Thermochimica Acta, 51 (1981) 297–306
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

THERMAL INVESTIGATION ON ELECTROSTATIC PRECIPITATOR KILN DUST *

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(Received 20 May 1981)

ABSTRACT

The electrostatic precipitator dust collected from a cement kiln was studied as received from the factory and when fired between 1000 and 1250°C. Two calcines (70:30 and 50:50) were prepared by blending the raw dust and kaolin, fired between 1000 and 1250°C, and the resulting phases were also studied. These investigations were undertaken by chemical analysis, DTA and X-ray diffractometry, as well as weight losses.

The results revealed that the dust consists of dolomitic limestone, minor amounts of alkalies and quartz, together with $2\,C_2S{\cdot}CaCO_3$ and $2\,C_2S{\cdot}CaSO_4$. The dissociation of these phases occurred at 1000°C while volatilization of alkalies occurred at ≥ 1200°C.

The 70:30 (dust:kaolin) calcine is found to be more suitable, being composed mainly of gehlnite, while the other calcine is mainly composed of β-dicalcium silicate. The appropriate calcination temperature was 1150°C for 2 h, as negligible variations in phase composition could be detected above this temperature.

INTRODUCTION

The utilization of by-products, from the various sectors of industry, is a present-day concern involving the problem of energy and sometimes even ecology. Cement plants generate solid waste air pollutants, and water pollutants during the course of their operation. The cement kiln exhaust gas contains substantial quantities of particulate matter and constitutes the largest source of air pollution in the plant. The solid waste problems generally arise from the disposal of kiln dust (a mixture of finely divided raw feed, partly calcined raw feed, cement clinker and condensed volatile salts) [1].

Particulate emissions from a cement plant arise from one of the following sources: (a) quarrying and crushing, (b) mixing and grinding, (c) clinker production in the

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* Cement notations are used in this work: CaO = C; Al_2O_3 = A; SiO_2 = S; Fe_2O_3 = F.

0040-6031/81/0000–0000/$ 02.75

rotary kiln, and (d) finish grinding, packing and shipping. The cement industry usually uses mechanical collectors, electrostatic precipitators, filter baghouse collectors, or combinations thereof to control the particulate [2]. The types of collectors used depend on the emissions and the temperatures of the effluents of the unit operation. In fact, approximately 12% of the kiln feed exits from the kiln with the gas (upstream of any air pollution control equipment). Throughout the industry, roughly 73% of the kiln dust is recycled to the cement-making process [3,4].

Dust emissions from all 95 plants in the German Federal Republic in 1967 was $\sim 0.15\%$ of the total clinker production [5]. The dry method of cement production results in dust three times more than the wet process. The present general production of cement in Egypt is by the wet process. Nevertheless, the on-going shift, in our cement industry, to the dry method is expected to increase the accumulated dust. Generally, the dust that is not recycled has excessive concentrations of alkali oxides and sulphates that may prevent the final product from meeting standard specifications.

Previous investigators reported the utilization of alkaline wastes collected from the electrostatic filters in cement kilns to produce porcelaneous objects [6–8]. Because the high calcium oxide content of the dust together with the considerable quantity of iron oxide and sodium and potassium oxides have powerful fluxing effects, it would be profitable to assess its possible use as a component of porcelain. It is supposed that if these oxides are in the form of complex silicate minerals or glasses, they would behave differently from the addition of the corresponding free oxide in porcelain.

The objective of this study is to investigate the thermal behaviour of this kiln dust at temperatures between 1000 and 1250°C. The possible use of this dust to prepare calcines for its use in porcelain is to be verified.

EXPERIMENTAL

The dust used in this study was collected from the electrostatic precipitator of Portland Cement Company, Alexandria, Egypt. Representative samples of the dust were collected weekly for a period of 2 months and were blended to offer the raw dust. The particle size distribution of this sample is as follows: $92.04\% < 71\ \mu m$, 6.20% between 107 and 71 μm, and $1.84\% > 107\ \mu m$. Table 1 shows the chemical analysis of the raw dust.

