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Influence of limestone content, fineness, and composition on the properties and microstructure of alkali-activated slag cement

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ABSTRACT

The influence of the fineness, concentration, and chemico-mineralogical composition of limestone on the workability, reaction kinetics, compressive strength, microstructure, and binder gel characteristics of sodium carbonate—based waste-activated waste slag cement pastes was investigated in this work. Alkaliactivated slag cements incorporated with limestone, containing 33–100% of calcite, at a content of up to 60% with a 28-day compressive strength of 26.2–48.8 MPa were proposed. The main reaction products of hardened alkali-activated cement pastes and those incorporated with limestone are C–S–H, CaCO₃, Na₂Ca(CO₃)₂·5H₂O, and Na₂CaSiO₄. "Physically active" limestone does not chemically react with the binder gel but it can improve the physical structure. The higher packing density of mixed cement, without an increase in the water demand, the satisfactory binding strength of limestone with the binder gel lead to the improvement in the physical structure and compressive strength of alkali-activated slag paste.

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1. Introduction

Alternative or non-traditional cements form a large group of binders, differing significantly from Portland cement and from each other by the composition and type of raw materials, nature of hardening products, mechanism of hardened cement paste formation, and the research experience, adoption, and application of each type of cement [1]. Some types of alternative binders also termed new cements for the 21st century, new cementitious matrixes, combining higher, in comparison with PC, 'ecological compatibility' and some technical characteristics are proving to be increasingly promising in terms of partial replacement of ordinary Portland cement (OPC) in the present climate of 'sustainable development' [1,2]. The non-clinker non-fired alkali-activated cements (AACs) belong to this category of cement [3–5]. Such materials usually consist of two components: an aluminosilicate precursor and an alkaline activator, with a variety of industrial byproducts and aluminosilicate solids having been used as raw

* Corresponding author. E-mail address: rahimova.07@list.ru (N.R. Rakhimova). One of the most popular mineral admixtures for OPC is limestone (LS) owing to its abundance and chemical-mineralogical composition [11,12]. Portland–LS cements are the most widely used cements in Europe. Two classes exist in EN 197-1 designated as CEM II/A-L and CEM II/B-L, in which the maximum contents of limestone are 20 and 35%, respectively. Several studies in the past

materials. At the present stage of development of AACs, ground granulated blast furnace slag (GGBFS) and fly ash are accepted as

attractive precursors for large-scale industrial production of AACs

[6]. However, fly ash and metallurgical slag are not available

everywhere nor has the supply chain for their distribution been

established in local markets; this is because the supply chain has an

interdependence on the existence of a ready market [4]. According

to past studies, a wide range of natural materials and by-products is

suitable for the replacement of GGBFS, which also has valuable

technical advantages and economic benefits [7–10]. The cost and

environment footprint of the alkali activator also holds importance

in the further development of alkali-activated slag cement (AASC),

which is why the application of widely accessible mineral admix-

tures that can effectively substitute for GGBFS in AASC activated by

appropriate alkali components, including alkali-containing wastes,

is of scientific and practical interest.







few years have stated the attractiveness of LS for blended nonclinker cements [13,14], including AACs [15–23]. Developed by Sakulich et al. [16], alkali-activated slag/limestone fine aggregate concrete had a compressive and tensile strength of up to 45 and 4 MPa at 28-day age, respectively. According to Bilek [17], the addition of up to 33% ground LS filler, with a S_{sp} of 360 m²/kg, to GGBFS activated by a blend of sodium water glass and potassium hydroxide improved its workability, decreased early strength, and almost did not affect the 28-day strength when compared to a reference sample. Gao et al. [19], investigating the properties of alkali-activated slag-fly ash blends with LS addition, stated that the LS powder mainly shows physical modifications with slight but non-ignorable chemical modifications of alkali-activated slag-fly ash blends. The additional nucleation sites provided by LS powder slightly accelerated the induction and acceleration/deceleration stage of the reaction; it also increased the total heat evolution within the tested 72 h and improved the strength of the blended alkali-activated binder system. The gel-characteristic analyses show that the reaction products of alkali activated slag-fly ash-limestone blends are governed by the chain structured C-(A)-S-H type gels. The presence of LS powder did not lead to the formation of new phases, but slightly increased both the physically and chemically bound water content. Yip [20] confirmed the dissolution of Ca²⁺ from calcium carbonates in alkali activated systems. It should also be noted that satisfactory surface binding between the LS powder and alkali-activated materials was suggested by Cwirzen [21]. Thus, according to the above-mentioned studies. LS is a promising mineral supplementary material, which has a positive effect on the properties of AAC mainly due to the "physical filler effect". At the same time, the properties of AACSs incorporated with supplementary materials depend on a number of influencing factors, including important factors of supplementary materials such as its chemical-mineralogical composition and fineness [8].

