

VACUUM BALANCE STUDIES OF PHOSPHATE-BONDED OXIDE CERAMICS

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ABSTRACT

Methods of phosphate bonding of oxide ceramics are summarised. Applications of vacuum balance techniques are described to study the sintering of lime, magnesia, alumina and kaolin in the presence of phosphoric acid and sodium polymetaphosphate additives. Changes in surface area, crystallite and aggregate sizes during sintering have been determined by gravimetric B.F.T. nitrogen gas sorption techniques, supported by X-ray diffractometry, optical and electron-microscopy.

Phosphoric acid has comparatively little influence on lime and magnesia sintering. There is no enhancement of sintering and even slight activation at temperatures between 800-1000 °C, when chemical reactions with the additive are completed. In contrast, sodium polymetaphosphate additive enhances sintering of lime and magnesia at temperatures between 500-1000 °C. When kaolin is calcined with sodium polymetaphosphate, the activated alumina in the intermediate metakaolinite readily forms aluminium phosphate to accelerate sintering.

INTRODUCTION

The mechanical strength and hardness of ceramics are important industrially. High-melting metal oxides, such as lime, magnesia and purified alumina are obtained generally from natural sources in finely-divided form and require sintering to produce strong dense bodies. Sintering is promoted by additives(1).

Kingery(2) has summarised the earlier literature on phosphate bonding and has studied the reactions and properties of cold-setting phosphoric acid bonds with metal oxides and hydroxides. His experimental data indicates that the formation of acid phosphates is responsible for bond formation at room temperature. With the more refractory and inert oxides, e.g., alumina, heat is required to achieve reaction and hence the setting of the cement. Fischer(3) has compared the effect of temperature on bond strength for alumina using different sources of phosphate radical and the two precipitation cements ethyl silicate and aluminium monoacetate. For the phosphate reaction bonds, strength increases and porosity decreases with increasing acidity of the phosphate. Further research (to 1977) on phosphate bonding has been reviewed by Cassidy(4). Phosphoric acid and monoammonium phosphate react too quickly with basic aggregates and so alkali polyphosphates are preferred. Sodium hexametaphosphate

( $\text{NaPO}_3$ )<sub>6</sub>, forms rubberlike polymers and yields high strength mortars with fireclay aggregates. These materials are used in high alumina refractory mortars and ramming mixes and are particularly useful as bonds for basic aggregates. (5). Foessel and Treffner (6), who reviewed the earlier literature on the use of sodium polyphosphates in basic refractories, showed that very high hot strength (1500-2500 psi) could be achieved at 2700 °F (about 1500 °C) in magnesite and magnesite chromic refractories under certain conditions. The most important criterion was the  $\text{CaO}:(\text{P}_2\text{O}_5 + \text{SiO}_2)$  ratio, for limes. Venables and Treffner (7) reported that the bonding phase was  $\text{CaNaPO}_4$ , sodium rhenanite.

The effect of natural impurities and additives such as chloride, sulphate, phosphate and iron oxide on lime sintering has been investigated earlier (1967) by the author (1). Thus in the present research, vacuum balance techniques are applied further to study the sintering of lime, magnesia, alumina and kaolin in the presence of phosphoric acid and sodium polymetaphosphate additives. Changes in surface area, crystallite and aggregate sizes during sintering have been determined by gravimetric B.E.T. nitrogen gas sorption techniques, supported by X-ray diffractometry, optical and electron-microscopy.

## EXPERIMENTAL

### Materials

Samples of calcium hydroxide and magnesium hydroxide (British Drug Houses) were intimately mixed with known amounts of phosphoric acid or sodium polymetaphosphate. The  $\text{M.H}_3\text{PO}_4$  produced partial dissolution, after which the solutions were carefully evaporated and the residues dried at 140-150 °C (1).

### Procedure

Separate portions of the calcium and magnesium hydroxides, with or without the additives, were calcined for various times at each of a number of fixed temperatures in air in an electrical furnace.

