

PREPARATION OF THE HIGH IRON SULFOALUMINATE BELITE CEMENTS FROM RAW MIXTURES INCORPORATING INDUSTRIAL WASTES

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High iron sulfoaluminate belites were synthesized using different kinds of raw components, maintaining the equal chemical composition of raw mixtures. A blast furnace slag, two kinds of brown muds and two kinds of fly ashes were used as waste raw components and limestone and bauxite as the natural raw components. Pure gypsum and gibbsite were used as the additional raw components. Raw mixture compositions were calculated by an especially designed procedure. The difference in properties of cements is seen from the development of their mechanical strength and from the rate of a heat liberation at early stage of hydration. The mechanical strength of specimens (28 days compressive strength in the range of 33 to 54 MPa) justifies the use of specified wastes for the preparation of title cement clinkers.

INTRODUCTION

The belite (C_2S)⁺ cements containing calciumsulfoaluminate phase ($C_4A_3\bar{S}$), anhydrite (CS) and calciumaluminoferrite (C_4AF) are low energy cements [1-3] and have the special capacity for being prepared from industrial wastes [4, 5].

The four mentioned clinker phases with a possible participation of free lime create the most frequently encountered phase assemblage to synthesize the laboratory clinkers of this kind [6-8], from among a fairly large set of phase assemblages possible [9, 10].

A preparation of the high iron oxide sulfoaluminate belite cements has been studied in detail in [11] using the reagent-grade chemicals. Frequently a variety of appropriate high tonnage wastes is available in certain districts and the question is how to combine them in an efficient way in order to create the appropriate raw mixtures. In case of Portland clinkers their composition tends to be settled into a narrow range of most convenient compositions. The sulfoaluminate belite (SAB) clinkers are much more flexible in this respect and

the suitable clinker phase combinations are only partially explored.

In this contribution a simple procedure for computation of the more complex raw mixtures from a set of available raw components is declared and demonstrated. Computed raw mixtures have the same overall chemical composition but differ in the raw components taken for their set.

By means of computed results the clinkers of equal chemical composition were prepared as the high iron SAB clinkers F1 and C2 studied in [11]. Subsequently the properties inside the two groups of these clinkers are compared.

The C_4AF content of clinkers is relatively high and so raw components, especially iron rich solid wastes, can be used for their preparation. The present clinkers were prepared from raw components, including the brown mud, the component high in iron oxide but also in sodium and potassium oxide.

⁺ An usual cement chemistry notation is used in which: C = CaO, S = SiO₂, A = Al₂O₃, F = Fe₂O₃, and \bar{S} = SO₃.

Table I. Chemical Composition of Raw Components

Raw Comp.	Oxides (wt.%)					MgO	TiO ₂	Na ₂ O	K ₂ O	LOI
	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃					
LIM	53.44	0.36	0.08	1.18	0.04	-	-	-	-	43.36
FA1	2.30	41.76	31.01	6.56	1.40	0.20	8.47	0.5	0.97	6.83
FA2	3.64	46.11	32.44	5.51	0.53	0.30	6.47	0.84	0.54	3.63
BM1	23.06	14.34	9.54	28.86	0.16	0.26	3.05	2.34	0.14	18.23
BM2	21.65	12.18	10.71	26.72	0.08	0.23	2.85	2.74	0.08	22.76
BFS	51.17	26.04	4.04	0.68	0.10	3.68	0.06	0.01	0.02	14.2
BAUX	0.96	17.17	45.22	18.05	0.06	0.16	2.16	0.11	0.29	15.82
GYP	32.59	-	-	-	46.4	-	-	-	-	21.01
GIB	-	-	65.37	-	-	-	-	-	-	34.63

LIM – Limestone, Rohožník; FA1 – Fly Ash, Tisová; FA2 – Fly Ash, Strážske; BM1, BM2 – Brown Muds 1 and 2, Žiar n. Hronom; BFS – Blast Furnace Slag, VSŽ-Košice; BAUX – Bauxite, Žiar n. Hronom; GYP – CaSO₄·2H₂O; GIB – Al₂O₃·3H₂O

EXPERIMENTAL PART

The composition of raw mixtures was calculated using program shortly described in the next paragraph.

Individual raw materials were weighed and milled together to a fine powder mixture. Nodules were prepared from the water plasticised paste. They were dried at ambient temperature and sintered in an electric furnace at 1200 °C for 0.5 h. The clinkers received were ground in a vibratory mill for 1 hr to produce cements. Their fineness was measured by Blaine method. The free lime content was determined by its extraction by ethylene-glycol and a subsequent titration by the benzoic acid.

Brown muds, prior to their use as raw components, were partially dealcalised by water leaching of the as received granular material.

The phase composition of product clinkers was determined by XRD analysis (Dron 2). Quantitative mineralogical composition of clinkers was calculated using the procedure given in [12].