This research aims to study the influence of LS content, fineness, and composition on the properties and microstructure of sodium carbonate—based waste-activated slag cement.

2. Experimental details

GGBFS was obtained from the Chelyabinsky factory. Three types of local LS differing in chemical and mineralogical composition were used as supplementary material. The chemical composition of GGBFS and LS is shown in Table 1. The main difference in the mineralogical composition of LSs is in the calcite content, which is 90%, 33%, and 100% in LS1, LS2, and LS3, respectively. LS1 also contains 9% of quartz and 1% of albite; LS2 includes 1% of quartz and 66% of dolomite.

The GBFS was ground in a laboratory planetary mill to a S_{sp} of 300 m²/kg, and the LSs were ground to S_{sp} ranging from 200 to 600 m²/kg (Blaine). The particle size distribution and the S_{sp} of the GGBFS and LS powders were tested using a Fritsch Particle Sizer ANALYSETTE 22 laser particle size analyser and a Blaine airpermeability apparatus.

Table 1	
Chemical composition of	of starting materials.

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The alkaline activation of the AASCs was carried out using alkaline solid waste, forming because of incineration of sewage of petrochemical company "Nizhnekamskneftekhim" (Russian Federation) which produces synthetic rubbers and plastics (Table 2). It consists mainly of sodium carbonate (91.4%). The alkaline solid waste content was 10 g per 100 g of GGBFS or GGBFS + LS.

Vicat tests were carried out according to EN 196–3 to establish the effect of LS on the standard consistency of the fresh AASC pastes.

All test mixtures were prepared by using an electrically driven mechanical mixer. Initially, GGBFS and LS were mixed in a dry state for a minute and then the activator solution was gradually added while mixing continued for about 3 min. Fresh pastes were cast into steel cubic moulds ($2 \times 2 \times 2$ cm). The compressive strengths of the cubes were tested after a 28-day storage under normal conditions (room temperature, humidity 95–100%). Average compressive strengths of six cubes were obtained from each mixture at each testing age.

Isothermal calorimetry experiments were carried out using the metering equipment "Thermochron". The pastes were mixed externally, loaded into the sealed glass ampoule, and loaded into the calorimeter. The time elapsed between the instant the activating solution was added to the powder and the paste being loaded into the calorimeter was around 2–3 min. The tests were run for 200 h.

The mineralogical composition of the LS and hardened AASC pastes was determined using a D8 ADVANCE X-ray diffractometer (XRD) with CuK α radiation operating at 40 kV and 30 mA. Fragments of selected 28-day cured samples were sprayed with an Au/Pd alloy for observation under a scanning electron microscope (SEM, Merlin of CARL ZEISS).

For qualitative analysis, a set of etalons established in the program Aztec has been used (reference standards for X-RAY microanalysis "Registered Standard No. 8842").

3. Results and discussion

3.1. The influence of LS on the properties of fresh and hardened AASC pastes

For study of the influence of LSs on the properties of fresh and hardened AASC pastes, the content of the LS was varied from 0 to 70%. Normal consistency of fresh AASC and alkali-activated slag-limestone cements (AASLSC) did not significantly increase with the content and S_{sp} of LS, and was about 25–26%. These results are in agreement with the results stated by Tsivilis et al. [24] about lowering the water demand of PC paste incorporated with LS powder and with those stated by Gao et al. [19] concerning the positive effect of increasing LS powder content on the flowability of alkali-activated slag–fly ash–limestone blends. This is explained by the microvoids of the paste being filled by fine LS particles, which leads to better particle packing and release of water lubricating the particles.

Starting material	Compon	Component (mass % as oxide)											
	SiO ₂	CaO	Al_2O_3	MgO	MnO	Fe ₂ O ₃	TiO ₂	Na ₂ O	K ₂ O	P_2O_5	SO_3	CO ₂	LOI
GGBFS	37.49	36.22	11.58	8.61	0.50	0.16	1.80	0.64	0.95	0.01	2.00	_	_
LS1	14.26	43.31	2.44	0.84	_	1.11	0.12	0.38	0.51	0.08	-	35.62	36.28
LS2	1.26	39.79	0.20	12.94	-	0.08	0.01	0.08	0.07	< 0.01	-	44.33	45.50
LS3	0.47	55.06	0.07	0.49	-	0.05	0.01	0.03	0.01	0.02	-	43.66	43.83

Table 2	
Chemical	composition of alkali waste.

