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Waste Materials in Construction: Putting Theory into Practice

LOW LIME BINDERS BASED ON FLUIDIZED BED ASH

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ABSTRACT

Cement, steelmill and energy industry are after organic mass decomposition the second major sources of CO_2 emission which create, with other gases, greenhouse effect, moreover, the waste discarded from the last ones is still not utilized to the extent the environmental problems of today call for.

The research team tested several sources of fluidized bed combustion (FBC) ashes with a goal to incorporate them into manufacture of building elements. Some of the FBC ash samples showed distinctly different both chemical and mineralogical composition from the prevailing majority indicating good potentials even as a constituent of alternative silica binder. This fact might lead towards considerable savings of traditional cement or lime which production exploits dwindling natural deposits and through thermal treatment of limestone (together with a fuel) releases large amounts of CO_2 to the atmosphere. In question are ashes from installations where low grade coals or coal waste are being combusted.

INTRODUCTION:

Since the nineties, our research team has been exerting efforts to solve the energy and building industry problems of handling and processing solid residues from the fluidized bed combustion (FBC) technologies.

In many areas worldwide one can meet with depositions of low grade coal or coal waste (slurry) which were either neglected due

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** Associated Professor, field of thermodynamics and kinetics of cementious phases to the state-of-the-art of energy generation technique by its shipment costs or simply for environmental aspects. This is the case of the Limburg Area, the Lorraine Area, the Upper Silesian Basin to name only some.

Fresh wind of the world energy crisis in the seventies attracted the attention to the forgotten energy depositions with a goal to develop technologies to make the most from the least. The FBC installations meet the goal, moreover, the reduction of SO_x and NO_x is another evident feature. The addition of SO_2 sorbent at the combustion process gives rise to larger amount of solid residues to be handled, deposited or better utilized than it is in case of conventional coal boilers.

FLUIDIZED BED ASH - MINERALS

Fuel feed consists of a powdered coal and sorbent calculated according to the sulphur content in the coal to create conditions for the reactions taking place at temperature around 850 °C when decomposition of sorbent and oxidation of the sulpherous constituents from coal are completed

$$CaO + SO_2 + {}^1/_2\, O_2 \longrightarrow CaSO_4$$

Calcium sulfate in the form of anhydrite II remains fixed in the ash cutting down the SO_x emissions by 96 %. As the combustion temperature is kept well below the decomposition temperature of anhydrite II also a glass phase present in conventional high temperature ashes doesn´t orginate.

Clay minerals in the coal are thermally decomposed during the combustion process to yield the ash hydraulic and pozzolanic reactivity.

The SO_2 sorbent is dolomite or preferentially limestone which undergoes decomposition within 650 °C to 850 °C.

PHASE COMPOSITION OF ASHES

Rough sand like bed ash creating the fluidized bed is collected separately from fly ash. Due to their chemical and mineralogical differences (9), the applications may differ substantially (10).

In the ash collected from AFBC and CFBC installations chemical analyses confirm presence of free lime, in PFBC installation the free lime is replaced by calcium carbonate. The main component of AFBC and PFBC ashes is anhydrite, the content of which exeeds sometimes 20 per cent. Further variable amount of quartz, hematite, magnetite and unburnt carbon are being detected. High content of Al_2O_3 originates from thermal decomposition of clays obtained in the coal. With the circulated and especially with the pressurized technologies contrary to the atmospheric ones increase of a residential time of a combustible particle in the fluid bed produce an ash of almost total carbon burnout (Table 1). These set facts make the FBC technology adoptable for the combustion of low grade fuels as coal waste, coal slurry, oil shales, wooden chips, peat, etc.

In The Nederlands, the fluidized bed ashes are employed in production of low grade binders - calcined products (4) which comply the building industry demands put on the end product.

The morphology character of fluidized bed ashes is different from conventional fly ashes due to the combustion temperature (5, 10, 11). FBC ash particles are of irregular shape, glassy phases and mullite are missing alltogether, there is no evidence of cenospheres. Specific surface area is higher depending on the type of separator installed. It is also worth to mention that different fractions differ not only by fineness but also in its chemical and mineralogical composition.

