

The Use of FBC Ash for Preparation of Types of Hydraulic Binders Similar to Portland Cement

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Abstract—The reduction of greenhouse gases emissions is highly discussed ecological theme at present. In addition to power industry also main production sectors of binders, i.e. cement, air and hydraulic lime are very sensitive to these questions. One of the possibilities how CO₂ emissions can be reduced directly at clinker burnout is represented by partial substitution of lime with a material containing limy ions at absence of carbonate group. Fluidised fly ash is one of such potential raw materials where CaO can be found free and also bound in anhydrite, CaSO₄. At application of FBC (fluidized bed combustion) fly ash with approximate 20% CaO content and its dosing ratio to high percent lime 1:2, corresponding stoichiometrically to the preparation of raw material powder, approximately 0,37 t CO₂ per 1 ton of one-component cement would be released at clinker burnout compared to 0,46 t CO₂ when orthodox raw materials are used. The reduction of CO₂ emissions thus could reach even 20%.

Keywords—FBC ash, cement, hydraulic binders.

I. INTRODUCTION

THE reduction of greenhouse gases emissions is highly discussed ecological theme at present [1]. In addition to power industry also main production sectors of binders, i.e. cement, air and hydraulic lime are very sensitive to these questions. Since lime, CaCO₃, is the main production raw material in all three cases, it is clear that production process also brings massive CO₂ emissions.

In cement industry the CO₂ emission share can be reduced by cement mixing. Within the standards the permit and emission intensive clinker can be considered to be substituted with pozzolana latent hydraulic materials and also with various inert materials. It is stated that using such a process the CO₂ emission share can be reduced by 10 to 15% per unit of produced mixed cement [2]-[6]. However, considering the present shortage of blast furnace slag this substitution depends mainly on application of fly ashes and FBC (fluidized bed combustion) ash type materials, undersize recycled products, dusts from crushed aggregates etc., therefore materials not yet completely tested in concrete practice [7].

Another possibility how CO₂ emissions can be reduced directly at clinker burnout is represented by partial substitution of limestone with a material containing Ca ions at absence of carbonate group. FBC fly ash is one of such potential raw materials where CaO can be found free and also bound in anhydrite, CaSO₄ [8]-[10]. At application of FBC ash with

approximate 20% CaO content and its dosing ratio to high percent limestone 1:2, corresponding stoichiometrically to the preparation of raw material powder, approximately 0,37 t CO₂ per 1 ton of one-component cement would be released at clinker burnout compared to 0,46 t CO₂ when orthodox raw materials are used. The reduction of CO₂ emissions thus could reach even 20%.

II. METHODOLOGY

A raw material mixture consisting FBC fly ash from Hodonín power plant and high percent limestone in weight ratio 1:2 with and without presence of Fe-correction was used for preparation of the raw material powder. The two-component raw material powder was marked as sample A, the three-component one with 0,06 weight part of Fe-correction as sample C. Both of the samples further underwent in laboratory a line of burnouts in temperature range from 1250 to 1450°C, after each 50°C with constant isothermal dwelling 5 hours. With burnt clinkers and original raw material powders chemical analysis was carried out together with monitoring of phase composition using methods of microscopic integration and X-ray diffraction analysis.

After separation or preparation of pastes respectively the formed clinkers were subjected to setting of technological properties, strength namely and monitoring of hydration processes.

Considering the low burnout extractions the strengths were realised on non-standard micro-beams 10x10x30 mm.

The hydration process course was regularly monitored using X-ray diffraction analysis method and with selected samples also by electron microscopy. Further the sample A with the closest composition to clinker which was burnt to 1450°C also underwent the phase composition quantification during the 28-day hydration.

III. RESULTS

A. Phase Composition of Clinkers

Phase composition of burnt clinkers was monitored using X-ray diffraction analysis methods and microscopic point integration. Photos of clinker abrasions from selected samples are clear at Figs. 1 and 2.

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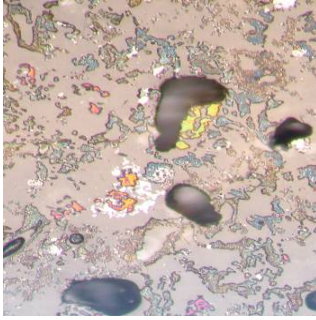


