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Alternative raw materials for the production of calcium sulfoaluminate cement: ladle slag and phosphogypsum

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ABSTRACT

Calcium sulfoaluminate belite (CSAB) cement clinkers were produced using two industrial by-products: ladle slag and phosphogypsum. The phase composition of the produced clinkers was identified using quantitative XRD analyses, and the chemical composition of the clinker phases produced from phosphogypsum was established using FESEM-EDS. We demonstrate that ladle slag and phosphogypsum can be used as alternative raw materials for the production of CSAB cement. We also show that phosphorous from the phosphogypsum can be incorporated into the larnite crystal structure. The mechanical properties of the hydrated/hardened cement are also presented and are comparable with those produced from reagent-grade materials.

Keywords: CSAB; Mortar; Cement; Alternative cement; Eco-cement

1| INTRODUCTION

Cement production is responsible for 8.6% of worldwide anthropogenic CO_2 emissions [1]. Over the past century, Portland cement (PC) has been the most commonly used binder [2]. The CO_2 emissions from PC manufacturing arise primarily from the embodied carbon released during the calcination process of the $CaCO_3$ source used, such as limestone ($CaCO_3 \rightarrow CaO + CO_2$). Secondary CO_2 emissions emerge from the burning of fossil fuels combusted to reach a clinkering temperature of approximately 1500 ℃ [2]. The growing demand of cement coupled with the increased societal pressures on the cement industry to lower their CO_2 emissions has boosted the international search for alternative low-CO_2 binders [3].

One option is to use calcium sulfoluminate (ye'elimite) binders that do not contain the high calcium-containing phase: alite (C_3S)[4]. The production process of calcium sulfoaluminate belite (CSAB) clinker has a ≈30% lower carbon footprint than that of PC, which can be attributed mainly to the lower lime factor (calcium content) of CSAB cement relative to PC [4]. The major phases of CSAB cements are: ye'elimite ($C_4A_3\$$), belite (C_2S) and ferrite ($C_2(A,F)$).

The use of industrial side-streams to produce calcium sulfoaluminate clinker is a topic of interest in the cement community. Clinkers composed of ye'elimite, belite and ferrite can allow for the usage of industrial by-products, such as slag, fly ash or sludge that would otherwise be landfilled [5]. The major benefits of using industrial side-streams is that they are a source of already decarbonised CaO and a valuable source of Al_2O_3, which can reduce the cost of the final product through reduced requirements for bauxite. Also, the economic and environmental cost of landfill can be avoided.

In the steel-making industry, ladle slag (LS) is a secondary metallurgical slag from the ladle treatment process when steel is refined before continuous casting. From estimations that 12–15 kg of unrecycled LS is produced for every tonne of crude steel [6] and that the annual crude steel production is 1691.2 Mt [7], it can be calculated that the annual production of LS is approximately 20–25 Mt worldwide. In Europe, with the same calculation procedure, the production of LS is calculated as roughly 1.9–2.4 Mt [6].

LS has been used as a filler material in concrete [6,8]; however, research concerning its usage as a raw material of CSAB cement is scarce. The use of LS as a raw material instead of bauxite and limestone can lead to a reduction of both CO_2 emissions and the production costs associated with CSAB cement manufacture. By replacing limestone with CaO containing industrial by-products, the CO_2 emissions from cement manufacture will decrease because the calcination of $CaCO_3$, which liberates CO_2, will have been avoided. The price of LS is estimated to be one-third the price of bauxite, with the latter having a price of 30€ per ton (as of 2017) [9].

Phosphogypsum (PG) is a by-product from the flue gas desulphurisation (FGD) process of using phosphate rock to produce phosphoric acid, which is used as a fertiliser. Approximately 4–6 tonnes of PG is produced for each tonne of phosphoric acid manufactured [10]. World mine production of phosphate rock in 2017 was estimated to be 263 million tonnes, and it is estimated that in the United States, 32 million tonnes of FGD gypsum was produced in 2017 [11,12]. One-half of the FGD gypsum was used for wallboard products [11]; however, PG is still underused globally.

