The use of limestone sludge for the geopolymer preparation

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Abstract. The study investigates the effect of sludge waste from mining and washing of limestone on the properties of geopolymer binders based on metakaolin and blast furnace slag. The effect of adding two types of limestone sludge on workability, setting time, compressive strengths, durability and pore distribution was investigated. Limestone sludge was dosed in an amount of 0–30%. Sodium water glass was used as an alkaline activator in the ratio of 5:4. A linear correlation between the flowability and limestone sludge content was observed, and very satisfactory results of compressive strength after 90 days were obtained for samples with sodium water glass (about 55 MPa). The positive effect of CaCO₃ on strength was confirmed. The increased content of clay components resulted in a reduction of compressive strength.

1. Introduction

The effect of the addition of waste sludge from limestone washing on the properties of geopolymers based on metakaolin and blast furnace slag was studied in this work. This waste is generated during the production of limestone, and it is landfilled at a sludge pond. The main component of this waste is calcite, so this raw material has no potential for use in alkali-activated materials at first sight. Geopolymers are a result of a reaction between aluminosilicate compounds and alkaline solutions. The main materials used in alkali-activated binders are kaolinitic clays, fly ash and blast furnace slag. During the reaction of the raw materials to the alkaline environment, dissolution occurs. After amorphisation and the formation of precursors, the geopolymer precipitates in an amorphous or semi-crystalline state [1]. There is an effort to reduce costs in the production of these materials. Therefore, alternative waste products are being sought, reducing the price and simultaneously maintaining or improving the final product properties.

In previous works, the beneficial effects of calcite on the properties of alkali-activated materials have been confirmed [2]. The addition of calcite and dolomite on the mechanical properties of metakaolin geopolymers is described in the study of Yip et al. (2008) [3], and improvement of strengths by the addition of 20% of calcite was confirmed. Qian (2015) [4] suggested that adding 10% to the metakaolin matrix resulted in a more compact structure. In Aboulayt’s work (2017) [5], the effect of the replacement of metakaolin by calcium carbonate was examined. Sodium and potassium hydroxides and alkaline solution were used as the alkaline-activator. The evolution of mechanical strengths vs the calcite contents was tested, and samples with calcite in the amount of 5–10% exhibited higher compressive strengths than the reference sample.

Cwirzen et al. (2014) [6] studied the effect of limestone on metakaolin-based geopolymers activated by sodium hydroxide solution. The study of Gao (2015) [7] deals with the influence of limestone powder (LS) on fresh mixture behaviour and mechanical properties of alkali-activated slag-fly ash blends in which the positive effect of limestone on workability and compressive strength was confirmed. Yuan
(2017) [8] studied the impact of LP on the reaction kinetics, workability, and compressive strength development of sodium carbonate activated slag. An optimal dosage of 10% of LP was determined to reaction kinetics and strength development.

This work aimed to verify the possibility of using dry waste limestone in a geopolymer mixture based on metakaolin and blast furnace slag. Two types of sludge with different compositions of 0–30% were used for the tests.

2. Experimental

2.1. Materials

Metakaolin (MK), blast furnace slag (BFS) and two types of limestone waste sludge (LS) were used as raw materials. MK Mefisto L05 was supplied by České lúpkové závody, a.s. (Czech Republic), finely ground BFS originated from Trinec (Czech Republic). LS comes from the production of Vitošov limestone (Czech Republic). Waste sludge is generated from washing during limestone mining and processing. Sludge with washing water is delivered to a sludge pond, where it sediments. The settled sludge is not used in any way, and its volume in the landfill is growing. Two types of samples were taken for the experiments, which differ in their composition. The samples were dried at 60°C and ground. Sodium water glass was used as the alkaline-activator (Ms = 1.65).

Chemical analysis of used materials is given in table 1. Characteristic particle diameters D_{10}, D_{50} and D_{90} are summarised in table 2.

