DOI: https://doi.org/10.24425/amm.2025.152564

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CHARACTERIZATION OF MINE TAILINGS AND FLY ASH FROM BULGARIA AS RAW MATERIALS FOR GEOPOLYMERISATION

Geopolymers present a modern low CO_2 footprint alternative of traditional building materials. The reuse of industrial waste or by-products as raw materials could address important ecological problems. The aim of this study is to evaluate the characteristics of mine tailings and coal combustion by-products from Bulgaria as raw materials for the preparation of geopolymers. Three mine tailings and two coal combustion by-products from thermal power stations were characterized. Appropriate validated analytical methods were combined to retrieve detailed information. The studied samples contented relatively high percentage of Al_2O_3 (17-21%) and SiO_2 (68-53%), and low concentration of sulfur (0.02-3.5% as SO_3). The alumosilicates, proved by XRD, are expected to show high reactivity in alkaline media, however some less reactive mineral phases were also observed. The aqueous slurry was alkaline pH 8-11, the fly ash contained the highest concentration of components ionized in water solution. Heavy metals content was found to be at micro or trace levels. The copper content was 56-818 mg/kg, Pb 127-2 mg/kg, Cr 1-71 mg/kg. The results showed that the studied mine tailings and fly ash could be used as precursors for geopolymer obtaining after fine adjustment of the technology to account for the specific characteristics of raw materials.

Keyword: Mine tailing; fly ash; geopolymers; chemical composition

1. Introduction

In recent decades, there has been an increase in the accumulation of tailings from the mining industry, which presents a high potential to be reused as raw materials for obtaining a substitute for Ordinary Portland Cement (OPC) [1]. The most effective substitutes are geopolymers or inorganic polymers synthesized using several raw materials, mainly metakaolin and reactive fly ash [2].

The geopolymers synthesis often requires low-temperature (<100°C) methods, thus lowering the emissions of greenhouse gases. In geopolymers, the binder is an aluminosilicate polymer gel formed from tetrahedral bonded silicon (Si) and aluminum (Al) with the oxygen atoms shared between them [3]. Two important constituents of geopolymer concrete are source materials and alkaline liquids. The source materials must be rich in Si and Al. These could be either natural minerals like kaolinite, clays, etc. or by-products like fly ash, blast furnace slag, silica fume, rice-husk ash, etc. The alkaline liquids are based on soluble alkali metals. The most common alkaline activator used is a combination of sodium or potassium hydroxide along with sodium or potassium silicate [4].

Fly ash has a high content of silica and alumina, which makes it a suitable base material for geopolymerization, a substitute for metakaolin. Since slag and fly ash are combustion byproducts, they are widely available [5,6]. However, fly ash is a heterogeneous material with a different chemical composition depending on the sources and could affect the final geopolymer product [7].

Due to the limited sources and availability of metakaolin and reactive fly ash, most research in recent years has focused on mine tailings. Globally, overview studies on geopolymers obtained based on mining waste are increasing confirming the research interest in the subject. The geopolymer materials derived from mine tailings have similar or even better physical and mechanical properties compared to OPC [8].

Parameters affecting fly ash geopolymer mixtures include the raw materials, alkaline activators, concentration and curing method. A combination of sodium silicate (Na_2SiO_3) and sodium hydroxide (NaOH) as alkaline activators have been used [9,10]. The ratio of sodium silicate to sodium hydroxide is an important technological parameter. In addition, since fly ash has a slow reactivity at ambient temperature, high temperature is essential to increase the kinetics and reaction rate of the geopolymer

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process, to develop a denser pore system, and to obtain appropriate mechanical properties [11]. The use of waste materials for geopolymer binder produced with copper mine tailings and low-calcium slag for potential applications in road construction was reported [12]. A study proved that the Ca content in fly ash based geopolymers as well as the liquid/solid ratio regulated the properties of the final product [13]. Relatively high mechanical strengths could be obtained using low Ca fly ash [14]. The addition of mine tailings from different sources has various effects on the characteristics of geopolymer products [8,15-18]. The inherently low reactivity of mine tailings affected the mechanical properties of geopolymers. The compressive and flexural strengths varied quite widely among all mine tailings-based geopolymers mainly due to different types of mine tailings. However, the influence of various types of additional aluminosilicate source materials, alkali activators, a wide range of alkali activator/binder ratios, curing duration and curing temperature, and humidity, etc. should also be considered when design the raw materials mixture [8,15-18]. Particle size of the precursor plays an important role in the geopolymerization process. Moreover, the particle size has influenced the physical and mechanical properties of geopolymers. Since geopolymerization demands material to leave the surface of precursors to take place in the reaction, the surface area needs to be maximized [19].