An early hydration of cements was measured by the differential calorimetry (ZIAC) at a water/cement ratio 0.5.

Test specimens were prepared by casting the cement slurry into moulds with dimensions 1 × 1 × 3 cm, using the water/cement ratio 0.34. The same water/cement ratio was used to determine setting and hardening of the cement by a standard Vicat test. After 24 hours of hydration the specimens were demoulded and left for curing in a humid atmosphere.

SETTING UP

THE COMPOSITION OF RAW MIXTURES

A simple program AltMix - alternative mixes was developed for this purpose. In a course of the com-

putation the overall (required) chemical composition of the mixture, with respect to the five major oxides (CaO, SiO₂, Al₂O₃, Fe₂O₃, SO₃) is pre-set to the specified value (in our case corresponding either to C2 or F1 compositions) [11]. The raw compositions (each raw mixture containing five raw components) are created then by the combination of raw components, from their given set, until an exhaustion of all combinations.

Table II. Chemical composition of clinkers C2 and F1 as given in [11]

Clinkers	Oxides (wt.%)				
	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃
C2	48.3	8.7	18.4	13.1	11.4
F1	49.5	9.4	18.2	16.8	6.1

Table III. Calculated mineralogical composition of clinkers C2 and F1

Clinkers	Content of minerals (wt.%)					Ref.
	C	C ₂ S	C ₄ AF	C ₄ A ₃ S̄	C ₂ S̄	
C2	-	25	40	20	15	[11]
	0.6	24.9	39.9	20.2	14.3	this work
F1	-	27	51	15	7	[11]
	0.2	26.9	51.1	15	6.6	this work

Table IV. Calculated raw mixture compositions for clinkers C11-F13

Raw Compon.	Content of raw mixture components (wt.%)					
	C11	C12	C13	F11	F12	F13
LIM	38.19	38.35	31.47	40.97	38.22	43.64
FA1	-	4.87	-	-	-	-
FA2	4.34	-	-	1.82	-	-
BM1	-	-	-	37.02	37.66	31.33
BM2	30.22	29.82	31.71	-	-	-
BFS	-	-	7.41	-	3.07	-
BAUX	-	-	-	-	-	9.77
GYP	5.97	15.83	16.31	8.30	8.39	8.34
GIB	11.26	11.11	13.07	11.86	12.64	6.89

Subsequently the linear equations (1) are set and solved for each raw mixture (raw components in the mixture and their chemical composition) ($W_{j,i}$) and the pre-set chemical composition of the raw mixture (b_j).

$$\sum_{i=1}^p W_{j,i} a_i = b_j \quad (1)$$

p - number of linear equations; $W_{j,i}$ - oxide (j) mass fraction in the (i) component; a_i - mass fraction of the (i) raw component in the mixture of raw components; b_j - oxide (j) mass fraction in the product clinker or in an anhydrous, decarbonated - i.e. burnt raw mixture

The method is essentially a trial and error one. From all possible calculated raw mixture compositions the physical meaning have only those in which the content of all participating raw mixture components is positive. The negative content means that the given chemical composition of the clinker is "outside" the considered "assemblage" of raw components.

The program written in Quick Basic is available from authors.

RESULTS AND DISCUSSION

Chemical composition of raw materials used for computation of raw mixtures and for preparation of clinkers is given in Table I. The chemical compositions of the respective clinkers C2 and F1 is listed in Table II.

By a computation two sets of raw mixtures were established which, after liberation of CO_2 and H_2O at burning and neglecting of minor oxides, nominally all were equal in chemical composition either to the clinker C2 or to the clinker F1, respectively. The three mixtures, C21-C23, given in Table III, were chosen from the first group of raw mixtures for the experimental preparation

of clinkers. Similarly three other mixtures, F11-F13, were selected for the experimental preparation of clinkers from the second group of raw mixtures.

Computed mineralogical composition of clinkers as given in [11] and also as received by an application of the procedure described in [12] is given in Table IV. Table IV shows a small difference in computed phase quantities. The results presently obtained envisage however a certain quantity of CaO to be nominally present what is a kind of the useful information. The mineral phases were taken to be stoichiometric in computation what, especially in the case of C_4AF is not the real case [13].

X-ray patterns examined shown only the presence of the four major phases with no presence of $\text{C}_5\text{S}_2\bar{\text{S}}$.

Free lime, specific surfaces of milled clinkers and time corresponding to setting and hardening of cements are given in Table V.

Content of alkalis in the raw mixtures of C2 group is nearly the same (0.8 wt. %). The content of alkalis in the case of the clinker F11 is slightly increased (1.5 wt. %).

