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# Alkali-activated binders by use of industrial by-products

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**Abstract**

Cement kiln dust (CKD) materials are used as alkaline accelerators for latent hydraulic substances and as alkali activators for different alumosilicate materials, including ground-granulated blast furnace slag, low-calcium fly ash and metakaolin. The dusts differ in their phase composition, especially in the amount of reactive phases and the kind and amount of alkali salts. The quantitative phase composition, pore solution composition and strength behavior of the activated blends is reported.

*Keywords:* Cement kiln dust; Alkali-activated cement; Hydration products; Pore solution

## 1. Introduction

Alkaline by-products with hydraulic properties originate from the manufacture of hydraulic binders, e.g., cements. The production of 1 t cement requires about 2.8 t raw materials, including fuels and other materials. Five to ten percent of the by-products are dusts from the dryers, mills, kilns, coolers and transportation facilities. These dusts arise from different sources. Altogether, 6000–14,000 $m^3$ dust-containing airstreams are generated per 1 t cement which contain between 0.7 and 800 $g/m^3$ of dust (depending on source and technology). The dust is separated in dry dust-separators from the airflow and may be put back into the cement, according to the technological and chemical conditions.

However, exhaust streams containing cement kiln dusts (CKDs) may be unsuitable to add to the process due to their chemical composition. The strategy is to eliminate CKD with high contents of special components (e.g., alkalis, chloride, fluoride, etc.) through a bypass from the production process. In order to produce a high-quality cement with defined chemical composition, up to 2% related to the raw material may be generated as CKD. Dusts with similar composition and comparable quality can also arise during cleaning of the exit gas. These dusts usually contain more than 2.0 mass% alkalis. The present state-of-the-art cements usually have an equivalent $Na_2O$ content less than 1.3 mass %.

The question arises if the high alkaline contents of CKD can be used for alkaline activation of alumosilicate materials.

## 2. Alkali-activation of alumosilicate materials

A reactive material for alkali-activated binders has to consist of a certain amount of highly solid energetic phases, like a glassy phase (fly ash, slag). Clays, for instance, kaolin, can be transformed into a reactive material by a thermal activation process in which the dehydroxylation of the clay mineral leads to a highly energetic, unstable and nearly amorphous solid. The reaction mechanism of alkali-activated materials can be described in two steps,

(1) The generation of reactive species (*alkaline activation*). The alkaline pore solution disintegrates the solid network to produce reactive silicate and aluminate species with low molecular weights. The activation of the solid is achieved with alkaline solutions containing alkali hydroxides, alkali silicates and/or alkali carbonates.
(2) The *setting* reaction. Pure alumosilicate materials, e.g., metakaolin and some types of fly ash, set by a condensation reaction which leads to the formation of alumosilicate polymers [1]. Typically, alumosilicate

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> polymers are forming three-dimensional networks in a similar structure than zeolites, but are almost completely amorphous.

As shown by several authors, the setting of alkali-activated slag and calcium-containing materials can be characterized by both a condensation reaction and a hydration reaction forming CSH (or Al-substituted CSH) and CAH phases, depending on calcium content and alkalinity [2–5].

Comparing the reaction products of alkali-activated calcium-containing materials, like slag, with those activated by Portland cement (latent hydraulic or pozzolanic materials), it becomes clear that there has to be a weak transition between both types [6]. In mixing CKD and alumosilicate materials, essentially CSH and CAH phases will be expected as reaction products, according to the high calcium content of CKD with only slightly higher pH value than in OPC pastes.

The use of CKD as alkaline activator of slag and fly ash has been occasionally discussed in the literature [7,8]. An extra addition of sodium hydroxide improved the performance of the alkali-activated fly ash [8]. Composites consisting of mainly OPC and only a small amounts of CKD as alkaline activator are reported in Refs. [9,10].

