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Alkali-Activated Mine Tailings and Solid Wastes as Precursors for Geopolymers

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Abstract - Former mining activities may pose a threat to the environment if not being handled correctly due to neglecting proper conservation methods at the time of mine closure. While dumping is the most common way of disposing of solid industrial waste such as tailings, fly and bottom ashes, slags etc., those materials are in fact a valuable source of secondary raw minerals. Thus, they could be recycled in a variety of products to turn the waste streams into value via the promising geopolymerisation technology. This article presents a study on the conversion of mine tailings and industrial by-products into geopolymers. Geopolymers based on alumino-silicate fines (steel-making slags and mine tailings) were synthesized using alkaline activation comprising sodium silicate. While the hardening of compositions occurs slowly at ambient temperature, elevated temperatures could change the leaching behaviour and decrease copper release from geopolymer matrix. Compressive strength of the proposed composition was 49±2 MPa after 90 days of curing. The results provide insights of possible reduction of the environmental footprints and potential economic benefits of mine tailings-based geopolymer composites for building applications utilizing mine tailings as suitable concrete material.

***Keywords*:** geopolymers, alkaline activation, mine tailings, industrial by-products, side product valorisation

1. Introduction

The total worldwide copper mine production amounted to an estimated 22 million metric tons in 2023. Global copper production has seen steady growth over the past decade, rising from 16 million metric tons in 2010 [1]. Owning one of the richest mineral deposits in the world makes Chile a leader in terms of copper reserves. Currently, operating mines address environmental and social responsibilities, while the former mine sites, lacking proper closer procedures in the 70s, may cause a substantial ecological burden [2]. At the same time, materials from secondary raw resources could stay overseen and underused ending up in landfills or open pit storages. Steel-making slags from the blast furnace process, fly ashes from energy production, and the tailings, which may contain residual copper after extraction/flotation procedure, are bright examples.

The main mineral phase of the aluminosilicate fines is quartz, making copper tailings poorly reactive and underused in construction industry. The copper tailings are powder material with high contents of aluminosilicates in the form of orthoclase or albeit. The normal state tailings are barely usable, because of their specific fineness, high weight, contamination of potentially harmful metals, etc. However, the copper tailings show a Si/Al ratio, which makes them suitable for use as precursors to manufacture geopolymer bricks or concrete substitutes and secondary raw source in the construction industry. With the regional economic specifics of Taltal city, where the copper tailings were dumped for years, geopolymer technology is a potential solution to rising ecological and social problems.

Geopolymers are a class of inorganic polymer materials with amorphous or semi-crystalline three-dimensional structures [3]. The geopolymer materials possess high compressive strength, chemical resistance, thermal and fire stability, low CO_2 footprint, and the possibility of utilizing industrial waste materials [4].

The geopolymers are multicomponent mixture of powder material (fines) and activator solution. The most commonly used activator is mixture of sodium silicate and potassium/sodium hydroxide. Recently, studies have showed suitable activator concentration to prepare alkali-activated geopolymers based on aluminosilicate fines and steel-making slags. This report provides detailed studies of selected geopolymer compositions based on mine tailings and steel-making slags to find recipes with suitable compressive strength for the preparation of geopolymer concrete and bricks.

2. Materials and Methods

2.1. Materials

The copper tailings were collected from the abandoned mine site near Taltal city (25° 24' 28.45" S; 70° 29' 8.97" W). The sample was sieved into two fractions <125µm and 125µm – 4mm. Additionally, the size distribution of material was determined on Hosokawa Alpine. Sodium hydroxide, acids, and analytical standards were purchased from VWR Chemicals. Sodium silicate – ZEOPOL 25 (42-46%, molar ratio SiO_2:Na_2O is 2.4-2.6) was purchased from JV Huber. Blast furnace slag was purchased from Finnsement Oy, and a steel-making slag was received from stainless steel production site in Finland, materials were used as received.

2.2. Methods

X-ray fluorescence spectroscopy (XRF, PanAnalytical Minipal 4) and flame atomic-adsorption spectroscopy (FAAS) were used to analyse the elemental compositions in solid and liquid phases. ICP-OES analysis was conducted in external laboratory service. Copper in the leachate solutions was determined using Perkin Elmer AAS 5000 at 324.8 nm, 15 mA. A powder X-ray diffraction method (XRD, a PANnalytical X´Pert PRO MPD diffractometer, Co Kα radiations generated at 40 kV and 40 mA, step width of 0.02°, Highscore software 3.0) was used to define the mineralogical composition. The compressive strength of the specimens was determined using the compression machine C089-10A.

