

CHEMICAL-MINERALOGICAL CHARACTERISATION OF BELITES FROM EXPERIMENTAL SAB CLINKERS

EMILIA MOSONYI^{a*}, JÓZSEF FAZAKAS^{b,c}, MARIA SPATARU^c,
TIMEA HALMAGYI^c

ABSTRACT. Guided by theoretical (sulphoaluminate belitic) SAB clinker chemical compositions, raw materials of known chemical composition (locally sourced from the Carpathian oroclinal), were mixed and tested by burning in laboratory conditions at different temperatures 1220, 1240 and 1260°C. The resulting materials were analyzed by optical transmission and reflection microscopy (using HF etching) and completed with XRD analyses. In this paper we describe chemical and mineralogical characterization of clinker belitic components manufactured in laboratory conditions. Belite nests and clusters with complex zoned structure are observed optically in interstitial material of the clinker that is composed of sulfoaluminate, ferrite and anhydrite. These structures display all three morphological types of belite, corresponding to the different polymorphs of belite, depending on the burning and quenching conditions of the clinker. The XRD patterns are interpreted to show that the appearance of β - and α' -belite and different $\alpha' \rightarrow \beta$ transition forms are due to cooling to room temperatures and presence of the belite polymorph stabilizing ions SO_3 , Al^{3+} , Fe^{3+} and alkali. The conclusions of the study were that belites were formed in various mixtures of raw materials treated at low burning temperatures, relatively slow cooling rates (resulting in different proportions of impurity absorption) and with some experiments run under reducing conditions during firing. Chemically, the lime saturation factor of clinkers is low ($\text{LSF} = 0.74 - 0.84$), such compositions favoring the clinker belite component; the silica ratio is low ($\text{SR} < 1.5$), which can improve the burnability of the clinker; the alumina ratio is medium ($\text{AR} = 1.5 - 2.5$), chemically restricting the solid solution of mineral phases, and the hydraulic modulus (HM) is under 1.7, enhancing resistance to chemical attack.

Keywords: SAB clinker, belite polymorphs, mineralogy, XRD

^a Babeş-Bolyai University, Faculty of Biology and Geology, Department of Geology, 1 Mihail Kogălniceanu str., RO-400082, Cluj-Napoca, Romania

^b Babeş-Bolyai University, Faculty of Economical Sciences and Management, 58-60 Teodor Mihali str, Campus FSEGA, RO-400591, Cluj-Napoca, Romania

^c C. VALDEK IMPEX SRL, str. 1 Decembrie 1918, Bl. 15, Sc. E, et. 3, ap. 9, Sfântu Gheorghe, Covasna, Romania

* Corresponding author: emilia.mosonyi@ubbcluj.ro

INTRODUCTION

The subject of this study, the sulphoaluminate belitic clinkers, “the third cement series” [1] contain calcium sulphoaluminate, belite, ferrite and anhydrite as main mineral phases [2, 3, 4].

As a low energy type clinker, its recipe may comprise natural raw materials or natural materials mixed with industrial waste or mining dump materials which are sinterized at about 200°C lower than normal Portland cement [5, 6]. These types of clinkers are environmentally friendly due to lowering greenhouse gas (CO₂) emission by 20 - 30% compared with Portland cement clinker production [7].

Our purpose was to test by burning in laboratory conditions, at different temperatures (1220, 1240 and 1260°C) few raw mix recipes for theoretical (tentative) SAB clinker compositions. The recipes were counted by reverse Bogue method, using mainly local raw materials of known chemical compositions.

The components of our experimentally produced SAB clinkers comprise, beside limestone, clay, diatomite, volcanic tuff or basaltic scoria, red mud and gypsum. The latter component is a mineralizer [8], which stabilizes the reactive β-belite form in the clinker composition and lowers the sintering temperature (1200 - 1250°C).

The clinkers' main component, belite (theoretic formula C₂S), in the cement industry may present 5 polymorphs [9, 10]:

The transition temperatures for: $\alpha \rightarrow \alpha'_H \rightarrow \alpha'_L \rightarrow \beta \rightarrow \gamma$, are 1425°C, 1160°C, 630- 680°C and <500°C respectively. The α polymorph is ditrigonal dipyramidal and optically is almost isotropic; α' is orthorhombic, having high refraction indexes ($n_\alpha = 1.719$, $n_\gamma = 1.732$) β -belite is monoclinic and posses the highest hydraulic activity; the γ polymorph is orthorhombic, having $n = 1.642 - 1.645$ and splintery fracture. The γ -belite has the lowest density and hydraulic properties.

The α , α'_H , α'_L , β structures are parts of the same species family of glaserite (K₃Na(SO₄)₂) (Moore, 1973) [11], but the γ polymorph is similar to olivine (Fe Mg)₂(SiO₄) [12, 13]. The α' and β polymorphs are generated from α structure form by progressive change of the lattice symmetry and density. The $\beta \rightarrow \gamma$ conversion implies a mechanical phenomenon, known as self-pulverization (dusting).