## 3. Investigation

### 3.1. Materials used

Two different CKD materials were selected from a multitude of CKDs from different cement-producing plants in Germany [11]. The reason for choosing is the different chemical compositions, especially chloride contents. The CKD has been extracted from various production locations, which means that they are based on different material resources and technologies. Fly ash, slag and metakaolin were used as alumosilicate materials one at a time; an inert calcite filler was used for comparison. The chemical composition of all materials are listed in Table 1. Selected physical properties of the materials used, e.g., density, surface area and mean grain size, are listed in Table 2.

Table 1
Chemical composition of materials

| wt.% | CKD | | Additives | | | |
|---|---|---|---|---|---|---|
| | BYP21 | BYP41 | Slag | Fly ash | Metakaolin | Filler |
| LOI | 32.14 | 19.8 | 4.91 | 2.0 | 1.0 | 40.8 |
| $SiO_2$ | 11.3 | 16.71 | 31.34 | 50.74 | 52.1 | 5.8 |
| $Al_2O_3$ | 4.02 | 4.92 | 10.39 | 29.5 | 43.0 | 1.1 |
| $Fe_2O_3$ | 1.71 | 2.32 | 1.08 | 7.32 | 0.7 | 0.4 |
| CaO | 39.25 | 53.68 | 42.61 | 2.06 | 0.0 | 50.6 |
| MgO | 1.32 | 1.79 | 7.52 | 1.84 | 0.3 | 0.3 |
| $K_2O$ | 10.27 | 2.79 | 0.66 | 4.84 | 2.5 | 0.16 |
| $Na_2O$ | 0.56 | 0.23 | 0.25 | 1.01 | 0.12 | 0.03 |
| Cl | 4.4 | 0.25 | 0.03 | $<0.01$ | | |
| $SO_3$ | 4.9 | 2.41 | 1.08 | 0.16 | | 0.8 |
| $P_2O_5$ | 0.05 | 0.03 | 0.13 | 0.97 | | 0.23 |

Table 2
Physical properties of materials

| | Density ($g/cm^3$) | Surface area, measured by | | Mean grain size (μm) |
|---|---|---|---|---|
| | | Blaine ($cm^2/g$) | BET ($cm^2/g$) | |
| BYP21 | 2.69 | | 19,700 | 12.9 |
| BYP41 | 2.99 | 5750 | | 47.7 |
| Slag | 2.9 | 8120 | | 15.8 |
| Fly ash | 2.48 | 3370 | | 55.9 |
| Metakaolin | 2.55 | | 11,600 | 3.9 |
| Filler | 2.69 | 7350 | | 17.3 |

### 3.2. Binder preparation and curing

Pure binder specimens were prepared by mixing the cement dust and the additive (alumosilicate material or inert filler) in the proportion 1:1. Water was added and has been leveled on the same workability of the paste. No aggregates are added. The mixtures are reported in Table 3. Before testing, all samples were cured 1 day at 35 °C without drying followed by 27 days at room temperature at 60% relative humidity.

### 3.3. Strength testing

The flexural strength (center point loading) on the specimen has been measured with a geometry of $10 \times 10 \times 60$ $mm^3$ and so is the compressive strength on the broken samples with a compression area of $10 \times 20$ $mm^2$.

### 3.4. Composition of pore solution

The pore solution has been analyzed for two different tests. First, the time dependence of the pore solutions was determined over 56 days for both dusts alone. Pastes of water to dust ratio of 0.6 have been prepared. The pore solutions were expressed from the cylindrical samples and the contents of $K^+$, $Na^+$, $Mg^{2+}$, $Ca^{2+}$, $SO_4^{2-}$, $Cl^-$ and $OH^-$ have been analyzed by different methods.

Second, the pastes of the above-mentioned blends with the CKD BYP21 were prepared and the pore solution has been expressed and analyzed after 28 days of hydration. In addition to the above-mentioned ions, the contents of silicon and aluminium were measured by ICP-OES.

