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# Origin and characterisation of fly ashes from cellulose industries containing high proportions of free lime and anhydrite

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## Abstract

Fly ashes from cellulose industries originate from different internal waste combustion processes. Because they contain considerable amounts of free lime and anhydrite, they are potential secondary raw materials for the production of building products. The source of the CaO is a Ca-bisulphite-sludge originating from the cellulose extraction process. The CaO/anhydrite ratio in this lime-sulphate fly ash depends on the extent of sulphur reduction by organic carbon during the combustion process. A second type of Al-bearing ash contains additionally lowly reactive calcium silicates and highly reactive calcium aluminate phases originating from combusted paper sludge containing kaolinite. Both ashes show a reduced reactivity compared to commercial lime as it is used for the production of autoclaved aerated concrete. The reduced activity is related to the coated surfaces of the CaO and elevated sulphate and alkali contents.

*Keywords:* Fly ash; Characterization; CaO; Reactivity

## 1. Introduction

Cellulose industries produce several thousand tons of fly ash by waste combustion, which have to be disposed. They contain considerable amounts of free lime and sulphate, which are potential secondary raw materials [e.g., for autoclaved aerated concrete (AAC)]. In the light of this application, the origin, composition, and properties of these fly ashes was investigated.

Cellulose is extracted by a process based on calcium bisulphite and subsequent reaction with calcium carbonate in suspension with water. After the extraction a sludge composed mainly of calcium lignin sulphonate remains, which is burned at temperatures between 1000 and 1200°C (lime sulfate ash). In a succeeding process the solid residues from waste water treatment are mixed with wood wastes and sedimentary sludge from a paper plant containing kaolinite and calcite and burned in a fluidised bed combustion plant, composed of quartz sand, at 650 to 700°C (Al-bearing ash).

The chemical and mineralogical composition as well as the reactivity of the ashes were characterised. Analogous mixtures using pure substances as well as ash samples were prepared and heated on a laboratory scale to simulate reactions during combustion. The variability of the CaO content in a series of 36 samples collected daily of lime-sulphate ash was analysed. Systematics and relationships with the combustion conditions were established. Finally, ashes were hydrated and autoclaved. Newly formed phases after each step gave indications on the reaction behaviour of the principal constituents CaO, $Al_2O_3$, $SiO_2$, and $CaSO_4$, as well as reaction sequences.

## 2. Analysis and experimental procedures

The chemical composition of the ashes was determined by X-ray fluorescence (XRF), inductively coupled plasma atomic emission spectroscopy (ICP-AES), coulometry (C, S), Carlo Erba instrument (S), ion selective electrode (F, Cl) [1] and wet chemical methods ($S^{2-}$, S) (Table 1). The amount of crystal water was calculated by subtracting $CO_2$, organic carbon, F, and Cl from the loss on ignition at 1050°C.

The mineralogical phases were identified by X-ray diffraction (XRD), differential thermal analysis (DTA), and infrared $H_2O$ and $CO_2$ analyser. Additional XRD analysis was performed on residues of samples leached with sugar solution or water and their corresponding precipitated solutions.

Various methods were applied to achieve quantitative phase composition. The contents of available lime were ob-

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Table 1
Major chemical composition of the ashes in wt %

| | Lime-sulphate ash | Al-bearing ash |
|---|---|---|
| $SiO_2$ | 0.42 | 14.51 |
| $TiO_2$ | 0.00 | 0.13 |
| $Al_2O_3$ | 0.26 | 9.30 |
| $Fe_2O_3$ total | 0.10 | 0.75 |
| MnO | 0.16 | 0.22 |
| MgO | 0.74 | 2.41 |
| CaO | 65.40 | 56.67 |
| $Na_2O$ | 2.34 | 0.44 |
| $K_2O$ | 1.87 | 0.68 |
| $P_2O_5$ | 1.22 | 1.26 |
| $CO_2$ inorganic | 4.2 | 5.9 |
| C organic | 0.2 | 0.2 |
| Cl | 0.62 | 0.48 |
| F | 0.0038 | 0.0339 |
| $H_2O$ 1050°C | −0.31* | 0.7 |
| $SO_3$ | 18.2 | 6.3 |
| $S^{2-}$ | 0.01 | n.m. |
| Total | 95.40 | 99.94 |