The higher temperature polymorphs on cooling to room temperature are stabilized by substituent ions. Such components could be Al³⁺, Fe³⁺ and S⁶⁺ which can replaces via coupled substitution 2Al³⁺+ S⁶⁺ for 3Si⁴⁺ [14] in the SiO₄⁴⁻ positions or Mg²⁺ replaces Ca²⁺ in the belite crystallochemical formula [15] or K, Na, P which can stabilize α' - polymorph [16].

In the case of the presence of fine grained belite (crystallites) the transformation to gamma form does not take place even if stabilizer ions are not present [17].

During $\alpha \rightarrow \beta$ transitions, the lower-temperature polymorphs are less able to accommodate substitute ions and the exsolution of substituting ions progressively greater, filling the spaces between belite twin lamellae as different phases [18] or mechanical twinning results due to density transformations. Hence, the interpretations of belite composition data are only tentative mainly due to exsolution effects [19].

The positive correlation between SO_3 content of clinkers and belite component was outlined by Regourd et al. (1969) [20] who sinterized β -belites and studied their cell parameters and microstructures. The authors indicated that in higher temperature polymorphs there are more substitutions, but in the same time the XRD analyses evidenced lowering crystallinity and peak intensities of these belites.

Ono et al. (1969), Ono (1975) and Yamaguchi and Takagi (1969) [21-23] described the optical properties of belite from clinkers. From morphological point of view, the belite can be classified [24] as: type I, with rounded grains of 20 - 40 μm , possessing skeleton structure, consisting of α and β forms of belite (interpreted [22], having two twinning directions owing to the symmetry transformation during $\alpha \rightarrow \alpha'_H \rightarrow \alpha'_L \rightarrow \beta$ transitions, although this form is mainly monoclinic β -belite; type II represents grains with irregular forms and having only one parallel twin lamellae, owing to $\alpha'_L \rightarrow \beta$ transition; type III, formed at lower temperatures, is untwined, but can display exsolution spots.

RESULTS AND DISCUSSION

Taking into consideration the chemical compositions of the clinkers raw materials (see the experimental section) and a tentative theoretical clinker composition, using the Bogue counting's, a few SAB clinker recipes were selected for burning and selected cement parameters were counted. In $\text{CaO} - \text{Al}_2\text{O}_3 - \text{Fe}_2\text{O}_3 - \text{SiO}_2$ system, the K \ddot{u} hl modules [25-28]: Silica Ratio SR, Alumina Ratio AR, Lime Saturation Factor LSF, (modified [29, 30, 31], Hydraulic Modulus HM and belite sulphate content S^*_b [32] are shown in Table 1.

Chemically, the LSF of clinkers are relative low, hence it stabilizes the belite component, the SR is under 1.5, AR is medium and HM is under 1.7. Based on the raw materials mixing recipe (Table 2) the sinterized products were analysed.

Table 1. The tentative chemical compositions (wt%), main mineral phases (%) (Bogue countings) and Kühl chemical ratios of resulting clinkers (lime saturation factor LSF), silica ratio SR, alumina ratio AR, hydraulic modulus HM, SO₃ content (%) of belites S^{*_b}

sample	CaO	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	SO ₃	C ₂ S	C ₄ A ₃ S*	C ₄ AF	CS*	LSF	SR	AR	HM	S ^{*_b}
2	54.13	3.94	18.84	9.03	14.06	54	13	12	21	0,84	1,45	2,29	1.71	17,6
3	55.15	7.23	19.53	10.63	7.46	56	12	22	10	0,87	1,07	1,47	1.54	9,5
8	51.38	7.56	15.00	18.86	7.20	43	28	23	6	0,76	0,67	2,49	1.56	9,1
11	53.11	4.93	17.44	12.17	12.36	50	18	15	17	0,74	1,02	2,47	1.24	15,5

Table 2. The composition of raw materials mixture (mixing recipe)

Sample	Raw materials mixture - %					
	Vârghiş Limestone	Oradea Red mud	Racoşul de Jos Basaltic scoria	Bodoc Clay	Racoşul de Sus Volcanic tuff	Nucşoara Gypsum
2	57.43	-	-	10.88	-	31.69
3	47.44	-	-	0.05	-	52,51
8	42.05	6.20	0.38	-	-	51.37
11	46.55	-	-	-	10.57	42.88

The thin section images of clinkers revealed calcium silicate particles (mainly belite C₂S) from few tens of micrometers up to 200-250 micrometers and dominantly olive- greenish to brownish interstitial material composed of sulphoaluminate, ferrite, anhydrite, amorphous glass material and circular to elliptical pores filled with alkali sulphates. The silicate particles are mainly belitic and they form nests and clusters of complex frequently zoned microstructure. In these structures, all three morphological belite types are developed with or without one or two directions of twin lamellae, presenting overgrowth zones or lamellar sometimes finger-like prolongations (ragged belite) or rough surfaces owing to the matrix corrosion effects. Not rare are situations in which belite rings developed around interstitial central pores. The belite grains present mainly rounded or irregular forms containing exsolutions or mechanical twin lamellae, sometimes spherulitic structures, the latter due to α'→β conversion [22]. The belite colors are pale yellow up to amber, the birefringence colors are first order yellow to orange (Δ= 0.017 - 0.018). The chemical compositions of belites could be only tentative, owing to many exsolution structures. The SO₃ content of belite is relatively high (Table 1, S^{*_b}= 9 - 18%) and was calculated in relation to the clinker SO₃ content. The S⁶⁺ enters the tetrahedral position replacing the Si⁴⁺ ions in the belite structure and stabilizes it at high temperature. Other stabilizing ions are Fe³⁺ and Al³⁺, resulting the greenish yellow or pale yellow up to amber belite color.