Table 3
Compositions of the activated blends

| Additive | Sign | Amount (wt.%) | | |
|---|---|---|---|---|
| | | CKD | Additive | Water |
| None | W | 64.1 | | 35.9 |
| Inert filler—calcite | I | 34.4 | 34.4 | 31.3 |
| Slag | S | 35.0 | 35.0 | 30.0 |
| Fly ash | F | 35.7 | 35.7 | 28.6 |
| Metakaolin | M | 29.1 | 29.1 | 41.9 |

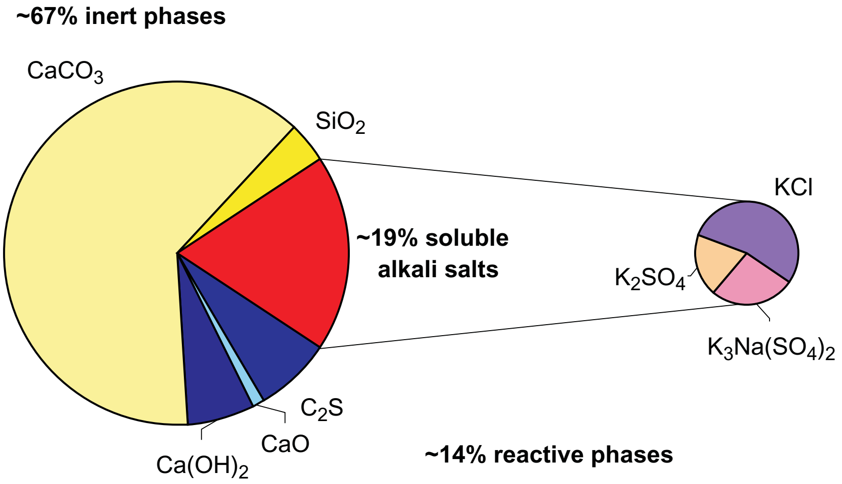

Fig. 1. Phase composition of CKD BYP21.

The ion concentration of the pore solution has been converted to mmol per dry mass of the binder for better comparison.

### 3.5. Phase composition

The composition of crystalline phases of the raw materials and the binders after 28 days were carried out by XRD and Rietveld program.

## 4. Results

### 4.1. Chemical and phase composition of CKD

The chemical composition of both CKD materials differ especially in contents of calcium oxide and chloride (Table 1). The material BYP21 contains a high content of alkali oxide and chloride but less calcium oxide than BYP41. The results of the quantitative phase analyses by XRD and Rietveld are shown in the Fig. 1 for BYP21 and Fig. 2 for BYP41.

In principle, three groups of phases could be detected by XRD:

- soluble alkali salts (sulphate and chloride)
- reactive cement and lime phases—containing calcium silicate, -aluminate and free lime, portlandite
- inert phases (calcite and quartz)

CKD BYP21 consists of a high amount (67% ) of inert phases, mainly calcite. Only a little amount of the calcium is bound as reactive cement or as lime phases (about 14%). The content of alkali salts is about 19% and half of that is potassium chloride.

The CKD BYP41 consists of a high amount of reactive cement and lime phases (about 45%). The high amount of portlandite is remarkable. The content of alkali salts is