*Negative value due to errors in loss on ignition analysis. Abbreviations: n.m. = not measured.

tained by the wet chemical sugar method [2] and the ethylene-glycol method [3]. Talvitie's method [4] was used to determine the contents of quartz. Anhydrite and calcite were calculated from $SO_3$ and inorganic C, respectively, whereas the $SO_3$ content was corrected for the amount of the apatite-structured phase (calculated as hydroxyl-ellestadite). Constrained by the bulk chemical composition and XRD peak intensities, the proportions of portlandite, hydroxyl-ellestadite, chlorides, and alkali sulphates were estimated. Soluble silica was determined in cold and hot HCl [5,6].

Quantitative XRD was applied to determine the mineralogical composition of a series of lime-sulphate ashes. Calibration curves were constructed by using ash samples that were quantitatively analysed by the methods explained above.

Specific surface area was determined following the method of Blaine. Material density was measured on a pycnometer using He gas. The rise in slaking temperature was recorded in a mixture of 200 g of ash and 800 mL of deionised water while stirring in a Dewar flask.

Hydration of the ashes was carried out by mixing with excess distilled water and subsequent drying at 50°C. Slurries of ash and water were autoclaved at 200°C for 4 h and dried in a vacuum oven at 50°C. The autoclaved samples were analysed by XRD and scanning electron microscopy (SEM). The proportion of chemically bound water was determined by the loss on ignition at 1050°C.

Calcination experiments were carried out using pure substances. Powders were mixed and heated in a laboratory oven for 90 min at temperatures between 1100 and 1200°C. Some mixtures were burned in Ar atmosphere to avoid oxidation of carbon. The calcined mixtures were examined by qualitative XRD. Samples of ashes were heated at 700°C for 24 h.

## 3. Results and discussion

### 3.1. Composition and reactivity of the ashes

Lime-sulphate ash consists mainly of lime and anhydrite (Fig. 1). Minor amounts of calcite and only traces of portlandite were detected. Calcite shows broad XRD peaks and weak DTA endotherms around 700°C, which point to a low degree of crystallinity due to recarbonation of CaO at atmospheric conditions. After leaching of soluble CaO with sugar solution, an apatite-structured phase and small amounts of halite could be identified in the residue. Traces of sulphide might originate from oldhamite, as will be discussed below. Based on calculations of the chemical composition of the remainder the presence of periclase and alkali sulphates is suggested. In the Al-bearing ash, lime and anhydrite contents are lower compared to lime-sulphate ash. About 15 wt% of $SiO_2$ are distributed among three silicate phases. Quartz represents a contamination originating mainly from the fluidised bed. Compared to lime-sulphate ash, more apatite-structured phases were estimated. The remaining amorphous proportion is composed mainly of CaO, $SiO_2$, and $Al_2O_3$ with molar proportions of about 4:2:1. Some unidentified peaks on XRD patterns showing increasing intensities when the sample is heated at 700°C for 24 h. These peaks might correspond to CA, $C_{12}A_7$, and gehlenite, which are observed in laboratory experiments [7–11]. However, due to the short combustion time and relatively low temperatures, the reaction sequence is incomplete [11,12].

The rate of temperature rise during hydration correlates with the reactivity of hydraulic materials (Fig. 2). The absolute temperature rise can be correlated with the content of free lime (Table 2). The reaction rates expressed by the increase of temperature per min of all ashes are generally lower compared to commercial lime, as used for AAC production. The surface of CaO crystals in the ashes are probably coated by less reactive materials [2]. The reactivity of lime-sulphate ash is lower than those of Al-bearing ash, although its specific surface area is almost doubled (Table 2). XRD measurements of the full width at medium height

