Assessment of mine tailings as precursors for alkali-activated materials for on-site applications

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HIGHLIGHTS

- Mine tailings can be valorised in alkali-activated materials for on-site use.
- The solubility of relevant chemical species in the tailings in highly alkaline solutions has been studied.
- The results of the leaching experiments have been used to facilitate the mix design for alkali-activated materials.
- Compressive strength of the alkali-activated materials is sufficient for underground backfill.
- Methods to increase the early strength of the materials have been studied additionally.

ABSTRACT

Year after year the mining industry generates 5–7 billion metric tons of tailings worldwide. They are mostly disposed rather than valorised. The substantial amounts of tailings has led to growing concerns about their ecological and environmental impacts such as occupation of large areas of land, generation of windblown dust, and contamination of surface and underground water. Over the past years the mining industry has been subjected to increase environmental principles. As the consequence, besides waste rock and water management, tailings management becomes a progressively important factor for ecologic and economic reasons.

Mine tailings from flotation processes are normally disposed in impoundments on the surface. This may cause environmental and safety problems including serious water pollution arising from contamination of surface water, groundwater, and soils due to the leaching of heavy metals, process reagents, and Sulphur compounds. Recently the process of alkali-activation and geopolymerisation has been explored as a potential method for tailings consolidation and heavy metal fixation. The tailings of many existing mining operations contain the aluminosilicate minerals needed for alkali-activation at least to some extent. From a sustainability point of view it makes sense to use alkali-activated products from tailings directly on the mine site as e.g. (1) backfill material applied to fill open cavities from the (underground) mining operation and (2) cover materials for surface deposits of tailings in order to store them ecologically safe and sealed off from the environment.

Mine tailings from different mining operations around the world have been investigated regarding their potential use as precursors for alkali-activated materials. An assessment of the release of gel forming elements into alkaline solutions was performed by leaching experiments under various conditions (time, concentration of the solvent, and temperature). Compared to traditional alkali-activated precursor materials the release of aluminium and silicon is in general low for the mine tailings investigated. However, results indicate a favourable ratio of Si/Al for the formation of gels similar to other alkali-activated products. Additionally, the leached calcium can contribute to the strength of the resulting products by forming C-S-H gels when a considerable amount of Si is present in the pore solution either from the activator or dissolved from the material itself.

The results of the leaching tests were used to facilitate the mix design for alkali-activated products. In order to increase the mechanical strength of the final product different approaches were considered: (1) addition of reactive materials (e.g. blast furnace slag), (2) increasing the reactivity of the tailings by grinding, and (3) increasing the reactivity by curing at elevated temperature. Depending on the tailings type, the mix design, and the curing conditions the final material shows a compressive strength in excess of 30 MPa even for curing at low temperatures.

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1. Introduction

Whenever a mine is developed, in general huge amounts of host rock have to be mined additionally and subsequently stored. The amount of (mostly valueless) waste rock varies much, depending on the ore body and whether the ore is mined from an open-pit or an underground mine. Due to intergrowth of minerals, even the mined ore itself contains valueless material. Furthermore, some ore might be left behind in the mine due to the chosen mining method, low grades, or other economic reasons. The dilution of the ore with waste rock can be substantial resulting in increased mineral processing costs and amount of tailings but no economic revenue [1].

One of the major environmental issues of the mining industry is the waste streams that can reach over 90% of the total mass for many ore types. When using a flotation process in mineral processing this waste stream (i.e. tailings), is a mixture of different minerals, process chemicals, and water in the form of a thick slurry. The tailings are mostly deposited in tailings storage facilities (TSFs) at the surface or sometimes used as paste backfill to fill underground cavities. Since the storage of tailings normally plays a minor role in the mining industry, little effort has been made regarding the valorisation of the tailings up to now.