In this work, both LS and phosphogypsum are used to produce CSAB cement clinker. The target phase composition was 40 wt.% ye'elimite ($C_4A_3\$$), 35 wt.% belite (C_2S), 20 wt.% ferrite (C_2F) and 5 wt.% anhydrite ($C\$$). A high iron content was chosen because of further interest in using high iron containing metallurgical slags with LS and PG. The raw material composition was assessed through X-ray fluorescence (XRF) analyses, and the clinkers were characterised via quantitative X-ray diffraction (XRD) and field emission scanning electron microscopy (FE-SEM) analyses. The mechanical properties of mortars were tested via compressive strength tests, and the results were compared with clinkers produced from pure reagent-grade chemicals and pure reagent-grade chemicals mixed with phosphogypsum (without LS).

2| MATERIALS

Three CSAB cement clinkers with the same phase composition were synthesised from reagent-grade chemicals and Finnish industrial by-products. The reagent-grade chemicals were calcium sulfate, calcium oxide, aluminium oxide, silicon dioxide and iron (III) oxide; information on the reagent-grade materials are provided in Table 1.

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(4) The following cement oxide notations are use throughout the current work: C = CaO, S = SiO_2, A = Al_2O_3, F = Fe_2O_3, M = MgO and \$ = SO_3.

Table 1 | List of the reagent-grade chemicals used for clinker synthesis.

Supplier Alfa Aesar	**Purity [%]**	**CAS-number**
Aluminium oxide (metals basis), fine powder	99	12553
Silicon(IV)Oxide(metals basis), Mesh fused amorphous powder	99	89709
Iron(III) oxide (metals basis)	98	012375
Calcium sulfate, anhydrous powder	99	40144
Calcium oxide, reagent-grade powder	98	33299

The industrial by-products utilised were LS from SSAB Europe Oy and phosphogypsum from Yara Suomi Oy. The main mineral phase of LS is mayenite, and it can hence be used directly as a supplementary cementitious material [13,14]; however, in many plants, LS still contains significant quantities of free lime, and the detrimental effects that free lime may have on hardened cement are well known [15]. When LS is combined with other industrial by-products to produce CSAB cement, the amount of replacement of reagent-grade chemicals with alternative raw materials can approach 100%.

Before XRF analysis, the phosphogypsum was dried at 250 °C for 24 h, and LS was dried at 105 °C for 24 h. The main chemical composition of the by-products were determined using an Omnian Pananalytics Axiosmax 4 kV XRF from a melt-fused bead. The melt-fused bead was produced from 1.5 g of each by-product material melted at 1150 ºC with 7.5 g of flux (66% LiB_4O_7 and 34% $LiBO_2$). Loss on ignition (LOI) at 950 °C was analysed by thermogravimetry using Prepash Precisa Gravimetrics AG 'prepASH automatic drying and ashing system'. For LS, LOI was ~0 wt.%, and for PG, it was 1.2 wt.%. The chemical composition of the by-products is presented in Table 2.

Table 2 | XRF analyses of the main oxide component of the industrial by-products.

XRF	**PG**	**LS**
CaO	40.5	48.4
Al_2O_3	0.1	32.3
SiO_2	0.5	7.2
Fe_2O_3	0.1	1.6
SO_3	54.6	0.7
MgO	0	5.7
TiO_2	0	0.8
MnO	0	1.4
P_2O_5	0.6	0
SrO	0.6	0
Total	97	98.1

3| EXPERIMENTAL AND RESULTS

3.1 Clinker preparation

In the current study, three different clinkers were produced: RGC (reagent-grade chemicals only), PGC (16.5 wt.% phosphogypsum and reagent-grade chemicals) and LSC (64.3 wt.% LS, 16.1 wt.% phosphogypsum, and reagent-grade chemicals). The target phase composition for all the clinkers was 40 wt.% ye'elimite ($C_4A_3\$$), 35 wt.% belite (C_2S), 20 wt.% ferrite (C_2F) and 5 wt.% anhydrite ($C\$$). C_2F instead of C_4AF was targeted in order to allow for most of the alumina to combine to form ye'elimite.