The utilization of natural minerals and wastes (fly ash) in geopolymerization as well as for immobilization of toxic metals was investigated extensively in the recent years [15,20]. Leaching tests are an informative tool to determine the degree of ion immobilization within a geopolymeric system [21]. Geopolymerization process was demonstrated to be effective in immobilization of various hazardous elements [12-25]. The most significant factor that controls the compressive strength of fly ash-based geopolymers is the pH of the alkali metal silicate precursor [26]. When cement is used as a setting additive in the geopolymeric matrix, the compressive strength increases almost exponentially with increasing pH. The higher alkali content was found to promote solid dissolution but also caused aluminosilicate gel precipitation at very early stages resulting in lower compressive strength [27]. Details of fly ash based geopolymers have been recently reviewed [28-31].

In Bulgaria, over 33 tailing dumps occur, 21 of which are recultivated, and 12 tailing dumps are actively operating. Different approaches for the reuse and valorisation of the tailing materials including in obtaining of geopolymers were studied [32-39]. In a line of recent studies, it has been shown that there are many potential geopolymer precursors in Bulgaria [32,33,36], however they need throughout study and characterization [32]. Geopolymers obtained using local materials such as metakaolinite [36], natural zeolite [37], fayalite slag [34-36,39] or fly ash [32,38] were described. The fayalite slag from a copper producing plant was found to be low reactive geopolymer precursor [39]. Usual practice in Bulgaria is the application of the thermal power plant (TPP) wastes in the construction of roads and embankments, the production of blended cements, concrete or mortars, also for production the plasterboard and plasters.

The obtaining of geopolymers requires detailed characterization of raw materials, such as: the component and phase composition, particle size, pH, conductivity of the waste and the degree of extraction of the main components in an alkaline medium, etc. These parameters influence the synthesis conditions of geopolymers and their properties.

This paper presents a comparative study of mine tailings and coal combustion byproducts from Bulgarian sources and assessment of their potential to be used as raw materials for geopolymer obtaining. The published data concerning the application of Bulgarian raw materials in geopolymer obtaining technology are reviewed.

2. Experimental

2.1. Sample description

Three copper mine tailings and two ashes from thermal power plants (TPP) were studied. The sampling was made by the corresponding company applying in-laboratory sampling plan. The samples were air-dried, homogenized without particle size reduction, and stored at room temperature. The samples description is presented in TABLE 1. A fraction below <200 μm was subjected to further analysis.

TABLE 1

Sample description

Sample name	Description	Waste type
MT1	Copper mine tailing from Ellatzite (active tailing dump)	Mine tailing
MT2	Copper mine tailing from (inactive tailing dump)	
MT3	Copper mine tailing from Assarel (active tailing dump)	
FA	Fly ash from TPP “Bobov Dol” thermal power station	Fly ash
MA	Mixed tailing from TPP “Maritza East 2” containing fly ash, bottom ash, and coal dust, etc.	Mixed ash

2.2. Granulometry

A particle size distribution was defined as the relative amount by mass of particles present according to size, retained on a series of sieves with different sized apertures.

2.3. pH and Electro Conductivity (EC)

The procedure for pH and EC testing of studied samples was validated using a certified reference material for clay soil for pH and EC: CRM498-100G, Lot LRAC5544. The pH and EC were measured as 20 g of air-dried and homogenized waste was transferred in a baker and 20 mL of distillate water was added [40]. The mixture was homogenized for 5 s and pH was measured in the supernatant after 10 min. A HI5521-02 Laboratory Research Grade Benchtop pH/mV and EC/TDS/Salinity/Resistivity Meter was used for measurements. Each measurement was done in duplicate, and the mean value was presented.