The specific surfaces,  $S$ , of the cooled samples were determined by a gravimetric B.E.T. method (8), using nitrogen (or occasionally oxygen) gas sorption at -183 ° or -196 °C recorded on an electrical sorption balance constructed by the author (quarter mg sensitivity using 5-10 g samples) or on vacuum microbalances ( $\mu\text{g}$  to  $\text{mg}$  sensitivity using 0.25 g samples or less), viz., Sartorius or CI Microforce Mark 2B. The adsorption isotherms also indicated any porosity present (from hysteresis) and pore size ranges. Average crystallite size ranges deduced from the specific surfaces of the less porous materials were compared with aggregate sizes observed by optical- and electron-microscopy (Phillips TEM 300).

To determine the nature of any chemical reactions between the lime, magnesia, alumina or clay and the additives, mixtures were made of stoichiometric amounts of oxide and additive. These mixtures were calcined at the temperatures and times employed for the studies of bonding and sintering. The components in the products were identified by X-ray diffractometry.

## RESULTS AND DISCUSSION

### Physical nature of activated lime and magnesia

The surface activities of lime and magnesia produced by thermal decomposition of the hydroxides are compared in relation to the changes in crystal structure during preparation at several temperatures up to 1000 °C, cf. Fig. 1-5. The magnesia samples have correspondingly much larger surface areas than the lime samples. This is due mainly to the greater volume decreases associated with the crystal changes and to the diminished sintering of the magnesia at the lower decomposition temperatures. Thus magnesium hydroxide almost completely decomposes within 5 h in air above 400 °C compared with temperatures of above 450 °C which are required for calcium hydroxide. Earlier research(9) has shown that the specific surface of the magnesia produced at 400 °C is 180 m<sup>2</sup>g<sup>-1</sup> compared with 28 m<sup>2</sup>g<sup>-1</sup> for lime at 450 °C, representing the maximum surface activities of magnesia and lime produced by thermal decomposition in air.

However, the magnesia and lime samples produced at the lowest temperatures have had little opportunity to sinter and have a low degree of crystallinity, especially the magnesia which has an appreciably dilated crystal lattice (2.3 vol-%) and shows some mesoporosity (Fig. 1). The nitrogen adsorption isotherm at -196 °C for the 400 °C sample in Fig. 1 was recorded on the CI Microforce balance. A good B.E.T. plot is given at lower relative pressures (0.05-0.3) indicating  $S = 175 \text{ m}^2\text{g}^{-1}$  in good agreement with 180 m<sup>2</sup>g<sup>-1</sup> from the nitrogen adsorption isotherm at -183 °C recorded earlier on the older electrical sorption balance(9). At higher relative pressures (0.40-0.96) there is some hysteresis over practically the whole of the mesopore range (pore size diameters of 2-50 nm). This isotherm is almost identical with that for a magnesia sample produced by calcining the hydroxide for a shorter time (½ hr) at 500 °C. Longer calcination at 500 °C to give a total time of 5 h enables the oxide to sinter and the surface area decreases to 126 m<sup>2</sup>g<sup>-1</sup>, while the unit cell dilation volume reduces to only 0.9 %. At higher temperatures the dilation diminishes still further and the mesoporosity becomes very small above 700 °C, as indicated in Fig. 1, where there is comparatively little hysteresis in the nitrogen isotherm of the 700 °C sample.

### Effect of additives on magnesia and lime sintering

Phosphoric acid has comparatively little influence on the sintering of magnesia.