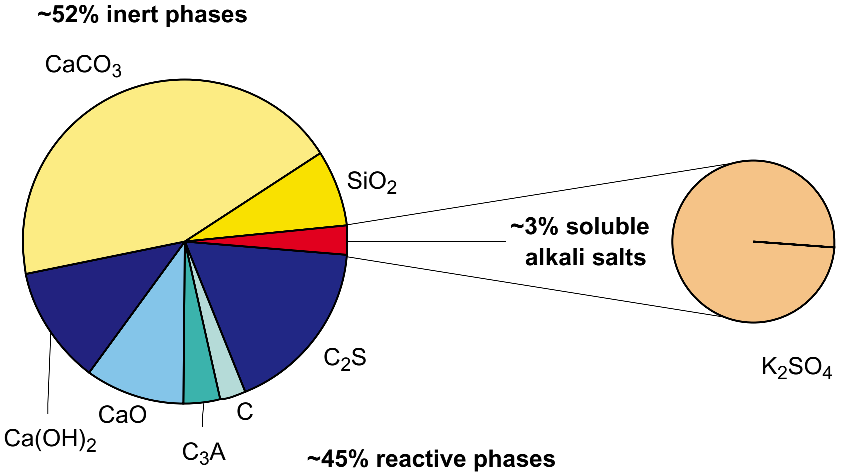

Fig. 2. Phase composition of CKD BYP41.

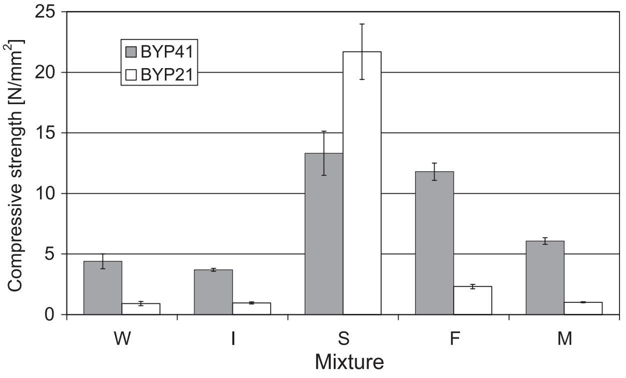

Fig. 3. Compressive strength of the binder after 28 days.

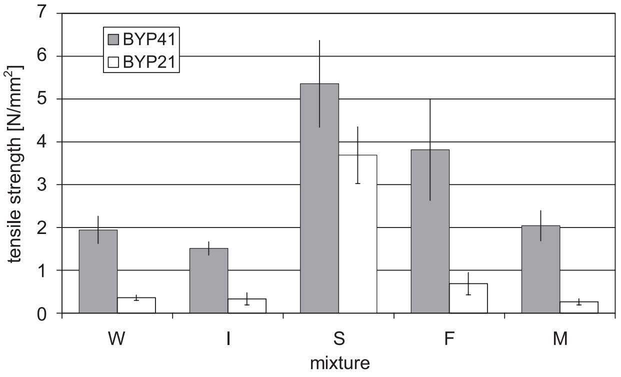

Fig. 4. Tensile strength of the binder after 28 days.

relatively low and is essentially potassium sulfate, half of the dust are inert components calcite and quartz.

A higher reactivity of the material BYP41 is assumed because of the larger amount of lime and cement phases.

### 4.2. Strength testing

The material BYP41 achieved higher strength than BYP21, as expected from the higher amount of reactive phases. This could be confirmed by the results (W) demonstrated in Figs. 3 and 4. The samples with the inert filler (I) showed corresponding lower strengths because of dilution effects. By adding slag (S) and fly ash (F), one can increase the strength. The samples with metakaolin (M) showed no significant increase. The mixture of BYP21 with slag performed well owing to sulfate activation of slag.

### 4.3. Composition of pore solution

The chemical composition of the pore solution is shown in Fig. 5 for BYP21 and in Fig. 6 for BYP41. The principal ions have been fixed to separate *y* axes for clarity. Comparing both diagrams, the different characters of the CKD become clearer. The higher pH value of the material BYP41 indicates a higher activation potential. The higher amount of alkali in BYP21 does not result in increasing the pH value as these alkalis exist as chlorides.

The pore solution of the blends with CKD BYP21 after 28 days of hydration are shown in Fig. 7. The chloride content in the pore solution is diluted by adding the alumosilicate or filler materials, but the chloride is dissolved completely in the pore solution. The high amounts of soluble salts causes efflorescence after drying the samples.