2.3. Geopolymer preparation

Bulk geopolymer was prepared by mixing of appropriate amount of mine tailings and slag with the alkaline activator in different solid-to-liquid ratios (S/L), fines percentage, Al/Si or Na/Si modulus, and curing temperatures. After intense stirring for several minutes, the material was poured into silicon moulds (35x35x35mm). The mixture was allowed to consolidate at ambient temperature for three days under polymeric foil, and the concrete-like monoliths were transferred to a water bath for curing. After 7, 28, or 90 days, the compressive strength of monoliths was determined. After the compressive strength test, monoliths were crushed with a jaw crusher to reduce the size of the particles to under 10 mm and subjected to a leaching test. The leaching test was performed according to standard method EN 12457-4. The moisture content of the crushed samples was determined using drying at 105°C overnight. The value of moisture is accounted for estimation of geopolymer mass for the leaching test. A crashed sample of 15.00±0.35 g was placed in a 250 mL HDPE bottle. The bottles were shaken 24h at 30 rpm. After leaching the filtrate was separated from the solid fraction using a Büchner funnel and Whatman#6 filter paper. The filtrate was acidified using 65% nitric acid for further atomic absorption spectrometry (AAS) analysis resulting in 0.05 mol/L HNO_3 in each sample.

3. Results and discussion

The XRF results of solid waste fractions are presented in Table 1. The copper as a target element for the leaching test was present at the levels of impurities 0.4% (Table 1). Aluminium and silicon oxides as well as sodium, calcium, magnesium, and iron oxides were present in significant quantities. Results for minor elements determined with ICP-OES are given in Table 2. The XRD patterns of the solid waste residues, e.g. geopolymer precursors, showed the presence of the characteristic diffraction peaks of albite, aluminium oxide and silicon oxides (quartz type). The amorphous halo located at 20–30◦ was probably attributed to various amorphous alumino-silicates and oxides. The XRD results of the prepared geopolymers did not show any significant differences from precursors. The main phases stayed mostly inert, for little exception of orthoclase, which probably was partly dissolved based on decrease of its intensities compared to quartz.

Although two different binders (BFS and SMS slags) had the same size distribution patterns, the amount of liquid required for SMS composition was higher (Table 3). Otherwise, it was not possible to transfer slurry to the mould and had got smooth surface for further mechanical characteristic testing. The optimum recipe for geopolymer brick preparation was chosen based upon results of the compressive strength tests (Table 3). Also, three additional compositions were prepared with tailing-to-BFS slag ratio 2.3 (70% tailings/30% BFS) and put for curing for the first 24h at different temperatures (40, 60, and 80°C). Although the curing temperature did not affect the compressive strength of the specimens (32 MPa), it had obvious influence on further leaching behaviour of copper from the geopolymer matrix.

Table 1: Chemical compositions of copper tailings and industrial by-products by XRF.

Constituent	Content (wt. %)		
	Copper tailings	BFS slag	SMS slag
Na_2O	1.3	<0.1	<0.1
Al_2O_3	17.9	6.1	3.6
SiO_2	53.3	28,5	26,2
SO_3	1.3	3.8	0.4
K_2O	3.5	0.5	<0.1
CaO	4.4	33.4	59.7
MgO	4.6	9.4	7.5
Fe_2O_3	11.9	0.6	0.5
Cu	0.4	<0.01	<0.01
Mn	0.1	0.3	0.3
Cr	<0.01	<0.01	0.9
Zn	0.02	<0.01	<0.01

Table 2: Level of minor elements in copper tailings and industrial by-products by ICP-OES.

Element	Cu tailing, mg/kg	BFS slag, mg/kg	SMS slag, mg/kg
Ag	< 2	<0.1	<0.1
As	41.4	<3	<3
Ba	7.69	550	630
Cd	4.79	<0.3	<0.3
Co	34.3	<1	<1
Cr	11.1	46	8960
Cu	1380	<2	<2
Ni	ND	1.2	<1
Mn	ND	2770	3140
Pb	ND	<3	<3
Zn	ND	<3	9.2

Footnote: NA-not determined

To estimate a copper leaching behaviour as the most probable contaminant originated from the copper mine tailings, a standard one-step leaching test at S/L ratio 10 (EN12457-4) was performed. The noticeable amount of copper leaching from the geopolymer matrix is observed only for samples with tailings content 60-80%, e.g. 0.9-2.4 mg/kg (Table 3). Lower percentage of mine tailings added (10-50%) gave results of leaching that were lower than method's limit of quantitation (0.05 mg/L or 0.5 mg/kg). For additional specimens (70% tailing content) treated under elevated temperatures, the copper leaching was 2.4±0.2, 0.6±0.3, 0.5±0.1 mg/kg for 40, 60, and 80°C, respectively.

