

Proceeding Paper

Formation, Characterization and SEM Microanalysis of Yeelimites[†]

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[†] Presented at International Conference on Raw Materials and Circular Economy, Athens, Greece, 5–9 September 2021.

Abstract: Yeelimites is one of the main components of SulfoBelite (SB) and Calcium SulfoAluminate cements which are promising low carbon alternatives to Portland ones. In this study, stoichiometric yeelimites, obtained at different temperatures, was characterized by XRD, Q-XRD and SEM-EDS. Additionally, mortars of the synthetic yeelimites, with and without standard sand, were studied in terms of the development of strength over time. The main result is that high yeelimites content samples were prepared by mixing stoichiometric quantities of analytical-grade raw materials at 1330 °C for 3 h soaking time, followed by rapid cooling. Moreover, an increase in the formed yeelimites results in increased strength values that meet the requirements to be classified at CEM 32.5.

Keywords: yeelimites grains; compressive strength of yeelimites; characterization; SEM depiction and microanalysis of yeelimites; yeelimites mortars



Citation: Kamitsou, M.D.; Kostakopoulos, E.; Kanellopoulou, D.G.; Hallet, V.; Petrica, P.; Christogerou, A.; Angelopoulos, G.N. Formation, Characterization and SEM Microanalysis of Yeelimites.

Mater. Proc. **2021**, *5*, 106. <https://doi.org/10.3390/materproc2021005106>

Academic Editor: Evangelos Tzamos

Published: 18 January 2022

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1. Introduction

Yeelimites ((CaO)₄(Al₂O₃)₃SO₃), also called “Klein’s salt”, is one of the main components of sulfoBelite (SB), calcium sulfoaluminate (CSA) and occasionally occurs in Portland-type cements [1–5]. CSA and SB cements can be promising alternatives to ordinary Portland cement (OPC), especially in the view of sustainable development and the circular economy [1,5], as their production requires less energy and produces less CO₂ emissions compared to OPC [1,2,5,6]. In order to study and interpret the hydration behavior of these “eco-friendly” cements, their individual components should be studied. Yeelimites is the one being studied in the present case, as the considered cements have a relatively high yeelimites content.

Hydrated yeelimites forms ettringite and contributes to the development of relatively high compressive strength values of cements, at 34 ± 5 MPa, from day 1 up to 3 years, which, however, then begins to decrease (5 years’ research) [2]. As CSA and SB cements are a mix of several phases, it is impossible to separate yeelimites from the other phases; therefore, there is a need to synthesize and examine yeelimites at the lab scale.

According to Lea’s Chemistry of Cement and Concrete 4th Ed. [2] and to the Handbook of Mineralogy [7], yeelimites starts to form at 900–950 °C, reaching its maximum quantity at 1200–1250 °C, while at 1350 °C, it begins to decompose, becoming unstable [2].

Furthermore, when yeelimite is formed by solid-state reactions, the final product contains krotite ($\text{CaO}\cdot\text{Al}_2\text{O}_3$), grossite ($\text{CaO}(\text{Al}_2\text{O}_3)_2$) and mayenite ($(\text{CaO})_{12}(\text{Al}_2\text{O}_3)_7$) as secondary phases, at temperatures $\leq 1300^\circ\text{C}$ [2,8–10]. Cuesta et al. [10] succeeded in producing stoichiometric yeelimite of 90.3 wt.% purity at 1300°C and a soaking time of 4 h, followed by slow cooling. Winnfeld and Barlag [8] synthesized pure yeelimite, according to XRD results, at 1300°C and a soaking time of 4 h, followed by slow cooling. On the contrary, Bullerjahn et al. [9] formed stoichiometric yeelimite of 87.9 wt.% purity at 1250°C and a soaking time of 3 h, followed by rapid cooling. In the present case, the typical procedure applied for OPC cement production [1,2] was followed. In addition, successful preparation of yeelimite by solid-state reaction(s) requires intermediate grinding steps and relatively high-temperature firings (at or even above 1250°C) [6,8].

Therefore, in the present study, yeelimite was formed at the laboratory scale by analytical-grade raw materials. Three different temperatures, i.e., 1300°C , 1330°C and 1350°C , and two different firing profiles were tested respectively, in order to examine the crystal structure and the compressive strength of the mortars.