Table V. Free lime content, specific surface area and setting and hardening time of prepared clinkers

Clinker	Free lime (wt.%)	Specific surface (m ² kg ⁻¹)	Setting time (min)	Hardening time (min)
C21	0	659	40	65
C22	0	632	42	70
C23	0.12	653	48	75
F11	0.21	326	47	70
F12	0.16	386	40	67
F13	0.13	377	35	60

Mechanical strength of test specimens is shown in Figure 1. It can be seen from this figure that the mechanical strength at early hydration correlates the fineness of cements and also the content of alkalis. At the age of the hydration corresponding to approx. 7 days there exists a cease of the strength increase, irrespective of the fineness of the cement. A relatively low water/cement ratio may contribute to this phenomenon. The strength of cement paste samples for samples C2 and F1 respectively, as given in [11], is really high (112 MPa after 5 days of hydration in the case of C2 and 88 MPa after 5 days of hydration in the case of F1 respectively). The mechanical strength of present samples is appreciably lower, nevertheless it is comparable to the strength of Portland cements. The main reason for this difference is believed to be the content of alkalis, since

they were shown to strongly interfere creation of ettringite. The content of the TiO_2 seems not to be critical. The SAB cements prepared with a high portion of Fly Ash Tisova [8], containing above 8 wt.% of TiO_2 , exhibited a high mechanical strength.

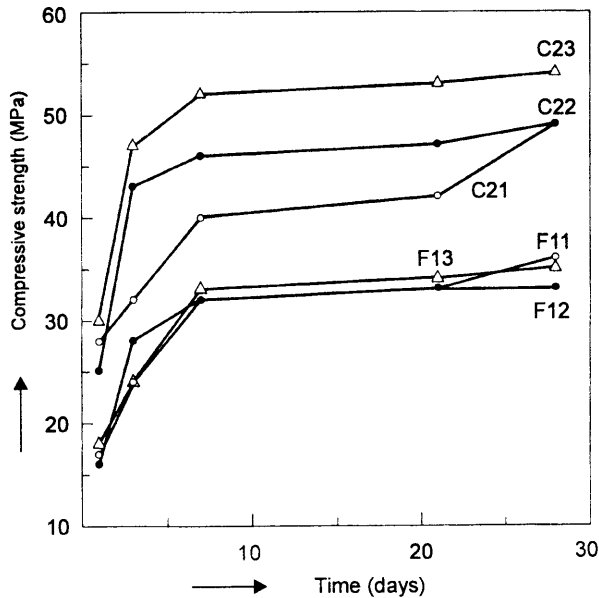


Figure 1. Compressive strength development of hydrated cement pastes of prepared cement clinkers

The deviation of the strength data inside the clinker group F1 with the low fineness is small. So in this case the origin of raw components does not play a significant role. On the other hand the fine clinkers exhibit a large deviation in the (final) strength.

Calorimetric curves (in Figures 2 and 3) reflect also preferentially the effect of fineness of cement. The strong early heat evolution in the case of the F1 group of clinkers is ceased after approx. of 30 hrs of hydration while in the case of the C2 group already after 6 hrs of hydration. Only small difference in the phase composition of clinkers inside of individual groups was expected. In spite of this the hydration curves also inside groups show expressive differences. However in the case of the F1 group they have no significant meaning in the strength development.

Only the partial conclusions can be drawn from results as for the effect of individual raw components on clinker properties because of the differences in the content of minor oxides. From strength data (clinker C1) it can be seen however that blast furnace slag may be a beneficial raw component.

In future it will be useful to extend computation of raw mixtures to those containing a higher number of raw components in order to keep the overall chemical

composition of mixtures equal also with respect to the minor oxides. The tests will be also desired for the change of the chemical composition of raw mixtures in course of their firing.