The mineral composition of the dust as received from the kiln was studied using a differential thermal analyzer (with a heating rate of $10°C\ min^{-1}$ between 25 and 1000°C) and a Siemens X-ray diffractometer D-5000 (using CuK_α radiation and a scanning speed of $2\theta = 2°C\ min^{-1}$). Weight losses in the range 1000–1250°C were performed on separate specimens by heating in a platinum crucible in an electric furnace.

To follow the effect of firing temperature on the phase composition of the ignited dust, it was wet mixed in a porcelain ball mill as a slurry. After drying, the paste was

TABLE 1

Chemical analysis of the raw dust

Oxide	%	Oxide	%
SiO_2	12.03	MgO	4.22
Al_2O_3	1.41	K_2O	8.05
Fe_2O_3	2.54	Na_2O	4.13
CaO	35.02	SO_3	2.96
		I.L.	30.8

made into pellets of ~ 10–20 mm and burned in a platinum crucible and kept for 1 h at each firing temperature. The specimens were cooled slowly in the furnace and ground to pass 63 μm ready for X-ray powder analysis. The free CaO was determined in the raw dust and its ignited samples using Franke's method [9]. Traces of CaO were found in the samples.

Two batches were prepared from blending the dust and Kalabsha kaolin (Aswan) in the ratios 70/30 and 50/50 parts by weight to produce the calcines. The batches were moulded into discs (4 cm $\phi \times 2$ cm thickness) at 1 kN cm^{-2}. The discs were fired at different temperatures between 1050 and 1250°C in an electric furnace, with 2 h soaking at each top temperature. The phase compositions were subsequently followed by X-ray analysis to choose the appropriate calcine mix and its suitable firing temperature.

RESULTS AND DISCUSSION

The differential thermogram of the raw dust as illustrated in Fig. 1 shows two exothermic effects and also five endothermic peaks. The exothermic peak temperatures are at about 520 and 605°C. The first effect may be attributed to the presence of sulphides and iron oxide, while the second is due to the polymorphous transformation of dicalcium silicate. The slight broad endothermic peak at 570°C is due to the α–β quartz transformation [10]. The sharp endothermic peak at 810°C is attributed to the calcination of calcium carbonate. The other two endothermic effects at 645 and 850°C are related to the presence of alkali sulphate or earth alkali sulphate as $K_2MgCa_2(SO_4)_4$. The lower effect is due to the polymorphous transformation, while the higher peak is attributed to the melting of this sulphate [11]. The endothermic effects at 710 and 850°C are attributed to the presence of montmorillonitic clay mineral [12]. The endothermic peak at 710°C could also be due to the dissociation of dolomite. The thermogram does not show any effects in the lower range which is due to the high temperature of the kiln during the clinker production and to the negligible amounts of free CaO where its presence may cause moisture absorption.

The X-ray diffractogram of the dust (Fig. 2) indicates that the dust consists of limestone as a main component. Minor amounts of quartz are detected together with