Table 1. Chemical composition of materials used in mixtures (%).

|       | SiO₂ | Al₂O₃ | CaO | Na₂O | K₂O | MgO | Fe₂O₃ | SO₃ | TiO₂ | LOI |
|-------|------|-------|-----|------|-----|-----|-------|-----|------|-----|
| LS1   | 19.60| 3.11  | 41.50| 0.09 | 0.46| 0.26| 1.40  | 0.01| 0.24 | 33.25|
| LS2   | 20.32| 9.04  | 34.37| 0.18 | 1.2 | 0.67| 3.16  | 0.02| 0.46 | 30.23|
| BSF   | 53.21| 42.94 | 0.20 | 0    | 0.78| 0.28| 0.92  | 1.56| 0.05 | 2.10 |
| MK    | 39.99| 8.99  | 38.70| 0.47 | 0.48| 8.71| 0.49  | 0.34| 1.84 | 0.71 |

Table 2. Particle diameters of materials (µm).

|    | D₁₀ | D₅₀ | D₉₀ | Mean diameter |
|----|-----|-----|-----|---------------|
| LS1| 1.43| 14.74| 54.11| 22.07         |
| LS2| 2.26| 17.14| 49.29| 22.13         |
| BSF| 1.66| 10.73| 28.63| 13.38         |
| MK | 1.21| 4.65 | 11.00| 5.52          |

The XRD analysis of these raw materials was performed. 83% of the amorphous phase was identified in MK. MK also contained quartz (SiO₂), kaolinite (Al₂Si₂O₅(OH)₄), illite (KA½(AlSi₃O₁₀)(OH)₂), anatase (TiO₂) and mullite (Al₅Si₃O₁₄). BFS contained calcite (CaCO₃), merwinite (Ca₃MgSi₂O₆) and melilite (Ca₂Al₂MgSi₂O₁₄). In addition, quartz (SiO₂) and a significant amount of the amorphous phase was present. The main component of LS1 was limestone (CaCO₃), quartz (SiO₂), albite (NaAlSi₃O₈), anorthite (CaAl₂Si₂O₈) illite (KA½(AlSi₃O₁₀)(OH)₂) or muscovite (KA½Si₃O₁₀H₂). More clay components were identified in LS2. Kaolinite (Al₂Si₂O₅(OH)₄) and feldspar group minerals were identified in the second limestone sludge LS2. The detailed phase composition of limestone sludges is given in table 3. The specific surface area was evaluated according to the Blaine method 230 m²·kg⁻¹ for LS1 and 436 m²·kg⁻¹ for LS2.
Table 3. Mineralogical composition of limestone sludges.

|       | LS1 | LS2 |
|-------|-----|-----|
| Calcite | 81.6 | 70.6 |
| Quartz  | 13.5 | 7.2  |
| Illite/muscovite | 3.1  | 8.3  |
| Kaolinite | -    | 4.8  |
| Feldspar | 1.8  | 9.1  |

2.2. Sample preparation

The weight ratio between MK and BFS was 1.25. MK and BFS were partially replaced by limestone sludge at 0–30%. Dry mixtures were homogenised and then mixed with sodium water glass in a mechanical mixer. Alkaline-solution had a molar SiO₂/Na₂O ratio of 1.65. The solids to solution mass ratio used was 1.25. Quartz sand was used for mortars preparation in a ratio of 1:1. Specimens 40 × 40 × 160 mm were stored at 20°C for 24 h in sealed moulds. After 24 h, hardened specimens were demoulded and stored in plastic bags under laboratory conditions (20°C) for 90 days.

2.3. Methods

The chemical composition of all raw materials was determined by XRF analysis (PANalytical Axios PW4400/30).

The particle size distribution was performed by the laser diffraction method on the CILAS 920L apparatus. The measuring range of the granulometry is 0.3–400 µm, and the measuring medium is isopropyl alcohol. The sample was sonicated for 60 seconds before measurement.

The composition of raw materials and final products was determined by X-ray powder diffraction. The X-ray diffraction analysis was conducted using Bruker D8 Advance apparatus with Cu anode (λKα = 1.54184 Å) and variable divergence slits at Θ-Θ Bragg-Brentano reflective geometry.

The extent of dissolution in an alkaline medium was studied for LS. A specified mass of LS was mixed with 2, 5 and 10 M NaOH solution at room temperature for 24 h using a magnetic stirrer. The samples were filtered (0.2 µm), and the clear liquid part was diluted by concentrated HCl. ICP-OES was used to analyse the concentration of Si, Al and Ca. The residue after filtration was analysed by X-ray powder diffraction.

The workability of the pastes was evaluated by the flow table test according to EN 1015-3 [9]. After mixing, the samples were applied into a conical ring with a diameter of 7 cm and a free flow without applying strokes was allowed.

