



Research article

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Alkali-activated bentonite clay-limestone cements

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Abstract. The development of sustainable cements requires the expansion and optimization of the mineral resources base. In this study, the medium-grade bentonite clay and limestone as a promising, available, low carbon, and abundant starting materials, were investigated as binary precursors for eco-friendly non-clinker alkali-activated cements development. Properties of fresh and hardened pastes of blended alkali-activated cements were investigated by standard techniques depending on the mineralogical assemblage, fineness of precursors, formulation details. The reaction products and microstructures of alkali-activated calcined bentonite clay-limestone hardened pastes were analyzed using thermal, XRD, and SEM/EDS analyses. As a result, calcined bentonite clays at 39–47 % content of clay minerals were stated to be suitable as a primary precursor for alkali-activated cements incorporated with high loading of raw limestone. Optimum compositions consisted of 20–30 % calcined clay and 70–80 % limestone with compressive strength up to 34.2 MPa. In the designed cement calcined bentonite clay is the main reactive precursor that forms a mineral matrix sodium aluminosilicate hydrate gel N-A-S-H, whereas calcium carbonate is a much less reactive secondary precursor that participates in the formation of sodium (calcium) aluminosilicate hydrate gel N-(C)-A-S-H.

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1. Introduction

Development of sustainable mineral binders that comply with increasing technical and ecological requirements and a general trend towards gradual decrease in their energy and resource intensities determines the expansion of the mineral resources range. The resource base of supplementary cementitious materials applied in increasing volumes for Portland clinker replacement in mixed cements has been reconsidered in recent decades to establish more available and wider range of mineral materials than traditional ones, such as blast furnace slag, fly ash, etc. As a result of ongoing studies conducted in this field, clays and calcium (magnesium) (C/M) carbonate rocks have been identified as the perspective sources for the production of low- [1–6] and non-clinker cements [7–13], including alkali-activated cements (AACs). The interest in these mineral sources is based not only on the large reserves and their ubiquitous availability, but also on their decreased global warming potential, lowered energy consumption, and multifunctional effect on the engineering performance of blended cements and concretes.

For a long time the limestone (LS) was assigned the sole role of an inactive filler for AACs. A great number of studies stated the beneficial effect of LS on the properties of fresh and hardened alkali-activated (AA) blast furnace slag, fly ash, calcined clays cements. The positive influence effect of C/M carbonates on the performance of AACs is based on the filler, nucleation, dilution, and chemical effects, which are conditioned by the chemical-mineralogical compositions of the primary precursors (Ca-free or Ca-rich), the nature and dosage of the alkaline component, and the content and fineness of LS or dolomite [14–21].

However, recent studies have stated that the chemical activity of LS in AA binder systems is underrated. Ortega-Zavala et al. [22], Aizat et al. [23], Yin et al. [24], Cousture et al. [25], and Lin et al. [26] reported that C/M carbonates can be used as primary precursors for AACs. However, LS and dolomite powders display noticeable reactivity only during long-term aging under a high alkaline dosage or pressure. Low chemical activity made it reasonable to use LS as a secondary precursor in AAC based on the low content of reactive calcined clays. Perez-Cortez et al. designed an AAC based on metakaolin (MK) and LS [10, 11]. The content of LS was as high as 80 % in optimal formulation, molar ratios of $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ and $\text{SiO}_2/\text{Al}_2\text{O}_3$ were 0.94 and 3.54 (4.7 % Na_2O respective to mass of MK+LS). The compressive strength (CS) of the designed cement after 24 h of treatment at 60 °C was 51.9 ± 0.7 MPa. The microstructure of the hardened pastes was a dense matrix of reaction products with partly reacted LS particles, and the main reaction products were mixed (C,N)-A-S-H with N-A-S-H, C-A-S-H, and C-S-H. The introduction of LS to sodium silicate (SS)-activated MK decreased alkali component consumption, and changed the chemistry and assemblage of the reaction products. The main reaction products were the mixed gels of N-A-S-H and (N-(C)-A-S-H) with 3D network structures where Ca^{2+} replaced Na^+ via an ion-exchange mechanism. Meanwhile, the properties of the proposed fresh and hardened AAC pastes were not comprehensively investigated, as the focus was on the CS of the hardened samples.