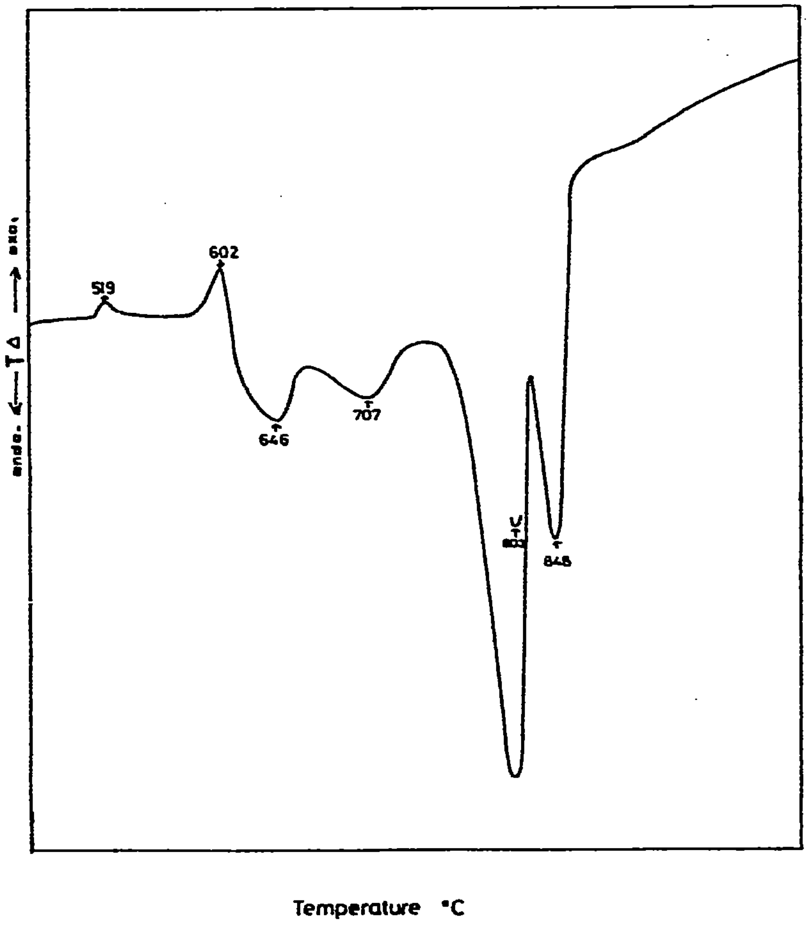

Fig. 1. DTA thermograms of raw kiln dust.

$CaSO_4$, KCl, NaCl, K_2SO_4, $2\,C_2S \cdot CaSO_4$ and $2\,C_2S \cdot CaCO_3$. The actual mechanism of sulphate formation is complicated; however, the following reactions are possible

$Na_2O + SO_3 \rightarrow Na_2SO_4$

$K_2O + SO_3 \rightarrow K_2SO_4$

$CaO + SO_3 \rightarrow CaSO_4$

During the clinker manufacture, SO_3 produced from the oxidation of sulphur in the raw materials and the fuels burned in the kiln combines with the alkali or alkaline earth oxides to produce sulphates. When the concentrations of the alkalies are low, SO_3 reacts with lime or $CaCO_3$ to form $CaSO_4$ [13]. Some 80–90% of the sulphur present in fuels could be accounted for the clinker by such a process [14].

From the results of chemical, X-ray and differential thermal analyses, it was concluded that the dust consists of dolomitic limestone with some alkalies which are more volatile and quartz. Some calcined phases such as $2\,C_2S \cdot CaCO_3$ and $2\,C_2S \cdot CaSO_4$ are also found.