2. Materials and Methods

Analytical-grade Al_2O_3 , CaCO_3 and $(\text{NH}_4)_2\text{SO}_4$ (MERCK) were dried at 100°C for 24 h. Subsequently, they were ground in a planetary mill (Siebtechnik TS 100) to achieve a particle size of less than $90\ \mu\text{m}$. The powdered raw materials were mixed in stoichiometric ratios corresponding to yeelimite [9,10], homogenized and pelletized, with a minimum addition of deionized water. Afterward, the pellets with a diameter of 12 to 15 mm were dried at 100°C for about 24 h. Following, they were placed in a lab-made chrome-magnesite refractory crucible (MAGNA P 201) with a cover lid of the same material and fired in a laboratory resistance furnace (Super Kanthal of Nabertherm–Mod: HT08/17). The heating profile followed a heating rate of $16.25^\circ\text{C}/\text{min}$ up to 1000°C and a soaking time of 30 min. The final heating temperatures were 1300°C , 1330°C and 1350°C respectively. Six yeelimite samples were obtained, which are presented in Table 1. To stabilize the formed crystals, the so-obtained samples were cooled rapidly by blasting air and simultaneous crushing by a hammer [1,9]. The so-obtained samples were brittle. Subsequently they were powdered and examined by SEM (EVO MA 10, Zeiss Company).

Table 1. Peak firing temperatures and duration of firing process of yeelimite samples.

Experiment	Yeel.1300_3	Yeel.1300_5	Yeel.1330_3	Yeel.1330_5	Yeel.1350_3	Yeel.1350_5
$T_{\text{Final}} (^\circ\text{C})$	1300	1300	1330	1330	1350	1350
Total time (h/min)	2:50	5:10	2:50	5:10	2:50	5:10

For the determination of the bulk density, a le Chatelier flask was used, filled with petroleum oil, according to ASTM C188-95: 2003. The fineness of the fired samples was measured according to the Blaine method (EN 196-6: 2010), and the specific surface area (SSA) was measured (ISO 9277: 2000) by nitrogen absorption measurements (BET, Gemini II 2375 of Micrometrics Company).

The mineralogical phases were determined by Bruker D2-Phaser XRD. Diffraction patterns were measured in the 2θ range of $10\text{--}70^\circ$ using $\text{Cu K}_{\alpha 1}$ radiation of 30 kV and 10 mA, with a 0.01° step size and a scan speed of $0.5\ \text{s}/\text{step}$. The samples were rotated at 15 rpm to have a more representative, random scan. Quantitative Rietveld analysis was performed by means of TOPAS software. For the accuracy of the results, adjustments were performed concerning instrument geometry, background, sample displacement, detector type and mass absorption coefficients of the refined phases.

Finally, for the determination of the mechanical resistance to compression, yeelimite mortar specimens were formed according to EN 196-1: 2005, but with dimensions of $20 \times 20 \times 80\ \text{mm}$. Moreover, mortars without standard silica sand addition were also formed. All test samples were kept in a cabinet at $20 \pm 1^\circ\text{C}$ and 90% humidity, as in the

case of OPC cement (EN 196–1: 2005), until the compressive strength tests. The loading rate of 8 mm/min was tested upon failure of the samples using an Instron press (Mod: 8802).

3. Results and Discussion

3.1. SEM Results

It was no need for sputter-coating of the samples for SEM observation, as yeelimite proved to be enough conductive. In Figure 1, it is observed that the crystals of the samples form a variety of sizes and many aggregates. Yeelimite of 5 h cured samples forms more and bigger aggregates than the 3 h cured samples. Yeel.1300_3 varies in size from approximately 1 μm to about 2 μm , while most of the grains of Yeel.1330_3 are less than 1 μm . So, Yeel.1330_3 consists of about 30–35 nm of nanocrystals. This result can be attributed to the fact that yeelimite is more stable at temperatures lower than 1330 $^{\circ}\text{C}$, as yeelimite is unstable over 1350 $^{\circ}\text{C}$ [2]. Moreover, according to the Mineralogical Society of America, crystals of yeelimite at cement are 15 nm in aggregates [7], so according to the results of the present study, stoichiometric yeelimite samples formed bigger crystals. In addition, crystals of Yeel.1300_3 and Yeel.1330_3 exhibit a polygonal shape, similar to that of yeelimite in CSA cement [11], while yeelimite in all other samples is more rounded.