The high cost and scarcity of the high-grade MK clay deposits have intensified the worldwide research on evaluating the potential of relatively more abundant clay minerals – illite, montmorillonite etc. [27–30]. Bentonite clay, meanwhile, has not yet been explored in AAC with high content of LS.

Several studies have investigated the suitability of natural clay-C/M carbonate blends in the form of carbonate-containing clays with varying mineralogical composition for AACs production [31–38]. Both the content of clay and carbonate minerals and the calcination temperature are determining factors in the reactivity of multimineral carbonate-bearing clays because the decomposition temperatures of calcium carbonate and clay minerals are different. Thus, the normal temperature range providing the clay minerals dehydroxylation at 600–800 °C is insufficient for the complete decarbonization of C/M carbonates. However, calcium carbonate began to decompose at 750 °C [37], indicating that carbonate-containing clays after calcination at temperatures range of 750–800 °C are composed of not only reactive Si and Al but also certain amount of reactive Ca. Consequently, thermally treated carbonate-containing clays used as geopolymer precursors are referred to as Ca-aluminosilicates. D'Elia et al. [35] designed a geopolymer binder based on 6 M sodium hydroxide activated thermally treated carbonate-rich illite clay with a 34.2 % clay mineral and 31.2% calcite content, and the 2 d CS was as high as 20 MPa, whereas 28 d was > 30 MPa. The presence of reactive Ca in the calcined clay induced the co-precipitation of a mix of aluminium-enriched C-A-S-H and N-A-S-H gels, in which sodium was partially replaced by calcium (N,C)-A-S-H.

It should be noted, the literature lacks data on the feasibility of using bentonite clay-limestone co-calcination for the purpose of AAC production.

The object of this study is alkali-activated cement based on bentonite clay and limestone, the subject is the investigation of the properties of fresh and hardened pastes, reaction products assemblage, and microstructural characterization of this binder system.

The goal of this study is the development of alkali-activated cements based on bentonite clay and limestone for general construction purpose. In light of these previous research works, the objectives of the research are:

- feasibility investigation of AACs designs based partially or co-calcined bentonite clay and limestone;
- study on the effect of mineralogical assemblage, fineness of precursors, formulation details, curing conditions on engineering performance, reaction products, and microstructure of AACs based on bentonite clay-limestone mixture;
- study of the role of calcined bentonite clay and limestone in formation of reaction products of the AAC hardened pastes.

2. Materials and Methods

The bentonite clays and LS applied to prepare the AAC paste samples were obtained from the Russian Federation (Republic of Tatarstan) deposits. The mineralogical composition of the Clay 1 (Fig. 1): kaolinite-1A – 5.03 %, montmorillonite-15A – 29.96 %, montmorillonite-18A – 12.02 %, quartz – 25.58 %, muscovite-2M2 – 14.61 %, orthoclase – 7.05 %, clinocllore – 5.28 %, pyrite – 0.46 %; Clay 2 (Fig. 2): montmorillonite – 39 %, quartz – 15 %, albite – 12 %, mica – 11 %, clinocllore – 8 %, hornblende – 7 %, microcline – 6 %, calcite – 2 %.