REACTIVITY OF THE FBC ASHES

These ashes exhibit cementitious properties. During hydration processes, lime and anhydrite react with Al_2O_3 yielding ettringite $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$ decreasing the initial higher pH value (6, 12). This reaction doesn´t take place with the PFBC ash or with ashes where the free CaO content is negligible.

Second reaction which contributes to the hardening process is the formation of an amorphous CS(A)H gel.

Third reaction which may be observed with mixes reach of calcium sulphate leads to hydration of anhydrite II to gypsum.

Fourth reaction taking place in systems containing periclase, magnesium oxide (from dolomite sorbent) is slow hydration to brucite. Worth note is that hydraulic properties of ashes with low content of either reactive CaO or $CaSO_4$ may be modified (PFBC ash, low grade coal feed installations) by adding the missing reagent and thus stimulate the ettringite or CS(A)H gel formation.

From this statement one may conclude a wider scope of utilization possibilities with systems where the ettringite complex is either missing or is controlled to the acceptable extent. Systems containing ettringite phase alone as a hydraulic binder are not known.

RELEVANT STANDARDS

The FBC ashes exhibit hydraulic and pozzolanic properties producing hydration products close to other constituents added to portland clinker listed in ENV 197-1. These constituents are clearly defined, results from long term durability tests and field application are available. Moreover, fly ash in concrete constructions is governed by EN 450 supervised by EN 206 standard. These standards, its stipulations and limitations were combined at our research work.

Conclusions from research affect the standard tests required, many procedures have to be modified. As these FBC ashes are steping out of the line of materials tested in building industry thus, the existing standards´ stipulations create an obstacle for their utilization.

This goes for L.O.I. - the procedure puts forward false data due to dissociation of calcium carbonate and magnesium carbonate.

Instead of determination of unburned carbon should be set next to carbon dioxide in case of presence of calcium carbonate or magnesium carbonate. If high level of iron oxide is detected, then determination of bivalent iron is recommended.

As quality parameters of ash from plant to plant differ, it seems to be prudent the standard limitations should be laid down on the final construction or construction element in phase of its production.

Pozzolanic activity plays an important role in assessment of materials employed. The determination by EN 450 fulfills its purpose, rapid thermochemical test largerly adopted may considerably speed up the quality assessment phase of the ash source (7,8).

EXPERIMENTAL

Based on preliminary tests the recent research activities were focused on the evaluation of a binder containing significant amount of FBC ashes together with other industrial by-products originating in the industrial part of Czech Republic - the Ostrava region in a civil engineering as a road base construction material.

The following by-products and activators were employed as basic constituents:

- Ordinary Portland cement CEM I 42,5 with specific area of 364 m^2/kg (Blaine).
- Ground granulated blast furnace slag (GGBFS) with specific area of 320 m^2/kg (Blaine).
- FBC fly ash with specific area of 415 m^2/kg (Blaine) collected by electrostatic percipitator from the power plant Třinec, where coal mine wastes are combusted (Figure 1a).
- Ground natural gypsum (60 % of $CaSO_4 \cdot 2H_2O$) with specific area of 310 m^2/kg (Blaine).
- Crystalline blast furnace slag (CBFS) 0 - 8 mm.
  The oxidic composition of the starting materials is given in the Table 2.

From blends of these constituents, mortars of identical workability (slump) were prepared. The workability was set by mortar A with water to binder ratio of 0,50, no plasticiser was added in any of the blends.

The initial setting time of the respective binder was determined according to the procedure described in EN 196-3 standard. The soundness Le Chatelier test according to the EN 196-3 on each binder was carried out. The SO_3 content in each of the binder was determined by EN 196-2 standard.

Test mortar specimens 40 x 40 x 160 mm were prepared, demolded after 24 hours and water cured. After different curing time the flexural and compressive strength together with the bulk density were determined. In mix D (Table 3a) a part of FBC minerals was replaced by equivalent part of gypsum.