Starting material	Component (mass % as oxide)								
	Na ₂ MoO ₄	Na ₂ SiO ₃	Na ₂ CrO ₄	H ₂ O	NaOH	Na ₂ CO ₃	Mechanical impurities		
Alkali waste	1.6	1.05	0.92	1.58	2.65	91.4	0.8		

The influence of the quantity and fineness of LSs on the 28-day compressive strength of hardened AASLC pastes is shown in Fig. 1.

As can be seen from the above data, the activation of AASC and AASLSC by alkali waste results in a compressive strength in the range of 26.2-39.0 MPa for hardened pastes aged for 28 days. The introduction of LS1 at 20% content and LS2 at 30% content, with a S_{sp} of 200 m²/kg, allows the replacement of GGBFS without loss in strength. The incorporation of LS, with a S_{sp} of 400–600 m²/kg, in AASC is more effective and allows the substitution of slag of up to 60% without loss in strength of blended cements. Moreover, the introduction of all three types of LS with a S_{sp} of 400–600 m²/kg improves the compressive strength of hardened AASLC pastes. The strength increment is highest at 30-40% content and grows with the increase of S_{sp} and calcite content. The incorporation of 30–40% content of LS1, LS2, and LS3 with a S_{sp} of 400–600 m²/kg improves the strength by 22.1-37.4%, 18.3-33.5%, and 29.7-48.8%, respectively. The increasing effect of LS incorporation depending on calcite content is caused by a higher bonding strength between the binder gel of AASC paste and calcite than that of quartz and dolomite. This is because, in sodium carbonate-activated slag cements, one of the reaction products is calcite [25-27]. Crystal-chemical similarity of the calcite in limestone with the calcite that forms as a result of the reaction between the Ca²⁺ of GGBFS and the alkali anion CO_3^{2-} of sodium carbonate and the carbon dioxide in air influence also contributes to a higher surface binding between the binder gel and LS particles. As a result, the higher effect on the strength of the AASLSC paste demonstrates LS3 characterizing by its monogene mineral composition.

According to previous studies [16,19], the LS admixture mostly acts as a mineral filler for AAC; it should be considered as a "physically active" mineral admixture that does not form hydration products, but it does affect the physical structure and properties of blended binders [8]. Therefore, it is reasonable to compare LS with another "physically active" mineral admixture—quartz sand. Analysis of the results shown in Fig. 1 and published in Ref. [9] revealed the higher efficiency of LS over quartz sand. The incorporation of ground quartz sand with S_{sp} 500–800 m²/kg and

content of up to 30% into sodium carbonate–activated slag cement led to a compressive strength increment of up to 14% when hardening at room temperature. However, along with S_{sp} particle size distribution is also an important characteristic of the fineness of the admixture. Thus, it was also stated that the compressive strength improvement was caused by an improvement in the grain-size composition of the mixed cement. The amount of particles smaller than 5 µm increases and is more than 30% [28] when the quartz sand is ground from a S_{sp} of 200 to 500–800 m²/kg (4.5 times); the grain-size distribution of the GGBFS at a S_{sp} of 300 m²/ kg is not optimum and improves when particles with sizes lesser than 20 µm are introduced [29].

The results depicted in Fig. 1 are in partial agreement with the data of Gao X [19]. who observed a positive influence of adding 30% limestone, which was characterized by a median particle size (d50) of 10.12 μ m, on the compressive strength of activated by sodium hydroxide and sodium silicate slag—fly ash blends.

As LS3 provides the best results in terms of influence on the compressive strength, its particle size distribution depending on S_{sp} was analysed, and the results are shown in Table 3. These data show that when the S_{sp} is increased from 200 to 400 and 600 m²/kg, the fraction content of LS particles with a size less than 20 μm is increased by 38.3 and 49.5%, respectively. Moreover, the grinding of LS3 increased the S_{sp} from 200 to 400 m²/kg, and the content of particles with a size smaller than 5 μ m increases by more than two times. The further grinding of LS3 increased the S_{sp} from 400 to $600 \text{ m}^2/\text{kg}$, and the content of particles with a size smaller than 5 µm increased by another 55%. It seems that the higher grindability of LSs compared to quartz sand provides a higher content of particles with a size less than 20 μ m, and especially less than 5 μ m. This results in an improved particle size distribution of the mixed binder, increased particle packing density at a constant liquid/solid ratio, and a decrease in porosity of the hardened paste. Consequently, there is an improvement in the strength characteristics.

