

Green remediation of tailings from the mine using inorganic agents

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Abstract

Increasing amounts of residues and waste materials coming from industrial activities in different processes have become an increasingly urgent problem for the future. The paper presents the problem of mine tailings generated in mine "Sase" (Republic of Srpska, Bosnia and Herzegovina) with high metal content (Pb, Cu and Zn). Dumpsite of this tailing represents potential risk for water bodies in the vicinity of this location. Chosen treatment process was stabilization/solidification (S/S). Inorganic agents used in this study were fly ash and red mud that represent secondary industrial waste generated on locations relatively near the mine. Therefore, their application can be used as an example of a sustainable solution of regional environmental problem. Further investigations are related to the impact of various factors on metals leaching from mine tailings solidified/stabilized material using the above mentioned immobilization agents. The performance of the immobilizing procedures was examined using several leaching tests: ANS 16.1, TCLP, DIN, MWLP. The results indicated that all S/S samples can be considered as non-hazardous waste, as all leached metal concentrations met the set criteria. These results will further enable the modelling of metals behaviour during long-term leaching from treated mine tailing. The data are invaluable in terms of economically and environmentally sound management of mine tailing.

Keywords: fly ash, red mud, mine tailing, stabilization/solidification, green remediation.

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Mining and industrial activities have caused extensive heavy metal contamination by introducing heavy metals directly into the surrounding environment. Mine tailings resulted from mining activities. Concerning the separation of ore concentrate, the land can be burdened with significant quantities of heavy metals. For this reason, finding new and improving existing tailings treatment techniques is very important. Toxic metals are one of the main contaminants present in mine tailings. An effective method for solving this problem is shown to be solidification and stabilization technology (S/S technology) [1–3]. S/S technology, which involves mixing the appropriate binding material with the contaminated material, protects the environment with immobilization of harmful components. Wastes from the solidification and stabilization technology will eventually be used for a specific purpose or deposition. During the S/S applications, the toxic constituents which are present in the waste are physically and chemically fixed. In this way their mobility is significantly reduced, so the threat to the environment is minimized, and also the compliance with existing regulatory

standards is ensured. In order to predict the long-term leaching behaviour, a diffusion model is frequently used to evaluate the leaching kinetics. The mechanisms governing heavy metal leachability in solids can be effectively examined using the American Nuclear Society's (ANS) semi-dynamic leaching test [4]. The ANS 16.1 provides substantially more information regarding the "real time" rate at which heavy metals are released from the solidified product as compared to other leaching tests [5]. The leaching results extend over a 90-day period instead of a single result at the end of the test. On the other hand, batch leaching tests are the preferred choice for regulatory assessment due to their simplicity, improved reproducibility, and shorter time requirements. However, as batch leaching tests are typically run over short time frames, it is debatable whether the compounds of interest behave similarly in the long term. Modelling can potentially predict the long term leaching of wastes providing a solution to problems inherent to batch procedures [6].

Over the last couple of years the term "green remediation" has been extensively used [7]. This term refers to the processes, products and activities that have little or negligible impact on the environment. This applies to finished products of remediation, and on the technology process, which should have little environmental impact. For this reason, in this paper fly ash was used as a stabilizing agent, in order to achieve

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the so-called “green concept” – immobilization and disposal of two types of waste. Owing to its pozzolanic nature, fly ash can be used in a variety of construction applications. Namely, combustion of bituminous coal produces a fly ash (fly ash class C) rich in calcium, with self-cementing characteristics, and the pozzolanic reactions lead to calcium aluminium and calcium silicate hydrate (CAH and CSH) cementations product formation. Class C is normally produced from the burning of sub-bituminous coal and lignite. Class C fly ash usually has cementitious properties in addition to pozzolanic properties due to free lime. Fly ash produced from the burning of younger lignite or sub-bituminous coal, in addition to having pozzolanic properties, also has some self-cementing properties. In the presence of water, Class C fly ash will harden and gain strength over time [8]. It has been reported that 26% of the total quantity of fly ash produced annually in the U.S. is used in construction materials [9]. In Serbia, the use of fly ash is still negligible.

