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THERMOGRAVIMETRIC AND X-RAY POWDER DIFFRACTION ANALYSIS OF PRECIPITATOR DUST FROM A ROTATING LIME KILN

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ABSTRACT

Precipitator dust was sampled from kilns six and seven of the Lime Acres plant, South Africa, and a mixture analysed for its chemical composition. It mainly consists of Si, Al and Ca compounds, with some Mg compounds also present. The phases were determined to be mainly calcite, with some portlandite, lime, $CaSO_4$ anhydrite, mullite and a small amount of carbon. Minute amounts of dolomite and magnesian calcite were also observed. Thermogravimetric analysis of the dust indicated a mass loss of between 2 and 3.5 % when heated to 600 °C with a further loss of 26 to 29 % when heated to 800 °C using a heating rate of 5 $°C.min^{-1}$. Upon treatment with water only a few percent of the available lime reacts with water to form $Ca(OH)_2$, while some $CaSO_4$ hemi- and di-hydrate also seem to form. Water treatment of precipitator dust has been shown to be ineffective because of the high percentage of lime that still remains in the product. The disposal of the water treated precipitator dust would therefore not satisfy environmental requirements.

Introduction

The Lime Acres plant, which produces most of the lime consumed in South Africa, is situated about 180 km west of Kimberley in the Northern Cape. During burning of the limestone in the kilns, a considerable amount of dust is generated. After collection in electrostatic precipitators behind the kilns, the dust is dumped on a waste heap. The disposal of this dust is complicated by its high content of free or "available" lime. This is not an environmentally favourable situation.

An environmental solution can be achieved by hydrating and subsequently utilising this hydrated precipitator dust as a landfilling material. This option, however requires a detailed investigation of the hydration behaviour of the precipitator dust, especially in view of the high lime content in the waste. The water demand, as well as kinetics of the hydration reaction requires investigation.

It was therefore decided to conduct a preliminary investigation into the hydration behaviour of a mixture of the precipitator dust, collected from kilns six and seven at the Lime Acres plant. The first aim of this study was to determine the chemical composition of the mixture of precipitator dust. Thermogravimetry and X-ray diffractometry were employed to determine the reactions and phase changes of precipitator dust upon heating to 1000 °C and subsequent water treatment.

Experimental

Sample Preparation. Excessive amounts of water were added to precipitator dust in porcelain crucibles. After 24 hours the wet samples were placed in a Term-o-mat drying oven at 75 °C for 24 hours to dry. All samples were then stored in a desiccator to prevent moisture uptake from the air.

Chemical Composition. The precipitator dust was dried and ground to a fineness of approximately 30 µm. The samples were analysed for their chemical composition using a Siemens MRS400 X-ray fluorescence (XRF) spectrometer. Table I contains the results of the XRF analysis.

Carbon was determined as 1.93 % by a method described in the literature (1). A LOI (Loss on ignition) value of 28.9 % was determined by recording the mass of a sample before and after heating at 1000 °C for one hour. In the lime industry, the CaO content is determined as the

TABLE I
Chemical Composition of Precipitator Dust as determined by XRF Analysis
(on a loss free basis)

Composition	Percentage
SiO_2	15.4
Al_2O_3	6.0
Fe_2O_3	.8
Mn_2O_3	.5
TiO_2	.4
CaO	43.9
MgO	1.7
P_2O_5	.4
SO_3	1.9
Cl	0
K_2O	.2
Na_2O	.3
CO_2	28.9
TOTAL	100.4

"available lime content" according to the standard ASTM method (2). The available lime content of the precipitator dust is 14.39 %.

X-ray Powder Diffraction Analysis. X-ray powder analysis was done on the precipitator dust, heat-treated precipirator dust and water-treated precipitator dust. The water treatment procedure is described in the sample preparation section. The heat treated precipitator dust samples were prepared by igniting at 500 and 1000 °C for two hours in a Carbolite furnace. The samples were then packed into standard plastic sample holders.

A Siemens D5000 X-ray diffractometer was used to acquire the data. Cu K_α-radiation was used in conjuction with a graphite diffracted-beam monochromator. Data were collected in the range $4° < 2\Theta < 80°$, with the divergence slit variable with 2Θ so that the irradiated area was constant at 20 mm^2. The receiving slit was 2 mm. DIFFRAC-AT software (V3.2 SOCABIM©, SIEMENS©, 1993) was employed to treat the data. The main quartz peak was used for displacement corrections.