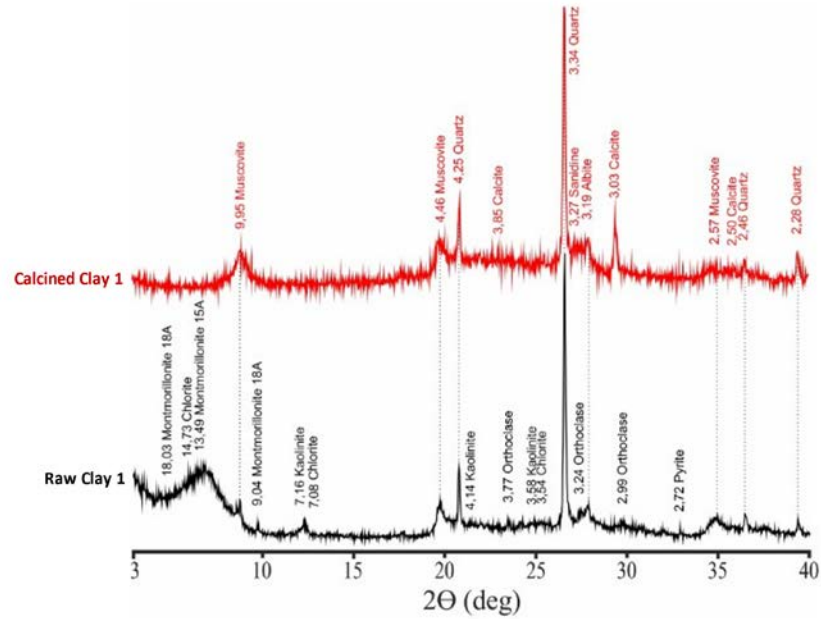


Figure 1. X-ray diffractograms of raw and calcined Clay 1.

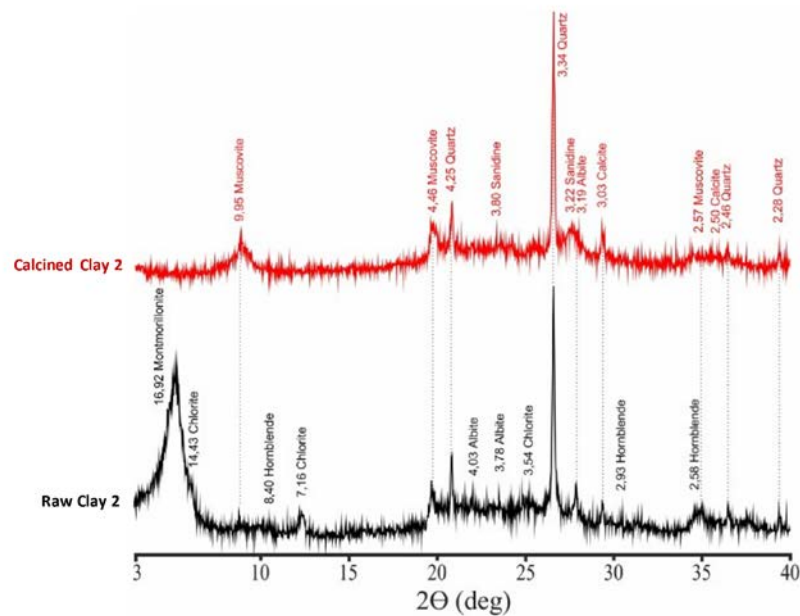


Figure 2. X-ray diffractograms of raw and calcined Clay 2.

Anhydrous solid sodium metasilicate (SSM) (Na_2SiO_3) provided by Meterra (RF) was used as the alkali reactant. An SS solution was prepared by dissolving SSM granules in deionized water and cooling it to room temperature for 24 h prior to use.

The bentonite clays or mixtures of bentonite clays and LS were calcined at 800 °C for 1 h. Calcined bentonite clay and LS were milled in a planetary mill MPL-1. The particle size distributions of the source materials were measured using a laser particle size analyzer (Horiba La-950V2). The materials were dispersed via ultrasound in ethanol as the dispersion medium. The particle size distributions of the starting materials are presented in Table 2 and Fig. 3.

Table 1. Particle size characteristics of the starting materials (μm).