Recently, more attention is paid to the deposition of tailings to TSFs at the surface by general public and especially legal authorities. Various problems are related to the storage of tailings at the surface [2]:

1. When tailings contain sulphide minerals, such as pyrite (FeS₂) or pyrrhotite (Fe₁₋ₓS), oxidation in the presence of oxygen and water (either from rainfall, surface water streams or from mineral processing) results in the formation of sulphuric acid. If not being captured this may lead to severe ecological problems and the so called acidic mine drainage (AMD).
2. The huge amounts of tailings results in very large deposits on the surface, which the authorities do not permit any more or a suitable large space cannot be found or is strongly opposed by the communities close to the mine.
3. When dams are used for the deposit a dam failure can result in an ecological disaster.

As a consequence the disposal of mine tailings is a major environmental liability becoming increasingly important for current and future mining operations especially on ore bodies with low grades. In order to prevent the problems related to tailings storage, new approaches are needed and might even become critical for future mining operations [1,2].

There are different ways and means to reduce the potential environmental hazards related to the storage of mine tailings and waste rock: (1) Isolation of waste materials from the nearby environment by capping, (2) chemical stabilization of especially mine tailings by adding chemicals or cementitious materials to immobilize heavy metals, and (3) a combination of these two methods. For the simultaneous use of isolation and stabilization techniques, the tailings surface can be treated by binders such as organic polymers, water glass or Ordinary Portland cement (OPC) to improve the resistance of the surface to erosion and reduce water infiltration, isolating the underlying tailings from the surrounding environment [3–5]. Although OPC has its benefits in the stabilization of certain mine tailings, it has several drawbacks such as low acid resistance, high cost as well as high energy consumption and CO₂ emissions related to the production of OPC.

Using the concept of alkali-activation, aluminosilicate raw materials can be turned into valuable cementitious-like materials. Depending on their composition, the resulting alkali-activated materials or geopolymers have comparable properties to OPC, but may also show additional advantages such as rapid development of mechanical strength, high acid resistance, immobilization of toxic and hazardous materials, and a considerable reduction in greenhouse gas emissions [6–9]. Simplified, geopolymers can be formed by the reaction of aluminosilicate raw materials with highly alkaline solutions by leaching of Al and Si from the solid precursors with subsequent formation of a gel with a molar ratio of M:Al:Si roughly equal to 1:1:4, where M represents an alkali earth metal [6,10]. Initially metakaolin and fly ash were used as the main raw materials for geopolymers and have become model compounds for the comparison with other precursor materials. In recent years a number of other raw material sources (e.g. various other types of fly ash, natural minerals, and metallurgical waste materials as well as their mixtures) have been studied to synthesise geopolymers [11].

The tailings of many existing mining operations contain the aluminosilicates needed for alkali-activation at least to some extent and therefore offer an interesting alternative source material for alkali-activated materials and geopolymers [11]. Even though natural rock can be thought of as a rather non-reactive material, the fine particle size distribution of the tailings might be advantageous right away or allowing for additional processes steps for substantially increasing the reactivity.

In a nutshell, this study addresses the valorisation of mine tailings as precursors to alkali-activated materials to be used for applications primarily at the mine site. The dissolution of relevant species is assessed by leaching in alkaline conditions and comparison to other precursor materials. Furthermore, the compressive strength of alkali-activated mixtures was determined in order to verify the suitability for the intended applications. The resulting alkali-activated materials can be used directly at the mine site as (1) a back fill material to fill underground cavities or (2) a covering layer for surface deposits of tailings. Depending on their properties the resulting materials could also be used for other applications (e.g. construction industry). The best-case scenario leads to a mining activity without any needs to deposit tailings on the surface or a minimized amount of tailings deposited on the surface using a covering layer for safely storing the tailings shielded from environmental conditions. Hence, in the near future mining operations can be more ecologically friendly and probably even more economically feasible compared to traditional mining operations.
2. Methodology

Four different mine tailings were used to study their application as precursors for alkali-activated materials. Relevant properties of the materials were determined by state of the art methods. In order to assess the reactivity of solid precursor materials the leaching of relevant species in alkaline solutions was studied at a constant solid to liquid ratio with varying conditions for time, temperature und solvent concentration.