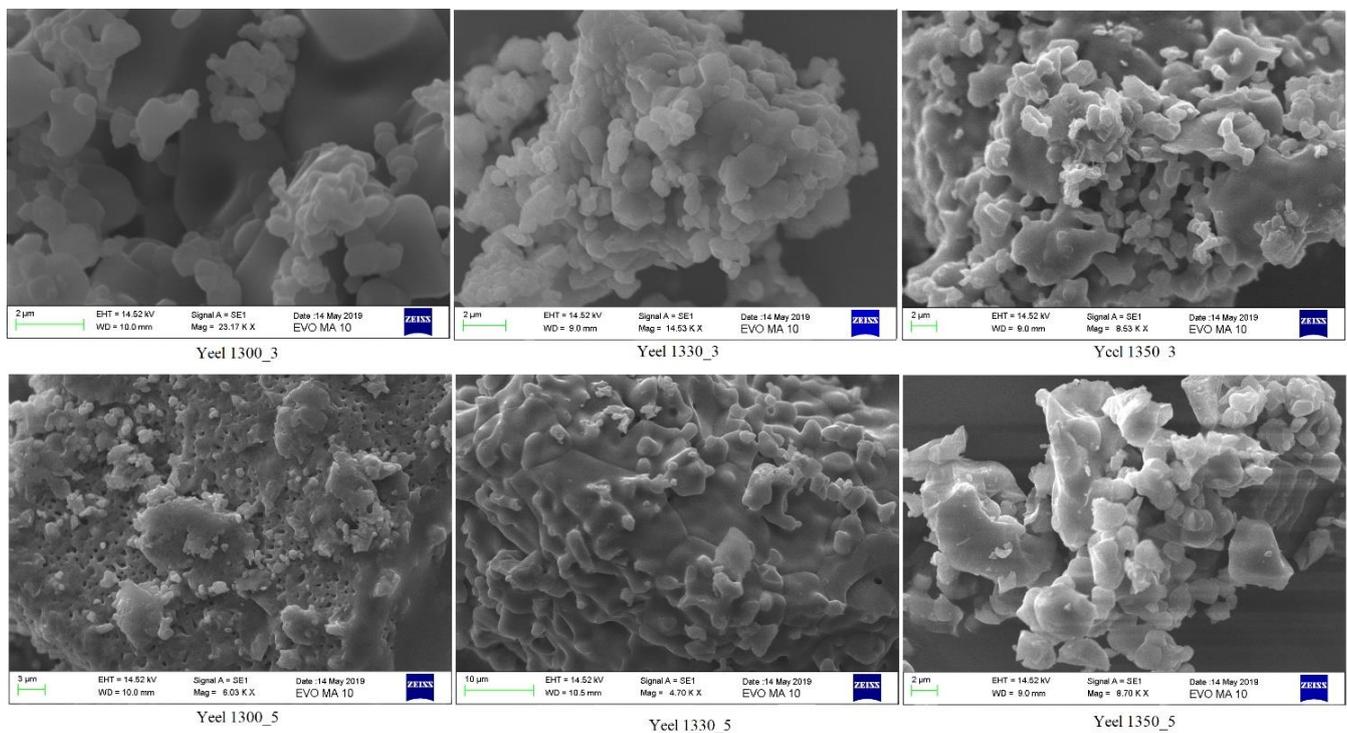


Figure 1. SEM images of crystals of the Yeel-experiments from 1300 (left) to 1350 (right) were obtained for 3 h (top) and 5 h (bottom).

The EDS analysis of the samples is presented in Table 2, showing that the produced crystals are not pure yeelimite. The atomic ratios Ca/Al/S of Yeel.1300_3 and Yeel.1330_3 are 4.0:4.3:0.9 and 4.0:4.4:0.9, respectively. Calculation was based on Ca = 4 wt. % and excluding O. Therefore, the samples, Yeel.1300_3 and Yeel.1330_3, were chosen for further analysis, as they exhibited better-formed crystals and a stoichiometry closer to yeelimite (4:6:1).