Thermogravimetric and Calorimetric Analysis. A NETZSCH STA 409 Simultaneous TG/DSC instrument was used to collect thermogravimetric and calorimetric data. Nitrogen was employed as a dynamic atmosphere (flow rate ≈ 20 $cm^3.min^{-1}$) and platinum pans were used. Temperature and enthalpy calibrations were achieved using the ICTAC recommended DTA standards. Sample masses varied between 30 and 40 mg. Although samples were ground and mixed before analysis, some differences in the data were observed due to the inhomogeneity of the samples.

Results and Discussion

XRD Measurements. The major phase in the precipitator dust is identified as calcite, $CaCO_3$ (Figure I). The two most intense peaks are clearly seen for quartz, SiO_2, but not so clearly for portlandite, $Ca(OH)_2$, and lime, CaO. $CaSO_4$ anhydrite and mullite, $Al_6Si_2O_{13}$, are easily identified. The presence of carbon is only identified as a small intensity hump in the XRD pattern. Upon closer investigation on a background-subtracted and smoothed XRD pattern, the main peak for dolomite, $CaMg(CO_3)_2$, was observed together with minute peaks for magnesian calcite, $(Ca_{1-x}Mg_x)CO_3$, $x < 0.5$ (Figure II). The XRD pattern for the precipitator dust, after heat treatment at 500 °C, is also given in figure I.

The comparison between the patterns for precipitator dust and that heated at 500 °C is given in figure III. After the precipitator dust had been ignited at 500 °C, the composition remains essentially unchanged, except for portlandite which appears to have decomposed completely:

$$Ca(OH)_2\,(s) \rightarrow CaO\,(s) + H_2O\,(g)$$

The calcite peaks for the sample heated at 500 °C are consistently less intense than those for the untreated precipitator dust, which would suggest some decomposition of the calcite having taken place. An increase in the main $CaSO_4$ anhydrite peak is observed, which can be expected when such phases as gypsum and hemihydrate dehydrate. Both these phases are however not detected in the untreated precipitator dust. The reason lies most likely in their being present in trace quantities or possibly that they are amorphous.

After heat treatment of the precipitator dust at 1000 °C, the calcite has decomposed completely to CaO, which is the major phase for these samples. The presence of a considerable