The results of the leaching experiments were taken into account for the mix design of alkali-activated materials and can also help to understand the possible reaction mechanisms during hardening. Enhancing the reactivity of the solid materials was investigated in order to increase the mechanical strength of the final products by the following approaches: (1) addition of other reactive materials, (2) increasing the specific surface area of the tailings, and (3) curing the products at elevated temperature. However, the main focus was put on using the tailings as delivered without further pre-treatment steps (like e.g. grinding or calcination) and thereby making it possible to apply solutions directly at the mine site without additional high investment into large infrastructures.

2.1. Materials

In this study the tailings from the following mining operations were investigated:

(1) MT 1 – tailings from a copper/nickel mine (Northern Europe, low content of sulphides).
(2) MT 2 – tailings from a copper/zinc mine (Southern Europe, high content of sulphides).
(3) MT 3 – tailings from a platinum mine (South Africa).
(4) MT 4 – tailings from an iron ore mine (South America).

All tailings samples were supplied wet (mostly as slurries) and dried at 110 °C until a constant mass was measured prior to any laboratory experiments. In order to prevent oxidation of samples containing a high amount of sulphides, only small portions were dried shortly before use.

Additionally to the tailings samples metakaolin (MK) and granulated blast furnace slag (GBFS) were used as solid additives. MK was delivered as a dry powder. GBFS was delivered moist with a maximum particle size of roughly 4 mm. The GBFS was dried at 110 °C and comminuted using a ball mill to a final specific surface area of approximately 3300 cm²/g.

The chemical composition of solid materials was determined by XRF on fused beads of the original sample after determination of the loss on ignition (LOI). The qualitative mineralogical composition was determined by XRD on loose powder bed samples. In order to assess the quantitative mineralogical composition of the tailings a Rietveld refinement was performed. Different particle size fractions of the samples were obtained by dry classification. The particle size distribution of the samples was determined by laser diffraction (dry dispersion).

Furthermore, a chemical grade concentrated sodium hydroxide solution (NaOH) and a sodium silicate solution (waterglass, Na₂SiO₃) were used. The concentrated NaOH solution was diluted to the desired concentration using deionized water. The waterglass solution used in this study has a solids content of approximately 35 m% with a mass ratio Na₂O to SiO₂ of 3:10.

2.2. Leaching experiments

Leaching of solid precursor materials in alkaline conditions was performed using a similar procedure as described in literature (e.g. Xu and van Deventer [12,13]) using a solids to liquid ratio of 2 g per 100 ml of solvent. The standard conditions for the leaching experiments were a duration of 24 h at a temperature of 40 °C using a 5 M NaOH solution, but additional parameter studies for relevant parameters have been performed for some materials. In order to prevent contamination of the leachates with Si from glass containers, plastic equipment was used for storage and during the experiments. The leaching was done by the following procedure:

(1) Preheating of the solid precursor material in a sealable plastic container.
(2) Addition of preheated solvent.
(3) Mixing of solids and solvent using a bottle roller with 60 rpm for the desired reaction time.
(4) Filtration of solids and leachate.
(5) Dilution of the leachate 1:50 with deionized water.
(6) Acidification to a pH between 2 and 3 using 4 M HCl to prevent precipitation prior to analysis.
(7) Determination of the concentration of leached species by ICP-MS.

The elemental concentrations of the leachates were corrected by the concentrations in the blank solvents treated by the exact same procedure.

In order to investigate the leaching residue after the experiment the filtration residue was washed with deionized water in order to eliminate excess NaOH of the leaching experiment. The residue was dried at 110 °C and further investigated. However, the change of mass of the dried solid residue compared to the initial sample was below the detection limit for the chosen experimental setup (<0,5 m%).

MT 3 was chosen for further leaching experiments with additional variation of the temperature. The experiments were carried out with 1 M, 5 M, and 10 M NaOH solution for leaching durations of 24 and 72 h.