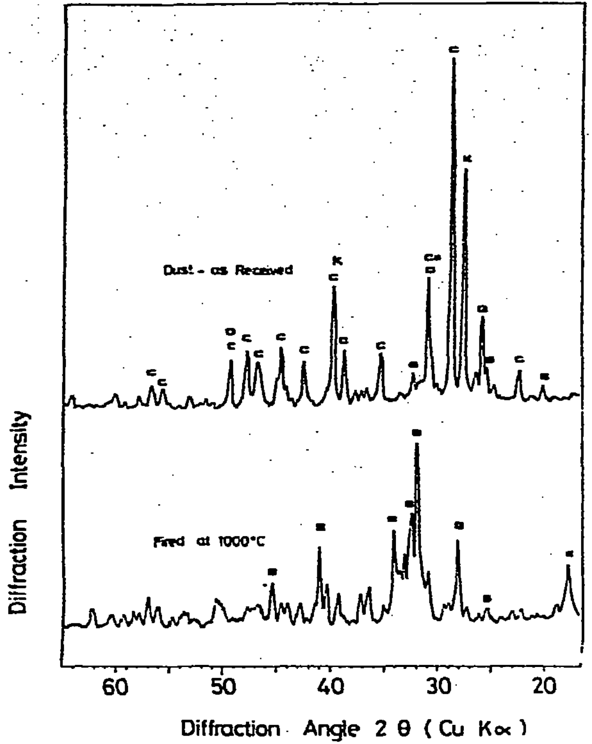

Fig. 2. XRD pattern of raw dust and when fired at 1000°C. β=β-C_2S; C=calcite; D=dolomite; Ca=$CaSO_4$; S=spurrite; Q=quartz; K=KCl; E=$C_{12}A_7$.

The X-ray patterns of the dust fired at temperatures between 1100 and 1250°C are shown in Fig. 3. On firing at 1000°C (Fig. 2), β-C_2S is detected as the main component with small amounts of $CaSO_4$, $C_{12}A_7$, C_4AF, NaCl, KCl, Na_2SO_4, K_2SO_4, $2\,C_2S \cdot CaCO_3$ and $2\,C_2S \cdot CaSO_4$, denoting small differences from the original dust received. Samples fired at 1100°C contain the same phases, either $2(C_2S) \cdot CaCO_3$(spurrite) which is characterized by a greater thermal stability than $CaCO_3$ [15]. Such stability is due to the substitution of the dissociable groups into the stable lattice. On increasing the firing temperature, a negligible difference in the patterns could be observed up to 1250°C. Alite (C_3S) could not be detected in the ignited samples. This is due to the lower Ca/Si ratio of the dust and also the presence of alkalies and gypsum which are known to retard its formation [16].

The present results coincide with the previous study [17] which indicated that by firing the raw meal containing high alkalies, compounds of $K_3Na(SO_4)_2$, $CaSO_4$, $C_{12}A_7$, $2\,C_2S \cdot CaCO_3$, $2\,C_2S \cdot CaSO_4$, β-C_2S and a very small amount of free CaO were detected by X-ray analysis.

Table 2 shows the weight loss values accompanying the phase changes, detected by X-ray analysis, during firing between 1000 and 1250°C. The dissociation of the spurrite phase and volatilization of CO_2 lead to the increase of the loss at 1100°C more than the value obtained at 1000°C. Values obtained at 1000°C are attributed mainly to the carbonates, while those at higher temperature are due to the spurrite