The centre of nest structures may contain prismatic alite (C_3S) or periclase (M) relics. The belite has mainly rounded shapes, sometimes rough surfaces due to the matrix corrosion (reducing burning conditions) or finger-like overgrowths (ragged belite, owing to the slow cooling conditions). In other cases belite presents dot-like exsolutions. Some microscopic images and interpretations of belite properties are presented in Figures 1- 7.

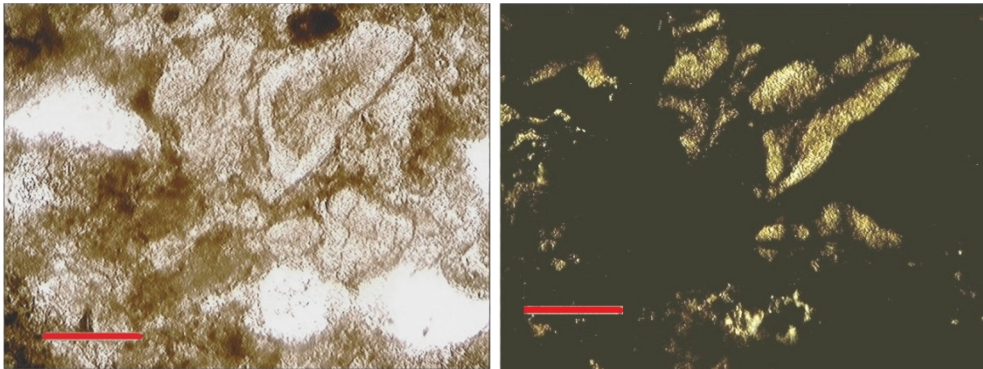


Figure 1. a (1N), b(N+). Sample 2 - raw mixture sinterized at 1220 °C: zoned belite spherulites (core zone brownish colored, overgrown by a light gray belitic ring with dot-like exsolutions- top center), corroded by matrix material. All these interpreted as formed under slow cooling conditions. Scale bar 50µm

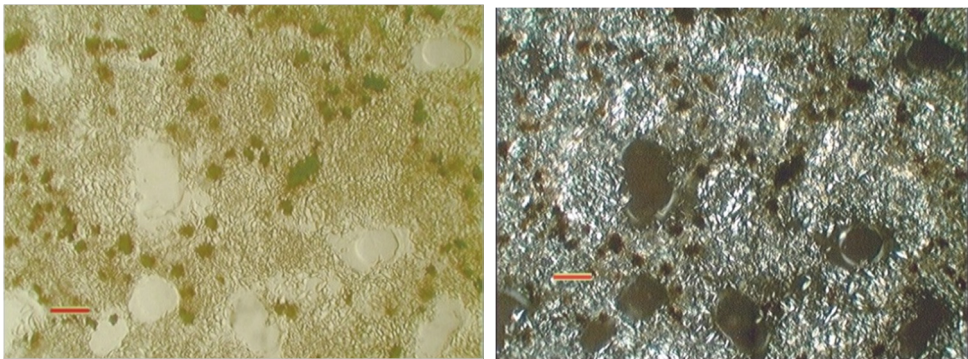


Figure 2. a (1N), b (N+). Sample 2A, burned at 1240 °C: pores filled with alkali sulphates (colorless, low relief), belite II (yellowish - white birefringence color and twin lamellae in one direction) chains and rings around pores; in the centre there is an alitic nest with belitic corona corroded by ferrite. Scale 50 µm

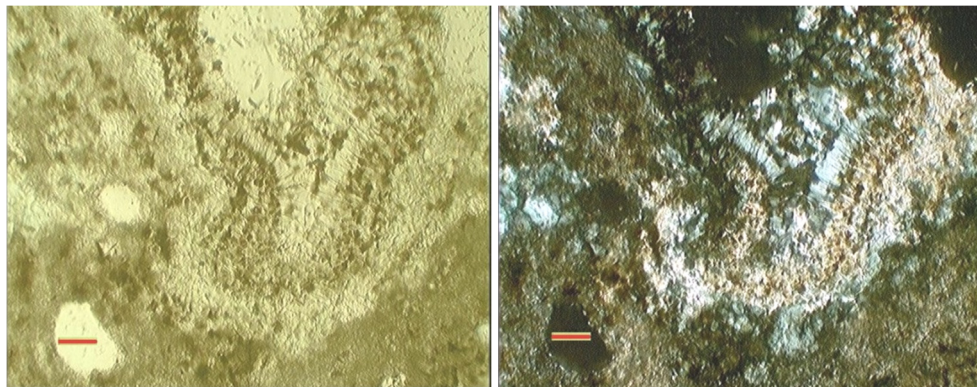


Figure 3. a (1N), b (N+) Sample 3, burned at 1220 °C: around the pore (top centre) was developed a ring with zonal structure: in the core - a radial lath - like alite ring overgrew by belite III with iron exsolutions and covered by belite I, the later being corroded by matrix phases (rough surface, due to reducing burning conditions). Scale bar 50 μm