In general, the composition of the pore solution does not change significantly by adding the alumosilicate or filler materials. Apart from the chloride, the concentration of the other ions is nearly constant. The mixture with metakaolin

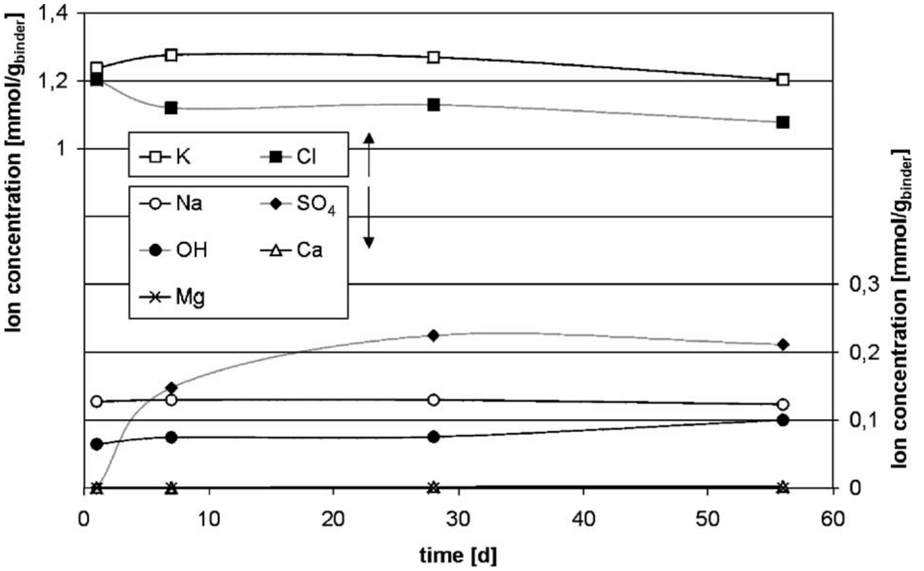

Fig. 5. Composition of pore solution of hydrating BYP21 alone over 56 days.

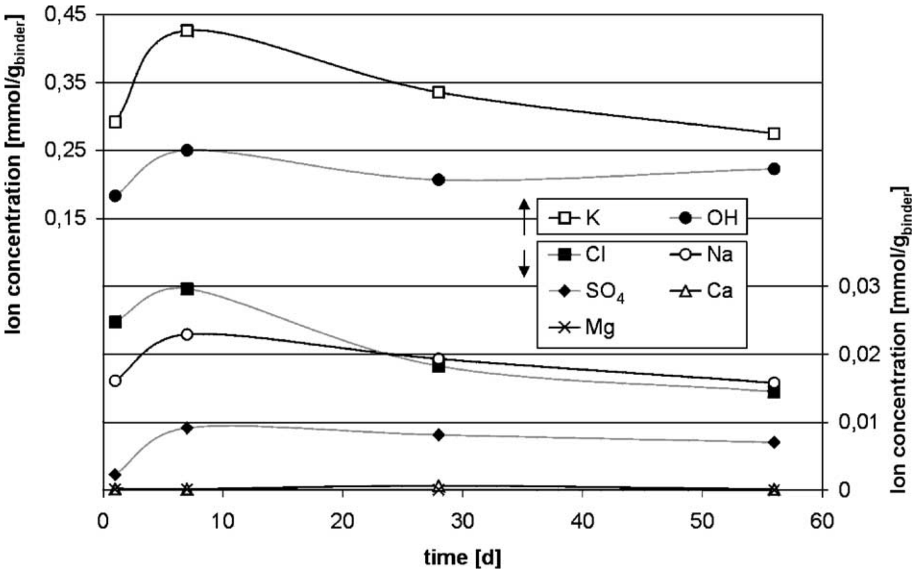

Fig. 6. Composition of pore solution of hydrating BYP41 alone over 56 days.

contains higher amounts of silicon and aluminium in the pore solutions. The proportion of silicon to aluminium corresponds to the composition of the alumosilicate material strictly speaking the composition of the reactive phase of the alumosilicate material.