2.4. Chemical and mineralogical composition

X-ray Fluorescence spectrometry was applied for determination of main components. The results are presented as corresponding oxides. ICP-OES measurement after aqua regia digestion was used for detailed study of chemical composition. A previously validated procedure for ICP-OES analysis of mine tailings leachates was applied. [41]. A measured weight of a sample of 2 g (±0.0001 g) was transferred in a beaker. Ten millilitres dist. water were added, 5 mL conc. HNO_3 and 15 mL conc. HCl was added to each sample and heated on a hot plate without boiling for 60 min, covered with watch glass. The obtained solutions were filtered and collected in volumetric flasks. The filters were washed with hot diluted HCl (1:4) [42]. The filters with residues were placed back in a beaker and was heated with 5 mL conc. HCl to fully digest the paper. The filtrate was collected in the same flasks. Ten millilitres conc. HCl was added, and the diluted to volume by dist. H_2O. The obtained solution was sent to ICP-OES measurement for determination of concentration of dissolved components. The loss of ignition (LOI) at 1000°C also was determined. X-Ray diffractometer system EMPYREAN with CuK radiation was used to determine the crystal structure of the studied industrial wastes. The step interval, integration time and angle interval used were 0.0530°; 53.8 s; 5-80 2θ, respectively.

3. Results and discussion

Characterization of industrial tailings by appropriately selected analytical methods allows assessing the suitability of industrial tailings for synthesis of geopolymers, evaluation of the potential toxicity of the wastes, as well as the level of encapsulation of the heavy metals after geopolymerization. It is known that the component composition, chemical and physical properties of raw materials affect the geopolymerization process and the physical properties of the obtained geopolymers [33,43]. To assess an industrial tailing suitability for geopolymer obtaining two groups of characteristics should be assessed: (i) characteristics of importance for the structure and properties of geopolymers and (ii) characteristics of ecological importance. The first group of parameters includes component and phase composition; particle size distribution, pH and conductivity of the waste and the degree of leaching of the main crosslinkers in alkaline media. These parameters influence the synthesis conditions of geopolymers and their properties. The second group of parameters includes heavy metal content, behaviour in aqueous medium and formation of ionized soluble components, as well as acidity of the generated leachates. These parameters could be applied to assess the environmental fate of the industrial tailings.

3.1. Particle size distribution

Particle size distribution of the studied samples is presented on Fig. 1. Percentile values d10, d50 and d90 indicating the size below which 10%, 50% or 90% of all particles are found are presented in TABLE 2.

As can be seen from the data the finest appeared the fly ash (FA1) with 90% of particles below 220 µm. The coarser material