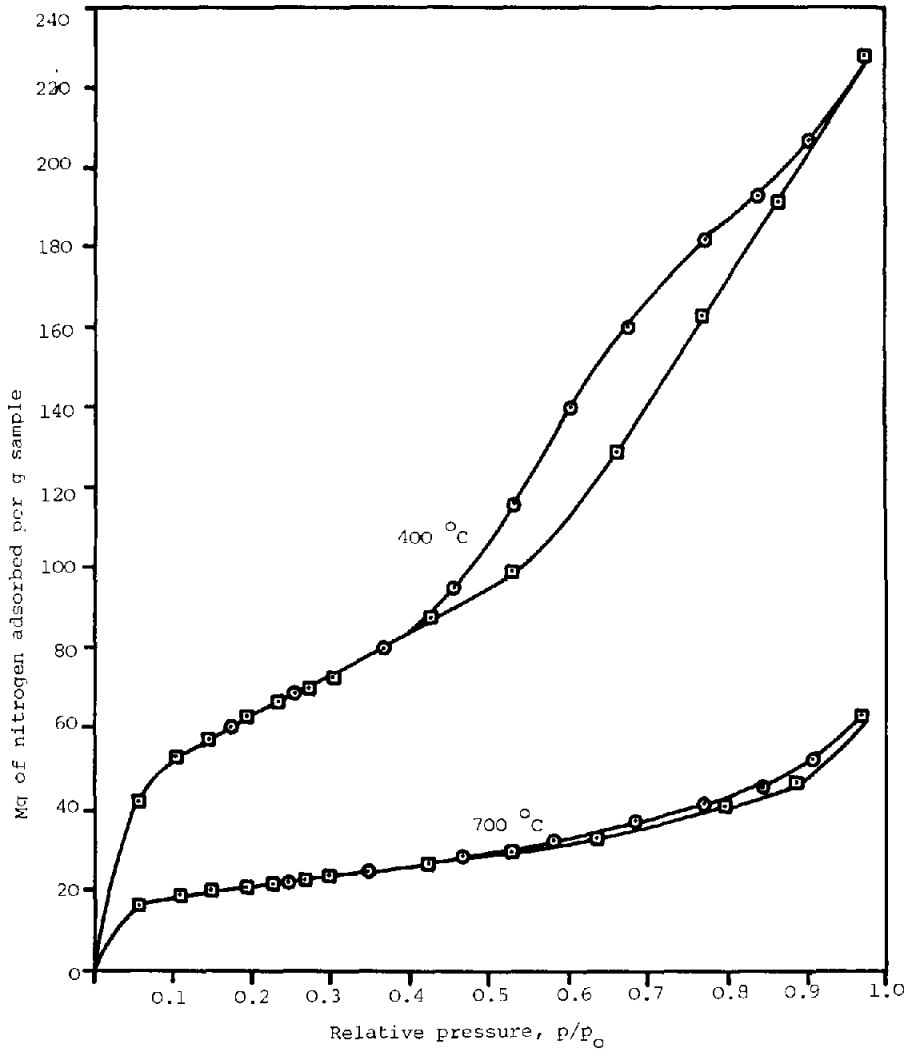


Fig. 1. Magnesium hydroxide calcined in air at 400 °C and 700 °C for 5 hours. Adsorption isotherms for nitrogen at -196 °C.

There is no enhancement of sintering and even slight activation at temperatures between 800 ° and 1000 °C when chemical reactions with the additive are completed. Thus the curves in Fig. 2 indicate that small amounts of additive (up to 0.5 %) cause some activation, but larger amounts give less activation. This is similar to what the author has found previously for lime(1). The Magnesium and calcium hydrogen phosphates initially formed with the phosphoric acid additive decompose at higher temperatures, first to pyrophosphates which then react with excess of magnesia and lime to give the normal phosphates,