2.3. Mix design and testing

The crucial property of the resulting alkali-activated materials for this investigation was the uniaxial compressive strength. It was tested using small cylindrical samples with a diameter of 40 mm and a height of 30 mm.

With regard to a possible installation of the alkali-activated mixes by pumping the consistency is of additional importance for the mix design. In order to ensure a desired viscosity of the mix the liquid to solids ratio was kept constant for a given solid raw material. Since there is a high variation of the density of the raw material. Since there is a high variation of the density of the raw mixtures were tested for homogeneity by hand in a small beaker with a rod until a homogeneous mix was obtained. The mix was poured into a fixed container at a fixed temperature until testing at the chosen curing temperature. The compressive strength was determined by recording the maximum force using a universal testing machine.

For MT 1 an activator screening with mixtures of NaOH and waterglass solutions was performed initially with a constant amount of 27.5 ml of activator solution for 100 g of solid mine tailings. The samples were cured for 7 days at a temperature of 60 °C prior to determination of the compressive strength. The results showed that the highest strength was achieved when using water-
glass solutions as an activator with only little to no further addition of NaOH. Therefore, further experiments were carried out using only waterglass solutions with concentrations between 10 and 30 m% of solid waterglass and testing after curing for 7, 14 and 28 days. Since the results were quite promising, further experiments were performed with the same recipes and curing at 40 °C and room temperature (RT) respectively. The other mine tailings were studied less extensive.

In addition to the determination of the strength of the final products, selected samples with high strength have been further investigated by XRD and SEM. Furthermore, calorimeter tests on fresh mixed samples have been performed in order to help understanding the reaction mechanisms resulting from the alkali-activation of the tailings. These tests were carried out using a TAM Air Isothermal Calorimeter. The paste samples were mixed in a small beaker at an ambient temperature of 25 °C for five minutes and subsequently poured into glass ampoules, which were then inserted into the calorimeter.

Additionally, the pore size distribution and pore surface area of selected samples with high strength have been investigated by sorption of nitrogen using a micromeritics ASAP 2020 after curing for 28 days at ambient temperature. Prior to testing the samples were dried at 105 °C for two hours in order to degas the samples. This procedure was chosen in favour of a long-term vacuum degassing process as previously described in [14]. The pore size distribution and the cumulative pore volume were determined from the measurement results applying the Barrett-Joyner-Halenda method [15].

3. Results and discussion

3.1. Material characterisation

Fig. 1 shows the particle size distribution of the mine tailings as delivered and Table 1 summarizes the characteristic parameters of their particle size distributions. The fineness is governed by the specific ore characteristics and related to the intergrowth of the valuable minerals with the matrix minerals. In general the tailings show a high fineness which is favourable for alkali-activation.

Table 1

| MT 1 | MT 2 | MT 3 | MT 4 |
|------|------|------|------|
| Cu/Ni tails | Cu/Zn tails | Pt tails | Fe tails |
| x90 [μm] | 54 | 25 | 90 | 9.0 |
| x50 [μm] | 7.5 | 4.6 | 11 | 2.4 |
| x10 [μm] | 0.9 | 1.0 | 1.6 | 0.8 |

Table 2 summarizes of the chemical composition of the solid precursor materials. The metakaolin (MK) used in this study is a technical grade stoichiometric metakaolin with at least 95 m% of Al₂Si₂O₅ and a x50 of 1.5 μm. The GBFS used has a x50 of 53 μm and a specific surface area of approximately 3300 cm²/g according to Blaine.

Table 3 gives an overview of the mineralogical composition of the mine tailings samples. The quantitative amount of individual mineralogical phases has been calculated by Rietveld refinement of the XRD measurements using Profex. The resulting XRD patterns of all mine tailings don’t indicate the presence of amorphous phase. Due to the granulation process the GBFS has solidified almost entirely in an amorphous state (>98%) and only minor indications of crystalline gehlenite and akelemanite peaks can be observed in the XRD pattern.