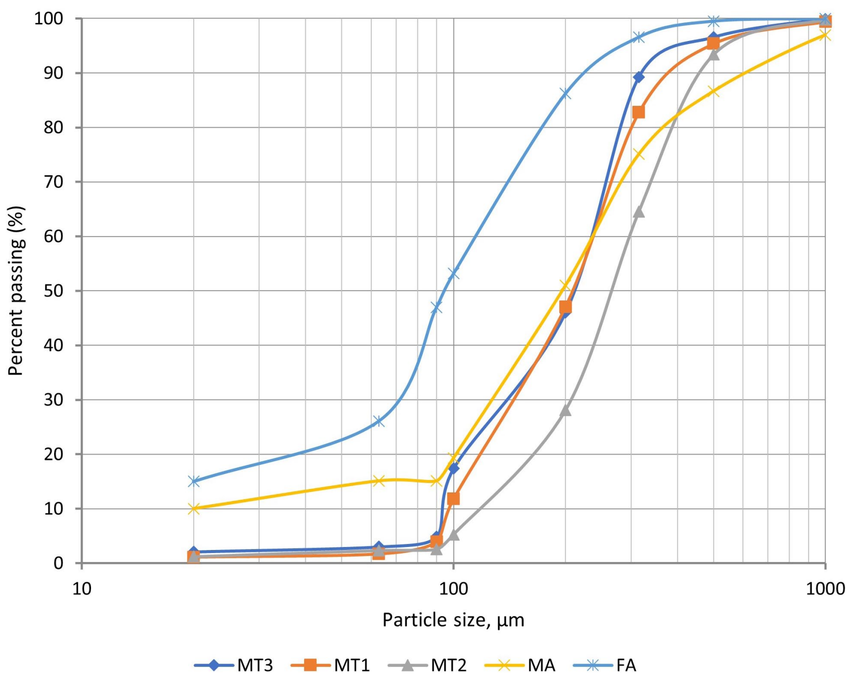

Fig. 1. Particle size distribution of the studied samples

was a mixed tailing (MA) with 90% of particles below 620 µm. The main part of particles in the studied samples is lower than 315 µm. 11.8% of sample MT1, 5.3% of MT2, 17.4% of MT3 copper mine tailings; 19.3% of MA and 53% of FA passed through a 100 µm sieve. The studied copper tailings showed very close particle size distribution pattern. It is well known that the particle size governs the reactivity of the raw material and geopolymerization process thus the finer are the raw material particles the more reactive is it [19,40]. Additionally, skipping the process of shredding the raw materials of waste will benefit economically the final product. Thus, the fine structure of the studied mine tailings (MT1-3) and fly ash (FA) appeared appropriate for geopolymer obtaining. The microstructure of geopolymers strongly depended on the particle size of the raw materials. The finer was the average particle size distribution, the denser and stronger was the geopolymer matrix [45]. It was explained by the larger surface area, which facilitated reactivity in alkaline media and densification of the structure. However, different size fractions may have a significant variation in chemistry, mineralogy, particle size distribution and glass content. Recent study demonstrated that the ratio SiO_2/Al_2O_3 showed increasing trend with increasing fineness, whereas Fe_2O_3, CaO and loss on ignition decreased [46].

TABLE 2

Particle size distribution d10, d50, d90 parameters

Sample	d10, µm	d50, µm	d90, µm
2364	99	216	375
2365	110	288	467
AM	94	206	319
M2	20	195	620
BD	8	92	220

3.2. Chemical composition

The chemical composition of the studied mine tailings and coal combustion by-products is presented in TABLE 3. Literature data concerning industrial tailings from Bulgarian sources as geopolymer raw materials are also summarized. It should be noted that the published studies concerning geopolymer obtaining using mine tailings, fayalite slag or fly ashes in Bulgaria are very limited. The samples contained relatively high Al and Si. However, some of the samples could not be used as a single precursor due to lower Si and Al and appropriate additives or mixture of the raw materials could address this problem. The sulfur oxide content was below 4%, except mixed coal combustion byproducts tailing (MA) were 19% was found. The high content of sulfur in MA sample could be explained by the coal dust contained in the tailing. According to the literature data the SO_3 content above 4% will negatively affect the performances of geopolymers [47]. The composition of tailing MA wasn't appropriate for geopolymers obtaining. The hazardous elements are found at impurities level between 1% and 0.1% and traces below 0.1%. Mainly Pb, Cd, As, Ni, Cu was found in the studied wastes; however, the level of heavy metals content needs more precise study. The results showed that copper mine tailings from "Assarel Medet" (sample MT3) and "Ellatzite Med" (sample MT1), as well as fly ash from TPP "Bobov dol" (sample FA) had a composition suitable for geopolymersation process.

However, the SiO_2/Al_2O_3 and CaO/SiO_2 ratios in raw material are crusial for geopolymerization [48]. The weight ratio of SiO_2 and Al_2O_3 in the studied mine tailings was between 4-6 (M1 ratio = 4.3, M2 = 4.1; M3 = 6.4), and of fly ash around 2 (M2 = 2; BD = 2.5), making the tailings appropriate precursors for geopolymer obtaining [48,49]. The rates of the release of Si and Al components from source materials can significantly affect their availability for reaction and their extent of participation in a geopolymer gel structure [44]. It was investigated that a finer size gradation and a high Si/Al ratio are favorable conditions to ensure the formation of a less porous and dense geopolymer gel, promoting the mechanical strength properties [19]. The variation with these parameters is aimed at enhancing the inclusion of the waste material in the structure of the geopolymer until the desired properties are achieved.