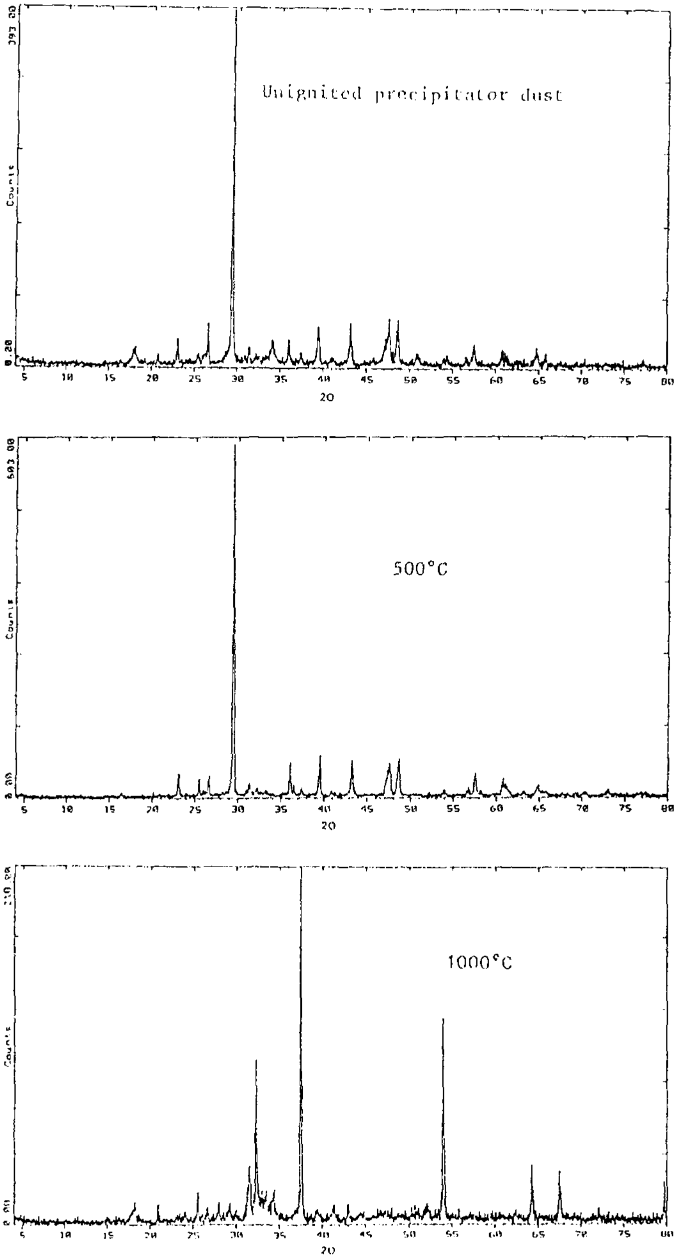

FIG. I.
XRD patterns of unignited precipitator dust, that ignited at 500°C and at 1000°C.

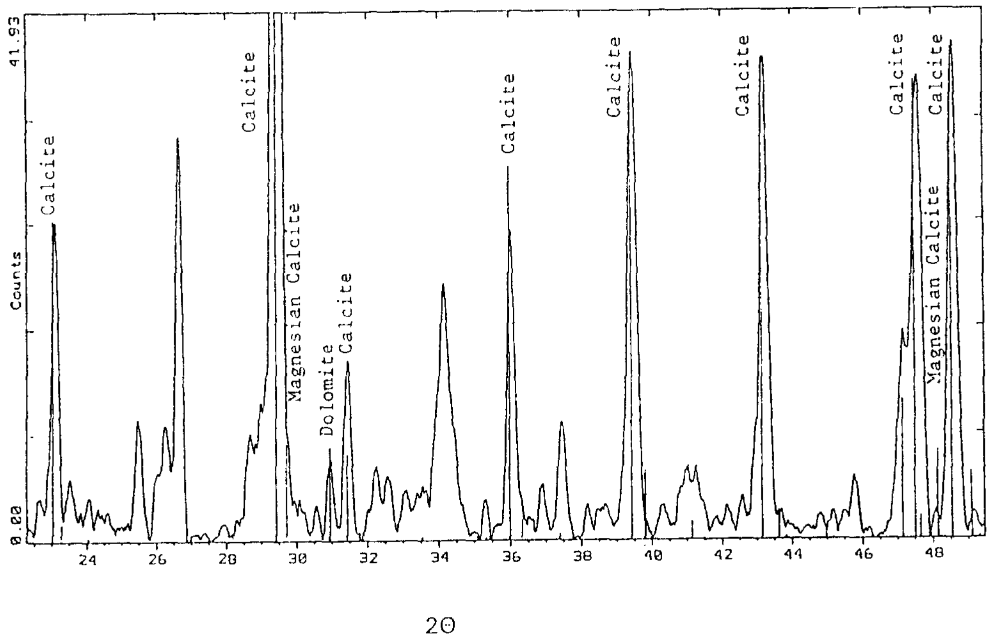

FIG. II.

Background-subtrated and smoothed XRD pattern of precipitator dust to show peaks for dolomite and magnesian calcite.

amount of lime in the sample complicates phase analysis. The sample expands upon X-radiation because the lime reacts with atmospheric moisture to form portlandite. This expansion results in movement of the particles contained in the sample and causes drift in the diffracted beam of X-rays for a particular reflection. This results in broad d-spacings.

After heat treatment at 1000 °C, mullite ($3Al_2O_3.2SiO_2$) has decomposed and reacts with CaO and two phases are observed: the major cement phase, C_2S ($2CaO.SiO_2$), and gehlenite ($2CaO.Al_2O_3.SiO_2$) (Figure I). The remaining Al_2O_3 reacts with CaO to form mayenite ($12CaO.7Al_2O_3$), also a cement mineral, presumably in the absence of reactive SiO_2. The three peaks for periclase, MgO, are clearly established. The MgO does not appear to react with CaO, Al_2O_3 and SiO_2.

For the samples that were treated with water, irregularities were observed in the intensities of phases such as quartz, which were not expected to change. These irregularities can be ascribed to the change in sample mass (and therefore a change in concentration) due to hydration. The main changes that are expected to be observed would be the hydration of lime to form portlandite and the hydration of anhydrite to form hemihydrate ($CaSO_4.\frac{1}{2}H_2O$) and gypsum ($CaSO_4.2H_2O$). The intensities for the $CaSO_4$ anhydrite and lime peaks are lower in the water treated samples.