3.2. Leaching of solid precursor materials in alkaline solution

The sample of MT 1 has been chosen to study the influence of leaching time in more detail for 5 M and 10 M NaOH. The results of the leaching experiments at 40 °C with test durations of 4, 8, 24 and 72 h are summarized in Figs. 2 and 3.

The results show that the amount of dissolved species is increased for a higher concentration of the alkaline solution (except for S and intermediate test durations). The maximum amount of dissolved species can be found after leaching durations of 24 h especially for the experiments with 10 M NaOH. This might be caused by subsequent formation of precipitates or gels from the solution reducing the amount of most of the species except Sulphur.

![Fig. 1. Particle size distribution of the tailings as determined by laser diffraction on dry dispersed samples.](image-url)
Table 2
Chemical composition of the solid precursor materials determined by XRF.

|          | MT 1 | MT 2 | MT 3 | MT 4 | GBFS |
|----------|------|------|------|------|------|
|          | Cu/Ni tails | Cu/Zn tails | Pt tails | Fe tails |      |
| Na₂O     | 0.30 | 0.32 | 1.48 | 0.03 | 0.69 |
| MgO      | 22.55 | 1.90 | 16.98 | 0.40 | 9.79 |
| Al₂O₃    | 2.06 | 8.04 | 9.79 | 5.73 | 10.50 |
| SiO₂     | 46.59 | 31.06 | 54.02 | 11.74 | 39.50 |
| P₂O₅     | 0.02 | 0.06 | 0.02 | 0.29 |      |
| SO₃      | 1.24 | 0.24 | 0.16 | 0.09 | 1.37 |
| K₂O      | 0.10 | 0.67 | 0.41 | 0.99 | 1.62 |
| CaO      | 13.42 | 0.94 | 6.80 | 0.82 | 32.20 |
| TiO₂     | 0.26 | 0.21 | 0.18 | 0.22 | 0.63 |
| Fe₂O₃    | 11.92 | 35.50 | 9.34 | 77.30 |      |
| LOI      | 2.35 | 18.37 | 1.82 | 2.92 |      |
| Σ        | 101.27 | 97.41 | 101.56 | 100.62 | 98.54 |

Table 3
Quantitative mineralogical composition of the mine tailings determined by Rietveld refinement of XRD measurements.

|          | MT 1 | MT 2 | MT 3 | MT 4 |
|----------|------|------|------|------|
| [g/100 g] | Cu/Ni tails | Cu/Zn tails | Pt tails | Fe tails |
| Albite   | 9.4  |      |      |      |
| Antigorite | 4.2  | 0.6  |      |      |
| Calcite  | 14.1 | 12.6 |      |      |
| Chlorite | 3.5  |      |      |      |
| Chromite | 21.3 | 14.2 | 25.3 | 5.1  |
| Diopside | 9.3  | 3.2  | 26.2 |      |
| Enstatite|      |      |      | 78.0 |
| Epidote  |      |      | 7.1  |      |
| Feldspar |      |      | 1.3  |      |
| Hematite |      |      |      |      |
| Lizardite|      |      |      |      |
| Magnesiohornblende | 5.7  | 15.3 | 4.4  | 21.0 |
| Muscovite/Biotite  |      |      |      |      |
| Magnetite| 3.6  |      |      |      |
| Olivine | 5.0  |      |      |      |
| Pyrite/Pyrrhotite | 2.5  | 11.0 | 2.4  | 0.4  |
| Quartz  | 53.4 |      | 2.2  |      |
| Siderite|      | 0.5  |      | 0.6  |
| Talc    | 0.9  |      |      | 7.5  |
| Tremolite| 23.5 |      |      |      |

Fig. 2. Dissolved species after the leaching of MT 1 in 5 M NaOH at 40 °C.
For leaching in 10 M NaOH approximately 1.4 m% of the initial Al and 0.6 m% of the initial Si have been dissolved which adds up roughly to the detection limit for the mass balance. However, subsequent analysis of the leaching residue by XRF, XRD and SEM did not reveal weather precipitates have been formed or from which mineral phases the individual species have been dissolved.