The amount of RGCs and by-products to achieve the phase composition of synthesised clinkers was calculated according to the stoichiometry of the target phases, and this is presented in Table 3. The amount of 'extra' components such as MgO, TiO_2 and so forth is calculated from the XRF results of the raw materials. Prior to weighing the components for firing, CaO was calcined at 800 °C for 4 h to remove any possible moisture, the anhydrite for RGC was dried at 250 °C for 2 h, phosphogypsum was dried at 250 °C for 24 h to form anhydrite and remove moisture, and LS was dried at 105 °C for 24 h. The materials for each clinker were separately mixed and ground using a mortar and pestle; then, they were compressed by hand in cylinder-shaped corundum crucibles. The firing was conducted in a Nabertherm chamber furnace. The crucible was placed in the furnace at 800 °C and then heated at a rate of 10 °C/min to 1300 °C and held for 4 h. After heating, the crucible was taken out of the furnace and placed on a copper table with water circulation, which provides fast cooling. Cooled clinkers were stored in a desiccator prior to grinding.

After firing, each clinker was first crushed using a hammer and then ground into a fine powder using a jar mill (Germantec TPR-D). A stainless steel jar with a volume of 10 L and d = 250 mm was used with grinding media of 180 stainless steel balls (d = 30 mm). The average grinding time for clinkers was 60 min, and 2-propanol was added to prevent agglomeration during grinding.

Table 3 | Chemical composition of synthesised CSAB clinkers calculated from the XRF analyses.

	RGC	**PGC**	**LSC**
CaO	48.6	48.6	48.6
Al_2O_3	20.3	20.3	20.3
SiO_2	12.2	12.2	12.2
Fe_2O_3	10	10	10
SO_3	9	9	9
MgO	0	0	4.4
TiO_2	0	0	0.7
MnO	0	0	1.5
P_2O_5	0	0.1	0.1
SrO	0	0.1	0.1
Total	100.1	100.3	106.8

The crystalline phases of clinkers were identified using X-ray diffraction (Rigaku SmartLab 9kW). The parameters of the XRD analysis were 2θ in the range of 5–120°, with Co K_α radiation under 40 kV and 135 mA, and the step size used was 0.02° with a scanning speed of 4.06°/min. The results of the XRD analysis are presented in Figure 1. A quantitative analysis was performed using Rigaku PDXL 2 software based on ICDD (PDF-4+) database and the Rietveld method. Clinkers were ground by hand in an agate mortar. The results of the Rietveld analysis are presented in Table 4. Weighted profile R-factor (R_{wp}) values were RGC 5.47%, PGC 5.27% and LSC 5.95%.

The Rietveld analysis was validated by calculating the oxide content using the stoichiometry of phases $C_4A_3\$$, C_2S, C_2F and $C_{12}A_7$, M and $C\$$; see Table 5. The oxide content according to the Rietveld analysis was compared with the original oxide content presented in Table 3. According to the calculations, in Table 5, in RGC and PGC, the amount of ferrite (C_4AF or $C_2(A,F)$) is slightly higher in the Rietveld analysis and Some SO_3 may have been lost during firing in LSC, however the accuracy of the Rietveld analysis is adequate.

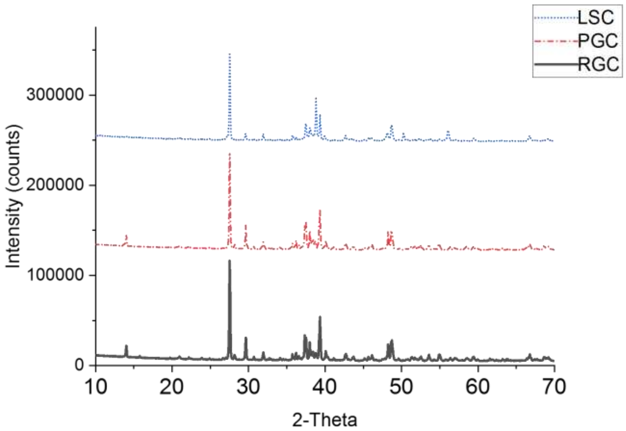

Fig. 1 | XRD analysis results of RGC, PGC and LSC.

Table 4 | Results of the Rietveld analysis.

DB-card number and reference	Phase	RGC	PGC	LSC
04-009-7268 [16]	Ye`elimite ($C_4A_3\$$)	37.3±0.2	36.5±0.2	39.7±0.6
04-013-6289 [17]	Larnite (C_2S)	32.5±0.2	36.6±0.2	32.0±0.7
04-006-8923 [18,19*]	Brownmillerite (C_4AF)	19±0.2	19.1±0.2	17.7±0.3
04-015-5592 [20]	Mayenite ($C_{12}A_7$)	2.2±0.2	0.0	0.7±0.3
04-008-3504 [21]	Periclase (M)	0.0	0.0	5.7±0.3
04-007-6682 [22]	Anhydrite ($C\$$)	8.0±0.1	7.8±0.1	4.2±0.7
	Total	99.98	100.03	100.0

*LSC only

Table 5 | Oxide content according to the Rietveld analysis ($C_4A_3\$$, C_2S, C_2F and $C_{12}A_7$).