A preference of the same workability with all tested blends over the same water-to-binder ratio (as the EN 196-1 standard requires) was preferred due to the selection of processing "Roller Compacting" technology.

Addition of gypsum in mix D should simulate the increase of the SO_3 content in FBC minerals and its effect on the binder quality, incorporation of industrial pozzolana like GGBFS should prove its impact on compressive strength at later ages. Composition of the blends with all summarized data are presented in Table 3a. Compressive strength development is shown in Figure 2.

The 90d compressive strengths led for the selection of the blend marked "C" to its further modification for the given purpose - Roller Compacting Stabilized Road Construction.

As this construction is not intended to be a top finish layer there is no necessity to carry out the deicing salt resistance and freeze-thaw resistance tests admitting bringing those interesting data with similarities as associated with cement-fly ash composites.

A gravel used in the laboratory prism tests was a CFBS 0-8 mm aggregate with a poor distribution curve in the area of the fine particles. A mixture marked H as shown in Table 3 was compacted by vibration and cured for three days in moist room, then demoulded and kept untill tested in wet burlap in plastic bags. To improve the deficiency of fine particles in the CFBS aggregate, increased portion of GGBFS was incorporated into the mix. Compressive and flexural strengths are listed in Table 3 b.

Simultaneously the binder itself was tested from the mineralogical point of view.

HYDRATATION, MINERALOGICAL TRANSITIONS

The scope of this part of the research was to enlighten on the mineralogical processes taking place in dry and low calcium content hardening composite.

Components focused on were the portlandite and CS(A)H phases, the former to be the most susceptible phase to carbonation creating the pH barrier of hydrated products against corrosion and carbonation respectively, the latter building the supporting skeleton of the hardened paste.

This research part has been split into test of standard curing conditions and hydrothermal curing conditions to bring forth data on the hydrated products and phases contributing to the strengths of the composite (13). Methods used were the XRD combined with DTA. Finally, from the autoclaved test it was expected to support the evidence once determined by previous Le Chatelier test - the soundness of the composite.

PREPARATION OF THE PASTE SAMPLES

The H paste blend 36,5 gr CEM I 42,5; 233,6 gr FBC; 206,5 gr GGBFS mixed with 13 % of water was compacted into briquetes which were moist cured in the desicator untill tested. In case of the autoclave test the briquetes after 1 day in desicator underwent the 3-6-3 hours regime at 190 °C and 12 atm.

COMMENTS OF RESULTS

Initial setting time

Replacement of cement by low free CaO content FBC ashes will prolong the initial setting time considerably as a consequence of C_3A and C_3S reduction accompanied by a low heat of hydration.

Water-to-binder ratio

Higher water demand is influenced by fineness and the particle characteristics of the FBC material.

Activity index

The value linked with the blend A suggests excellent both 28d and 90d pozzolana activity index.

Consumption of cement

It´s evident that the use of FBC material plus other pozzolana constituents as GGBFS enhances the reduction of cement consumption drastically.

Soundness of the composite

Le Chatelier tests confirmed conformity of all binders tested with the standard condition. Also the autoclave test performed on the paste blend H proved it´s soundness. However, this test is highly recommended to be carried out with blends whenever the utilization of FBC ash is considered as the behaviour of the thermally activated clay minerals and it´s impact on durability has not yet been elucidated.

Detected phases exhibiting binding properties where CSH (II) and ettringite in case of standard curing and CSH (I) in hydrothermal process conditions, presence of portlandite has not been detected (Figure 1b, c, d, e).

Blend sensitivity to the temperature during hardening

Additional test focused on the H mortar sensitivity towards the lower temperature during curing period brought in data that limit the adoptability of the set "Roller Compacting" processing technology as a result of low cement inclusion connected with low evolution of heat of hydration.

CONCLUSIONS:

Tested blend H with the FBC ash employment proved compliance with the set standards´ stipulations for the considered processing technology.