The Vicat needle method was used to determine the initial and final setting time (EN 196-3) [10] of pastes.

The specimens (40 × 40 × 160 mm) were tested according to EN 196-1 [11], and compressive and flexural strength were evaluated at the ages 28, 56 and 90 days.

Total porosity of prepared material was determined by mercury porosimetry (MIP) performed on the apparatus Carlo Erba Strumentazione model 200, measuring a range of 3.75–10,000 nm. Various levels of pressure were applied to a sample immersed in mercury. The samples were tested after 90 days.

The freeze-thaw test was performed according to ČSN 72 2452 [12] on water-saturated specimens (40 × 40 × 160 mm), repeatedly subjected to freezing and thawing. The freezing cycle lasts four hours at -20°C. Thawing takes place in a water bath for 2 hours at 15°C. The flexural strength was determined on the specimens, and then the compressive strength was determined on the fractions of specimens. Comparisons were made with specimens aged 56 days after 25 cycles and 50 cycles. Two-month-old samples were used for the test.
3. Results and Discussion

The extent of dissolution in alkaline media was monitored in limestone samples. The content of Al, Si, Ca was determined in the filtrate after dissolving the initial materials in sodium hydroxide.

Limestone sludge is not an essential source of Si and Al due to its composition, but at the same time, it cannot be considered only as a filler that does not participate in the geopolymer structure [3]. The graphs (figure 1 a, b, c) show an increase in the ion content depending on the concentration of the sodium hydroxide solution [13]. LS1 decomposed more significantly only when it was exposed to 10 M NaOH. A more significant increase Ca, Al and Si are evident, especially in LS2. The concentration of Si in the filtrate may be higher due to the greater content in the material or due to the higher intrinsic extent of dissolution compared to Al [13]. As the X-ray diffraction results confirm (See figure 2), the kaolinite peaks disappeared, and the calcite peak decreased in samples treated with NaOH solution. Portlandite (CaOH$_2$) was identified in a decomposed sample with 2 M NaOH solution, and portlandite content increased with NaOH solution concentration. The LS2 sample disintegrated more significantly under the action of NaOH solution due to higher surface area and a larger ratio of clay and feldspar minerals.

The slump flow of the fresh alkali-activated pastes is presented in figure 1d. The data show that the addition of LS1 slightly increases workability. Slump flow increased from 250 mm to 290 mm when 30% of limestone was used due to relatively low water demand of limestone particles compared to slag and metakaolin [7]. That is consistent with the results of Yuan (2017) [8], who has observed improvement in the workability of pastes in BSF and PC-based materials after incorporating LS. On the contrary, the LS2 decreased workability from 250 mm to 141 mm. Probably due to the kaolinite content and its plate-like structure, which resulted in inter-particle friction [14].

![Figure 1](image_url)
Ca content in the filtrate (c), results of flow table test (d).

Figure 2. XRD diffractograms of samples of LS after dissolution in NaOH solution a) LS1 
b) LS2 (C-calcite, P-portlandite, Q-quartz, A-albite, Mi-microcline, K-kaolinite, 
Mu/I muscovite or illite).

The effect of LS on the setting of the mixture is shown in figure 3. The reference sample based on 
metakaolin and slag had an initial setting time of about 260 minutes, and the end of the setting occurred 
10 minutes later. As the LS content in the mixture increased, the initial setting time increased up to 
320 min (30LS1), and the final setting time was increased up to 360 minutes. Longer setting times were 
oberved by using LS2. 5% LS2 prolonged the setting time by 60 minutes. The higher content of LS2 
in the mixture had only a slight effect on the setting. The final setting time was observed up to 
380 minutes in the sample 30LS2. The main reason for prolonging the setting time is the reduction 
of the slag content in the mixtures. Gao (2015) [7] studied geopolymer mixtures based on fly ash, blast 
furnace slag and calcium carbonate and found the effect of limestone on setting time as negligible. In 
another work [3], a small content of finely ground CaCO$_3$ in the metakaolin matrix increased the setting 
rate.

The setting time and polymerisation process of LS2 samples could be partly influenced by clay and 
feldspar minerals, which are present in LS2 in an amount of about 22%. Xu and Deventer (2000) [13] 
dealt with the geopolymerisation properties of various natural Al-Si minerals, including kaolinite and 
anorthite. They confirmed the complexity of the reaction mechanisms involved in dissolution, setting 
and formation of the gel structure, and it is impossible to predict their behaviour effectively.
significant changes were seen. The concentration of these ions in the system remains low to form a separate hydrated gel with surface binding to unreacted mineral particles.