TABLE 3

Type of waste / Components	Fayalite slag from copper industry		Mine tailing					Coal combustion by-products			
	[34, 39]	**[35,36]**	**[50]**	**[51]**	**MT1**	**MT2**	**MT3**	**FA**	**MA**	**Fly-ash TPP Maritsa East 2 [33]**	**Fly ash TPP Galabovo [32]**
SiO_2, %	29.34	25.77	69-71	**	68.20	57.50	74.81	52.45	25.7	52.66	46.18
Al_2O_3, %	4.40	3.73	12.8-14.2	**	16.90	14.02	11.67	21.44	12.96	23.37	24.73
Fe_2O_3, %	58.42	61.68	5.7-8.0*	5.0-61.0*	2.61	12.70	3.52	7.85	3.92	8.72	10.39
CaO, %	2.66	2.12	**	**	1.77	6.97	0.73	8.89	27.65	5.75	8.42
K_2O, %	0.71	0.76	**	**	5.95	4.03	4.70	1.75	0.40	**	**
Na_2O, %	0.58	**	**	**	3.39	1.13	0.97	0.70	0.43	**	1.43
MgO, %	0.89	0.81	**	**	2.84	10.08	1.52	2.04	1.18	2.75	2.36
MnO, %	**	0.08	**	0.56*	0.04	0.18	0.02	0.04	0.07	**	0.08
TiO_2, %	0.30	0.34	**	**	0,40	0.54	0.32	1.12	0.65	**	0.67
P, %	**	**	**	**	0.05	0.23	0.04	<0.01	0.01	**	**
SO_3, %	0.26	2,2*	3,9-6,6*	**	0.02	0.06	0.07	3.519	18.70	5.75	4.04
LOI, %	**	**	**	**	1.44	10.08	4.0	3.34	26.58	**	**

** unidenfied by XRF spectrometry analysis

3.3. Mineralogical composition

XRD study of mineralogical composition showed the presence of different alumosilicate minerals, as well as silica as quartz, zeolite, and albite, which were submitted to successful geopolymerization process [52]. The cooper mine tailings (MT1) contained: quartz (O2 Si1), Albite (Al1 Na1 O8 Si3) and Zeolite A (C16 H53.66 N1 O25.33 Si8). The XRD output of the cooper mine tailing (MT2) is presented on Fig. 2. The phases were identified by the characteristic interplanar distances of the most intensive peaks (%) at 2theta: Quartz ref. code 98-015-6196 (69.9%) 26.68; (30%) 26.66; (19.92) 20.88; (12.58) 50.19 and (3.09) 54.93; (4.81) 67.81, Orthoclase 98-003-0650: (100.0) 26.91; (77.60) 27.58; (62.54) 21.04; (37.34) 34.87, Albite (heate treated) 98-008-7660: (100.0) 27.93; (97.26) 22.03; (41.95) 24.35, Clinochlore IIb-2 98-006-6258: (100) 12.46; (96.6) 18.73; (91) 6.23; (19.56) 31.46 and Coesite 98-017-2295: (100) 28.92; (73.18) 25.89; (28.32) 29.02. The following phases could be identified: Quartz, Orthoclase, Albite, Clinochlore and Coesite. Copper mine tailing sample (MT3) was found to contain: quartz (O2 Si1), Clinochlore (H8 Al1.881 Cr0.004 Fe0.22 Mg4.882 O18 Si2.96 Ti0.004); Albite low (Al1.005 Na0.986 O8 Si2.995), Zeolite (O2 Si1) and Muscovite 2M1, phengitic (H1.56 Al2.61 F0.19 Fe0.22 K0.92 Mg0.1 Na0.08 O11.81 Si3.17).