	RGC	PGC	LSC
CaO	48	48	45
Al_2O_3	20	18	20
SiO_2	11	13	11
Fe_2O_3	11	11	10
SO_3	10	9	8
MgO	0	0	6
Total	100	100	100

3.2 Mortar preparation and compressive strength

Mortar samples for compressive strength were prepared using synthetic clinkers (RGC, PGC and LGC), phosphogypsym, tap water and standard sand. In mortars 15 wt.% of cement clinker was replaced with phosphogypsum and water to cement ratio (w/c) was 0.5. Preparation of the mortar samples was done according to cement standard EN 196-1 [23] with slight modifications. Here, 20 x 20 x 80 mm prisms were used instead of 40 x 40 x 160 mm prisms. All mortar specimens that were fabricated were cured in 98% air humidity at room temperature (22℃±1) for 1 and 7 days prior to being tested.

The unconfined compressive strength tests were done using a Zwick testing machine with a maximum load of 100 kN, here employing a loading force of 2.4 kN/s. The test measurements were done from both ends of 20 × 20 × 80 mm mortar prisms, totalling six measurements. The reported compressive strengths are average values. The compressive strength test results are presented in Figure 2.

After 1 day of curing, all mortars reached approximately 20 MPa strength, and the strength developed to approximately 40 MPa after 7 days of curing. The strength development behaviour was similar with each clinker used. The compressive strength results show that phosphogypsum can be used as a replacement for reagent-grade gypsum in the cement blend.

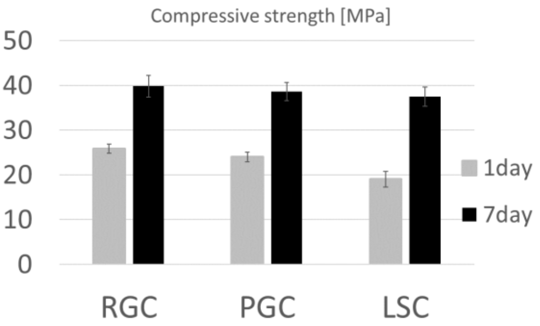

Fig. 2 | Compressive strength test results of RGC, PGC and LSC.

3.3 FE-SEM analysis

To assess the influence of phosphogypsum on the clinker mineralogy, a FE-SEM was carried out on the PGC sample. A polished section was prepared for analysis by mixing a piece of nonground PGC cement clinker with optical-grade epoxy resin (Struers Epofix) and casting this in cylindrical 40-mm mould in a vacuum, the casted sample was cured in a 40 ℃ oven for 24 h. After curing, a thin section was cut from the middle of cured (d=40 mm) sample, epoxy-impregnated in a vacuum into a 25-mm cylindrical mould, and cured again in a 40 ℃ oven for 24 h. After second curing the excessive epoxy was removed using lathe and the sample was polished with wheel polisher (Struers LaboPol-6) using ethanol (98%) as lubricant. Before back scattered electron (BSE) imaging and chemical composition analysis with energy dispersive spectrometry (EDS), the polished section was coated with carbon. The BSE images are presented in Figures 3 and 4, and the point EDS chemical composition analysis is presented in Table 6.

Table 6 | FESEM-EDS point analysis of PGC (wt.%).

Element	Larnite	Ferrite	Ye'elimite
O	34.67	28.42	38.00
Na	0.26	0.00	0.00
Mg	0.74	0.29	0.00
Al	0.79	5.69	24.87
Si	14.83	0.80	0.40
P	0.25	0.00	0.00
S	0.49	0.82	5.10
Ca	45.07	30.07	25.79
Fe	1.17	30.30	2.34
Total	98.3	96.4	96.5

Three main phases can be identified from the BSE images, ye'elimite, larnite and ferrite, descending from darkest to lightest. The amounts are averages of the total EDS point analysis points from a single phase with the total amount of points: ye'elimite 6, ferrite 7 and larnite 20.