Fig. 2 depicts the progress of the reactions of the fresh AASC and AASLSC pastes containing 30% of LS3 (AASLS3C(30%)) with different S_{sp}s of the mineral admixture. As can be seen at the initial period of



Fig. 1. 28-day strength of hardened AASC and AASLSC pastes as a function of the amount and S_{sp} of LSs.

Table 3					
Particle size	distribution	of LS3	depending	on Ser	

S _{sp} , m ² /kg	Particles content (%) in fraction (µm)									Fraction content < 5 μ m (%)	Fraction content < 20 μ m (%)
	≤1	1-5	5-10	10-20	20-40	40-80	80-100	100-150	≥150		
200	0	18.45	22.62	15.16	5.10	10.47	5.02	7.83	15.34	18.45	56.23
400	2.83	36.81	25.92	12.22	6.35	10.41	3.65	1.34	0.47	39.64	77.78
600	25.03	36.58	14.82	7.65	5.21	7.88	2.33	0.51	0	61.61	84.08



Fig. 2. The hydration rate of AASC and AASLS3C(30%) as a function of the S_{sp} of LS3.

the reaction, the temperature rise curve of the reference sample is characterized by two initial peaks: the first is at 100 min and 25 °C, and second one is at 49 h and 26 °C; we also observe one accelerated hydration peak at 183 h and 24.5 °C. Thus, our results in terms of the two initial peaks and temperature are in agreement with study of sodium carbonate—activated slag cements by Shi et al. [30]. The first initial peak is attributed to the wetting and dissolution of slag particles, and the second one is attributed to the formation of CaCO₃; the third peak is associated with the formation of more CaCO₃ and first occurrence of C–S–H [30]. With regard to the temperature rise of fresh AASC pastes incorporated with LS3, their behaviour is significantly interrelated with the fineness of LS3. As can be seen in the case of LS3 with a S_{sp} 200 m²/kg, there is only one initial peak that appears at 69 h and at a lower temperature than that for the reference sample. The temperature curve of AASLS3C(30%) incorporated with LS3 with a S_{sp} of 400 m²/kg has similarities with that of the reference sample; the first initial peak and accelerated hydration peak have lower temperature, but the second initial peak is observed at the same temperature as the reference sample. When the LS3 incorporated in AASC has a S_{sp} of $800 \text{ m}^2/\text{kg}$, the first initial peak is registered at a lower temperature (23.5 °C and 9 h) compared to the reference sample, which is probably similar to that observed for LS3 with a S_{sp} of 400 m²/kg, caused by the lower amount of particles that are able to wet and dissolve in the alkali medium. However, the second initial peak occurred at higher temperature (27 °C) but at the same time (49 h) as the reference sample. This fact indicates that LS3 with a S_{sp} of 800 m²/kg, as opposed to LS3 with a S_{sp} of 200 and 400 m²/kg, accelerates the reaction process. These results are in agreement with earlier studies that also indicated that LS with a d50 value of 10.12 μ m and when present at 0–30% content promotes the reaction process of sodium hydroxide-sodium silicate activated slag-fly ash blends [19]. The incorporation of LS powder introduces more fine particles in the system, which provides additional nucleation sites for the formation and growth of reaction products, and then as a result, the reaction process is accelerated [31]. The intensification of the acceleration effect of blended cements depending on LS particle size has also been reported by Vance et al. [32]. Thus, it can be concluded from our results that the LS accelerates the reaction process of sodium carbonate-based waste-activated slag pastes,



Fig. 3. X-ray diffractograms of 28-day cured AASC, AASLS1C, AASLS2C, AASLS3C pastes.





Fig. 4. X-ray diffractograms of 28-day cured AASC, AASLS3C(30%), and AASLS3C(60%) pastes.



50µm



Fig. 6. SEM image of 28-day cured AASLS3C(30%) paste.

and the acceleration effect can be achieved when the content of particles with a size less than 5 μ m was no less than 61%.

3.2. The influence of LS on the hydration products composition and microstructure of hardened AASC pastes

It is well-known that the alkali activation of GGBFS results in a majority C–A–S–H gel [33–35], but it is undetectable by XRD analysis. The XRD patterns of the samples of hardened pastes of AASC with a slag of content 100%, pastes with slag content of 70%, and LS1 (AASLS1C), LS2 (AASLS2C), and LS3 (AASLS3C) with LS additions of 30% (S_{sp} of 800 m²/kg) are presented in Fig. 3. Fig. 4 shows the XRD patterns of AASC and AASLS3C incorporated with 30% and 60% of LS3 with the same S_{sp}.