Adoptability of this technology is, however, profoundly temperature dependant.

Cheap lightweight building elements manufactured at elevated temperature accompanied with production of dry mortars may be the viable processing solution to the examined FBC ash.

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Table 1. Combustion technology and phase composition of solid residue (in mass %)

		Fluidized bed combustion (sorbent - limestone)	
	High Temperature combustion	Atmospheric AFBC, CFBC	Pressurized PFBC
0/C	> 1200	860	860
Glass phase	50 - 90	0	0
Mullite	3 - 20	0	0
X - Ray amorphous AS	0	30 - 50	30 - 50
Clay, shale	0	1 - 3	1 - 3
Feldspar	0 - 1	1 - 2	1 - 2
Dead burnt lime	0 - 3	0	0
Free reactive lime	0	5 - 22	0 - 2
Periclase	0 - 1	0 - 2	0 - 2
Hematite	2 - 20	3 - 10	3 - 15
Magnetite	2 - 10	4 - 15	2 - 6
Anhydrite II	0 - 2	10 - 25	10 - 25
Calcite	0	0 - 1	10 - 15
Quartz	2 - 8	3 - 10	3 - 10

Table 2. Oxidic composition of the starting materials
Method used: XRF, gravimetric analyses

	CEM I 42.5	FBC	GGBFS	CBFS
SiO_2	22,46	41,8	37,3	37,6
Al_2O_3	5,13	21,4	6,6	7,2
Fe_2O_3	3,24	5,7	1,6	0,7
CaO	61,42	10,7	37,8	40,8
MgO	1,29	6,2	14,4	10,6
K_2O	0,90	2,3	0,4	0,5
Na_2O	0,52	0,9	0,3	0,2
TiO_2	0,35	1,2	0,3	0,1
MnO	n	0,1	0,6	0,5
P_2O_5	n	0,8	0,1	0,1
SO_3	2,55	3,75	1,71	1,65
free CaO	0,20	1,48	-	-
L.O.I.	1,92	n	-	-
C	-	4,9	-	-

