CHARACTERISATION OF CEMENTS FROM DOMINANTLY VOLCANIC RAW MATERIALS OF THE CARPATHIAN BEND ZONE

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This paper presents the results of laboratory investigations regarding the production of cements from local raw materials, such as limestone from Varghis, gypsum from Nucsoara, basaltic scoria from Racosul de Jos, volcanic tuff from Racosul de Sus, diatomite from Filia, and red mud from Oradea. The raw mixtures, based on modified Bogue calculations, contain limestone, gypsum, and one or two of the above-mentioned materials. The cements resulted from clinker grinding in a laboratory gas furnace at 1260–1300 ºC, with one hour at the peak temperatures, and were characterised for Blaine specific surface area, specific density, and mineral phases. Physico-mechanical properties, such as water content for normal consistency, setting time, soundness, and compressive strength were also determined. Results show that these cements contain belite, ferrite, calcium sulphoaluminate, anhydrite, and some minor compounds.

Keywords: experimental cement, Varghis limestone, Racosul de Sus volcanic tuff, setting time, mechanical properties

1. Introduction

Manufacturing of Portland cement is energy consuming, globally accounting for 2% of primary energy and 5% of industrial energy consumption. Moreover, Portland cement production contributes significantly to greenhouse gas emission in the order of 5% of the global CO_2 emissions due to anthropogenic sources [1]. New civil engineering requirements impose the production of a new type of cement, which is of good quality, environmentally friendly, and requires low energy utilization. Low-energy cement manufacturing is economically and ecologically preferable. These cements could be used in places where high early strength or expansion compensation and also increased durability are required.

In cement chemistry, notation of oxides are abbreviated by their first capital letters: C=CaO, S=SiO_2, A=Al_2O_3, F=Fe_2O_3, C$\overline{S}$=SO_3, and H=H_2O. Low-energy cements comprise those that belong to the CaO-SiO_2-Al_2O_3-Fe_2O_3- C$\overline{S}$ system. They are mainly sulpho-aluminate belitic and sulphoferroaluminate belitic cements [2]. These can be produced from both natural raw materials or raw material mixtures, containing by-products or industrial waste, by firing at lower temperatures than for Portland cement clinkers. A large variety of cements was developed in China based on the composition $C_4A_3\overline{S}$. These were standardized and named as "Third Cement Series" [3]. These cements have special features such as quick setting time, good impermeability, and rapid strength development even at low temperatures.

There are numerous investigations on the laboratory-scale production of sulphoaluminate belite (SAB) cement [4–18]. SAB cement can be classified into three major categories according to the content and proportions of the phase compositions. The tentative naming and some basic properties are summarized below:

1. *Calcium sulphoaluminate-rich belite cement:* They are mostly composed of only two main phases of SAB cement, the major components being $C_4A_3\overline{S}$ (around 55–75 (g/g)%) and C_2S. This type of cement is typically used for applications requiring rapid setting and high early strength [4, 6, 8, 9, 19, 20].

2. *Expansive belite-rich calcium sulphoaluminate cements*: Besides the main components of the SAB cements they contain free lime up to 10 (g/g)% which promotes expansion. This type of cement can be used in restricted areas requiring shrinkage-resistant and self-stressing cements [4, 12, 16, 20, 21].

3. *Non-expansive belite-rich calcium sulphoaluminate cements*: These cements have higher belite, lower calcium sulphoaluminate, and much lower or completely deficient of free lime content than those of commercially produced SAB cements. Industrial by-products with high sulphate content can be used in high

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Table 1. Chemical compositions of the raw materials in (g/g) %.

oxides	Varghis limestone	Oradea red mud	Racosul de Jos basaltic scoria	Racosul de Sus volcanic tuff	Filia diatomite	Nucsoara gypsum
CaO	89.61	12.71	10.38	2.88	0.71	28.31
SiO_2	4.01	8.93	46.10	64.53	92.52	9.83
Al_2O_3	5.16	17.04	18.78	11.80	3.24	2.73
Fe_2O_3	-	48.37	9.93	2.57	2.18	1.07
Na_2O	-	3.68	3.23	1.89	-	0.15
K_2O	-	-	1.69	2.75	0.46	0.55
MgO	-	1.30	7.21	0.45	-	0.39
TiO_2	-	6.80	1.61	0.27	-	0.13
V_2O_5	-	0.19	-	-	-	0.04
P_2O_5	1.22	0.98	1.07	-	-	0.04
SO_3	-	-	-	-	0.89	37.08
Mn_2O_3	-	-	-	-	-	0.02
P.C.	-	-	-	12.40	-	19.90

Table 2. Theoretical mineralogical and chemical compositions of the cements in (g/g) %.