The main peak intensity for anhydrite is reduced for the precipitator dust that had been ignited at 500 °C, after being treated with water. This can be ascribed to the hydration of anhydrite to form hemihydrate and gypsum. This hydration reaction cannot however be expected

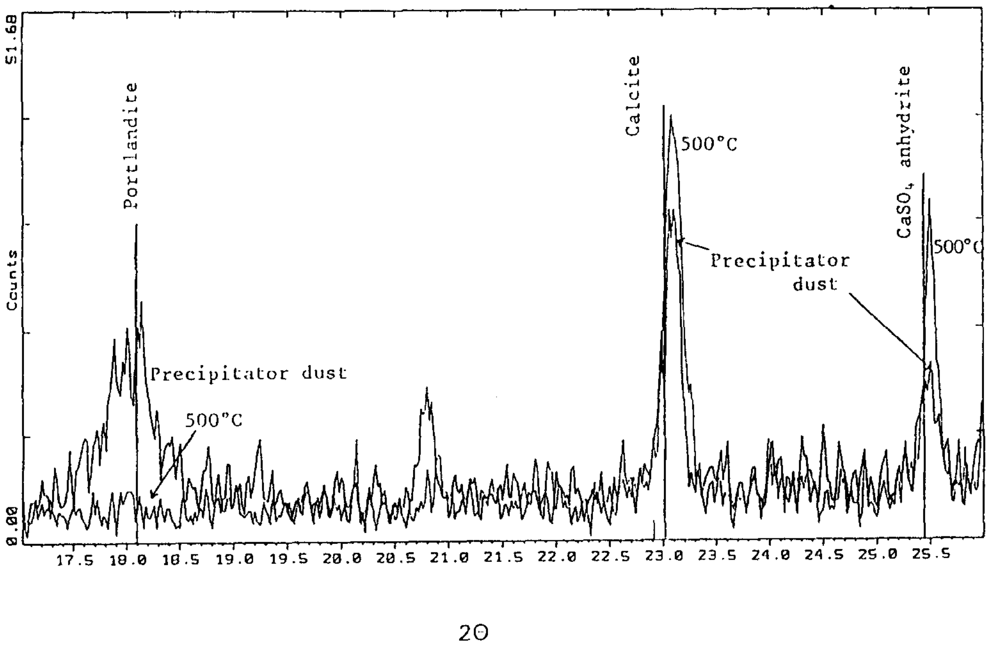

FIG. III.
Comparison between the XRD patterns for precipitator dust and precipitator dust heated to 500°C.

to be effective, because any soluble tetragonal anhydrite that may be present in the precipitator dust is at least partially rendered to the orthorhombic insoluble form (3). Insoluble anhydrite is formed from soluble anhydrites or the hydrates of $CaSO_4$ at about 900 °C. Conversion is noticeable at lower temperatures, but the rate decreases considerably (3). This is confirmed by the observation that anhydrite appears to be more hydrated in the unignited samples.

The main peak for C_2S in the precipitator dust that is ignited at 1000 °C, is reduced in intensity in the water treated samples. The cementitious C_2S phase has therefore partially hydrated to form calcium silicate hydrates (C-S-H) (4).

$$Ca_2SiO_5\ (s) + H_2O\ (\ell) \rightarrow C_2S_2H_3\ (s) + Ca(OH)_2\ (s)$$

Here the calcium silicate hydrates is presented as $C_2S_2H_3$, which can be written as $2CaO.2SiO_2.3H_2O$.

Thermogravimetric Measurements. Using a heating rate of 5 °C.min^{-1}, the precipitator dust shows a slow gradual mass loss of between 2 and 3.5 % from 50 to 600 °C (Figure IV). Between approximately 600 and 800 °C a mass loss varying from 26 to 29% is observed. The enthalpy accompanying the first mass loss is approximately 90 J/g and that for the second reaction 1300 J/g. Since the samples are not homogeneous, only approximate values can be determined.