Material	d10	d50	d90
Calcined Clay 1	7.7	24.1	116.2
Calcined Clay 2	9.8	20.9	88.6
Limestone	3.0	9.5	108.0

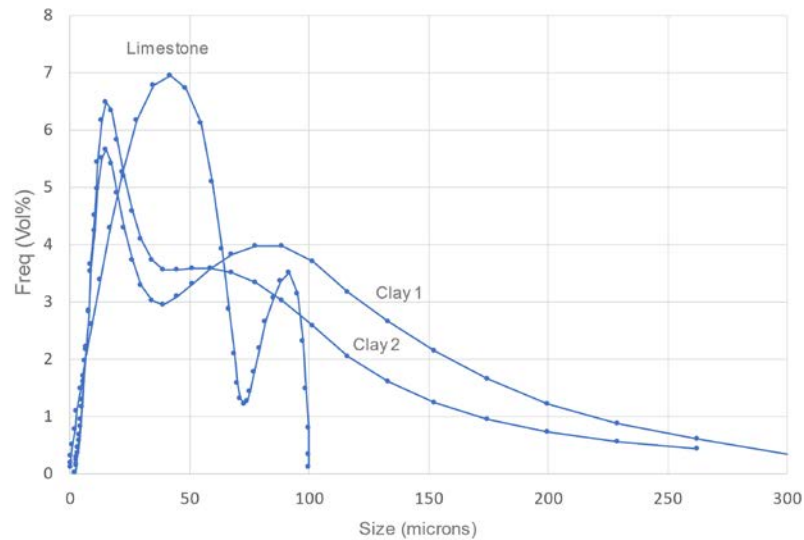


Figure 3. Particle size distribution of starting materials.

The dry mixes were kneaded for approximately 10 min with an alkali reactant solution (Fig. 4). The fresh pastes were manually cast into 25×25×25 mm cubic moulds and vibrated for 1 min to remove entrapped air. Two sets of samples were then prepared. CS of the hardened AAC pastes was tested after steam curing, following a thermal curing program of 24 h of presetting, 4 h to reach the desired temperature, 12 h of dwell time at 80 °C, and 3 h of cooling. Mechanical tests were conducted by applying a vertical load between the two parallel surfaces during casting. Each CS determination quoted was based on the average of six measurements from the same cast.



Figure 4. Preparation of AACs hardened pastes.

X-ray diffraction (XRD) and thermal analyses (TG/DSC) were conducted on ground clays and AAC hardened pastes. The XRD results were obtained using a D2 Phaser X-ray diffractometer in a Bragg-Brentano θ - 2θ configuration with Cu K α radiation operating at 40 kV and 30 mA. Data analysis was performed using the DIFFRAC plus Evaluation Package EVA Search/Match and PDF-2 ICDD database. The mineralogical composition of the clays was determined by analyzing the X-ray diffractograms of the software product Diffrac.eva V3.2. An STA 443 F3 Jupiter simultaneous thermal analysis apparatus was used for the TG/DSC. The clays and hardened AAC pastes were heated from 30 °C to 1000 °C at a heating rate of 10 °C/min. The data were analyzed using Netzsch Proteus Thermal Analysis software. Scanning electron microscopy (SEM; FEI XL-30ESEM) was performed at accelerating voltage of 20 keV.

The workability of the fresh pastes was evaluated using flow-table tests according to EN 1015-3. The water/binder ratio was regulated to maintain constant flowability ranging from 29.5 to 30.0 cm. The fresh pastes were placed into a standard conical ring, and free flow without jolting was allowed. Two perpendicular diameters were determined, and the mean value was recorded as the slump flow. The initial and final setting times were measured using the Vicat needle method according to EN 196-3. The determined values are the averages of three samples.