The main phases in PGC contained various impurities from the raw materials. The chemical impurities may dissolve into the structure of the main mineral phases of CSAB through ionic substitution of Ca, Si, Fe and Al. Larnite (C_2S) contained P, Na, Mg, Al, S and Fe as foreign elements. Phosphorous (P) and sodium (Na) were not detected in any other phases. The main impurity in ye'elimite is iron (Fe). In the ferrite phase, there is aluminium (Al) present; the ferrite phase was calculated to be $C_2(F_{0.72},A_{0.28})$ or $C_4(F_{1.44},A_{0.56})$.

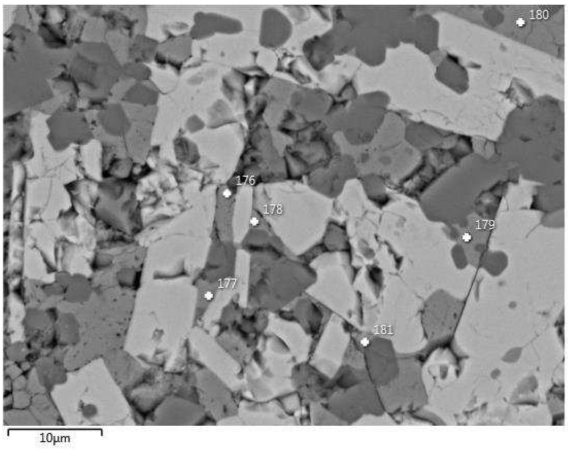

Fig. 3 | BSE image of PGC from a polished section using EDS analysis points 176–181 (Larnite).

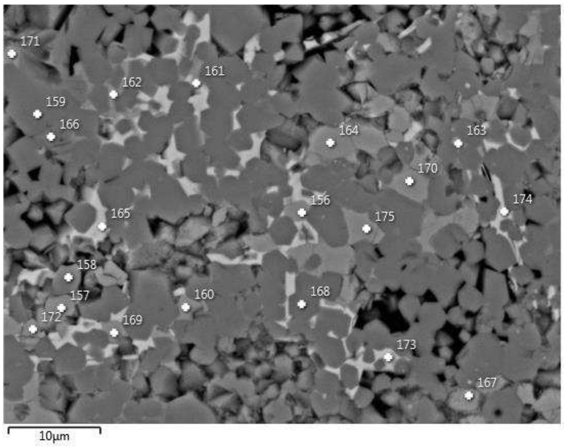

Fig. 4 | BSE image of PGC from a polished section using EDS analysis points 156–175 (Ye'elimite 168, Ferrite 165, Larnite 175).

5| CONCLUSIONS

In the current paper, we demonstrated that LS and phosphogypsum can be used as alternative raw materials for the production of calcium-sulfoaluminate-based clinkers. LS is a valuable source of aluminium oxide required to form ye'elimite, while phopshogypsum can provide the necessary SO_3.

The use of phosphogypsum instead of reagent-grade anhydrite to manufacture CSAB clinker does not seem to affect the overall clinker phase assemblage; however, a FE-SEM EDS analysis reveals that phosphorus becomes incorporated into the larnite crystal structure through ionic substitution.

The compressive strength of cement produced from LS and phosphogypsum are comparable with what is produced from reagent-grade materials. In addition, phosphogypsum was successfully used as a replacement for traditional gypsum blended with clinker to produce the final cement.

Although the use of LS and phosphogypsum as alternative raw materials for the manufacture of cement is limited because of their limited availability, significant economic and environmental benefits can be realised through their use.

Future work will focus on assessing the long-term behaviour of the produced clinkers regarding its mechanical properties and durability.

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REFERENCES

[1] Miller, S.A., Horvath, A., Monteiro, J.M., 2016. Readily implementable techniques can cut annual CO2 emissions from the production of concrete by over 20%. Environmental Research Letters, 11(7).

[2] Londono-Zuluaga, D., Tobon, J.I., Aranda, M.A.G., Santacruz, I., De la Torre, A.G., 2017. Clinkering and hydration of belite-alite-ye´elimite cement. Cement and Concrete Composites, 80(2017): 333-341.

[3] Miller, S.A., John, V.M., Pacca, S.A., Horvath, A., 2017. Carbon dioxide reduction potential in the global cement industry by 2050. Cement and Concrete Research, 114(December 2018):115-124.

