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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.
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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 air-streams 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 10×20 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

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