Table 3: Compressive strength and leaching behaviour of the selected specimens.

Sample code	Tailing, wt. %	Tailing-to-slag ratio	MPa[1]	Liquid-to-solid ratio	Cu, mg/kg
Blast furnace slag recipes					
MT80-BFS20	80	4.0	20	0.30	2.4±0.2
MT70-BFS30	70	2.3	31	0.30	1.9±0.6
MT60-BFS40	60	1.5	48	0.30	<0.5
MT40-BFS60	40	0.67	49	0.30	<0.5
MT20-BFS80	20	0.25	71	0.30	<0.5
MT0-BFS100	0	-	70	0.30	<0.5
steel-making slag recipes					
MT80-SMS20	80	4.0	5	0.32	1.1±0.1
MT70-SMS30	70	2.3	9	0.32	1.4±0.4
MT60-SMS40	60	1.5	11	0.32	1.3±0.5
MT40-SMS60	40	0.67	16	0.32	<0.5
MT20-SMS80	20	0.25	15	0.35	<0.5
MT0-SMS100	0	-	10	0.40	<0.5

Footnote: [1]compressive strength is measured on 28th day of curing.

After consideration of benefits and requirements to a final product, the next composition for geopolymer bricks were chosen: BFS is binding material, tailing-to-BFS slag ratio is 2.3, L/S ratio is 0.22, Si/Al ratio is 0.6. The specimens with dimensions of 10x10x10cm were prepared in the standard moulds in triplicates and left for consolidation under water at ambient temperature for 7, 28, and 90 days. The compressive strength was 12.8±0.3, 32.4±0.6, 49±2 MPa on 7th, 28th, and 90th day of curing time, respectively. The results of MT70-SMS30 depicted for comparison on Figure 1. The leaching of copper from the specimens after 90 days of curing time was 1.8±0.4 mg/kg, which makes the geopolymer bricks prepared according to this recipe potentially non-hazardous waste after its demolition [5]. The set limits for copper are between 2 and 10 mg/kg depending on application and thickness of coverage.

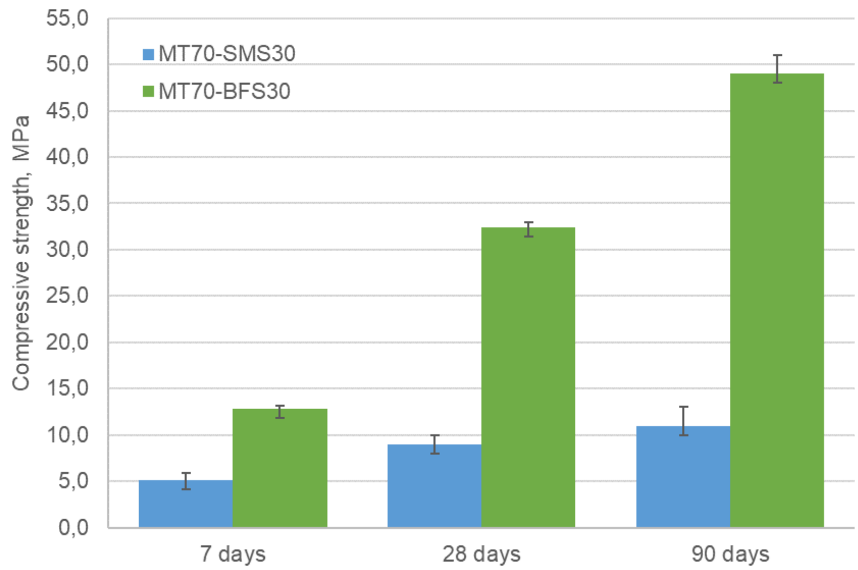

Fig. 1: Average compressive strength of geopolymer blocks versus curing age.

4. Conclusion

The present work showed that former copper mine tailings and industrial slags could be successfully used as fines and binders for preparation of geopolymers. The proposed compositions had compressive strength sufficient for manufacturing of construction materials locally (blocks or bricks). Even then alkali activation occurs at ambient temperature, leaching behaviour of demolished specimens allows the further reuse of construction and demolition waste in land construction (the set limits for copper is 10 mg/kg for coverage in road construction). Further, more detailed studies are needed for in-depth characterisation of proposed materials and their practical applications. The study demonstrated a new approach that could facilitate sustainable mineral recovery from abandoned mine sites especially in low-populated sites with economic and environmental challenges.

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