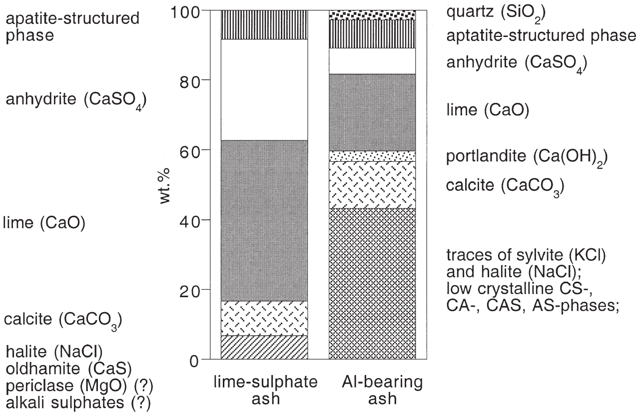

Fig. 1. Mineralogical phase composition of the ashes normalized to 100 wt%.

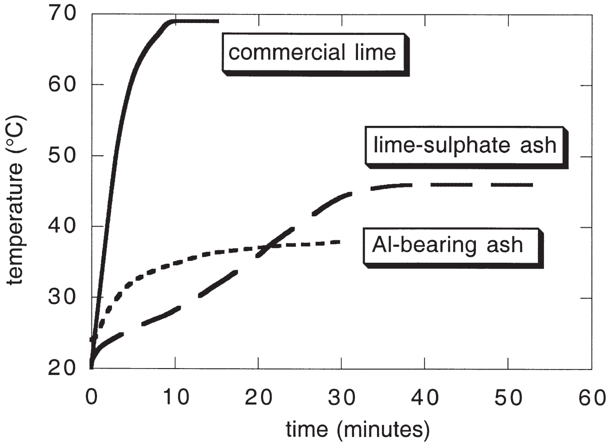

Fig. 2. Reactivity of the ashes given as rise in temperature against time of hydration.

(FWMH) at d(002) = 0.236 nm showed that the crystallinity of the CaO in lime-sulphate ash is not significantly different compared to CaO in commercial lime. Therefore, hard burnt lime is not the reason for its low reactivity. Retardation effects on the hydration of lime are known to originate from sulphate and alkalis [2,13,14]. Increasing anhydrite contents from Al-bearing ash to lime-sulphate ash might cause a flattening of the curve, reflecting the lowered reactivity.

### 3.2. Free lime in lime-sulphate ash

Free CaO in lime-sulphate ash does form from gypsum through a desulphurisation reaction with coal, as reported by Klauss [15], who proposed the reaction depicted in Eq. (1):

$$\begin{aligned} &CaSO_4 + 2\,C \rightarrow CaS + 2\,CO_2 \\ &3\,CaSO_4 + CaS \rightarrow CaO + 4\,SO_2 \end{aligned} \tag{1}$$

Analyses of a series of 36 samples collected daily allowed additional insights on the systematic of the lime-forming process. The results for lime and anhydrite were corrected for the dilution by hydration and carbonation. The variability of the initially free CaO lies between 31 and 47 wt% and anhydrite scatters between 33 and 41 wt%. Negative relationships between CaO and anhydrite [Fig. 3(a)] and between CaO and organic C content [Fig. 3(b)] confirm the reaction proposed above.

Positive correlation between the initial CaO content and the specific weight of the ashes indicates higher sintering effects [Fig. 3(c)], which is also confirmed by decreasing FWMH for CaO (002) [Fig. 3(d)].

### 3.3. Properties of the amorphous part of the Al-bearing ash

Indications on the kind of the silicate compound were obtained by comparing the solubilities in hot and cold HCl. For comparison the same analyses were carried out for cement. $SiO_2$ of cement is almost entirely soluble in hot HCl but also in cold HCl (Table 3). The amount of $SiO_2$ included in the amorphous part is calculated as a lower limit since the apatite-structured phase (calculated as hydroxyl-ellestadite) was not exactly quantified. With respect to this the solubility of silica of the ash is estimated to be in the same range as $SiO_2$ from cement.

Low crystalline phases cannot be detected by XRD, but experimental data of similar systems from literature show that $C_2S$ is the most probable calcium silicate to occur under these conditions [7,10,12,16], where it usually exists as its low reactive $\gamma$-modification [17]. Low reactive $C_2S$ obtained form calcined mixtures of calcite and kaolinite was also observed by Cottin et al. [8].