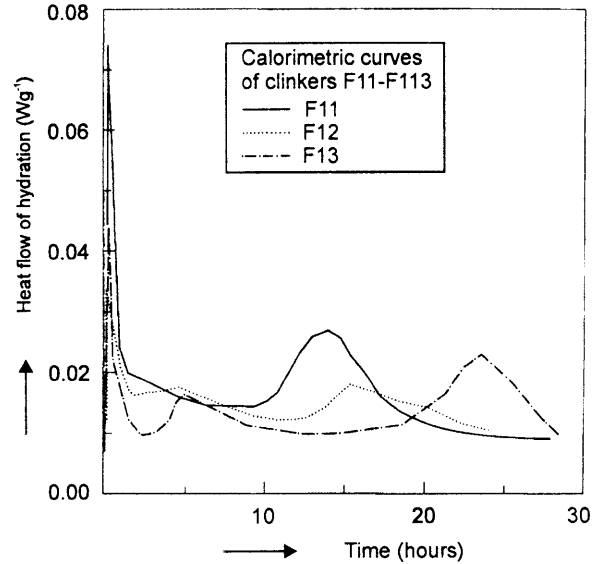


Figure 2. Heat evolution in the early period of hydration of clinker F11-F13

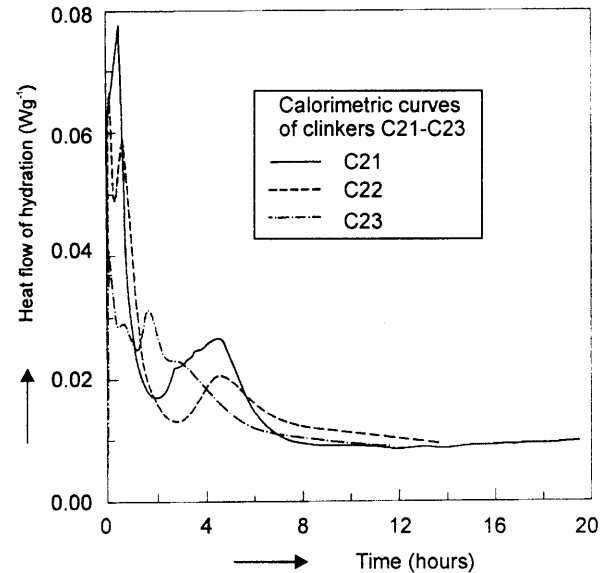


Figure 3. Heat evolution in the early period of hydration of clinker C21-C23

Many questions need further clarification. The ones belong to the optimization of the clinker composition with respect to its practical exploitation, e.g. with respect to the availability of raw materials, especially of wastes. The corresponding raw mixtures can be quite complex and may be completely based on wastes.

The second ones belong to the precise characterization of a phase composition of clinkers, including chemical composition of individual phases, as well as of their granulometry. This would create much more convenient basis for interpretation of results.

Finally, a long term durability test are needed before proceeding to a major production of these clinkers, especially when considering the increased content of alkalis.

CONCLUSION

An attempt has been made to compare properties of clinkers prepared from different sets of raw components, which were however equal in chemical composition with respect to the five major oxides present. Only partial conclusions can be drawn from results as to the role of individual raw components for clinkers preparation.

At lower specific surfaces of clinkers the strength development is nearly the same irrespective of the origin of raw components and the fluctuation in a content of minor oxides. At higher specific surfaces of clinkers the differences in the ultimate strength of test specimens are quite significant. Calorimetry shows differences in hydration curves at early period of hydration also in cases of clinkers with the approximate equal strength development.

Further effort in this field should be directed to rigorous maintaining the equal chemical composition of raw mixtures also with respect to the minor oxides present. Described program for the computation of raw mixtures may be quite beneficial to this purpose.

Nevertheless, also in cases in which chemical composition of clinkers can be maintained exactly the same in respect to all oxides present the assessing of the role of individual raw components in raw mixtures and especially an interpretation of calorimetric results can be done only on the ground of the precise mineralogical and particle size characterization of final clinkers. In principle the brown mud is approved as a raw component for the preparation of SAB clinkers.

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PRÍPRAVA VYSOKOŽELEZITÝCH SULFOALUMINÁT-BELITOVÝCH CEMENTOV ZO SUROVINOVÝCH ZMESÍ OBSAHUJÚCICH PRIEMYSLOVÉ ODPADY

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Sulfoaluminát-belitové slinky (SAB) sú nízkoenergetické slinky. Na ich prípravu možno využiť viaceré veľkotonážne anorganické odpady.

V práci sa uvádza postup výpočtu zloženia surovinových zmesí pre výrobu slinky zo zadaného súboru surovinových zložiek, medzi ktoré možno zahrnúť aj priemyslové odpady, pri zadanom celkovom chemickom zložení surovinovej zmesi a tým aj pri určenom nominálnom chemickom a mineralogickom zložení slinky.

Pri výpočte sa zohľadňuje 5 základných makrozložiek sústavy (CaO, SiO₂, Al₂O₃, Fe₂O₃, SiO₂, SO₃). Princípom výpočtu je systematická generácia päťc surovinových zložiek a zostavovanie a riešenie lineárnych rovníc (päť rovníc o piatich neznámych).

Postup sa aplikoval na výpočet zmesí k príprave dvoch druhov vysokoželezitých SAB slinkov, ktoré boli už predtým pripravené (z čistých chemikálií) a v literatúre boli opísané ich vlastnosti.

Na základe vypočítaného zloženia surovinových zmesí sa pripravili cementové slinky a určil sa vývoj tlakových pevností zatuhlých cementových pást. Kalorimetricky sa zmeral tiež vývoj tepla v počiatočnom štádiu hydratácie.

Výsledky ukazujú, že aj pri zvýšenom obsahu alkálií v dôsledku použitia hnedého, i keď čiastočne dealkalizovaného kalu ako surovinovej zložky možno získať slinok a následne maltovinu s dostatočným nadobúdaním pevností.