Thermochimica Acta, 85 (1985) 203–206
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

PHOSPHATE BONDING OF LIME, MAGNESIA AND CLAY

D.R. GLASSON

John Graymore Chemistry Laboratories, Department of Environmental Sciences,
Plymouth Polytechnic, Plymouth PL4 8AA, Devon, England, U.K.

ABSTRACT

Formation of lime, magnesia and metakaolinite has been studied by TG and DTA of the corresponding hydroxides, carbonates and clay, alone or in the presence of sodium polymetaphosphate additive. The sintering of the products has been studied by gravimetric B.E.T. nitrogen gas sorption and X-ray techniques.

Sodium polymetaphosphate is effective in enhancing sintering of lime and magnesia at temperatures between 500-1000°C, especially above its melting point at 650°C. Sintering of metakaolinite formed from clay is accelerated by sodium polymetaphosphate only at higher temperatures of 1000-1200°C, when the additive reacts chemically to form an aluminophosphate and a silicate glass.

INTRODUCTION

In the ceramics industry, high-melting metal oxides such as lime, magnesia, purified alumina and clay are obtained generally from natural sources in finely-divided form and require sintering to give products of good mechanical strength and hardness. Sintering is promoted by use of additives (often termed mineralisers). In the metal and glass-melting industries, ceramics are needed which can be shaped cold and on heating will form dense, strong bodies with minimal shrinkage. Thus alumina powder may be bonded by a number of reaction cements, including phosphates. Earlier research on phosphate bonding (to 1977) has been reviewed by Cassidy (ref.1) and extended by the author (ref.2). Phosphoric acid and monoammonium phosphate react too quickly with basic aggregates and so alkali polyphosphates are preferred. Thus in the present research, thermoanalytical, X-ray diffraction and vacuum balance (gas sorption) techniques are applied further to study the sintering of lime, magnesia, alumina and metakaolinite in the presence of sodium polymetaphosphate additive.

EXPERIMENTAL

Preliminary TG and DTA studies showed that the calcium and magnesium hydroxides and clay decompose at temperatures below the melting point of sodium polymetaphosphate (about 650°C), whereas the carbonates decompose mainly above this temperature. Hence the hydroxides afford a wider temperature range for studying the effect of sodium polymetaphosphate on the sintering of lime and magnesia.

Samples of calcium hydroxide (I.C.I. "Limbux"), magnesium hydroxide, α- and

0040-6031/85/$03.30

γ-alumina (British Drug Houses) and kaolin (English China Clays "Supreme" grade) were intimately mixed with known amounts of sodium polymetaphosphate.

Separate portions of the materials, 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 (ref.3), using nitrogen gas sorption at -196°C recorded on a CI Microforce Mark 2B vacuum microbalance (μg to mg sensitivity using 0.25g samples or less). The adsorption isotherms also indicated any porosity present (from hysteresis) and pore size ranges. Average crystallite sizes were deduced from the specific surfaces of the less porous materials. For determining the nature of any chemical reactions between the lime, magnesia, alumina or clay and the additives, stoichiometric amounts of oxide and additive 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 and further information on their conditions of formation was obtained from TG and DTA, using a Stanton-Redcroft Thermal Analyser 781.

RESULTS AND DISCUSSION

Sintering of lime and magnesia

Earlier research (ref.2) has shown that sodium polymetaphosphate considerably enhances sintering of lime and magnesia at temperatures between 500-1000°C. The oxides did not react chemically with the sodium polymetaphosphate at 500°C, but reactions with stoichiometric amounts were practically complete after 20h at 1000°C, viz., $CaO + NaPO_3 = NaCaPO_4$ and $MgO + NaPO_3 = NaMgPO_4$. The sodium magnesium phosphate was molten above 800°C and crystallised from the melt on cooling. In the present research, TG and DTA traces (for $10^{\circ}C\ min^{-1}$ heating rates) showed that practically all of the magnesium hydroxide had decomposed to magnesium oxide below 600°C and then between 600-800°C there was sufficient reaction with the sodium polymetaphosphate to produce enough $NaMgPO_4$ for a small DTA peak at its melting point of 800°C, in accord with earlier findings.

Sintering of alumina and clay (metakaolinite)

Earlier research (ref.2) showed that α-alumina did not react appreciably or sinter with 5% sodium polymetaphosphate additive at 1000°C. Larger amounts of the additive formed a matrix around the alumina crystals. More active γ-alumina also showed no appreciable reaction, although in the present research the 5% additive somewhat enhanced sintering. Thus after 5 h calcination at 1000°C, the specific surface of the $\gamma\text{-}Al_2O_3$ decreased from 84 to 80 m^2g^{-1} without additive, but from 84 to 65 m^2g^{-1} with the additive. Calcination at higher temperatures, 1000-1200°C, causes more extensive sintering and densification as the $\gamma\text{-}Al_2O_3$

converts to α-Al_2O_3. Thus after 5h calcination at 1200°C, the product has a surface area of only 7 m^2g^{-1}. However, the presence of 5% $NaPO_3$ does not appreciably enhance sintering at this temperature, the product having an almost identical surface area. X-ray data indicates that the additive slowly reacts chemically with the alumina at 1200°C, all remaining unreacted alumina having been converted to the α-form.