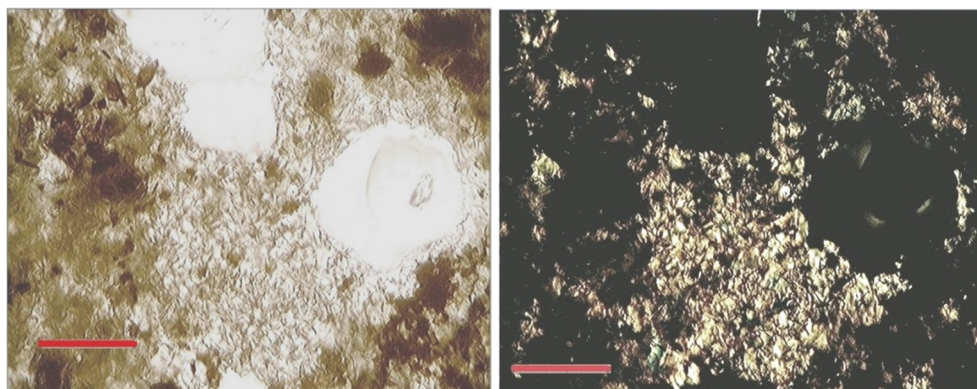


Figure 4. a(1N), b (N+). Sample 8A, burned at 1240 °C. External part of sample: around pores were crystallised alite and belite rings. In the centre of images is a complex belite cluster containing from core to rim: belite III with exsolution dots, belite I, belite II. The cluster has belite II satellite overgrowth and can contain alite prism relics (bottom of image). Scale 50 μm

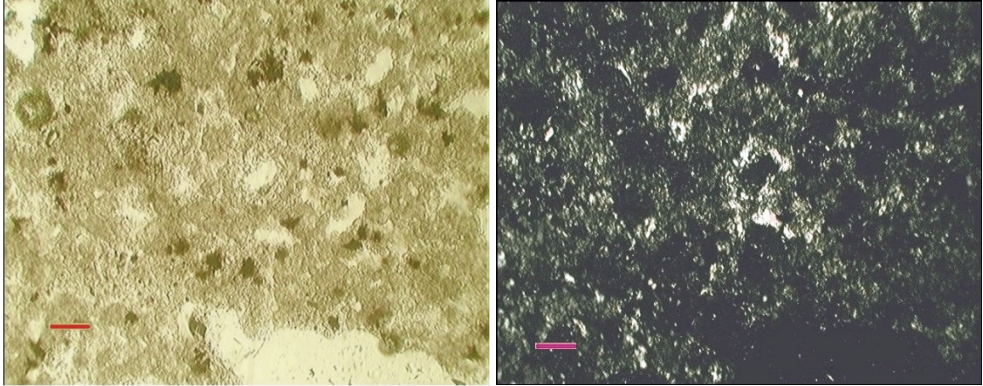


Figure 5. a (1N), b (N+). Sample 11A, burned at 1240°C: slightly differentiated interstitial material consists of yellowish green sulphoaluminate and ferrite; in the image centre there is a little pore with belite I ring overgrew by a belite II. Low cooling rate. Scale 50 μm

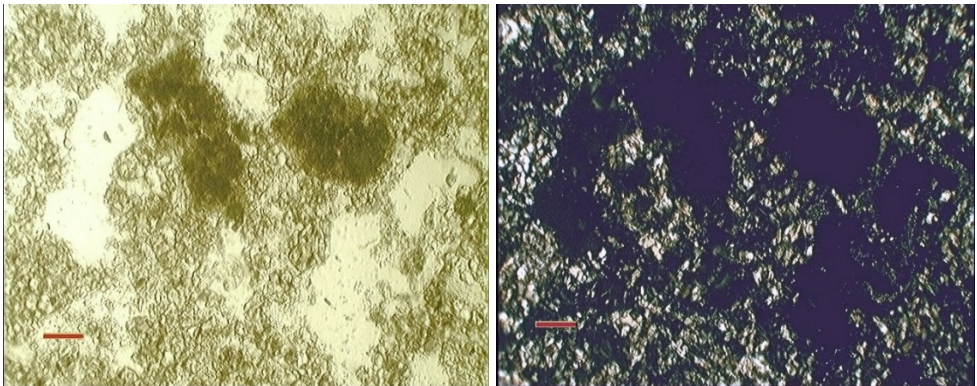


Figure 6. a (1N), b (N+). Sample 11B, fired at 1260°C: two drops of brownish olive interstitial material (isotropic sulphoaluminate in N+) between alitic (bottom left: polygonal grains) nests, belite I and belite III spherulites with rare alitic relics (dark grey birefringence). Scale bar 50 μm

The belite could be also evidenced in reflected plane polarized light on clinker surface etched with HF (method in [33]). The belite appears as bluish colored, mainly rounded grains, sometimes corroded by matrix phases, alite is brownish, the ferrite is white, other interstitial phases are grey, or not etched. (Figure 7).