[4] Hanein, T., Galvez-Martos, J.L., Bannerman, M.N., 2018. Carbon footprint of calcium sulfoaluminate clinker production. Journal of Cleaner Production, 172:2278–2287.

[5] Chen, I. A., Juenger, M.C.G., 2009. Synthesis of Portland Cement and Calcium Sulfoaluminate-belite Cement for Sustainable Development and Performance. Dissertation (PhD), the University of Texas.

[6] Nguyen, H., Carvelli, V., Adesanya, E., Kinnunen, P., Illikainen, M., 2018. High performance cementitious composite from alkali-activated ladle slag reinforced with polypropylenefibers. Cement and Concrete Composites, 90:150-160.

[7] World Steel Association, January 2018. World Crude Steel Production – Summary. Brussels Belgium. Available at https://www.worldsteel.org

[8] Anastasiou, K.E., Papanayianni, I., Papachristoforou, M., 2014. Behavior of self-compacting concrete containing ladle furnace slag and steel fiber reinforcement. Materials and Design Volume, 59: 454-460.

[9] Bray, E.L., 2018. U.S. Geological SurveyMineral Commodity Summaries, Bauxite and Alumina. Available at https://minerals.usgs.gov/minerals/pubs/mcs/

[10] Rashad, A.M., 2017. Phosphogypsum as a construction material. Journal of Cleaner Production, 166(2017):732-743.

[11] Grangle, R.D., 2018. U.S. Geological Survey,Mineral Commodity Summaries, Gypsum. Available at https://minerals.usgs.gov/minerals/pubs/mcs/

[12] Jasinski, S.M., 2018. U.S. Geological Survey, Mineral Commodity Summaries, Phosphate Rock. Available at https://minerals.usgs.gov/minerals/pubs/mcs/

[13] Adesanya, E., Sreenivasan, H., Kantola, A.M., Telkki, V.-V., Ohenoja, K., Kinnunen, P., Illikainen, M., 2018. Ladle slag cement – Characterization of hydration and conversion. Construction and Building Materials, 193:128-134.

[14] Nguyen, H., Adesanya, E., Ohenoja, K., Kriskova, L., Pontikes, Y., Kinnunen, P., Illikainen, M., 2019. Byproduct-based ettringite binder – A synergy between ladle slag and gypsum. Construction and Building Materials, 197:143-151.

[15] Chatterji, S., Jeffery, J.W., 1966. Mechanism of expansion of concrete due to the presence of "dead burnt" CaO and MgO. Magazine of Concrete Research, 18(55):65-68.

[16] Saalfeld, H., Depmeier, W., 1972. Silicon-free compounds with sodalite structure. Kritall und Technik, 7(1-3):229-233.

[17] Mori, K., Kiyanagi, R., Yonemura, M., Iwase, K., Sato, T., Itoh, K., Sugiyama, M., Kamiyama, T., Fukanagu, T., 2006. Charge states of Ca atoms in *β*-dicalcium silicate. Journal of Solid State Chemistry, 179(11):3286-3294.

[18] Colville, A.A., Geller, S., 1972. Crystal structures of $Ca_2Fe_{1.43}Al_{0.57}O_5$ and $Ca_2Fe_{1.28}Al_{0.72}O_5$. Acta crystallographica 28B (11):3196-3200.

[19] Redhammer, G. J., Tippelt, G., Roth, G., Amthauer, G., 2004. Structural Variations in the brownmillerite series $(Ca_2(Fe_{2-x}Al_x)O_5$: Single-crystal X-ray diffraction at 25 ℃ and high-temperature X-ray powder diffraction (25℃<T<1000 ℃). American Mineralogist 89 (2004) 405-420.

[20] Palacios, L., Cabeza, A., Bruque, S., García-Granda, S., Aranda, M.A.G., 2008. Structure and electrons in mayenite electrides. Inorganic Chemistry, 47(7):2661-2667.

[21] Bragg, W.L., 1920. Crystal structure. Nature(London), 105:646-648.

[22] Morikawa, H., Minato, I., Tomita, T., Iwai, S., Clinkering and hydration of belite-alite-ye´elimite cement. S., 1975. Anhydrite: a refinement. Acta crystallographica 31B(8): 2164-2165.

[23] EN 196-1, 2005. Methods of testing cement – Part 1: Determination of strength