Table 2. EDS atomic wt.% measurements of yeelimite samples.

Element.	Atomic wt.% of Experiment.					
	Yeel.1300_3.	Yeel.1300_5	Yeel.1330_3	Yeel.1330_5	Yeel.1350_3	Yeel.1350_5
O *	60.58	59.57	62.30	65.69	63.33	59.87
Al	18.43	20.23	17.89	16.79	18.71	19.71
S	4.02	2.67	2.98	2.30	2.09	1.82
Ca	16.97	17.53	16.83	15.21	15.87	18.60

* Calculated from stoichiometry.

3.2. Characterization of the Samples

The bulk density of the samples Yeel.1300_3 and Yeel.1330_3 was measured (ASTM C188-95: 2003) to be 2.86 g/mL which is in relative accordance with 2.6 g/mL, found in the literature [8].

The Blaine of the samples was measured (EN 196-6: 2010) at 5800 ± 100 cm²/g after 30 seconds of dry milling. This indicates a very brittle material, which is also confirmed by Winnfeld and Barlag [8], where the fineness of “pure” yeelimite is 5200 cm²/g after milling.

Finally, the specific surface area (SSA) was measured at 0.5791 ± 0.0150 m²/g for sample Yeel.1330_3 and at 0.6473 ± 0.0223 m²/g for sample Yeel.1300_3. Moreover, it was observed that yeelimite formed at 1300 °C had higher porosity than the one formed at 1330 °C. Therefore, it is assumed that as the temperature increases and the pores are reduced, solid-state reactions, as well as other processes such as local melting, occur, so more phases are formed resulting in a denser structure.

Q-XRD analysis is presented in Table 3. Approximately 6 wt.% more yeelimite is formed at Yeel.1330_3 than Yeel.1300_3 sample, confirming that reactions are favored by increasing the firing temperature, and in the present case only by 30 °C. Moreover, according to the Q-XRD anhydrite (CaSO₄), krotite (CaO·Al₂O₃) [2] and mayenite ((CaO)₁₂(Al₂O₃)₇), were formed which are common to yeelimite most probably by solid-state reactions [2,8–10].

Table 3. Q-XRD analysis of Yeel.1330_3 and Yeel.1300_3.

Crystal Phase (wt.%).	Yeelimite	Anhydrite	Krotite	Mayenite	SUM
Yeel.1300_3	80.6	4.3	9.7	5.4	100
Yeel.1330_3	86.1	2.5	5.9	5.5	100

3.3. Compressive Strength of the Samples with and without Standard Sand

Two types of specimens were formed for the mechanical tests. The first one was formed by using deionized water and yeelimite with a water/yeelimite ratio of 30 wt.%. The second one was formed by mixing yeelimite, standard silica sand (3 times by weight of yeelimite) and deionized water with a water/yeelimite ratio of 53.2 wt.%. The compressive strength was measured for all specimens on the 28th day of hydration and is presented in Figure 2.

The compressive strength of yeelimite samples with standard sand is lower than that of the ones without sand (Figure 2). The decreases in the compressive strength values are attributed to the fact that the hydrated phases are divided into silicon-free phases that contribute to strength and silicon phases that do not contribute to strength. Moreover, according to EN 197-1: 2000, all compressive strengths of yeelimite samples meet the requirements to be classified at the category of cement CEM 32.5.