3. Results and Discussion

3.1. Development of AACs based on calcined bentonite clay and raw LS

3.1.1. Properties of fresh and hardened AAC pastes based on calcined bentonite clays and raw LS

The influence of the quantity of LS, calcined clay minerals, and SSM dosage on the CS of hardened AAC pastes is shown in Fig. 5. It can be observed from the presented data that the CS of the samples based on thermally treated Clay 1 is higher than those derived from Clay 2 due to greater amount of reactive phase provided by higher content of metamontmorillonite as well as presence of metakaolinite. Moreover, higher content of quartz in Clay 1 compared to Clay 2 can improve the CS by slowing down the crack growth in the AA cementitious materials [39]. As for the dosage of SSM, 5–10 % was optimal, and the use of a higher percentage of 15 % was not productive. An increase of the SSM percentage from 5 to 10 % logically positively affects the CS by ensuring higher completeness of the reaction process between the precursor and alkali component. The highest mechanical performance up to 34.2 MPa corresponded to a low content of calcined clays (20–30 %) and high content of LS (70–80 %), which agrees with the results of Perez-Cortez et al. [10, 11]. However, the CS values of MK-LS optimal formulations were lower than those obtained by Perez-Cortez et al. [10, 11]. This can be attributed to the differences in curing conditions and lower reactivity of 2:1 type clay mineral metamontmorillonite compared to metakaolin. The improvement in CS followed by an increase in LS replacement up to 80–90 % is probably attributed to several reasons. First, the filler effect of LS provides better packing density of precursor particles; secondly, an increase in the SSM/reactive phase ratio at higher LS dosages against the backdrop of LS poor chemical activity intensifies the formation of binder gel. The SSM/reactive phase ratio supposedly reaches optimal value for formation of continuous mineral matrix with CS and in a volume sufficient to solidify high content of LS when the dosage of calcined clay minerals is 9.4 % and 10.8 % in Clay 1 and Clay 2, respectively.

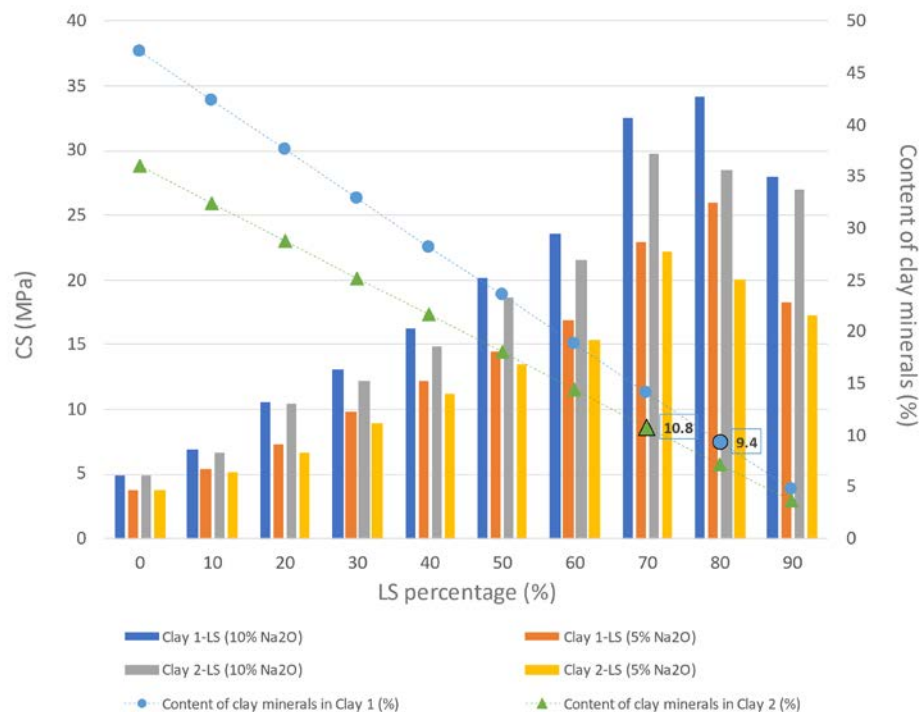


Figure 5. The influence of the quantity of clay minerals, LS, and SS dosage on the CS of the hardened AAC pastes.