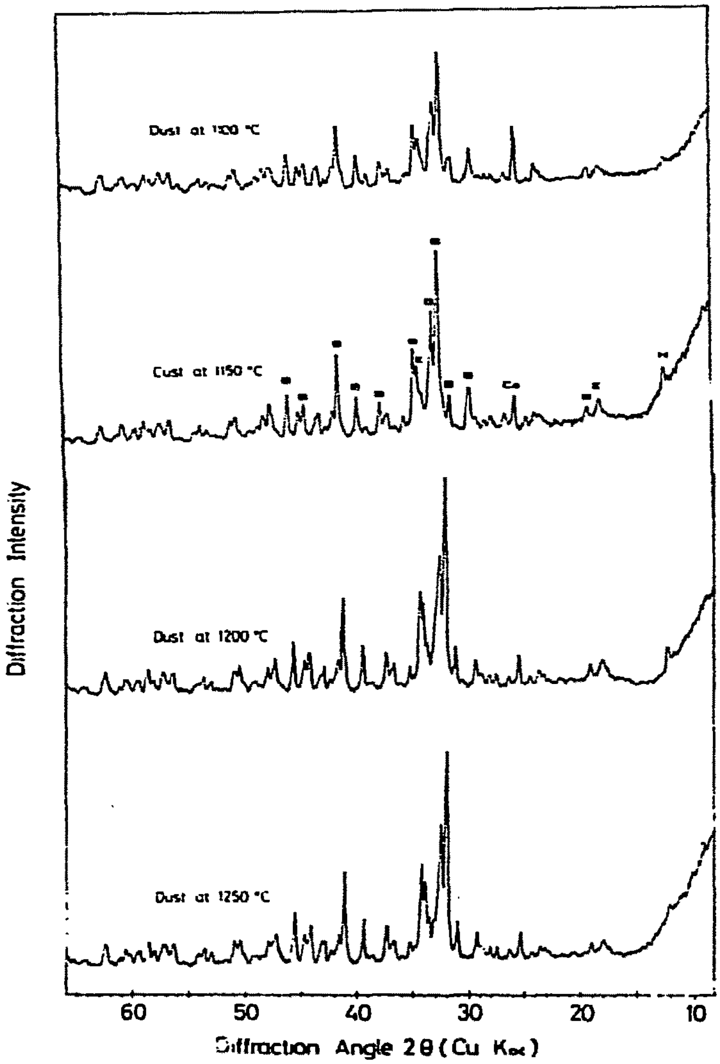

Fig. 3. XRD pattern of fired dust at different temperatures (1100–1250°C). β=β-C_2S; Ca=$CaSO_4$; E=$C_{12}A_7$; H=C_4AF.

TABLE 2

Weight loss of the dust at various temperatures

Temperature (°C)	Weight loss (%)
1000	30.07
1100	39.60
1150	40.03
1200	40.35
1250	43.13

since its dissociation is known to occur at a higher temperature than the $CaCO_3$ itself [15]. The higher value obtained at 1250°C is attributed to the volatilization of the alkalies and the dissociation of $2\,C_2S \cdot CaSO_4$ [18]. The samples were fused when fired at temperatures $> 1250°C$, producing a glassy phase with holes, denoting sublimation.

Consequently, based upon the above results two calcines having the chemical composition given in Table 3 were prepared. These oxide percents were computed from the chemical analysis of the dust (Table 1) and that of the Kalabsha Kaolin *. When the calcines were fired at 1250°C signs of expansion and high porosity were observed especially for calcine 73 containing the higher alkali content. Therefore the chosen calcine should be fired below this temperature.

The unexpected white colour is more obviously observed at 1150°C in calcine 73 although the dust has a greyish colour and the kaolin is creamy grey. This could be attributed to the formation of the calcium-rich phases such as gehlenite and calcium aluminate. The XRD traces of the two calcines when fired at 1000°C are shown in Fig. 4 where the numerical notations are identical with Table 3. Depending on the ratios of the dust/kaolin, individual differences appeared in the mineral compositions. Calcine 73 shows wollastonite β-($CaO \cdot SiO_2$) as the main phase along with gehlenite (C_2AS) and also some calcium aluminate ($C_{12}A_7$). Calcine 55 with higher kaolin content shows β-C_2S as the main phase together with other phases of $C_{12}A_7$ and C_2AS but all phases are of lower intensity compared with that of calcine 73. The study proceeded with calcine 73 as the other calcine is composed mainly of β-C_2S. This phase is not useful in porcelain production.

Firing calcine 73 produced gehlenite as the main phase and minor amounts of anorthite. The calcium aluminate phase disappeared. The XRD traces of calcine 73 fired at 1150°C are presented in Fig. 4.

The phase formation of the CaO and Al_2O_3 and/or SiO_2 might have proceeded through the formation of C_2AS and β-C_2S. The gehlenite was detected at 1000°C, in calcine 73, and at higher temperatures it increases at the cost of β-CS and $C_{12}A_7$. The present results are in agreement with the work of Schwiete and Hechler [19] which indicated the formation of β-C_2S and C_2AS in $CaCO_3$: clay mixes at temperatures as low as 900°C. In the case of calcine 55, the results indicate that the β-C_2S formation proceeded directly without intermediates, in agreement with the work of Mackenzie and Hadipour [20].