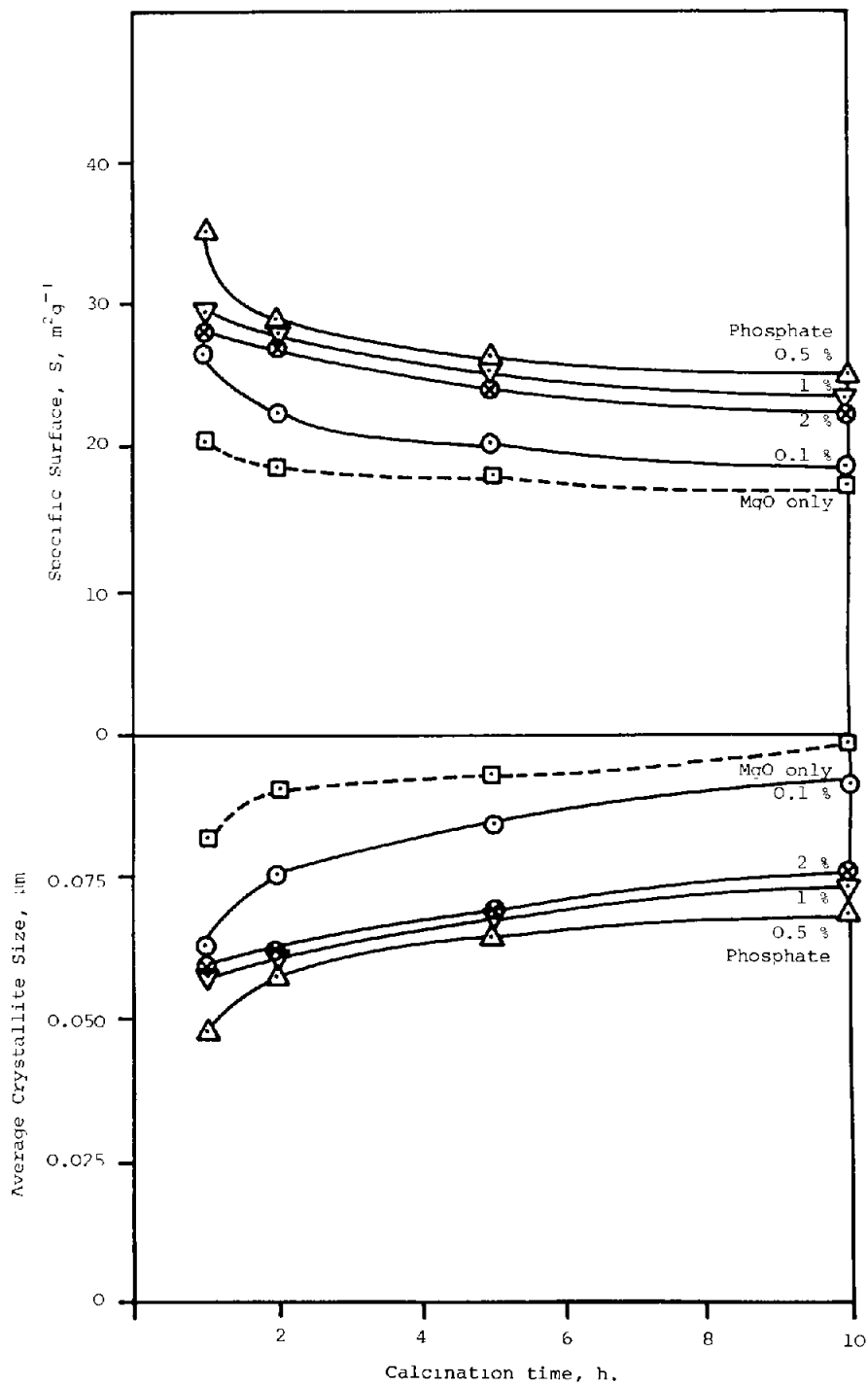


Fig. 2. Magnesium hydroxide (+H<sub>3</sub>PO<sub>4</sub>) calcined at 1000 °C in air.