### *4.4. Phase composition of binder*

Upon adding water to the CKD materials, the soluble phases are dissolved in the pore solution and the cement phases start to react. Crystalline calcium aluminate phases which contain carbonate and chloride (only BYP21) were detected as reaction products of the pure materials (W). CSH phases could not be detected because of their low crystallinity. But ettringite and an increased amount of portlandite can be proven.

The crystalline phase composition of the mixtures supports the results found by strength measurements.

- The mixture with slag showed a similar phase composition to that of the pure CKD. There are additional amount of $C_2S$ and $C_3S$ from the slag and similar amounts of calcium aluminate hydrate.
- The mixture with calcite showed only more calcite because of dilution effect.
- A consumption of portlandite and increased amounts of calcium aluminate hydrate could be proved in the mixtures with metakaolin and fly ash.

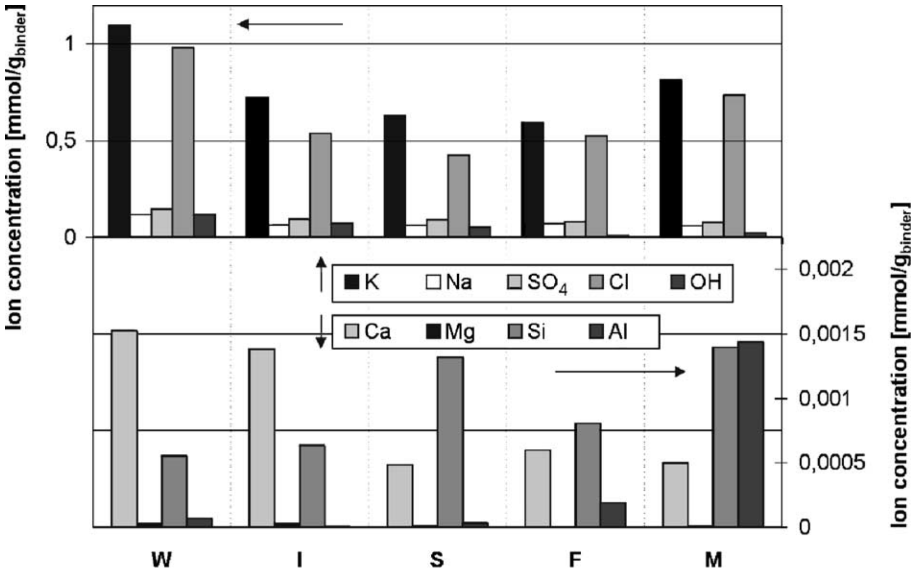

Fig. 7. Composition of pore solution in blends with CKD BYP21 after 28 days of hydration (see Table 3 for lettered composition).

## 5. Conclusion

The investigations should ideally give primary statements about the suitability of two quite different CKD materials for an alkali activation of different alumosilicate materials. However, the measurements have not been optimized for strength performance. The focus has been set on the composition of the pore solution and the phases of the hydrated blends to understand the influences on the setting process.

The results verify the suitability of both CKD materials in principle. The phase analyses confirm the reaction of the reactive lime and cement phases to calcium aluminate hydrate phases. We assume the formation of calcium silicate phases also accursed because of the simultaneous release of silicate and aluminate into the pore solution.

The additional phases led to a measurable increase in strength. The different water contents and late-age pore volumes misrepresent the strength values. Therefore, the formation of new phases led not to a rise of strength with the adding of metakaolin compared to fly ash.

To assess the reactivity of a CKD, the chemical analysis of the oxides can only be the first clue. The quantitative phase composition gives information on the content of reactive phases. A high equivalent $Na_2O$ content does not necessarily lead to a high pH value of the pore solution: if the alkalis are present as chlorides, they will dissolve, without affecting pH values. Besides, they cause efflorescence.

A future investigation will focus on the variation of chemical composition and rheological parameters of the CKD. Furthermore, it has to prove its basic practical value as a binder material especially in light of its potential for chloride binding.

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