From the calculated chemical composition of the two calcines (Table 3), the CaO/SiO_2 mole ratio and the CaO/Al_2O_3 mole ratio are 1.17 and 4.05, respectively, for calcine 73, and 0.8 and 1.96 for calcine 55. It is clear that the CaO/Al_2O_3 ratio is 2:1 for the 73 and 55 calcines. Therefore, the condition for the gehlenite and wollastonite formation is more suitable in the first calcine. On the other hand, formation of β-C_2S is more probable in calcine 55. Calcine 73 shows more gehlenite and some anorthite at the expense of β-CS and $C_{12}A_7$ at temperatures higher than 1000°C.

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* Report III Electrical Insulators, N.R.C., Cairo, 1977.

TABLE 3

Calculated chemical constitution of the prepared calcines

Cal-cine	Dust/ kaolin	Oxide (%)								
		SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	SO_3
73	70/30	27.12	14.44	3.66	0.30	35.03	4.18	4.29	8.02	2.95
55	50/50	33.85	23.20	3.21	0.51	25.18	2.99	3.22	5.73	2.11

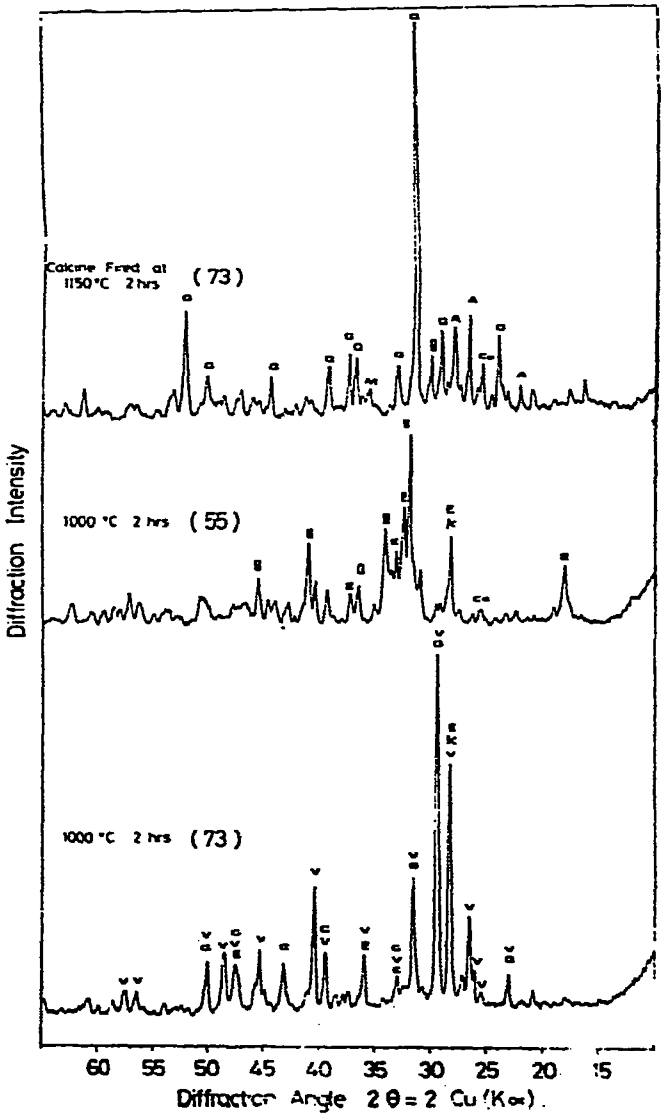

Fig. 4. XRD pattern of two calcines (73 and 55) fired at 1000°C and calcine 73 at 1150°C. A=Anorthite β=β-C_2S; Ca=$CaSO_4$; E=$C_{12}A_7$; G=gehlenite, K=KCl: V=CS; C=calcite.