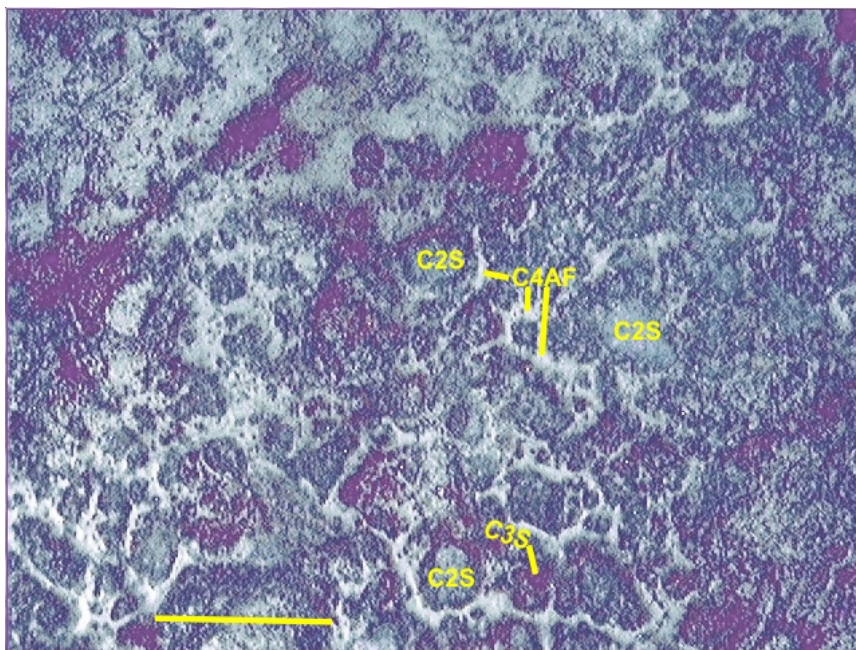


Figure 7. HF etched surface of sample 8, burned at 1220°C (in reflected plane polarised light). The belite I (C_2S) grains are rounded, bluish colored, frequently corroded by interstitial material, alite (C_3S) - brownish colored. The white colored phase = brownmillerite (C_4AF). Scale bar = 50 μm

The interpretations of XRD pattern of all samples revealed the presence of main phases from SAB clinkers: belite ($C_2S = B$), sulphoaluminate ($C_4A_6S^* = Sa$), ferrite (brownmillerite $C_4AF = Bw$) and anhydrite ($CS^* = Ah$) (**Figures 8, 9**) beside low quantities of: alite (C_3S), ettringite ($C_6AS^*_3H_{32}$), gehlenite (C_2AS), limeite (C), periclase (M), Na- alunite ($N_{0.5}K_{0.42}A_3S^*H_{16}$), Na-sulphate (N_2S^*) etc.

The polymorphic structure of studied belites could be evidenced in the XRD pattern detail ($2\theta = 30 - 35^\circ$) from Figure 9. The β -belite- is the most important polymorph and it is developed in all presented samples ($2\theta = 30.95^\circ, 31.83^\circ, 32.07^\circ, 32.18^\circ, 32.67^\circ, 32.80^\circ, 33.85^\circ, 34.20^\circ$). The α' -belite peaks were revealed in samples 2A, 3, 8A, 11A ($2\theta = 30.6^\circ, 31.2^\circ, 31.8, 31.95^\circ, 32.20^\circ, 32.90^\circ$). The best fitting belite standard, for example sample 3 (Figure 10) has orthorhombic symmetry which reveals α' -polymorph.

CHEMICAL-MINERALOGICAL CHARACTERISATION OF BELITES ...

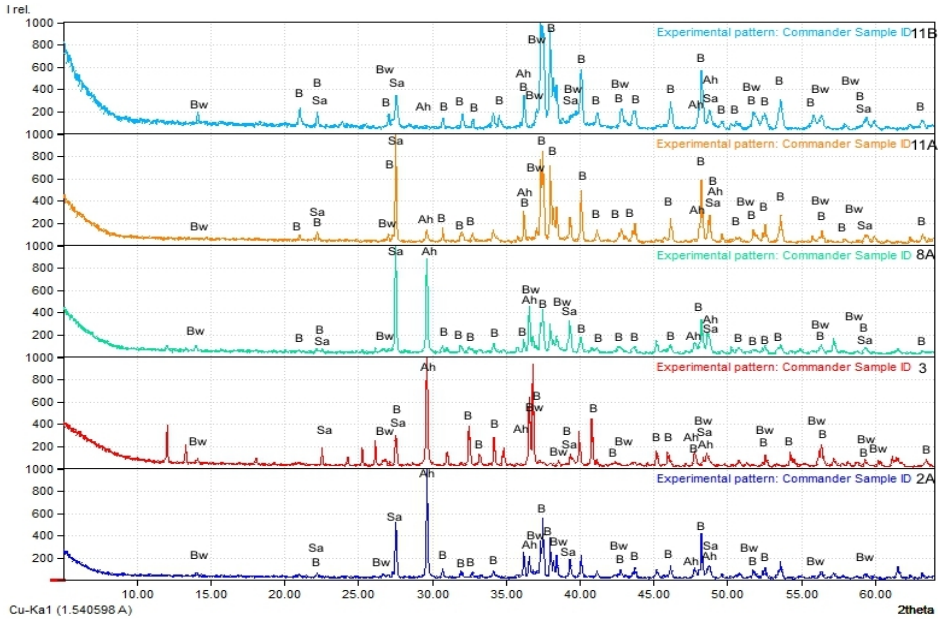


Figure 8. XRD pattern of few selected clinker samples (2A, 3, 8A, 11A, 11B). The sample 3 was fired at 1220°C, samples: 2A, 8A, 11A – at 1240°C and sample 11B - at 1260°C. (Reflections were recalculated for Cu-K α 1 for comparison with pdf2 database). C₂S = B = belite; CS* = Ah = anhydrite; C₄A₆S* = Sa = sulphoaluminate; C₄AF = Bw = brownmillerite.