Assuming the calcium silicate to be $C_2S$, the composition of the calcium aluminates in Al-bearing ash can be calculated. The molar C/A ratio is lower than 1, which implies a considerable Ca deficiency to form the proposed calcium aluminates and calcium aluminium silicates, CA, $C_{12}A_7$, and gehlenite. It is expected that a part of the kaolinite included in the raw material did not react with calcium and remained as metakaolinite. Rapid reaction in aqueous environment of the Al compounds as presented in the next section points to the presence of mainly CA, $C_{12}A_7$ [18], and metakaolin [8,10,19–21].

### 3.4. Hydration and hydrothermal treatment of the ashes

Hydration of lime-sulphate ash caused the formation of portlandite and gypsum. Both of these phases were also detected after autoclaving at 200°C under saturated steam pressure for several hours. The presence of gypsum in the autoclaved sample might be due to the rehydration of anhydrite during drying, whereby the XRD intensities for the apatite-structured phase remained about constant during hydrothermal treatment.

In contrast to lime-sulphate ash in which hydration and autoclaving produced only hydrates of the original phases, Al-bearing ashes formed ettringite during hydration, and $C_4AH_{13}$ occurs as a second Al-bearing phase. During hydrothermal treatment, both phases decomposed to form anhydrite and hydrogarnet. XRD patterns indicate a composition

Table 2
Specific surface area (Blaine), CaO content, and FWMH of CaO of ashes and commercial lime

| | Commercial lime | Lime-sulphate ash | Al-bearing ash |
|---|---|---|---|
| Specific surface area (Blaine) ($m^2/g$) | 0.99 | 1.41 | 0.83 |
| CaO (wt%) | 90.5 | 43.9 | 22.1 |
| FWMH CaO at d(002) = 0.236 nm (°2 theta) | 0.131 ± 0.003 | 0.137 ± 0.005 | 0.170 ± 0.003 |