CONCLUSIONS

From the results obtained it can be concluded that:

(1) The electrostatic precipitator dust consists of dolomitic limestone with some alkalies, quartz and a few calcined phases such as $2(C_2S)\cdot CaSO_4$ and $2(C_2S)\cdot CaCO_3$;

(2) On firing the dust at 1000°C, β-C_2S is formed as the main phase along with alkaline sulphates as well as $C_{12}A_7$ and C_4AF;

(3) At higher firing temperature (1100°C), spurrite $2(C_2S)\cdot CaCO_3$ is decomposed while other phases are still present. At 1250°C, the $2(C_2S)\cdot CaSO_4$ is decomposed also with some dissociation of $CaSO_4$. These reactions are identical with the weight loss values;

(4) On firing at 1000°C, the main phases formed in calcine 73 are gehlenite and wollastonite whereas the other calcine 55 has β-dicalcium silicate as the main component. On firing at 1150°C, calcine 73 is composed mostly of gehlenite;

(5) When the C/A ratio is > 4, gehlenite and wollastonite are formed while when the ratio is < 2 β-dicalcium silicate is formed. The results indicate the possibility of using calcine 73 in porcelain mixes. The other calcine with a lower dust content and having β-C_2S as the main phase is not advisable due to the cementing and hydraulic nature of this compound.

ACKNOWLEDGEMENT

Thanks are due to the N.R.C. for providing the facilities for performing the present investigation with financial support of the project Ceramic Articles from Industrial Wastes, 6/9/2/80 Industry.

REFERENCES

1 K.E. Daugherty and A.O. Wist, Bull. Am. Ceram. Soc., 54 (1975) 189.
2 R. Kester, Proc. Electrostatic Precipitator Symp., Birmingham, Al, Div. Process Control Energy, EPA, Durham, 1971.
3 T.A. Davis and D.B. Hooks, EPA-670/2-75-043, U.S. Environmental Protection Agency, Cincinnati, OH, 1971, p. 720.
4 R.F. Smith, J.E. Levin and A.T. Kearney, EPA-670/2-75-043, U.S. Environmental Protection Agency, Cincinnati, OH, 1979, p. 44.
5 W. Koehler and G. Franke, Proc. 2nd Int. Clean Air Congr., 1971, p. 720.
6 I.A. Bulavin, Stroit. Mater., Silikat. Prom., 9(2) (1968) 9; Chem. Abstr., 69, 5 (1968) 38431 d.
7 P.P. Budnikov, I.A. Bulavin and A.F. Belkov, Steklo Keram., 22(1) (1965) 22; Am. Ceram. Soc., Abstr., 6 (1967) 82i.
8 A.F. Belkov, Tr., Mosk. Inst. Nar. Khoz., 46(1968) 138; Chem. Abstr., 71, 6 (1969) 53063 V.
9 B. Franke, Z. Anorg. Allg. Chem., 247 (1941) 180.
10 D.N. Todor, Thermal Analysis of Minerals, Abacus Press, Tunbridge Wells, Kent, 1976, p. 103.
11 V.P. Ivanova, Zap. Ross. Mineral. Ova., 90 (1961) 50.

12 J. Lucas and N. Tranth, Bull. Serv. Carte Geol. Alsace Lorraine, 18 (1965) 4.

13 R. Plass and H. Haaland, Electrostatic Precipitation Seminar, Pennsylvania University, University Park., 1957.

14 S. Seigbert, Tonind. Ztg., 89 (1965) 124.

15 H. Scholze and U. Hildebrandt, Zem.-Kalk-Grips, 23 (1970) 573.

16 N.H. Christensen and V. Johansen, J. Am. Ceram. Soc., 62 (1979) 313.

17 W. Danowski and J. Kieser, Proc. 6th Conf. Silicate Ind., Budapest, Siliconf., 1963, p. 289.

18 P.E. Halstead and A.E. Moore, J. Appl. Chem., 12 (1962) 413.

19 H.E. Schwiete and R.W. Hechler, Proc. 8th Conf. Silicate Ind., Budapest, Siliconf., 1965, p. 93.

20 K.J.D. Mackenzie and N. Hadipour, Trans. Br. Ceram. Soc., 77 (1978) 168.