Sample	mineral composition				oxidic compositions				
	C_2S	$C_4A_3\overline{S}$	C_4AF	$C\overline{S}$	CaO	Fe_2O_3	SiO_2	Al_2O_3	SO_3
C1, C2, C3	56	12	22	10	55.15	7.23	19.53	10.63	7.46
C4	50	18	15	17	53.11	4.93	17.44	12.17	12.36
C5	43	28	23	6	51.38	7.56	15.00	18.86	7.20

percentages in production. This type of cement shows high mechanical strength both at early and late ages comparable to ordinary Portland cement and has the potential to replace it [4, 6, 8, 14, 16].

There is no commercial production of the belite-rich calcium sulphoaluminate-type of cement. Mehta [18] produced SAB cements containing no free CaO, but large amounts of belite rich in $CaCO_3$, silicic acid, hydrated alumina, iron oxide, and gypsum. The clinkers were obtained by heating the raw materials in an electric muffle furnace at 1200 °C for about 1 hour. Clinkers were ground to a Blaine specific surface area of about 400 m^2 kg^{-1}.

Microstructure examinations of the clinkers showed that $C_4A_3\overline{S}$ appears as cubic crystals whereas belite appears as large rounded grains. The clinkers were very easy to grind due to their brittleness [4]. Sahu *et alia* [12] produced cements of Types 2 and 3 from limestone, fly ash and gypsum at 1200 °C, for a bearing time of 30 minutes and cooled by fresh air. Kasselouri *et alia* [17] in 1995 obtained cement of Type 3 at 1280 °C from limestone, gypsum, bauxite, silica sand, and iron-rich industrial by-products. Cements composed from a mixture of baghouse dust, F-class fly ash, and scrubber sludge, sintered at 1175–1250 °C for bearing times of 30, 45, and 60 minutes, and cooled by natural air were obtained according to Arjunan *et alia* [10]. Mixtures composed of limestone, bottom ash, baghouse filter ash, bauxite, and gypsum fired at 1250 and 1300 °C, for a bearing time of 60 minutes, lead to SAB cement of $C_4A_3\overline{S}$ – ye'elimite, C_2S-larnite (belite), C_4AF-brownmillerite, and $C\overline{S}$- anhydrite compositions [4]. The absence of tricalcium aluminate (C_3A) in these cements indicates that the decomposition of the desired mineral $C_4A_3\overline{S}$ does not take place at these temperatures. The presence of the desired minerals and the absence of $C_5S_2\overline{S}$ confirmed the formation of the SAB cement at 1250 °C and 1300 °C after 1 hour.

This article presents our study on the cement series sintered using local raw materials, such as volcanic tuffs from Racosul de Sus, basaltic scoria from Racosul de Jos, and diatomite from Filia (all in the Carpathian orocline), and red mud.

2. Experimental

The raw materials used for the cement experiments carried out as part of this study are natural (Varghis) limestone, Bodoc clay, Nucsoara gypsum, Racosul de Jos basaltic scoria, Racosul de Sus volcanic tuff, Filia diatomite, and artificial industrial waste (Oradea red mud). The selected raw materials were investigated for chemical compositions.

The chemical compositions of the limestone, red mud, diatomite, and basaltic scoria were analysed by SEM/EDAX. The volcanic tuff and gypsum analyses were performed by wet chemical methods, according to the SR EN 192-2 (*Table 1*). The theoretically estimated mineralogical, chemical compositions based on modified Bogue calculations [1, 4, 22] are given in *Table 2*. The compositions of the raw material mixtures are presented in *Table 3*. The raw material mixtures were obtained by grinding them in a laboratory ballmill up to a sieve residue of 90 μm about 12%. Afterwards, the raw material mixtures underwent a process of briquetting and drying followed by firing in a laboratory gas oven for one hour at a constant temperature of 1260–1300 °C. The inside temperatures of the furnace were estimated with a thermocouple thermometer. Fast cooling was achieved in the air. The obtained cements from grinded clinkers (five hours in a mill, balls:clinkers ratio of 2:1) were tested. Mineralogical

Table 3. The compositions of raw material mixtures in (g/g) %.

Samples	Varghis limestone	Oradea red mud	Racosul de Jos basaltic scoria	Racosul de Sus volcanic tuff	Filia diatomite	Nucsoara gypsum
Cement 1	48.90	-	36.67	-	-	14.43
Cement 2	54.08	-	-	-	13.70	32.22
Cement 3	54.35	-	-	23.37	-	22.28
Cement 4	54.66	0.98	31.53	-	-	12.83
Cement 5	47.45	1.19	20.66	-	-	30.70

Table 4. Mineral compositions in (g/g) % of the cement samples C1-C5 according to the IL-LAB-41 testing method.