In previous works [3], it was confirmed that the CaCO$_3$ content in the matrix increases compressive strength after 90 and 560 days in geopolymers where metakaolin was replaced by 20% calcite. A positive effect on compressive strength was observed for the alkali-activated blast furnace slag, which was replaced by 30% LS [15]. Yip (2008) [3] submits that Ca$^{2+}$ cations play a limited structural role in the geopolymer gel formation. The concentration of these ions in the system remains low to form a separate hydrated gel with surface binding to unreacted mineral particles.

The samples of the paste after 28, 56 and 90 days were ground to analyse phase composition by X-ray diffraction. The XRD pattern of all samples had a broad hump in the range of 26-29° (2 Θ).

Calcite (CaCO$_3$), quartz (SiO$_2$), akermanite (Ca$_2$MgSi$_2$O$_6$), merwinite (Ca$_2$MgSi$_2$O$_6$) and anatase (TiO$_2$) were identified in the reference sample after 28 days. No significant changes were seen on the XRD patterns after 90 days. Illite (KAl$_2$(AlSi$_3$O$_10$)(OH)$_2$) or muscovite (KAl$_3$Si$_3$O$_10$H$_2$) were identified in all samples with LS. Kaolinite (Al$_2$Si$_2$O$_5$(OH)$_4$) peaks are not noticeable after 28 days already, which is consistent with other works [10]. Feldspar mineral, albite (NaAlSi$_3$O$_8$) and anorthite (CaAl$_2$Si$_2$O$_8$), which are components of the LS sludge, were identified in samples with more than 5% LS.

The replacement of calcite does not result in the formation of new phases. The calcite peaks increase in intensity with increasing LP content. The XRD results show that although calcite dissolves in an alkaline solution, it does not actively form the new crystalline phase. Yuan (2017) [8] reported that Ca$^{2+}$ can increase the release of Al and Si ions from metakaolin, and then carboaluminates are formed in the metakaolin-based system. In the slag-based system, the effect of Ca has not been confirmed, and LP acts as a filler. Ca$^{2+}$ ions released from slag can affect the dissolution of Ca$^{2+}$ from LP. The samples were analysed even after 90 days and, no visible changes in structure were found.

Flexural strengths and compressive strengths were tested on mortar specimens after 28, 56 and 90 days. The reference sample with 0% of LS had 6.5 MPa flexural strength and 55 MPa compressive strength after 28 days. The flexural strength increased to 8.5 MPa and the compressive strength to 63 MPa, after 90 days.

Comparable results with the reference specimen were obtained with sample 5LS1 after 90 days. The higher LS1 content resulted in a slight decrease in flexural strength. The amount of LS2 in the mixture had no significant effect on the flexural strength, which in all samples exceeded 6 MPa after 28 days and over 7 MPa after 90 days.

The compressive strength decreased after 28 days with the increasing amount of LS1 in the matrix. In the case of sample 30LS1, it is up to 45 MPa and 30LS2 35 MPa. All samples with LS1 had a compressive strength of about 55 MPa after 90 days, about 12% less than the reference sample. It has been shown that calcite is an inert filler but dissolves in an alkaline environment. X-ray records of LS samples dissolved in NaOH solution identified portlandite peaks. In previous works [3], it was observed for the alkali-activated blast furnace slag, which was replaced by 30% LS [15]. Yip (2008) [3] submits that Ca$^{2+}$ cations play a limited structural role in the geopolymer gel formation. The concentration of these ions in the system remains low to form a separate hydrated gel with surface binding to unreacted mineral particles.
On the contrary, the presence of LS2 results in a lower compressive strength after 28 and 90 days. For the samples 20LS2 and 30LS2, a decrease in strengths after 90 days was observed compared to 56-day strengths. The compressive strength decreased by 25% to 39% after 90 days for LS2 samples.

Low strength can be attributed to the lower reactivity of clay and feldspar minerals in LS2, which needs a longer time for reaction and gel structure formation [13, 16, 17]. Due to the layered structure of kaolinite at almost zero charge on the surface, the penetration of alkalis through the structure is very slow, which results in the formation of a weak structure in most clay-based geopolymers. Kaolinite is not completely incorporated into the polymer structure [13, 14, 18].