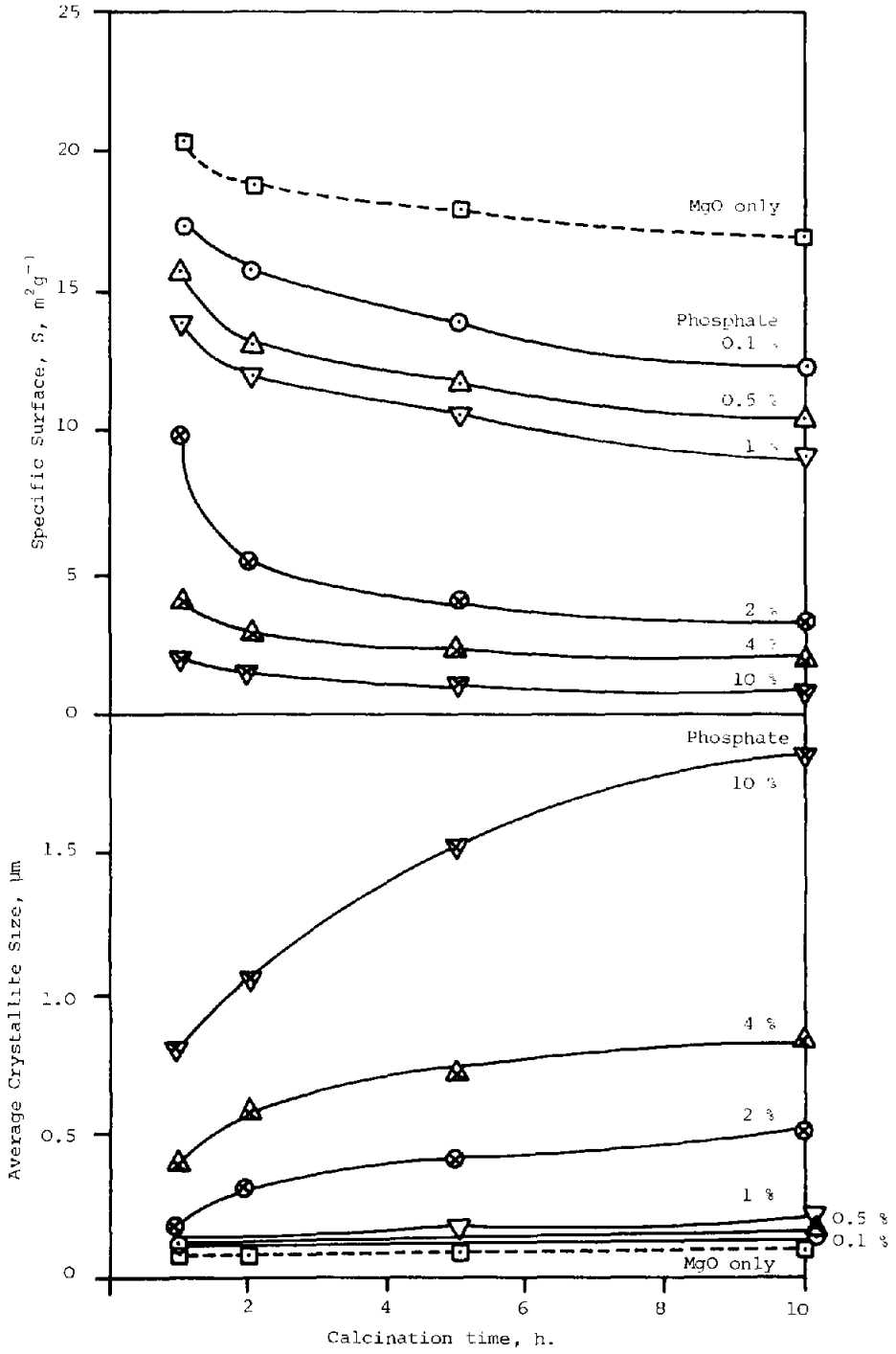


Fig. 3. Magnesium hydroxide (+NaPO<sub>3</sub>) calcined at 1000 °C in air.

$Mg_3(PO_4)_2$  and  $Ca_3(PO_4)_2$ , as the final products. Since these phosphates are high-melting, they are not very effective in promoting sintering of the magnesia and lime.

The curves in Fig. 3, 4 and 5 indicate that sodium polymetaphosphate has much more influence on the sintering of magnesia and lime. Fig. 3 shows the effect of the additive with time of sintering of magnesia at  $1000^\circ C$ , while Fig. 4 compares the effect of the additive at different temperatures for equal calcination times of 5 h. Although the limes have correspondingly smaller surface areas and larger crystallite sizes than the magnesias, their sintering is still enhanced by the sodium polymetaphosphate as shown in Fig. 5. Hence sodium polymetaphosphate considerably enhances sintering of both magnesia and lime at temperatures between  $500^\circ$  and  $1000^\circ C$ .