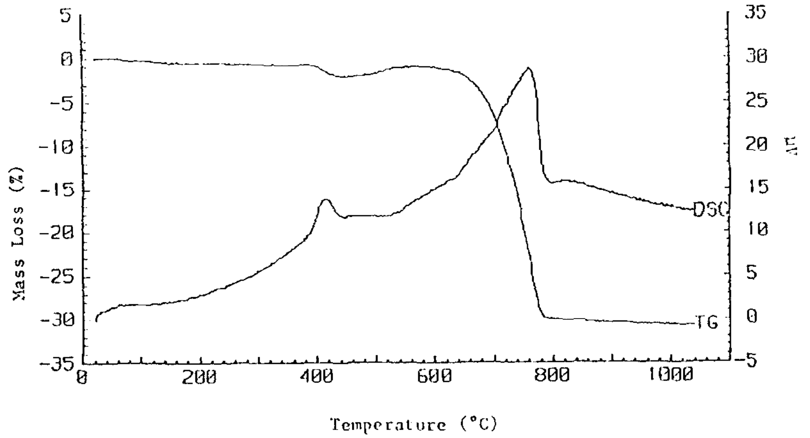

FIG. IV.
TG and DSC curves of precipitator dust heated to 1000°C at 5°C.min^{-1}.

After treatment of the precipitator dust with water and using the same conditions, a gradual mass loss of between 3.5 and 5.0 % from 50 to 600 °C is obtained (Figure V). A second decomposition reaction results in a mass loss between 27.4 and 29.0 % and occurs from 600 to 820 °C. The enthalpy change accompanying the first mass loss varies between 122 and 300 J/g and that for the second reaction between 1500 and 1950 J/g.

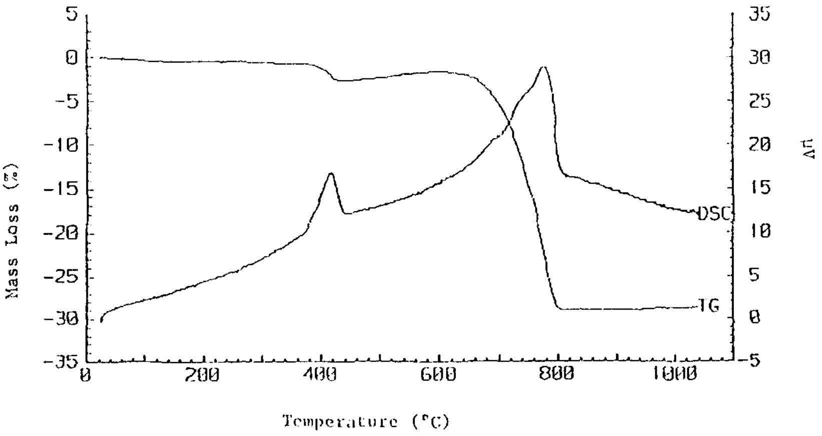

FIG. V.
TG and DSC curves of precipitator dust heated after water treatment to 1000°C at 5°C.min^{-1}.

Conclusion

Chemical composition of the precipitator dust indicates that it mainly consist of Si, Al and Ca compounds, and minor quantities of some Mg compounds. XRD analysis indicates that calcite is the major phase in the precipitator dust. Although a high lime content of 14.4 % was observed, only a few percent of it takes up water when the precipitator dust is treated with water. The mass loss curve of the sample treated with water only shows a 1.5% increace in the first decomposition reaction in comparison to the untreated sample, which seems to be mainly due to the following two reactions:

$$Ca(OH)_2\,(s) \rightarrow CaO\,(s) + H_2O\,(g)$$
$$CaSO_4.xH_2O\,(s) \rightarrow CaSO_4\,(s) + xH_2O\,(g)$$

Both these reactions only contribute to an increase of approximately 1.5 % in mass loss, indicating that only a few percent of the CaO in the precipitator dust has reacted with water to form $Ca(OH)_2$, and the same is valid for the hydration of $CaSO_4$. The increase in the enthalpy value for this decomposition step for the water treated sample is in good correlation with the increase in mass loss.

The second decomposition reaction mass loss percentage (29%) remains more or less the same. This decomposition reaction is mainly due to the decomposition of calcite to lime:

$$CaCO_3\,(s) \rightarrow CaO\,(s) + CO_2\,(g)$$

It is not clear at this stage why a higher enthalpy value is observed for this second decomposition step for the water treated sample in comparison to the untreated precipitator dust.

The treatment of precipitator dust with water does not appear to be successful in diminishing the amount of lime to an extent which is favourable for the environment. Other means for decreasing the amount of lime must therefore be investigated. The reasons why the lime in the precipitator dust does not react completely with water need to be resolved and will receive further attention. Heat treatment of the precipitator dust at 1000 °C forms cementitious phases, which upon hydration could satisfy the properties of a landfilling material, but the cost of heat-treatment would not warrant such a procedure.

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