Copper mine tailing sample: AM (MT3) was found to contain: quartz (O2 Si1), Clinochlore (H8 Al1.881 Cr0.004 Fe0.22 Mg4.882 O18 Si2.96 Ti0.004); Albite low (Al1.005 Na0.986 O8 Si2.995), Zeolite (O2 Si1) and Muscovite 2M1, phengitic (H1.56 Al2.61 F0.19 Fe0.22 K0.92 Mg0.1 Na0.08 O11.81 Si3.17). The typical phases of aluminosilicates – quartz, albite, where proved to participate effectively in geopolymerization process [51]. The phases as zeolite and orthoclase were reported to be reactive in geopolymerization with the resultant geopolymers showing a high compressive strength [52]. Clinochlore is a clay mineral with the nature of kaolin/kaolinite, which has been used for production of geopolymers with improved properties (its resistance to water absorption and mechanical performance) [53].

3.4. Physicochemical characteristics of the aqueous leachate

pH, redox potential and electroconductivity of aqueous leachates could be used to estimate the rate of dissolution of waste components in water. The physicochemical characteristics of leachate are presented in TABLE 4. The studied samples were alkaline with pH varied between 7.90 and 10.06. The relatively high alkalinity of could favour the geopolymerisation process and should be considered in adjustment of quantity of alkaline activator during geopolymer obtaining. However, it should be considered that the higher pH of the waste leads to faster fixation of geopolymer, which can lead to technological problems in the synthesis process [48]. The relatively high concentrations of CaO (above 10%) in PPT tailings could partially explain the high alkalinity of the leachate pH 10-12. Copper tailings leachates were typically alkaline pH ≈ 8-9, as it was reported for copper tailings from other sources [40]. The high pH showed that no sulfide containing minerals was presented in the samples [52], confirmed by the obtained results XRD results. The electroconductivity of aqueous leachates was used to estimate the total concentration of dissolved charged components of the studied tailings. The highest EC and correspondingly, highest concentration of dissolved charged components was observed in fly ash sample indicating the high reactivity of the raw material. The lowest EC was measured in MT2 sample (material from closed tailing dump) 297 μS/cm. It is possible that the