However, optical- and electron-microscopic observations show that at  $500^\circ C$ , the increased aggregation of the lime and magnesia crystallites is accompanied by very little crystal growth, the sodium polymetaphosphate evidently forming

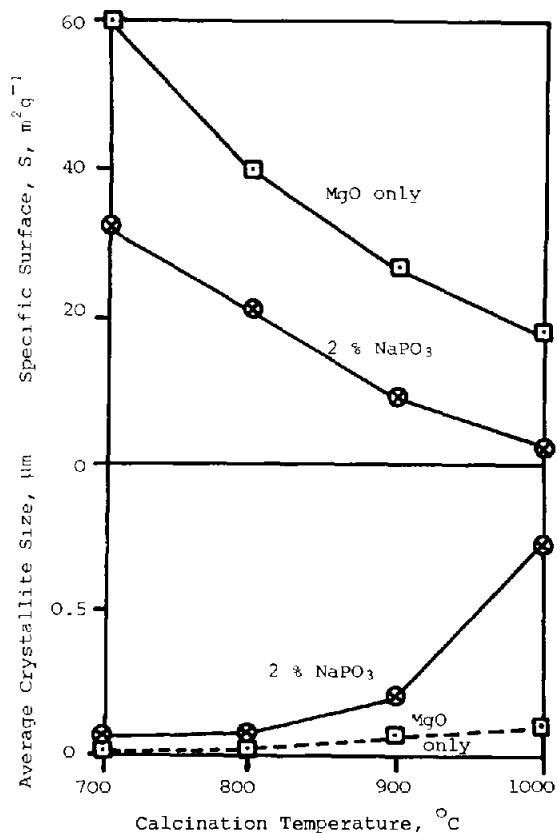


Fig. 4. Magnesium hydroxide calcined for 5 hours at different temperatures.