For MT 3 the absolute amount of dissolved Si and Al in dependence of leaching duration and temperature are summarized in Figs. 4 and 5. Similar trends as for MT 1 can be observed from the leaching experiments of MT 3 although the maximum concentration of dissolved species is not reached after a leaching duration of 24 h. The amount of dissolution is directly proportional to the concentration of the solvent but its dependence is not as strong as the influence of the leaching temperature. Increasing the temperature from 40 °C to 80 °C increases the amount of dissolved species roughly by a factor of 2. The results show when using a 1 M NaOH solution at a temperature of 80 °C the absolute amount of dissolved species is still higher than using a 10 M NaOH solution at 40 °C even for shorter leaching duration. This means that a short thermal treatment at a higher temperature might be favourable for alkali-activated materials in contrast to curing at moderate temperatures for a longer time.

The experiments with MT 1 and MT 3 suggested performing further tests with other materials with 5 M and 10 M NaOH solution for a leaching duration of 24 h. A temperature of 40 °C was chosen due to more simple and safe handling. The results are summarized in Table 4. The mine tailings show little reactivity in alkaline solutions compared to granulated blast furnace slag and metakaolin. For the mine tailings the amount of dissolved species corresponds to below 5 m% of the initial amount in the tailings sample whereas for GBFS roughly 60 m% and for MK roughly 80 m% are dissolved after a leaching duration of 24 h.

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3.3. Mechanical properties of alkali-activated mine tailings

The results of mixtures with MT 1 and waterglass are summarized in Fig. 6. In general a lower curing temperature resulted in lower strength especially for short curing times. The strength of MT 1 activated with waterglass solutions and cured for 28 days at RT ranges from 3.8 MPa up to 14.2 MPa depending on the concentration of solid waterglass in the activator solution. The early strength after curing for 7 days at room temperature was around 1 MPa only. In order to increase the early strength of the alkali-activated products two options have been tested:

(1) Grinding of the original tailings with $x_{50}$ of 7.5 μm to a product with $x_{50}$ of roughly 6 μm increased the strength after curing at room temperature to 7.5 MPa for an activator solution with 15 m% of solid waterglass in the activator solution.

(2) Replacing 10 m% of the original tailings with ground granulated blast furnace slag increased the strength in a similar way as (1).

The investigations with the other mine tailings have not been carried out as extensive as for MT 1. Hence, the results are not shown as detailed as for MT 1, but summarized in Table 5 instead. For MT 2, MT 3, and MT 4 mixtures of waterglass and NaOH have been used as activator solution using a similar screening process as for MT 1. Similarly, the amount of liquid activator has been adjusted in order to result in a mix with desired viscosity. In general a higher strength can be reached with a higher concentration of activator components in the solution. MT 2, MT 3, and MT 4 show lower strength compared to MT 1.

For MT 4 the addition of metakaolin was successfully tested to increase the strength of the final product. Compressive strength up to around 30 MPa was achieved for curing at 60 °C for 28 days. Due to the fine particle size of metakaolin the amount of liquid activator solution had to be adjusted.

Unfortunately XRD and SEM could not clearly identify the source related to the high strength of these materials. In contrast to geopolymers or alkali-activated materials the degree of reaction is rather low so that the microstructure of the alkali-activated materials is different from that of geopolymers.

![Fig. 5. Absolute amount of dissolved Al from MT 3 for different leachate concentrations at various temperatures.](image)

Table 4
Summary of the absolute amount of selected species dissolved from MTs, GBFS, and MK in NaOH solutions at a temperature of 40 °C and a leaching duration of 24 h with a solids to liquid ratio of 2 g per 100 ml of solvent.