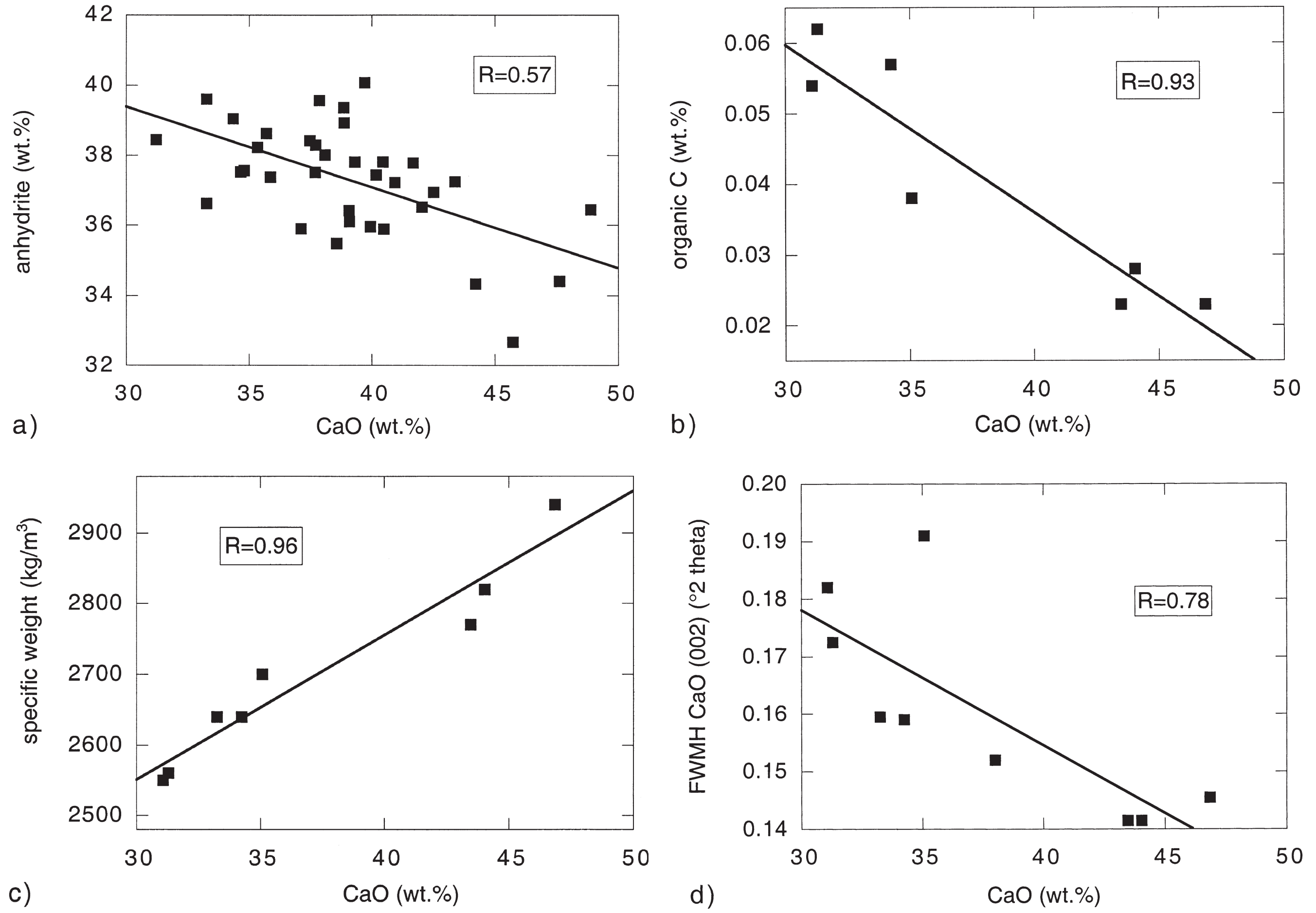

Fig. 3. Relationship between CaO and other ash properties in a series of samples of lime-sulphate ash. (a) Anhydrite, (b) organic carbon, (c) specific weight, and (d) FWMH for CaO at d(002) = 2.36 Å, respectively, where *R* is the correlation coefficient.

near $C_3AH_6$ and more apatite-structured phase is observed. Calcium silicate hydrate phases were not detected by XRD or SEM. The crystal water of portlandite and hydrogarnet was calculated by introducing the amount of available lime measured by the sugar method and the total amount of $Al_2O_3$, which is assumed to form hydrogarnet, giving the value of 13.08 wt%. The amount of chemically bound water as determined by loss on ignition measurement is less (11.49 wt%), which indicates that no significant amount of other hydrates exist besides portlandite and hydrogarnet. Therefore the silicate compound is nearly inert.

Table 3
Solubility of amorphous $SiO_2$ in hot and cold HCl

| | Cement | Ash 2 | Al-bearing ash |
|---|---|---|---|
| Amorphous $SiO_2$ (wt%) | 20.21 | <6.45 | <10.62 |
| $SiO_2$ soluble in hot HCl (wt%) | 18.5 | 4.3 | 9.0 |
| $SiO_2$ soluble in hot HCl/ amorphous $SiO_2$ (%) | 91.5 | >66.7 | >84.7 |
| $SiO_2$ soluble in cold HCl (wt%) | 17.3 | 3.0 | 7.2 |
| $SiO_2$ soluble in cold HCl/ hot HCl (%) | 93.5 | >69.8 | >80.0 |

## 4. Conclusions

Fly ashes from cellulose industries are fine-grained, lime and sulphate-rich materials with a lowered reactivity compared to commercial lime; they mainly controlled the high sulphate and alkali contents as well as impurities coating the surfaces of CaO. Evidence from XRD, calculated composition, and hydration experiments indicate that the low crystalline phases of Al-bearing ash must be mainly $C_2S$, CA, unreacted metakaolin, and probably small amounts of gehlenite and $C_{12}A_7$. Calcium silicate is highly resistant to hydration, even under hydrothermal conditions: no calcium silicate hydrate phases were formed. Calcium aluminates are very reactive in aqueous environment and combine with sulphate and $Ca(OH)_2$ to form ettringite and $C_4AH_{13}$, which react further to hydrogarnet during hydrothermal treatment.

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