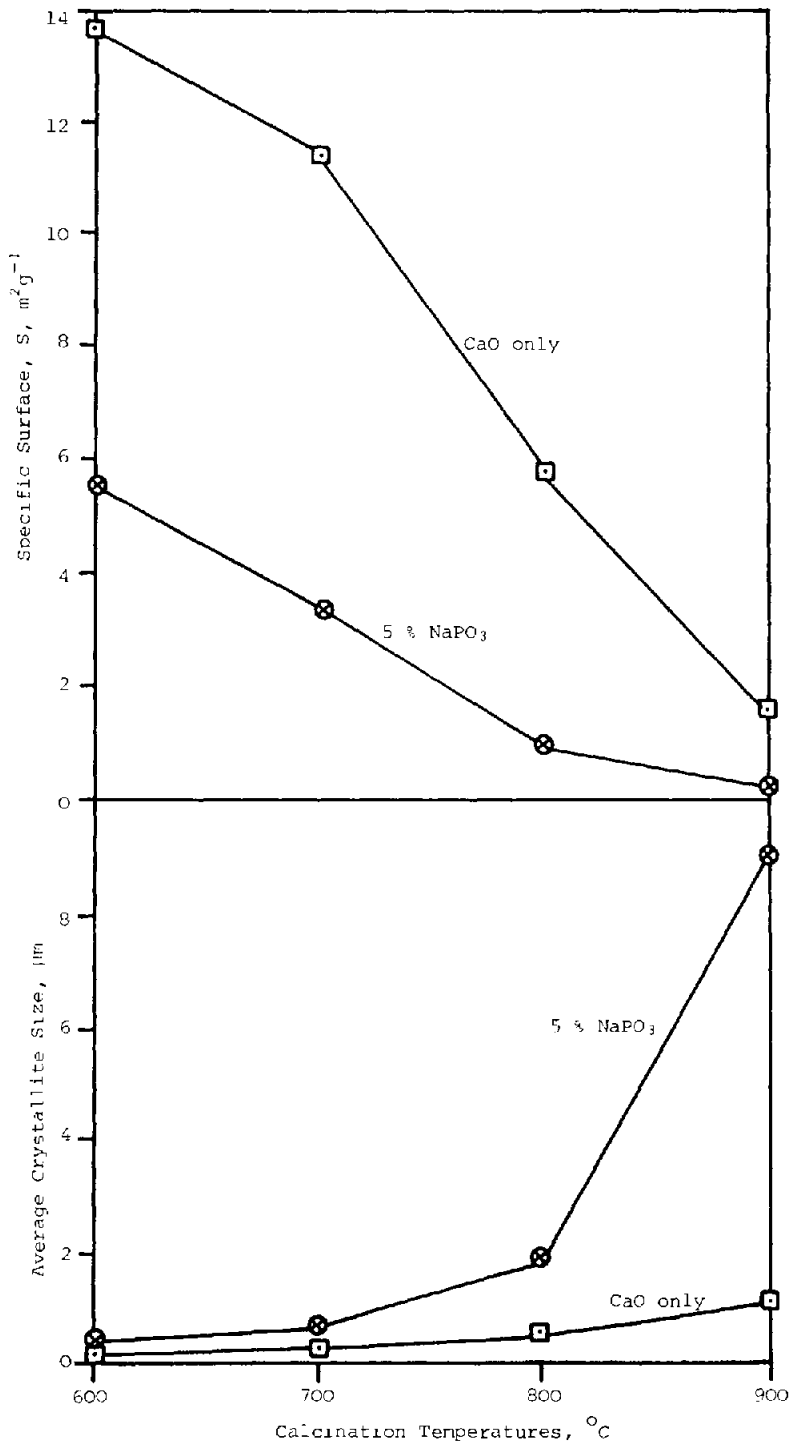


Fig. 5. Calcium hydroxide calcined for 5 hours at different temperatures



a matrix around the oxide crystallites. Extensive surface and crystal lattice diffusion of the sodium polymetaphosphate is possible, since  $500^{\circ}\text{C}$  is well above its Tammann temperature (equivalent to  $\frac{1}{2}$  m.p. in K) and indeed near to its m.p. of about  $650^{\circ}\text{C}$ . At higher temperatures, especially between  $800^{\circ}$  and  $1000^{\circ}\text{C}$ , sodium polymetaphosphate reacts chemically with lime and magnesia and becomes even more effective in enhancing sintering, since it forms lower-melting  $\text{NaCaPO}_4$  and  $\text{NaMgPO}_4$  compared with the  $\text{Ca}_3(\text{PO}_4)_2$  and  $\text{Mg}_3(\text{PO}_4)_2$  formed with the phosphoric acid additive.

#### Phosphate bonding of lime and magnesia with sodium polymetaphosphate

To understand more fully the action of the sodium polymetaphosphate additive, stoichiometric amounts of lime and magnesia were reacted with  $(\text{NaPO}_3)_x$  at  $500^{\circ}$  and  $1000^{\circ}\text{C}$  according to the equations:  $-\text{CaO} + \text{NaPO}_3 = \text{NaCaPO}_4$  and  $\text{MgO} + \text{NaPO}_3 = \text{NaMgPO}_4$ . X-ray examination showed that there was no appreciable formation of  $\text{NaCaPO}_4$  or  $\text{NaMgPO}_4$  at  $500^{\circ}\text{C}$  even after 20 h calcination, but the reactions were practically complete after 20 h at  $1000^{\circ}\text{C}$ . The  $\text{NaMgPO}_4$  is molten when formed above  $800^{\circ}\text{C}$  and crystallises from the melt on cooling. The X-ray data showed that  $\beta\text{-NaCaPO}_4$  was formed, orthorhombic with  $a = 5.20 \text{ \AA}$ ,  $b = 9.32 \text{ \AA}$  and  $c = 6.84 \text{ \AA}$  in good agreement with A.S.T.M. data. The  $\text{NaMgPO}_4$  was found also to be orthorhombic with  $a = 4.76 \text{ \AA}$ ,  $b = 11.17 \text{ \AA}$  and  $c = 5.94 \text{ \AA}$ .

The magnesia formed and sintered without additive was still quite finely-divided even when calcined at  $1000^{\circ}\text{C}$  in air for 20 h; its specific surface was about  $20 \text{ m}^2\text{g}^{-1}$  with an average crystallite size of about  $0.1 \mu\text{m}$  cf. Fig. 6(a), but the sodium magnesium phosphate crystallising from the melt had a considerably different morphology and larger crystal size, cf. Fig. 6(b). The magnesia mainly consisted of aggregates of submicron-sized crystallites, but the phosphate bonding and crystallisation led to material mainly above micron size. The crystal size of lime sintered without additive at  $1000^{\circ}\text{C}$  is already above micron size, but nevertheless the phosphate bonding with sodium polymetaphosphate considerably increases most of the crystal sizes to above  $10 \mu\text{m}$ . The effectiveness of the sodium polymetaphosphate on lime sintering at lower temperatures may be assessed from the data in Fig. 5, to calculate the multiple decreases in the number of crystallites,  $(S_2/S_1)^3$  where  $S$  and  $S_1$  are the surface areas of lime sintered with or without additive; at  $600^{\circ}$  and  $800^{\circ}\text{C}$ , the multiple decreases are 15 and 200-fold.