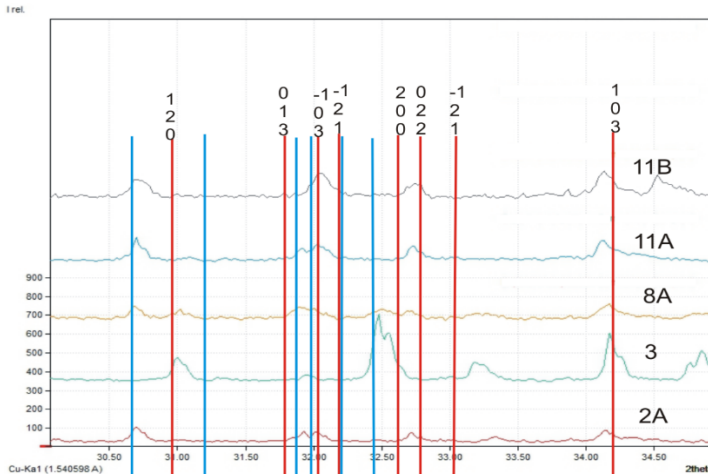


Figure 9. Detail of XRD patterns ($2\theta = 30 - 35^\circ$ and reflections were recalculated for Cu-K α 1 for comparison with belite database) of samples 2A, 3, 8A, 11A, 11B. The reflexions of α -belite and β -belite were marked with different colors. The Miller indexes of β -belite crystallographic faces are indicated.

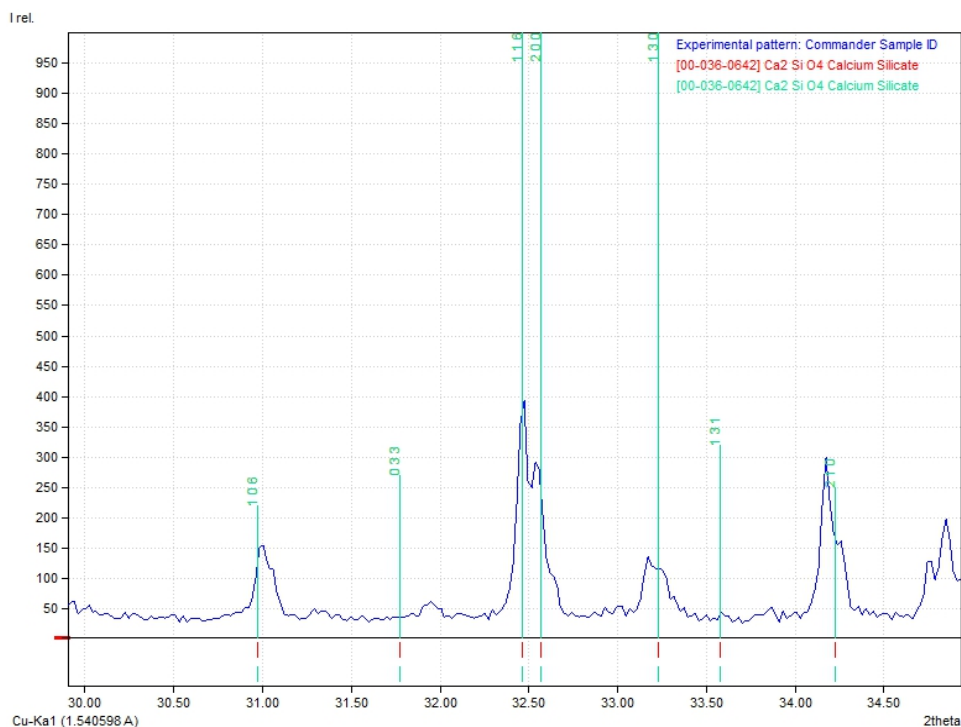


Figure 10. XRD pattern of sample 3 in range $2\theta = 30 - 35^\circ$. Are also marked the crystallographic Miller indexes. The best fitting belite standard has orthorhombic symmetry (α' - polymorph).

CONCLUSIONS

The optical features of belite presented here mirror the raw mix chemical compositions, relative low burning temperatures, slow cooling rate, differences in absorption of impurities, sometimes reduction conditions during firing. Taking into consideration the correlation between optical properties of clinker belites, firing conditions and hydraulicity of resulted cement, established by Ono and Campbell [34, 35], we can say, that: observed yellowish brown pleochroism of belite grains means slow cooling rate and low hydraulic properties, but sometimes the greenish yellow color indicates a clinker hydraulicity of medium quality. The measured belite birefringence of 0.017 - 0.018 could be interpreted as low hydraulicity of clinkers, low burning grade and very low or missing reactive α - belite content. Microstructures such as ragged belite or corroded rough grain shapes reveal low hydraulic activity and reducing burning conditions.