The properties of the fresh AA calcined Clay 1-LS pastes are shown in Fig. 6. By increasing the amount of LS in the range of 0–90 %, a reduction can be observed in the water/binder ratio from 0.7 to 0.54, which agrees with numerous studies stating the dilution effect of LS [40–42]. Moreover, the setting times of the fresh pastes were shortened by an increase in LS loading. The reason of it is the lower amount of liquid phase at higher loadings of LS, greater ratio of SSM/reactive phase, and chemical reactions intensity between the alkali reactant and precursors blend.

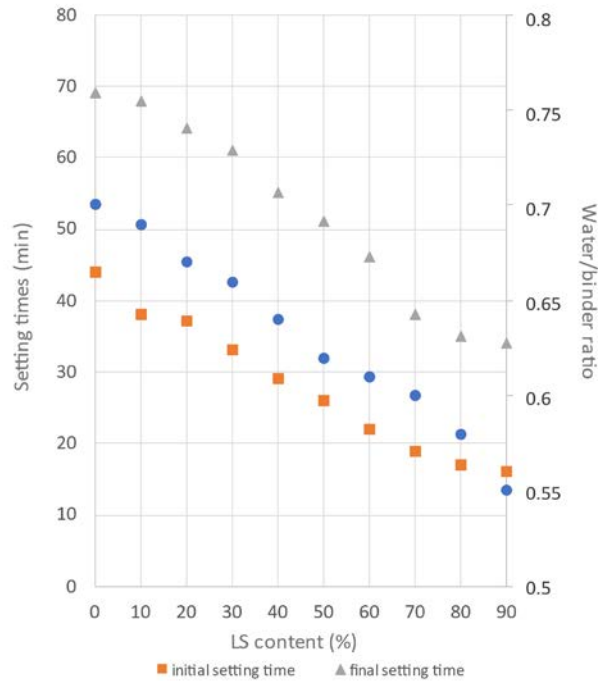


Figure 6. The properties of the fresh AAC pastes.

3.1.2. Reaction products and microstructure of hardened pastes based on calcined bentonite clays and raw LS

The results of the X-ray diffraction, thermal, and SEM/EDS analyses are shown in Figs. 7–9, performed for the optimal formulations of AAC hardened pastes based on calcined Clay 1 incorporated with 80 % of LS and activated by SSM solution (10 % by Na_2O). According to XRD, the main reaction product of hardened paste, based on the amorphous hump which is centralized between 26 and 29° 2θ , is a mixed N-A-S-H and N-(C)-A-S-H gel-like product [11], along with relic unreacted quartz, mica, and calcite. The binder hydrate gel is also supported by the results obtained through thermal and SEM/EDS analyses. The water loss of 4.52 % detected in the area of 50–175 °C reflects water evaporation and dehydration from the gel reaction product. However, the reactive phase composition in the studied cementitious system requires further more detailed investigation.

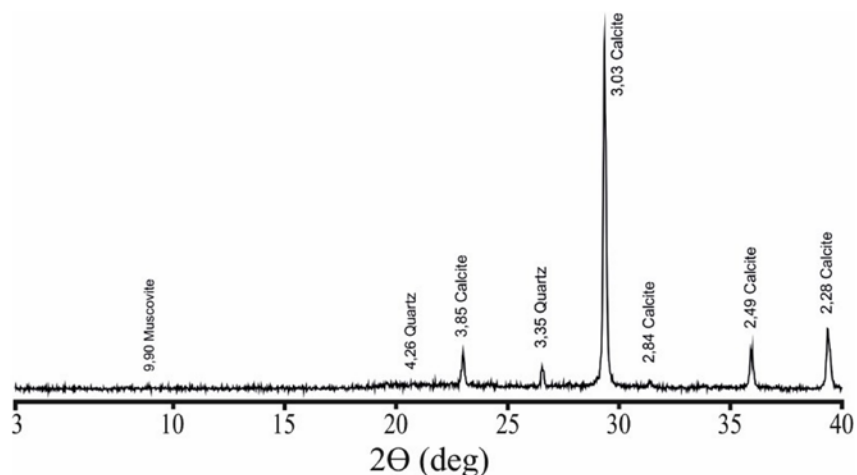


Figure 7. X-ray diffractogram of calcined Clay1(20)-LS(80)-based hardened paste.