#### Phosphate bonding of alumina and kaolin with sodium polymetaphosphate

Optical micrographs showed little change in crystal size for  $\beta\text{-Al}_2\text{O}_3$  calcined in air for 20 h at  $1000^{\circ}\text{C}$  with or without 5 %  $\text{NaPO}_3$  additive. The size remained mainly between 20–100  $\mu\text{m}$  averaging about 70  $\mu\text{m}$ . In longer calcination (20–120 h) with 10–25 %  $\text{NaPO}_3$ , the material formed lumps of up to 10 mm size less easily

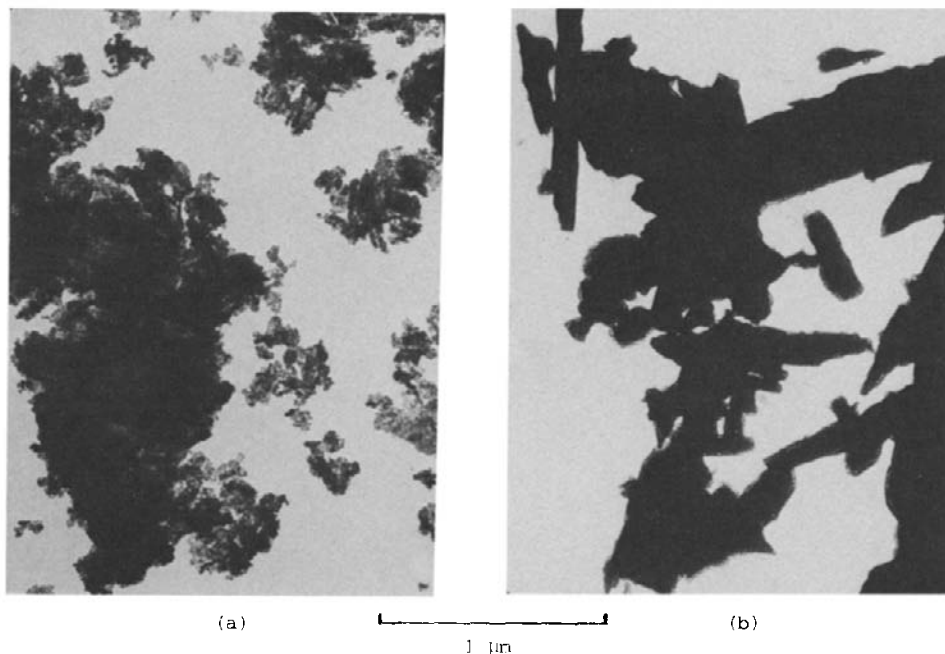


Fig. 6. Transmission electron-micrographs of (a) MgO (b) MgO + NaPO<sub>3</sub> (1:1 mol ratio) after 20 hours sintering at 1000 °C in air.

crushed when more NaPO<sub>3</sub> was present. Evidently the NaPO<sub>3</sub> was forming a matrix around the Al<sub>2</sub>O<sub>3</sub> crystals. Thus when equimolecular proportions of Al<sub>2</sub>O<sub>3</sub> and NaPO<sub>3</sub> were calcined for 20 h, practically all of the material formed one hard mass, with the surface containing small glass nodules of 4-10 μm. However, no appreciable amounts of AlPO<sub>4</sub> were shown on the X-ray traces, not even when more active γ-Al<sub>2</sub>O<sub>3</sub> was used. But when kaolin and NaPO<sub>3</sub> were calcined at 1000 °C, a glass product containing AlPO<sub>4</sub> was obtained; dehydration of the kaolinite to metakaolinite provided very active alumina and silica, so that aluminium phosphate was formed more readily to accelerate sintering.

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