The details of XRD pattern of the studied clinkers indicate the presence in all samples of β -polymorph reflections and different structural transformations or stabilization forms of α' -belite quenched to room temperature.

The established chemical and mineralogical features of belites could help to improve the clinker raw mixture recipe and sintering conditions. By increasing the quenching rate or by using different belite stabilizing components could induce a greater proportion of reactive belite and interstitial amorphous material, which all lead to the better hydraulic activity of cement.

EXPERIMENTAL SECTION

The raw materials used for the present SAB clinkers experiment are natural (Vârghiş limestone, Bodoc clay, Nucsoara gypsum, Racosu de Jos basaltic scoria, Racosu de Sus volcanic tuff, Filia diatomite) and industrial waste (Oradea red mud), the later resulted in the bauxite ore processing by Bayer method at "Alumina" factory from Oradea. The selected raw material compositions previously were chemically and optically (under polarizing microscope) studied. The chemical compositions of raw materials were analysed by SEM-EDX, or by wet chemical method. (Table 3).

Table 3. Chemical compositions of clinker raw materials, wt%

oxides	Vârghiş Limestone (SEM- EDX)	Bodoc Clay (wet chem)	Oradea Red mud (SEM- EDX)	Racoşul de Jos Basaltic scoria (SEM-EDX)	Racoşul de Sus Volcanic tuff (wet chem)	Filia Diatomite (SEM- EDX)	Nucşoara Gypsum (wet chem)
CaO	89.61	1.66	12.71	10.38	2.88	0.71	28.31
SiO ₂	4.01	67.97	8.93	46.10	64.53	92.52	9.83
Al ₂ O ₃	5.16	15.41	17.04	18.78	11.80	3.24	2.73
Fe ₂ O ₃	-	4.88	48.37	9.93	2.57	2.18	1.07
Na ₂ O	-	1.54	3.68	3.23	1.89	-	0.15
K ₂ O	-	2.43	-	1.69	2.75	0.46	0.55
MgO	-	1.59	1.30	7.21	0.45	-	0.39
TiO ₂	-	0.81	6.80	1.61	0.27	-	0.13
V ₂ O ₅	-	-	0.19	-	-	-	0.04
P ₂ O ₅	1.22	-	0.98	1.07	-	-	0.04
SO ₃	-	-	-	-	-	0.89	37.08
Mn ₂ O ₃	-	0.13	-	-	-	-	0.02
L.O.I.	-	3.58	-	-	12.40	-	19.90
Total	100	100	100	100	100	100	100

The raw materials were dried in oven then grinded for two hours in the porcelain mill with balls. The raw materials mixed as in recipes from **Table 2** were homogenized for one hour in the porcelain mill. From the raw mix materials cube - like briquettes of 25x25x25 mm sizes were made, then burned in a laboratory electrical kiln until a constant peak temperature of 1220°C, 1240°C (samples ID marked as „A”) and 1260 °C (samples ID marked as „B” in **Figure 8**) for one hour.

For the present chemical-mineralogical study were selected five samples of clinkers, burned at 1220°C (sample 3), 1240°C (Samples 2A, 8A, 11A) and 1260°C (sample 11B) and were studied in dry-prepared **[33]** thin and thick sections under optical transmission and reflexion polarising microscope (using also HF etching). Were took microphotos in plane polarised light (1N) and in cross polarised light (N+)

The crystallised mineral phases from clinkers were also investigated by XRD analyses at the University Babeş- Bolyai using a Bruker D8 Advance diffractometer with Bragg-Brentano geometry, CoK α 1 with $\lambda = 1.78897$, Fe filter and a one-dimensional detector. Corundum (NIST SRM1976a) was the internal standard. The data were collected on a $2\theta = 5 - 64^\circ$ interval, at a 0.02° , with the measuring step of 0.2 seconds. The identification of the mineral phases was performed with the Match 3.1 software, using the PDF2 (2012) database.

ACKNOWLEDGMENTS

Acknowledged Professor Nicholas Culshaw, Dalhousie University, Canada for discussions and suggestions which improved the scientific content of paper. Also thanks for unnamed references for criticism and advices.

REFERENCES

- [1] L. Zhang, M. Su & Y. Wang, *Advances in Cement Research*, **1999**, 1, 15-21.
- [2] K. Quillin, *Cement Concrete Resources*, **2001**, 31, 1341.
- [3] M. Palou, J. Majling and I. Janotka, *Proceedings of the 11th International Congress on the Chemistry of Cement (ICCC) Durban, South Africa*, **2003**, 1896.
- [4] A. Alaoui, A. Feraille, A. Steckmeyer & R. Le Roy, *Proceedings of the 12th International Congress on the Chemistry of Cement (ICCC), Montreal, Canada paper 258 (W3-11.3)* **2007**, 1-8.
- [5] İ. Soner, “Utilization of Fluidized Bed Combustion Ashes as Raw Material in the Production of a Special Cement”; In partial fulfilment of the requirements for the degree of Master of Science in Chemical Engineering, Middle East Technical University, Haziran, Turcia, June **2009**.