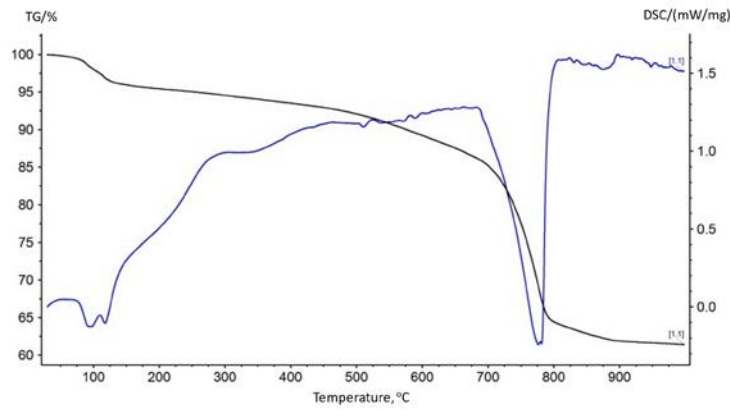


Figure 8. Thermal analyses (TG/DSC) of calcined Clay1(20)-LS(80)-based hardened paste.

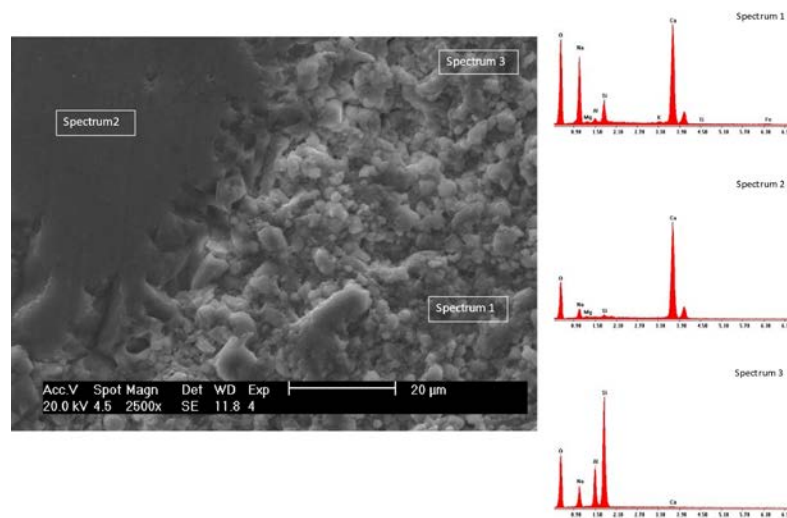


Figure 9. SEM/EDS of calcined Clay1(20)-LS(80)-based hardened paste.

3.2. Development of AACs based on calcined bentonite clay and raw LS

The mechanical properties of hardened pastes obtained by alkali activation of the calcined mixtures of bentonite clays and LS were not significantly different from those based on calcined clays and LS. Therefore, the joint thermal treatment of bentonite clay and LS did not result in formation of calcium silicates as it was stated for mixtures based on kaolin and limestone [38]. These hypotheses were confirmed by XRD and thermal analysis data presented in Figs. 10, 11. As can be seen from the presented data, the calcination of bentonite clay-LS mixtures leads only to dihydroxylation of clay minerals and decomposition of calcite.