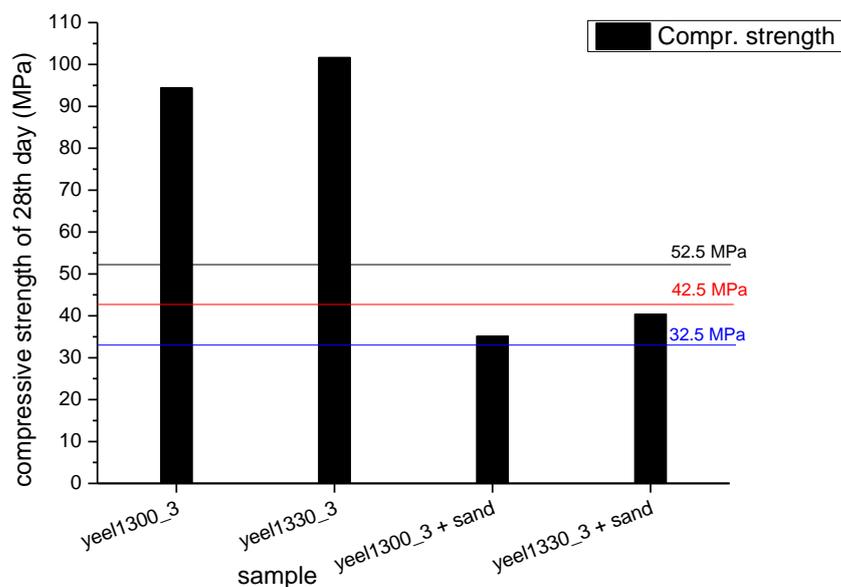


Figure 2. Compressive strength of Yeel.1330_3 and Yeel.1300_3 specimens with and without standard sand at the 28th day of hydration. The 3 lines correspond to values of the 28th day of EN 197-1:2000 classification of cement.

4. Conclusions

High yeelimite content samples, up to 86.1 wt.%, were prepared by mixing stoichiometric quantities of analytical-grade raw materials at 1330 °C and a soaking time of 3 h, followed by rapid cooling. The purity of yeelimite formed at 1330 °C (86.1 wt.%) is close to 87.9 wt.% reported by Bullerjahn et al. [9], which was also formed at 1250 °C using a 3 h firing profile, followed by rapid cooling.

Other conclusions of this study are:

- The production of pure yeelimite is not feasible, neither by analytical-grade materials according to this study which is in line to the literature [8–10].
- Yeelimite, formed at temperatures ≥ 1300 °C, contains krotite ($\text{CaO} \cdot \text{Al}_2\text{O}_3$), anhydrite (CaSO_4) and mayenite ($(\text{CaO})_{12}(\text{Al}_2\text{O}_3)_7$) as secondary phases.
- The shape of the produced yeelimite grains is polygonal.
- The crystals of the so-formed yeelimite are larger (30 nm) than the yeelimite crystals of the CSA cement (15 nm) [7]. This is because stoichiometric yeelimite is not 100 wt.% pure yeelimite, and secondary phases are formed.
- The formed stoichiometric yeelimite is brittle.
- By increasing the yeelimite content, the compressive strength increases.
- The compressive strength at the 28th day of hydration of yeelimite exceeds 95 MPa.

Author Contributions: Authorship is limited to those who have contributed substantially to the work reported. Conceptualization and methodology, M.D.K., D.G.K. and G.N.A.; software, M.D.K., D.G.K. and A.C.; validation, M.D.K., and D.G.K.; analysis M.D.K.; investigation M.D.K., D.G.K., E.K., V.H. and P.P.; resources G.N.A. and D.G.K.; data curation, M.D.K., D.G.K., V.H. and P.P.; writing—original draft preparation, M.D.K.; writing—review and editing, M.D.K., D.G.K., A.C. and G.N.A.; supervision, G.N.A.; project administration, G.N.A.; All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Acknowledgments: The authors M.D.K., D.G.K., A.C. and G.N.A. acknowledge the support of this work by the project “INVALOR: Research Infrastructure for Waste Valorization and Sustainable Management” (MIS 5002495) which is implemented under the Action “Reinforcement of the Research and Innovation Infrastructure”, funded by the Operational Program “Competitiveness, Entrepreneurship and Innovation” (NSRF 2014–2020) and co-financed by Greece and the European Union (European Regional Development Fund). In addition, authors acknowledge the contribution of Laboratory of Applied Mechanics and Vibrations of Mechanical Engineering and Aeronautics of the University Campus, GR 265 04 Patras, for the compressive strength tests and Yiannis Pontikes, MTM, KU Leuven, Kasteelpark Arenberg 44, B 3001 Leuven, Belgium.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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