- [6] I.A. Chen & M.C.G. Juenger, *Journal of Material Science*, **2009**, *44*, 2617.
- [7] G.S. Li, G. Walenta & E. Gartner, *Proceedings of the 12th International Congress of the Chemistry of Cement (ICCC)*, Montreal, CA, paper 398 (TH3-15.3), **2007**, 1-12.
- [8] G.K. Moir and F.P. Glasser, *Proceedings of the 9th International Congress on the Chemistry of Cement (ICCC)*, New Delhi, India, **1992**, 125-152.
- [9] P. Barnes, C.H. Fentiman & J.W. Jeffery, *Acta Crystallographica*, **1977**, *A36*, 353.
- [10] S.A. Guinier and M. Regourd, *5th International Symposium on Cement and Concrete*, **1969**, Vol. 1, p. 1.
- [11] P.B. Moore, *American Mineralogist*, **1973**, *58*, 32.
- [12] S. Udagawa, K. Urabe, M. Natsume, and T. Yano, *Cement and Concrete Research*, **1980**, *10*, 139.
- [13] W.G. Mumme, R.J. Hill, G. Bushnell-Wye and E.R. Segnit, *Neues Jahrbuch für Mineralogie*, **1995**, *169*, 35.
- [14] L. Bonafous, C. Bessada, D. Massiot, J.-P. Coutures, B. Le Rolland, & P. Colombet, *Journal of the American Ceramic Society*, **1995**, *78*, 2603.
- [15] Y.J. Kim, I. Nettlehip and W.M. Kriven, *Journal of the American Ceramic Society*, **1992**, *75*, 2407.
- [16] D.H. Campbell, "Microscopical Examination and Interpretation of Portland Cement and Clinker". Edited by: Natalie C. Holz, Portland Cement Association, Published by: Portland Cement Association USA, **1999**.
- [17] N. Yannaquis and A. Guinier, *Bulletin de la Société Française de Minéralogie et de Crystallographie*, **1959**, *82*, 126.
- [18] C.J. Chan, W.M. Kriven, and J.F. Young, *Journal of the American Ceramic Society*, **1988**, *71*, 713.
- [19] T. Taylor, "Cement chemistry", second edition, Thomas Telford Publishing, **1997**, London.
- [20] M. Regourd, M. Bigare, J. Forest and A. Guinier, in *5th International Symposium on Cement and Concrete*, **1969**, Vol. 1, p. 44.
- [21] Y. Ono, S. Kawamura and Y. Soda, in *5th International Symposium on Cement and Concrete*, **1969**, Vol. 1, p. 275.
- [22] Y. Ono, "Microscopic Analysis of Clinker," Onoda Cement Co., Central Research Laboratory, 1973/12/15 and 1975/6/22. Paper supplied to students at Hawaiian seminar, **1975**.
- [23] G. Yamaguchi and S. Takagi, in *5th International Symposium on Cement and Concrete*, **1969**, Vol. 1, p. 181.
- [24] H. Insley, "Structural Characteristics of Some Constituents of Portland Cement Clinker," *Journal of Research of the National Bureau of Standards*, Vol. 17, Research Paper RP917, Washington, D.C., September **1936**, pp. 353-361.
- [25] H. Kühl, „Der Kalkstandard der Portlandzemente". *Tonindustrie-Zeitung*, **1933**, *57*, Heft 40, S. 460-464.
- [26] H. Kühl, „Hydraulischer modul und Hydraulefaktoren- Verhältnis im Portlandzement". *Protokoll des VDPCF*, **1913**, S. 399-408.
- [27] H. Kühl, „Der junge Zementchemiker", *Zement* **1926**, *15*, Heft 36. S. 636/639,
- [28] H. Kühl, Der Kalksättigungsgrad, *Zement*, **1931**, *20*, Heft 6, S. 123-125.
- [29] S. Nasir and H. El Etr, *Qatar University Science Journal*, **1996**, *16(2)*, 315.

- [30] M.S. Idris, K.N. Ismail, S.B. Jamaludin, C.R., Ghazali and K. Hussin, *American Journal of Applied Sciences*, **2007**, 4(5), 328.
- [31] N.H. Deborah & D.E. Thomas, *Journal of Cleaner Production*, **2009**, 17, 668.
- [32] C. Hall and K.L. Scrivener. *Journal of Advanced Cement-Based Materials*, **1998**, 7(1), 28.
- [33] J. Ingham, „Geomaterials under the microscope, a colour guide, building stone, roofing slate, aggregate, concrete, mortar, plaster, bricks, ceramics and bituminous mixtures, in transmitted polarised light, under Jenapol petrographic microscope and by XRD method”. Manson Publishing, **2013**.
- [34] Y. Ono, *Proceedings of the Third International Conference on Cement Microscopy*, International Cement Microscopy Association, Houston, Texas, **1981**, pp. 198-210.
- [35] D.H. Campbell, “Microscopical Examination and Interpretation of Portland Cement and Clinker”. Edited by: Natalie C. Holz, Portland Cement Association, Published by: Portland Cement Association USA, **1999**.