n .... not determined

Fig. 1a XRD pattern of FBC ash

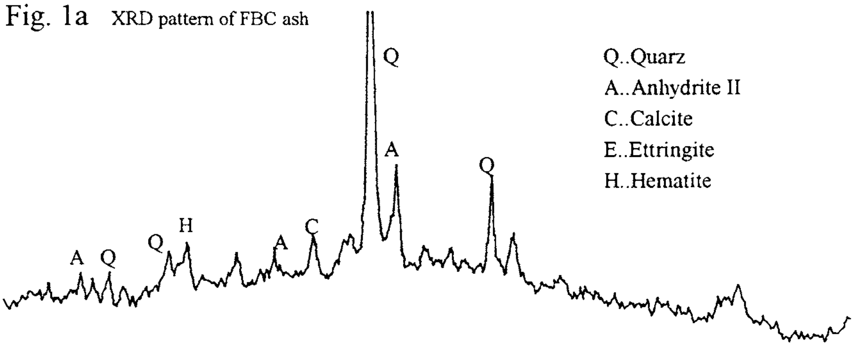

Fig. 1b XRD pattern of H paste after 60 days of standard curing

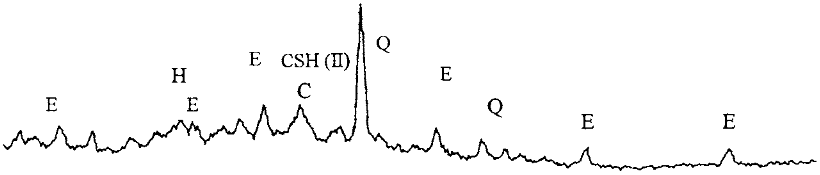

Fig. 1c XRD patttern of H paste after hydrothermal process

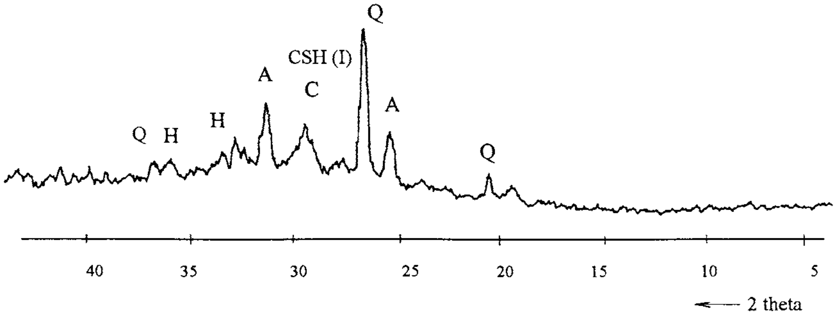

Fig. 1d DTA-TG curves of H paste after 60 days of standard curing

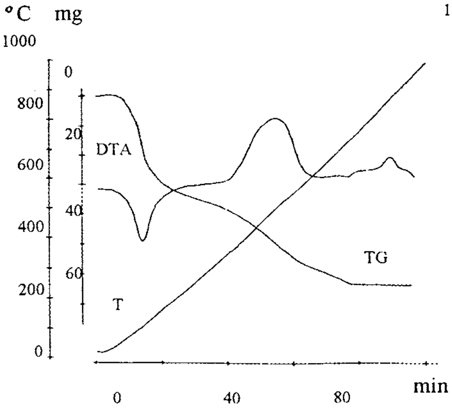

Fig. 1e DTA-TG curves of H paste after hydrothermal process

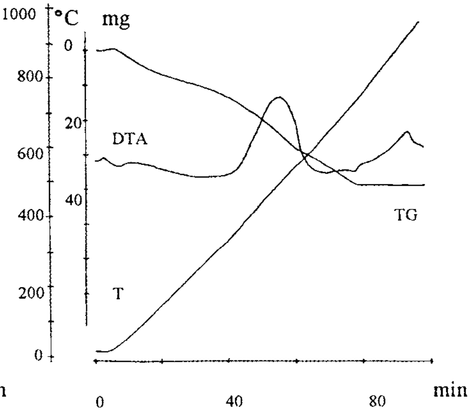

Table 3 a) Composition of the mortars in grams, the same workability

	R ref.	A	B	C	D	H	H kg/m^3
CEM I 42,5	450	315	225	180	180	36,5	40
FBC	-	135	225	135	130,5	233,6	254
GGBFS	-	-	-	135	135	206,5	225
Nat. gypsum	-	-	-	-	4,5	-	-
CBFS 0-8	-	-	-	-	-	1324,4	1441
Quartz sand	1350	1350	1350	1350	1350	-	-
W	0,38	0,5	0,59	0,51	0,53	217	234
Initial setting time (min)	120	210	220	220	290	n	n
Le Chatelier (mm)	0,0	5,0	5,0	5,0	0,0	n	n
Binder SO_3 cont (%)	2,55	2,91	3,15	2,66	2,91	n	n
Unit weight, 90 d (kg/m^3)	2246	2227	2240	2198	2236	2194	2194

Table 3 b) Strengths, flexural/compressive, MPa

Days	R	A	B	C	D	H
1	3,26/15,7	1,29/5,1	0,60/2,2	0,40/2,0	0,43/1,9	-
2	4,12/22,2	3,36/15,3	1,30/5,2	1,40/5,8	1,28/5,6	-
7	5,94/35,2	6,09/28,9	3,95/17,0	4,4/19,2	4,47/18,5	3,14/10,4
28	6,66/43,7	9,29/49,4	7,58/34,5	7,37/36,8	7,05/33,3	5,16/14,2
90	13,5/51,6	12,8/53,9	11,5/45,9	11,7/47,6	14,5/50,1	5,9/17,0
180	14,1/60,3	12,8/59,2	12,2/51,9	12,5/49,7	15,3/52,0	6,4/19,0
90 d. per cent	100,0	104,5	88,9	92,2	97,1	-

Fig. 2 Compressive strength developement