After 90 days of curing under laboratory conditions, the pore structure of mortars was investigated by MIP (figure 5). Mesopores (2 < 30 nm) are the most represented, considered spaces between individual precipitates with free water [19]. The total porosity is slightly affected by the addition of LS. The reference sample has an overall porosity of 0.074 cm$^3$·g$^{-1}$, with LS1 and LS2 slightly increasing to values around 0.085 cm$^3$·g$^{-1}$ and 0.095 cm$^3$·g$^{-1}$, respectively.

The pore distribution was slightly changed by the addition of LS. The reference sample has a bimodal pore distribution: 5–7.5 nm small gel pores and transition pores 7.5–30 nm. Other samples except 30LS1 have a similar pore distribution. For 30LS1 the pore volume disappeared in the region 5–7.5 nm [20].

The pore distribution of LS2 samples was changed. The distribution curve has only one peak in the range of 3.75–25 nm, and the pore volume in this area increased. Changes in the pore distribution can be attributed to the particle distribution of the raw materials rather than the formation of new products that have not been confirmed by XRD. Evidenced by results shown in figures 5a and 5b, LS2 contrary to LS1, in combination with BFS and MK, was involved in forming a structure with smaller pores up to 10 nm.

**Figure 4.** The extent of flexural strength (2a, 2b) and compressive strength (2c, 2d) after 28, 56 and 90 days.
The durability of specimens was tested by freeze-thaw cycles (figure 6). Specimens were tested after 56 days of curing. The compressive and flexural strengths decreased with increasing LS content in the matrix. Compared to LS2, LS1 specimens showed worse freeze-thaw resistance. The strength characteristics after freeze-thaw cycles of 20LS1 and 30LS1 were not possible to be determined because of cracking and deterioration of samples. The compressive strength was reduced by 6% and 7%, respectively, in the reference sample. 5LS1 and 10LS1 had lower compressive strengths, 48 MPa and 45 MPa, respectively, but no significant degradation occurred during cycling, as in the reference sample. The flexural tensile strengths were comparable to the reference sample.

Degradation of samples with a higher content of limestone sludge does not occur if LS2 was used. This is probably due to the finer LS2 granulometry and different types of pores formed due to the higher content of clay and feldspar minerals.

Figure 5. Pore diameter distribution of samples with LS.

Figure 6. Compressive and flexural strength of samples after freezing-thawing test.
MIP performed pore characterisation on samples after 50 cycles of freeze-thaw tests. It has been shown that the total porosity decreased due to the effect of frost. An increase in pores diameter below 10 nm was monitored. The gel pores are refined by continual polymerisation, which is caused by immersing the samples in water. In previous work [21, 22], the beneficial effect of freeze-thaw tests on pore volume reduction was confirmed, which increased in strength. Figure 7 shows the pore diameter distribution of samples after 50 test cycles. A significant increase in gel pores was observed, especially in LS2 samples, due to the slower dissolution of clay and feldspar components.

The worse resistance is probably because a sufficiently strong structure was not formed, which is evidenced by the lower volume of gel pores (below 10 nm) in the structure of samples 20LS1 and 30LS2 (See figure 5).

![Figure 7. Pore diameter distribution of samples after 50 cycles of freeze-thaw test.](image)

4. Conclusions
The possibility of using waste limestone sludge to prepare geopolymer based on metakaolin slag was investigated in this work. The influence of LS on workability, setting time, compressive strength and flexural strength was studied. The samples were subjected to the freeze-thaw cycles. A positive effect of CaCO$_3$ on workability was found out while the higher content of clay and feldspar minerals in waste material had the opposite effect. The effect of waste sludge on the prolongation of setting time can also be assessed positively. The results of compressive and flexural strength and frost resistance tests suggest using a maximum of 10% limestone sludge with higher CaCO$_3$ content. The compressive strength was found to be around 55 MPa after 90 days.

A higher ratio of clay and feldspar components in waste sludge resulted in a strength decrease. The sufficient strengths of about 35 MPa were achieved using 30 % sludge in the matrix after 90 days of curing in laboratory conditions. After 50 cycles of freeze-thawing tests, there is no significant degradation of prepared samples. The maximum dosage that can be recommended is 20% in the matrix due to reduced workability. The incorporation of LS contributes to strength improvement and lowered costs.

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