Kaolinite dehydrated to metakaolinite almost completely (94.3%) in the 5 h calcination in air at 500°C. Fig.1 shows that the 5% sodium polymetaphosphate additive only appreciably enhanced the sintering of the metakaolinite above 1000°C. The nitrogen adsorption isotherms showed that the samples calcined at lower temperatures had some mesoporosity (pore size range 2-50 nm diameter) which largely disappeared at higher temperatures, becoming negligible above 1000°C.

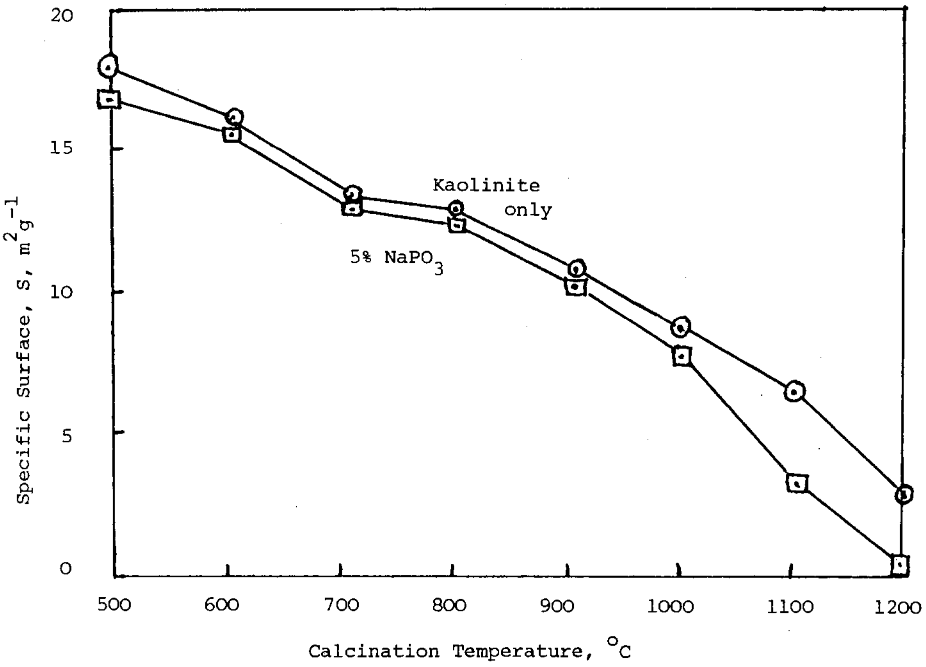

Fig.1. Kaolinite calcined for 5 hours in air at different temperatures.

The considerable effect of the additive on the sintering at the higher temperatures is further illustrated in Fig.2, showing the variations in average crystallite sizes, calculated from the surface areas.

At temperatures between 1000-1200°C, the metakaolinite (composition Al_2O_3 + $2SiO_2$) converts to sillimanite, $Al_2O_3.SiO_2$, and/or mullite, $3Al_2O_3.2SiO_2$ (ref.4)

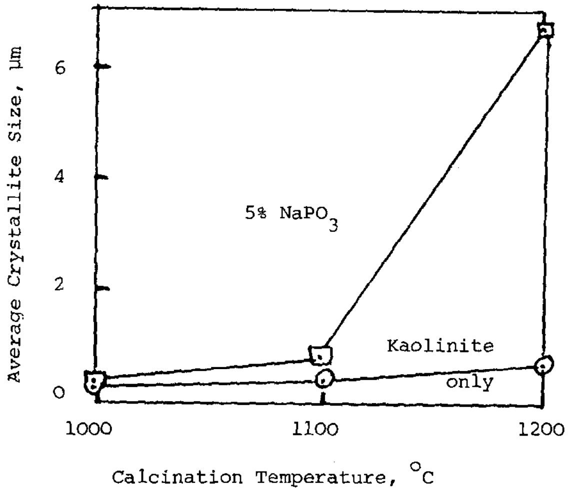

Fig.2. Kaolinite calcined for 5 hours in air at higher temperatures.

(which gives almost identical X-ray diffraction patterns) and cristobalite, SiO_2. The sodium polymetaphosphate additive evidently reacts with the alumina component of the metakaolinite, since it gives the same product as that obtained from γ-Al_2O_3 and $NaPO_3$ at 1200°C. The presence of the silica makes the clay product more glass-like in appearance and this evidently contributes to the greater effectiveness of the sodium polymetaphosphate in enhancing sintering.

ACKNOWLEDGMENTS

The author thanks Mr. K. Adams and Mr. P. Davis for their assistance in the thermoanalytical and X-ray testing of materials, also Imperial Chemical Industries and the Science and Engineering Research Council for sponsorship.

REFERENCES

1 J.E. Cassidy, Amer. ceram. Soc. Bull., 56 (1977) 640-643.
2 D.R. Glasson, Thermochim. Acta, (1984), in press.
3 D.R. Glasson, J. chem. Soc., 1956, pp. 1506-1510.
4 D.R. Glasson, "Analysis of Calcareous Materials", Society of Chemical Industry, London, 1964, Monograph No. 18, pp. 401-406.