Fig. 1 (a) Clinker abrasions: line A, 1250°C

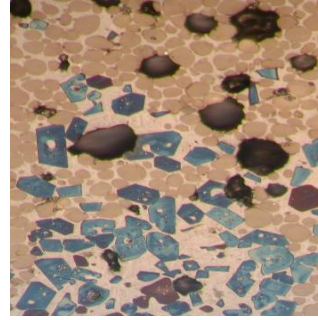


Fig. 2 (b) Clinker abrasions: line C, 1350°C

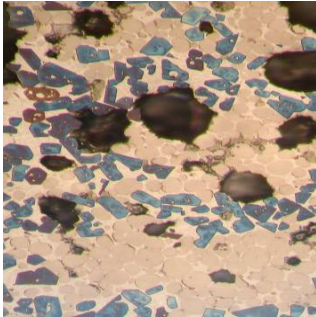


Fig. 1 (b) Clinker abrasions: line A, 1350°C

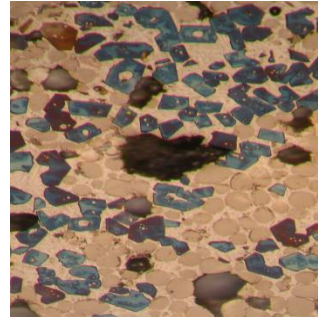


Fig. 2 (c) Clinker abrasions: line C, 1450°C

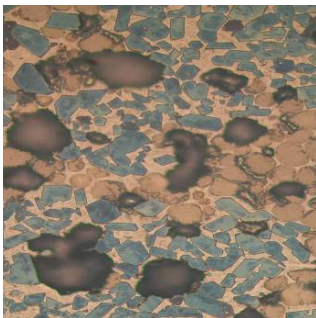


Fig. 1 (c) Clinker abrasions: line A, 1450°C

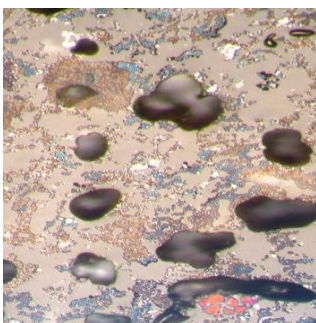


Fig. 2 (a) Clinker abrasions: line C, 1250°C

The presence of alite (blue grains) is already evident in the samples were burned at a temperature of 1250°C. In the pictures is evident a gradual development of alite grains (blue grains) with increasing temperature. At comparing of line A and C (the two-component and three-component raw mix), the clinkers regularly differed only in notably increased brownmillerite content with C line samples. The samples burnt under 1250°C definitely showed presence of Klein complex (Calcium sulfoaluminate), above this temperature its residual share was noticeable only with A line clinkers. Regarding Klein complex presence the clinkers burnt to 1250°C showed significantly lower content of C_3A than clinkers burnt under higher temperatures where due to absence of this phase the whole content of Al_2O_3 could practically apply only for formation of C_3A and C_4AF . In all clinkers the presence of β - C_2S and C_3S was further identified. In addition to the stated it was found that none of the clinkers contained any anhydrite II in identified amount.

B. Technological Properties of Burnt Clinkers

Results of test of technological properties are shown in Table I. Separation of samples was realized as on-time milling process and on that ground the different values in specific surfaces should be considered as primarily influenced by grindability of given clinker. The best grindability showed samples with burning temperature 1250°C, which due to very soft burnout contained low portion of still present free lime and in finely disperse condition already present clinker minerals.

TABLE I
TECHNOLOGICAL PROPERTIES

Monitored property	Burnout temperature [°C]					
	Samples of line A			Samples of line B		
	1250	1350	1450	1250	1350	1400
Grinding fineness Blaine [m ² /kg]	442	228	244	384	267	185
Normal consistency w [-]	0,300	0,325	0,270	0,331	0,306	0,300
Compressive strength [N/mm ²]	1 day	26,1	7,0	23,8	19,0	8,5
	3 days	31,0	25,8	28,0	27,5	16,0
	7 days	42,3	39,8	40,0	29,5	21,8
	28 days	60,8	48,4	53,1	42,0	36,3

With consolidation of clinker mineral structure less than 1300°C the grindability intensely worsened and at 1400°C it reached its minimum when clinkers contained higher belite share. Grindability improved again at burnout to 1450°C, when compared to preceding temperature alit share grew by 10% on account of worse grindablebelite. However, all the samples burnt to temperatures above 1250°C were coarse-grained compared to common Portland cements. Water-cement ratio of the samples was subjectively set to approximately same consistency of cement pastes and on that ground it has a low explanatory power in relation to character and sorting of given clinker. At the same time the subjectivity of this setting partially projected even to strength values. Not only samples burnt to highest temperatures but also ones burnt to 1250°C obtained the highest strengths. Considering the adequate rate between specific surface and water-cement ratio we can tend to opinion that also clinker very composition also contributed to higher strengths. Samples burnt to 1250°C contained a significant belite and alit portion already due to high share of C-A-F phases supporting sintering. However both of C-S phases have been very finely disperse so far due to which the clinker were in condition of high free internal energy content and thus of perfect reactivity. At sharper burnouts to 1350°C a balanced status for reactions in firm phase was obtained, i.e. the alit and belite contents were not changed in principle. On the contrary proportionally to the burning temperature the inner setup of these two phases structure improved which resulted in worse reactivity. Reactivity increased and therefore strengths too only with temperatures over 1350°C, when further portions of alit started to occur. Kinetics of this reaction was evidently increased at burning temperature 1450°C, when due to finished formation of alit also strengths grew.