|                | MT 1 | MT 2 | MT 3 | MT 4 | GBFS | MK |
|----------------|------|------|------|------|------|----|
| Cu/Ni tails    | Ca   | Mg   | Al   | Fe   | S    |    |
| 5M NaOH        | 4.4  | 0.5  | 11.6 | 35.2 | 97.2 |    |
| Absolute amount dissolved [mg/l] | 4.1 | 2.5 | 15.3 | 57.0 | 132 | |
| 10M NaOH       | 3.7  | 9.2  | 28.0 | 37.0 | 70.0 | 70.0 |
| Absolute amount dissolved [mg/l] | 4.1 | 2.5 | 58.0 | 57.0 | 13.2 | 880 |

3.3. Mechanical properties of alkali-activated mine tailings
3.4. Additional parameters of selected alkali-activated mine tailings

Selected samples of MT 1 have been chosen to evaluate the pore size distribution of the hardened products after curing for 28 days. Fig. 7 summarizes the measurement results showing the cumulative pore size distribution as a function of pore size. The volume of the smallest pores up to a pore diameter of approximately 6 nm is very similar for all samples. Replacing parts of the tailings by fine tailings leads to an increase in the amount of larger pores. This can be explained by less optimal particle packing of the total solids – the amount of fines is too high in this mixture. The addition of GBFS to the combination of fine tailings and original tailings lead to a decrease of the pore volume. Due to the larger particles the mixture has a more optimal particle packing. Furthermore the formation of reaction products of the alkali-activated GBFS in the larger pores can be an additional factor reducing the pore volume.

The calorimeter experiments were performed on the same recipes of MT 1 as have been used for pore size measurements. These mixtures were chosen because they showed a favourable strength development over time. However, the calorimeter tests didn’t show a clear trend as would be expected from the results of the strength development of these samples. Some mixtures showed a considerable heat evolution already while mixing whereas other mixtures didn’t show a significant heat release at

| Additives | Activator Amount | Composition | Curing T [°C] | t [days] | $\sigma_c$ [MPa] |
|-----------|------------------|-------------|--------------|---------|-----------------|
| MT 1      | 27.5 ml/100 g    | waterglass  | 60           | 7       | -5 to -15       |
|           |                  |             | 7            | 7       | -5 to -15       |
|           |                  |             | 14           | 14      | -5 to -20       |
|           |                  |             | 28           | 28      | -5 to -20       |
|           | 27.5 ml/100 g    | waterglass  | 40           | 7       | -1 to -6.5      |
|           |                  |             | 14           | 14      | -3 to -15       |
|           |                  |             | 28           | 28      | -3 to -15       |
|           | 27.5 ml/100 g    | waterglass  | RT           | 7       | -1 to 1.5       |
|           |                  |             | 14           | 14      | -3 to 8         |
|           |                  |             | 28           | 28      | -3.5 to 14      |
| Fine tails to reach $x_{50} \approx 6 \mu m$ | 27.5 ml/100 g | waterglass  | RT           | 7       | -4 to 7.5       |
| GBFS (10 m%) | 27.5 ml/100 g | waterglass  | RT           | 7       | -5 to 12        |
| MT 2      | 38.75 ml/100 g   | NaOH and waterglass | 60 | 7 | -1 to 3.5 |
| MT 3      | 33.75 ml/100 g   | NaOH and waterglass | 60 | 14 | -1.5 to 5 |
|           | 33.75 ml/100 g   | NaOH and waterglass | RT | 14 | -1.0 to 2 |
|           |                  |             | 28           | 28      | -1.5 to 4       |
| MT 4      | 37.5 ml/100 g    | NaOH and waterglass | 60 | 7 | -1 to 1.5 |
|           |                  |             | 14           | 14      | -1.5 to 2       |
|           |                  |             | 28           | 28      | -2 to 3         |
| Metakaolin (10 m%) | 40 ml/100 g | NaOH and waterglass | 60 | 7 | -1.5 to 3 |
|           |                  |             | 14           | 14      | -3.5 to 6       |
|           |                  |             | 28           | 28      | -5 to 30        |
all even though their physical properties indicate the formation of hydration products resulting from the alkali-activation. A clear conclusion of possible reaction mechanisms cannot be drawn from the calorimeter tests. Therefore these results are not shown here. However, a different experimental setup of the calorimeter tests might lead to a better comprehension of possible reaction mechanisms resulting from alkali-activation of the mine tailings.