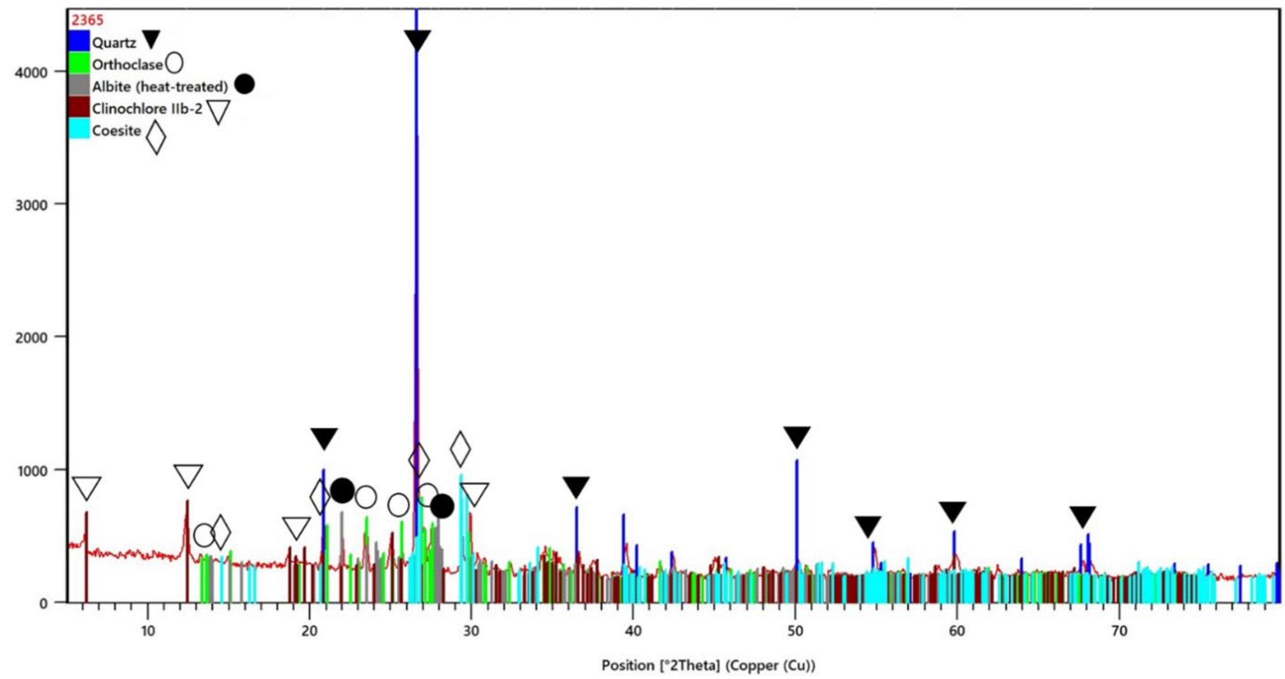

Fig. 2. Mineralogical composition by XRD of MT2 mine tailing

material of the inactive tailing dump was subjected to chemical and phase transformation which lower the dissolution capacity of the components. The redox potential of copper mine tailings was positive indicating slight oxidative capacity of the slurry, in contrast fly ash slurry redox potential was reductive.

TABLE 4

Physicochemical characteristics of the slurry

Sample	pH ± 0.02 28°C	EC σ, mS/cm 28°C	Ep, V (vs Ag/AgCl)
MT1	7.90	0.790	134.9
MT2	8.19	0.297	138.5
MT3	9.01	1.796	122.4
FA	10.06	2.485	–72.6
MA	8.18	2.218	254.5

3.3. Heavy metal content

The results from determination of heavy metals content in the studied samples by ICP-OES after aqua regia digestion are presented in TABLE 5.

It should be noted that the total heavy metal content could not be applied for the estimation of environmental risks of the tailings as their mobility and bioavailability are dependent on heavy metals speciation and distribution in geochemical fractions. Moreover, comparatively low levels of heavy metals found in the virgin material could guarantee low mobility and high level of encapsulation in geopolymers matrix. Thus, additional reduction of the flow to the environment could be expected.

TABLE 5

Heavy metal content of the studied tailings by ICP-OES after aqua regia digestion

Elements, mg/kg	Mine tailing			Coal combustion tailings	
	MT1	**MT2**	**MT3**	**FA**	**MA**
Cu	491	818	56	1.6	12.2
Zn	<0.5	195	2.7	<1.0	2.6
Mn	223	1176	21	3.1	36
As	<1	<1	<1	<1	1.2
Cr	20	71	<0.5	0.8	2.3
Cd	<0.5	<0.5	<0.5	<0.5	<0.5
Ni	33	46	6.7	0.8	20
Co	<0.5	28	<0.5	<0.5	1.1
Pb	29	127	5.8	1.9	9.4

4. Conclusion

This study presents the results from evaluation of the potential three copper mine tailings and two coal combustion by-products from Bulgaria as raw materials for the preparation of geopolymers. Detailed characterization of the waste materials was done by applying appropriately validated analytical methods. The results showed that the studied mine tailings contained relatively high percentage of Al and Si, and low concentration of sulfur, which make them an appropriate raw material for geopolymers obtaining. The aluminosilicates in the studied waste materials were expected to show high reactivity in alkaline media, however some less reactive mineral phases were also observed. The aqueous slurry was alkaline pH 8-11, the fly ash contained the highest concentration of components ionized in water solution. Heavy metals were found at micro or trace levels. The fly ash FA has low the particle size, low CaO and SO_3 content which supposed to be successful initial material for geopolymerization. The obtained results showed that the studied mine tailings and fly ash could be used as precursors for geopolymer obtaining. However, a fine adjustment of the technology and the composition of the raw mixture should be considered in order to account for the specific characteristics of raw materials from Bulgarian sources.

Acknowledgments

This study is supported by the Bulgarian National Science Fund under the contract KP-06-DO02/5 "RecMine – Environmental footprint reduction through eco-friendly technologies of mine tailings recycling" in the frame of ERA-MIN3 program, Horizon Europe. The authors acknowledge the support of Ellatzite Med Concentrator Plant, Assarel Medet JSC Bulgaria, TPP "Bobov dol" and TPP "Maritsca East 2" for providing tailings materials for this study.

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