Minerals	C1	C2	C3	C4	C5
Belite	24.2	69.1	65.9	52.7	58.4
Ferrite	7.5	13.1	8.5	24.6	20.8
Cubic aluminate	8.5	0.4	0.0	0.2	4.7
Orthorhombic aluminate	20.5	0.0	0.0	1.5	0.0
Free lime	1.4	0.5	1.7	0.6	0.1
Anhydrite	2.1	6.8	3.8	1.5	5.3

Table 5. Physical properties of cement samples C1-C5.

Sample	Blaine specific surface area, $cm^2\,g^{-1}$	Heat of hydration, $J\,g^{-1}$	Specific density, $g\,cm^{-3}$
C1	7367	29	3.17
C2	8745	123	3.04
C3	7963	32	3.07
C4	6501	44	3.14
C5	7553	110	3.26

Table 6. Physico–mechanical properties of cement samples C1-C5.

sample	water for normal consistency, cm^3	setting time, hour : minutes early	final	soundness, mm	compressive strength, $N\,mm^{-2}$ 2 days	28 days
C1	135	0:44	1:44	2.75	0.24	0.42
C2	225	0:13	0:35	0.50	4.12	26.67
C3	124	3:35	4:29	3.00	0.23	8.42
C4	185	1:57	> 10 hour	1.00	0.53	0.72
C5	178	0:05	0:15	2.00	1.44	2.28

compositions of cements made by XRD analyses with a Panalytical-Philips Cubix PRO X-ray spectrometer, according to IL LAB 41 proceedings are presented in *Table 4.* Experimental laboratory-produced cements were tested in conditions provided by the Romanian CRH CEMENT S.A. plant in Hoghiz (Brasov county). The Blaine specific surface area, specific density, heat of hydration (*Table 5*), volume of water for normal consistency, setting time, soundness, and compressive strength (*Table 6*) have been determined. Identification of mineral phases formed during the burning of clinkers was carried out by means of the Cubix PRO spectrometer.

3. Results and Discussions

The mineralogical compositions of the experimental cements are summarized in *Table 4*. All cement samples contain belite, ferrite, anhydrite, and many other phases in small amounts. The largest amount of belite found in a cement sample is in the raw mixture containing diatomite (sample C2 with C_2S = 69.1%), followed by the sample prepared with volcanic tuff (sample C3 with C_2S = 65.9%). Soner *et alia* reported [4] that the mineral $C_4A_3\bar{S}$ is stable between 1250–1350 ºC, but probably it can decompose during cooling. Furthermore, it was demonstrated that aluminium could be substituted by iron in the ye'elimite structure forming $C_4A_{3-x}F_x\bar{S}$ [23–26]. The experimental cement samples were characterized with regards to specific density and fineness, representing the Blaine specific surface area
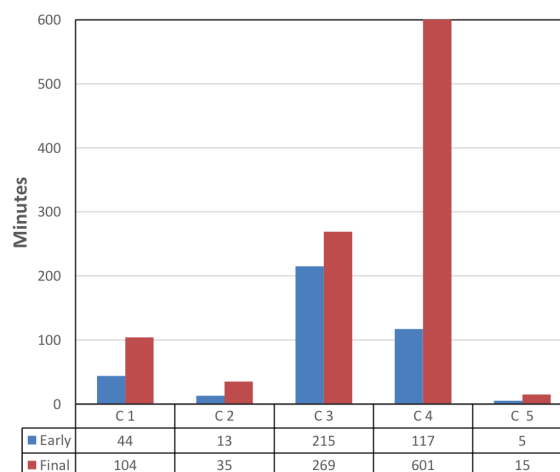

	C 1	C 2	C 3	C 4	C 5
Early	44	13	215	117	5
Final	104	35	269	601	15

Figure 1. Early and final setting times of the cement samples in minutes.

[27]. The heat of hydration according was also determined to the SR EN 196-9/2006 method [28]. The physical properties of experimental cements are presented in *Table 5*.