C. Monitoring of Hydration Process

Qualitatively the hydrated clinker samples of lines A and C practically did not differ. In all samples there were identified quite high belite portions, further portlandite, sometimes carbonated to calcite as a by-product of alit hydration or as a direct product of free lime residues hydration. According to constant intensity of its diffractions brownmillerite present in the clinkers practically did not participate in the hydration process. On the contrary Klein complex was in the environment of Ca(OH)₂ saturated solution and as early as after one day hydration transformed in monosulphate and C₃A

with residues of calcium sulphate or alkali sulphates eventually and lime ions rather to ettringite. In semi-quantitative respect it can be stated that compared to hydrated Portland cements monosulphate strongly dominated ettringite. Higher ettringite portion was recorded regularly only with A sample burnt to 1450°C. Another difference of this sample was also a lower portlandite level given by total lime absence, higher consumption of limy ions for ettringite formation and higher saturation with lime in non-hydrated alit.

IV. CONCLUSION

It can be stated that burnout of p-clinker type binder with FBC fly ash as partial raw material base is possible.

Contrary to the natural raw material resources the FBC ashes contain relatively high anhydrite portion and in order the Portland clinker burnout on base of FBC ashes is possible at all, first the question of possible leak of SO_x into air at reverse CaSO₄ disintegration must be resolved.

The danger of CaSO₄ disintegration does not practically exist within approx. 1300°C, due to its still sufficient thermodynamic stability and also due to fact it is mostly bound to Klein complex. However if it is necessary to increase the temperature over the above mentioned limit, i.e. at clinker burnout, the Klein complex and CaSO₄ thermodynamic stability decreases under critical level and they start to disintegrate resulting in risk of SO_x escape and change of burnout conditions and clinker phase composition. At Klein complex disintegration a high portion of calcium aluminate phase is released resulting in essential change of conditions for formation of particular clinker minerals. Mainly consolidation of share of dark and light space matter occurs on account of belite and principally alit formation. Roughly in the period of Klein complex the FBC ash based raw material obtains character of especially well burnable set with high portion of liquid phase. This fact, however it appears as positive one can have a negative impact. At first burnout of sample A to 1450°C it was completely melted due to high portion of liquid phase. In real conditions a sticking part portion would significantly grow under these circumstances.

Sulphate ions, formed by CaSO₄ disintegration are immediately bound to alkali present in the set, primarily to K₂O. After saturation of present alkali other sulphate portions pass to dicalcium silicate structure which is generated by reaction in solid phase. But only to sintering moment when also C₂S comes to the melt, even half of the present sulphate ions are released and in laboratory burnout conditions they volatilise into air as sulphur oxides.

Therefore the differences in laboratory burnout conditions and real burnout ones in rotary furnace were examined. From consultations with cement industry experts it was found that SO_x escapes at burnout in furnaces with heat exchanger only at sulphido-sulphur oxidation. Present sulphates are bound with alkali and in form of congruently melting alkali sulphates they volatilise out to the heat exchangers where due to cooling condense and return together with the raw material powder back to the furnace. In addition part of them leave as by-products with clinker and generally they are removed by

bypass together with dust. Sulphates, released from FBC ashes, therefore do not enter in the air as SO_x at real burnouts at rotary furnaces with heat exchanger; they do not influence common composition of flue gases.

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REFERENCES

- [1] Garcia-Diaz, J.G. Palomo, F. Puertas, Belite cements obtained from ceramic wastes and the mineral pair. $\text{CaF}_2/\text{CaSO}_4$, *Cem. Concr. Comp.* 33-10 (2011).
- [2] Singh M, Upadhyay SN, Prasad PM, Preparation of special cements from red mud. *Waste Manag*; 16:665–70. (1996)
- [3] Ozturk, A.; Suyadal, Y.; Oguz, H., The formation of belite phase by using phosphogypsum and oil shale, *Cement and Concrete Research*, 30 967-971 (2000)
- [4] Raupp-Pereira F., James Ball R., Rocha J., Labrincha J.A., Allen G.: "New based clinkers: belite and lime formulations" *Cement and Concrete Research*. 38, 511 (2008).
- [5] Singh M, Upadhyay SN, Prasad PM.: Preparation of special cements from red mud. *Waste Manag*; 16:665–70. (1996)
- [6] Zapata A, Bosch P. A combustion method to synthesize a belite cement clinker. *J Am Ceram Soc*; 93:987–92. (2010)
- [7] Meyer, C., Baxter, S.: Use of recycled glass and fly ash for precast concrete, Final Report to New York State Energy Research and Development Authority, Rep. 98–18, Albany, NY, Oct. 1998
- [8] Poon, C.S., Kou, S.C., Lam, L., Lin, Z.S., Activation of Fly Ash/Cement Systems Using Calcium Sulfate Anhydrite (CaSO_4), *Cement and Concrete Research*
- [9] GAZDIĆ, D.; Slag-Sulphate Binder Preparation. *Advanced Materials Research*. 2013. 2013(818). p. 68 - 71. ISSN 1022-6680
- [10] Keppert, M., Reiterman, P., Pavlík, Z., Pavlíková, M., Jerman, M., Černý, R.: Municipal solid waste incineration ashes and their potential for partial replacement of Portland cement and fine aggregates in concrete. *Cement WapnoBeton*. 2010, vol. 15/77, no. 4, p. 187-193. ISSN 1425-8129.

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