4. Conclusions

The results of the leaching experiments showed, that in general the dissolution of significant species from the mine tailings is little compared to reactive materials like granulated blast furnace slag or metakaolin. However, alkali-activation can lead to final products with considerable strength depending on the curing conditions. Furthermore, finer ground tailings or the addition of other reactive materials have a positive effect on the strength of the final products.

One possible on-site application of alkali-activated materials is mine backfill. Depending on the mining method and whether a primary or secondary stope is being filled, the ultimate strength of installed backfill ranges from 0.2 to 5 MPa. Secondary stopes, or areas where tailings are being placed for safe disposal only require sufficient strength to resist liquefaction, whereas primary stopes may need strength to stand vertical up to a height of 50 m. Cut and fill operations – where quick access is crucial – often require a more rapid strength development (i.e. more than 2 MPa in approximately the first seven days after installation).

The results for alkali-activated products from the mine tailings indicate that an application as mine backfill seems possible. However, further material properties of the final products (e.g. water resistance) have to be determined additionally. Additionally, the setting behaviour of the backfill can be of importance, especially for long pumping distances between the backfill mixing plant and the place of installation.

For the covering layers of surface deposits of tailings a parameter set of physical and chemical properties can only be defined knowing the environmental conditions on the site of installation. Geochemical modelling can assess if such an application is possible with a specific alkali-activated product taking relevant physical and chemical properties into account.

Unfortunately a further assessment of high strength products did not reveal the source of the strength. The following reaction mechanisms are theoretically possible for the given chemical system when adding NaOH and waterglass as an activator:

(1) Waterglass bond: Formation of a gel due to a reaction with polyvalent cations or due to a reaction with CO₂ leading to silification of dissolved Si according to: Na₂OₙSiO₂ₓH₂O + CO₂ → nSiO₂ₓH₂O + Na₂CO₃.

(2) Formation of a C-S-H gel: Formation of a gel due to the reaction of dissolved Ca from tailings with dissolved Si from the addition of waterglass and/or leached from the tailings.

(3) Formation of a N,C-A-S-H gel: Formation of a gel as for the alkali-activation of granulated blast furnace slags or fly ash.

(4) Formation of a geopolymer gel.

The first three reaction mechanisms seem likely depending on the concentration of relevant species in the pore solution of the mix. However, the formation of a geopolymer gel seems rather unlikely when using mine tailings only as the solid precursor material. Unfortunately, the calorimeter tests that were performed within this study didn’t result in a clear picture of the actual reaction mechanisms. A different experimental setup with in situ mixing of the alkali-activated pastes in the calorimeter might lead to a better understanding of reactions taking place as a result of alkali-activation. Therefore, these experiments will be carried out in a later study.

The determination of the pore size distribution of hardened alkali-activated mine tailings revealed the importance of a proper mix design regarding particle packing. Additionally, the results indicated that in mixtures with GBFS reaction products likely formed in the vicinity of the GBFS particles and consequently decreased the amount of larger pores within the structure.

5. Outlook and further procedure

The results currently available don’t allow for a direct link between the specific chemical and mineralogical composition of
the tailings and their leaching behaviour or performance in alkali-activated materials. However, the data from the leaching experiments can be used for geochemical modelling to link dissolution to certain mineral phases. For that purpose a more detailed mineralogical assessment of the raw material as well as the leaching residues needs to be done by e.g. QEMSCAN. Additionally, modelling can help to assess the formation of gel phases while hardening of the alkali-activated products.

As stated above, the calorimeter tests could help to understand possible reaction mechanisms when using a different experimental setup. These experiments will be performed in a later study.

CRediT authorship contribution statement

R. Obenaus-Emler: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing - original draft, Writing - review & editing, Visualization, Project administration. M. Falah: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing - review & editing. M. Illikainen: Conceptualization, Writing - review & editing, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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