Bernal et al. [36] investigated hardened paste based on sodium carbonate—activated GGBFS with a composition similar to that of the GGBFS used in this study; she identified calcium silicate hydrate (C–S–H), calcite, traces of hemicarbonate and gaylussite, and two layered double hydroxide—type phases: manasseite (Mg₆Al₂CO₃(OH)16·4H₂O) and Mg₆Al₂(OH)18·5H₂O. Kovtun et al. [26] found tobermorite Ca_{2.25}Si₃O_{7.5}(OH)1.5H₂O, \geq alcite, and gaylussite in sodium carbonate—activated slag pastes. Our results are consistent with the above in terms of the detection of C–S–H, calcite, and gaylussite. Moreover, sodium calcite silicate Na₂CaSiO₄, which could form due to the presence of Na₂SiO₃ in alkali waste, was also identified. With regard to the composition of AASLS1C, AASLS2C, and AASLS3C pastes incorporated with LS, there are no "new" hydration products, which is in agreement with study by

Gao et al. [19], who stated no evident chemical reaction between LS and sodium hydroxide and sodium silicate activated slag—fly ash paste. Along with the reaction products, which were identified in the reference AASC sample, the peaks of the relict minerals of the LS in all samples were found to be calcite and dolomite in AASLS2C. The increase in LS concentration just leads to intensification of the relict LS mineral peaks.

Figs. 5 and 6 show SEM images and examples of the qualitative analysis of 28-day cured reference AASC and AASLS3C(30%) pastes (S_{sp} of 800 m²/kg).

As can be seen, compared to the reference sample, the microstructure of the hardened AASC paste incorporated with LS3 is characterized by lesser amount of shrinkage of the microcracks and a less stressed microstructure. The analysis of Fig. 6 also revealed the presence of unreacted slag (spectrum 4) and LS particles. The assumption made in section 3.1 on the sufficiently good binding of the binder gel and LS3 particles is confirmed by Fig. 6. With regard to binder gel composition (Fig. 5, spectrums 1, 2, and 3, Fig. 6, spectrum 3 and 5) the atomic ratios of Ca/Si, which were determined by EDS, were 1.3 (\pm 0.21) and 1.24 (\pm 0.3) for the reference and blended AASC-based samples, respectively. The higher Ca/Si ratio than that inherent for alkali-activated slag pastes (≈ 1) [3,4,37,38] is caused by the high content of calcite in the binder system. A higher Ca/Si ratio (1.09 ± 0.23) in sodium carbonate-activated slag cement paste at 1-day age was also reported by Kovtun [26], and this was explained by the intermixing with gaylussite and calcite. Thus, the results of the XRD analysis shows similar values of the Ca/Si ratio for the reference and blended alkaliactivated samples, with visible LS3 particles, with a size up to 5 μ m, in the SEM images (Fig. 6) that indicate that LS does not react with binder gel of the AASC paste.

4. Conclusions

In this work, the influence of the fineness, concentration, and chemical-mineralogical composition of limestone on the normal consistency, reaction kinetics, compressive strength, microstructure, binder gel characteristics of sodium carbonate-based wasteactivated slag cement pastes were studied. The application of alkali waste as an activator results in compressive strength in the range of 26.2-39 MPa for hardened alkali-activated cement paste and those incorporated with limestone up to 60% content at 28 days. The ground limestone with calcite content of 33-100% is a promising "physically active" mineral admixture for alkaliactivated slag cements for replacement of ground granulated blast furnace slag up to a content of 60% without strength loss and a compressive strength improvement up to 48.8% depending on the concentration and fineness of limestone. The "physical activity" of limestone increases with the increase in calcite content and fineness of limestone. The LS containing more than 39% of particles with a size lesser than 5 µm provides nucleation sites and accelerates the reaction process of blended alkali-activated cements. The main reaction products of hardened alkali-activated cement pastes and those incorporated with limestone are C-S-H, calcite (CaCO₃), gaylussite $(Na_2Ca(CO_3)_2 \cdot 5H_2O)$, and sodium calcite silicate (Na₂CaSiO₄). Limestone does not chemically react with the binder gel but it improves the physical structure and compressive strength, while providing the following features:

- higher packing density of mixed cement without increasing the water demand when the content of particles with a size less than 20 μm and 5 μm are more than 77% and 39%, respectively
- has good compatibility with ground granulated blast furnace slag, including chemical-mineralogical similarity with one of the reaction products of sodium carbonate alkali-activated slag paste calcite
- shows satisfactory binding strength with the binder gel.

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