_2O_3 and SiO_2 interact in this system to form aluminium silicate with no effect of both compounds on the reduction rate of $Ca_3(PO_4)_2$ by carbon. Accordingly, the value of activation energy is nearly the same as that given by reaction (a), i.e. no additions of Al_2O_3 or SiO_2. The formation of aluminium silicates at these relatively low temperatures was also investigated by some authors[13,14].

The X-ray analyses of the products are summarised in Table 3. It is noted that the reduction of $Ca_3(PO_4)_2$ in presence of Al_2O_3 gives mainly $CaAl_2O_4$, while a mixture of $CaSiO_3$ and $Ca_3Si_2O_7$ are the main products on adding silica. The compound $Ca_2Al_2SiO_7$ could be noticed clearly, only at temperatures higher than 1150 °C on adding the mixture of Al_2O_3 and SiO_2. Calcium aluminate was not easily detected from the patterns obtained by X-ray analysis of the reduction products on using an Al_2O_3–SiO_2 mixture. These results confirm the above-mentioned discussion, concerning the break obtained in curve d in Fig. 8.

REFERENCES

1 H. H. Franck and H. Fuldner, *Z. Anorg. Allg. Chem.*, 204 (1932) 97.
2 R. R. Videnova, *Khim. Ind.* (*Sofia*), 37 (1965) 10; *Chem. Abstr.*, 63 (1964) 2657 f.
3 A. T. Khvichiya, S. G. Samkharadze and Z. A. Mutadova, *Izv. Vyssh. Ucheb. Zaved., Chern. Met.*, 8 (1965) 17; *Chem. Abstr.*, 62 (1964) 8893 d.
4 J. Hgwliezek and B. Tendoj, *Chem. Stosow., Poland*, 6 (1962) 68; *Chem. Abstr.*, 57 (1962) 1851 e.
5 V. A. Ershov, *Zh. Prikl. Khim.* (*Leningrad*), 40 (1967) 953; *Chem. Abstr.*, 67 (1967) 83493.
6 N. N. Poznikov and A. D. Mikhailin, *Issled. Khim. Tekhnol. Udobr., Pestits., Solei*, (1966) 9; *Chem. Abstr.*, 67 (1967) 47607 b.
7 Y. Kenichiro and K. Akio. *Kogyo Kagaku Zasshi*, 17 (1968) 367; *Chem. Abstr.*, 69 (1968) 24136.
8 K. D. Jacob and D. S. Reynolds, *Agr. Ind. Eng. Chem.*, 20 (1928) 1204.
9 K. D. Jacob, D. J. Reynolds and W. L. Hill, *Ind. Eng. Chem.*, 81 (1929) 1126.
10 M. K. Hussein, G. A. Kolta, I. F. Hewaidy and A. El-Roudi, *J. Chem. U.A.R.*, 14 (1971) 289.
11 H. H. Mayer, *Mitt. Kaiser-Wilhelm, Inst. Eisenforsch., Duesseldorf*, 9 (1927) 273.
12 J. H. Sharp, G. W. Brindley and B. N. N. Achar, *Numerical Data for some Commonly Used Solid-State Reaction Equations*, Brindley and Ray Scientific Report No. AFCKL-65-606, 1965, pp. 94–104.
13 N. A. Torpov and F. Ya. Galakhov, *Dokl. Akad. Nauk SSSR*, 78 (1951) 301.
14 S. Aramaki and R. Roy, *J. Amer. Ceram. Soc.*, 42 (1959) 644.