The experimental Blaine fineness data are characterised by large specific surface areas. The biggest Blaine specific surface area was found in sample C2 (with diatomite) followed of sample C3 sample (with volcanic tuff). These samples have the smallest specific densities in the same order. The binding behaviour of the cements was estimated by measuring the setting time, volume of water for normal consistency, soundness, and compressive strengths (after second and twenty-eighth days). To determine the
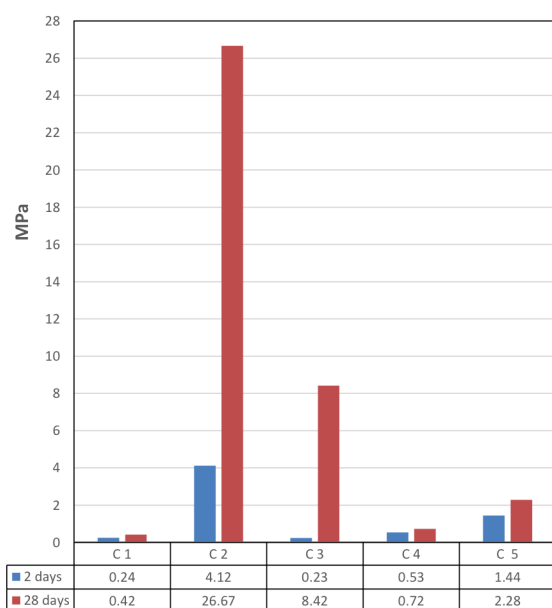
	C 1	C 2	C 3	C 4	C 5
2 days	0.24	4.12	0.23	0.53	1.44
28 days	0.42	26.67	8.42	0.72	2.28

Figure 2. Compressive strength of cement samples after 2 and 28 days in MPa.

setting times, the quantity of water required to form cement paste of standard (normal) consistency was determined previously [29]. The water data for standard consistency are presented in *Table 6*. The setting time for the paste with standard consistency was measured using a Vicat device. The initial and final setting data of the investigated cements are also shown in *Table 6* and *Fig.1*. The compressive strengths have been determined according to the SN EN-1/2006 method [30] and the data are shown in *Fig.2*.

The investigated cements exhibited different mechanical strengths, as a function of their mineral compositions. The strength of SAB cements depends mainly on the mineral ye'elimite ($Ca_4Al_6O_{12}SO_4$ or $C_4A_3\bar{S}$) during the initial minutes up to hours of hydration [31, 32]. Ye'elimite is almost entirely responsible for the hydration reactions at early ages of CSA-type cements [23]. The presence of belite was found to be responsible for compressive strength at late ages. The compositions of raw material mixtures for these experimental cements influenced their mineral contents. Taking into consideration these, the initial strengths are better for the cements containing diatomite (sample C2), volcanic tuff (sample C3), basaltic scoria (sample C4), and red mud (sample C5). A higher content of red mud is favoured over sample C4 (see *Tables 3* and *4*, *Fig.2*).

A good evolution of mechanical strength over time is shown for samples C5 and especially for the C2 cements. C3 cement sample is also notable, but with lower initial strength, which is an important characteristic for a favourable evolution of specific surface area. This is clearly the largest value for cement sample C3. The cements containing basaltic scoria generally developed lower mechanical strengths in comparison to those containing diatomite or volcanic tuff. The cement containing diatomite is noticeable due to its very high initial strength (*Table 6*). For this

cement, the compressive strength, after two days increased, which may be a consequence of the increased specific surface area. In terms of practical applications, the development of cement of good mechanical strength and workability depending on the setting time is of importance. The setting time of investigated cements was decisively influenced by the content of raw material mixtures (see *Table 3*). In the order of C4→C3→C1→C2→C5, the setting time becomes shorter. For the cement samples containing 1.2% red mud, 20.7% basaltic scoria (C5) and 13.7 % diatomite (C2), the setting time is quick. This is a consequence of rapid hydration processes. Because of this, these latter samples can be considered for practical applications only as retarding admixtures or super-plasticizers due to their set-retarding effect. Soundness shows reasonable values, which is required to be less than 10 mm for Portland cement.

4. Conclusion

Based on investigations into cement samples in the laboratory of the Hoghiz plant, it can be concluded that from all raw material mixtures, heated at temperatures of between 1260 and 1300 ºC, resultant clinkers contain more belite, ferrite, and anhydrite. Physico-mechanical properties show good compressive strength at early ages, good soundness, the biggest Blaine specific surface area (S_{sp} = 8745 cm^2 g^{-1}) for cement containing limestone, diatomite, and gypsum, as well as belite and anhydrite. The use of the local raw materials from the Carpathian orocline area, e.g. Varghis limestones, Bodoc clays, Nucsoara gypsum, volcanic tuffs from Racosul de Sus, basaltic scoria from Racosul de Jos, and Filia diatomite, facilitated the formation of cements that are more belitical than sulphoaluminate.

Acknowledgement

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