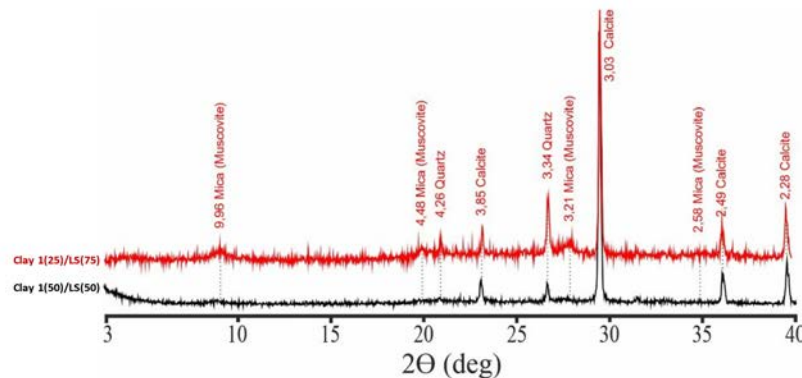


Figure 10. X-ray diffractogram of calcined mixtures Clay1(25)-LS(75) and Clay1(50)-LS(50).

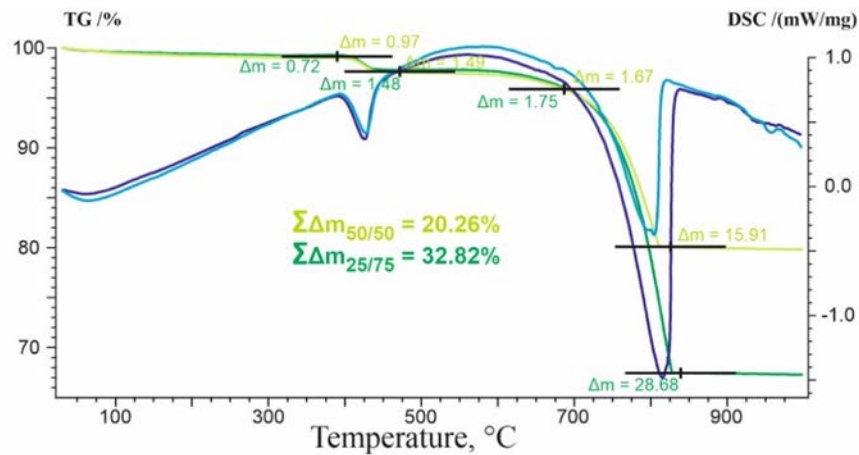


Figure 11. Thermal analyses (TG/DSC) of calcined mixtures Clay1(25)-LS(75) and Clay1(50)-LS(50).

4. Conclusion

The paper presented study results on the effects of formulation-processing factors (individual or complete thermal treatment of bentonite clay-LS, dosages of precursors and alkali reactant) on the properties of sodium-silicate activated fresh and hardened cement pastes, reaction products assemblage, and their microstructure. The following conclusions were drawn. Calcined bentonite clays at 39–47 % content of clay minerals were found to be suitable for AACs incorporated with high loading of raw LS. The thermal treatment of bentonite clay followed by mixing with raw LS was a more reasonable way to obtain mixed AAC compared to joint calcination of bentonite clay and LS. Optimum compositions consisting of 20–30 % calcined clay and 70–80 % LS had compressive strength up to 32 MPa. In the designed AAC based on the binary calcined clay-LS precursor, calcined clay is the main reactive precursor that forms a mineral matrix in the form of sodium aluminosilicate hydrate gel N-A-S-H, whereas calcium carbonate is a much less reactive secondary precursor that modifies the main binder gel by forming sodium (calcium) aluminosilicate hydrate gel N-(C)-A-S-H. An intermixed mineral matrix consisting of N-A-S-H and N-(C)-A-S-H gels binds the LS particles by forming a consolidated material. The effect of LS on the properties of fresh AAC pastes, which manifests in water demand and setting times reduction for blended fresh AAC paste, was based on the dilution effect. The strengthening effect of LS was based on filler, nucleation, and chemical effects.

Predominant content of raw LS contributes to low energy consumption of the proposed AACs. Presented outcomes contribute to the development of the raw materials base of sustainable cements.

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