Another type of industrial waste that has been used as stabilization agent, to achieve “green concept”, was red mud. Red mud is the solid waste residue of the digestion of bauxite ores with caustic soda for alumina (Al_2O_3) production. Approximately 35–40% of the processed bauxite ore goes into the waste as alkaline red mud slurry which consists of 15–40% solids [10,11]. The chemical and mineralogical composition of the complex industrial waste is widely different, depending on the source of bauxite and the technological process parameters. However, six major oxides in the red mud are CaO , SiO_2 , Fe_2O_3 , Al_2O_3 , TiO_2 and Na_2O [12]. It is estimated that annually 70 million tons of red mud is produced all over the world [13]. Red mud is known as an extremely fine material in terms of particle size distribution, having an average particle size $10\ \mu\text{m}$, which makes it hard to precipitate and many organic or inorganic compounds have to be added for its separation. Typical values would account for 90% volume below $75\ \mu\text{m}$. The specific surface area (BET) of red mud is around $7.3\text{--}34.5\ \text{m}^2\ \text{g}^{-1}$ [14], which can be substantially increased using certain treatment methods as well as enhancing its internal catalytic activity [15,16]. Red mud particles are reported to carry a significant negative charge under basic conditions due to ionized hydroxyl groups on their surfaces [17].

The paper presents the problem of waste sludge from mine tailings with high metals concentration, as well as the methods of treatment process stabilization/solidification. The goal of this study was to investigate the possibility of immobilization heavy metals in the mine tailings using fly ash and red mud as immobilization agents and determining their efficacy depending on a number of factors. Efficiency of immobilization procedures was followed by the use of so-called leach-

ing tests. Metals concentrations were determined in order to establish whether after a certain time they crossed from the immobilized into the mobile phase which is considered potentially hazardous and bioavailable. The results from simulation of these conditions will further enable modelling of behaviour in terms of long-term metal leaching from treated tailings and evaluate the effectiveness of fly ash and red mud for the immobilization of various metals in the tailings.

MATERIALS AND METHODS

Study area and sample preparation

Mine tailing used in the experiment originated from lead and zinc mine “Sase” municipality Srebrenica, Bosnia and Herzegovina. Coal fly ash was provided from the Ugljevik (Republic of Srpska, Bosnia and Herzegovina) thermal power plant and red mud was obtained from dehydrated aluminium oxide factory Birac (Republic of Srpska, Bosnia and Herzegovina). In order to analyze the chemical and mineral composition of the fly ash and red mud, X-ray fluorescence (XRF-1700) analyzer and X-ray diffraction (XRD) system were applied. Pseudo-total trace metal content was assessed on sample triplicate after nitric acid digestion employing USEPA standard method [18] and mean values were used. The relative standard deviations (RSD) obtained ($n = 3$) were below 10%. Metal content was determined by AAS (Perkin Elmer Analyst™ 700) according to the standard procedure [19].

Samples were designated by the capital letter (F: fly ash, R: red mud, J: mine tailing) followed by a number indicating the percent weight of the given attribute. The fly ash and red mud content was expressed as percentage of the total solids weight. During the leaching test, 8 types of specimens were tested: F10J90, F20J80, F30J70, F50J50, R10J90, R20J80, R30J70 and R50J50.

Samples were prepared in the form of monolithic cubes ($(3\pm 0.1)\times(3\pm 0.1)\times(3\pm 0.1)\ \text{cm}^3$) by compaction at an optimum water content, defined as the water content at which the maximum dry density is achieved for a given compactive effort. The compaction was performed according to ASTM D1557-00 [20], providing a compactive effort of $2700\ \text{kN}\cdot\text{m}/\text{m}^3$ [4]. Density of specimens ranged from 1.38 to $1.54\ \text{g}\ \text{cm}^{-3}$. Samples were cured at $20\ ^\circ\text{C}$ in sealed sample bags for 28 days and then subjected to the different tests.

Leaching tests

Leaching occurs when a leachate contacts a waste and carries away contaminants from the waste. A leachate can contact the waste either by flowing around the waste or by flowing through the waste, or in a combination of both. In an actual landfill situation,

the relative importance of these two ways of contact is dependent on the permeability of the solidified waste and its surrounding materials. Several leaching procedures have been developed to simulate the leaching processes of hazardous wastes in landfills or natural environments in order to evaluate the possibility of human health hazard threats of tested wastes. Semi-dynamic leaching test, ANS 16.1, was conducted in order to assess the long-term leaching behaviour of tested metals, and three different single-step leaching tests, TCLP, DIN and MWLP, were applied to evaluate the extraction potential of pollutants in the waste.

ANS 16.1 test

The long-term leachability of Cu, Pb and Zn from the S/S treated materials was evaluated using the ANS method 16.1 [4]. By applying this test we get the cumulative fraction of metals leached versus time. Mathematical diffusion model based on Fick's second law is used to evaluate the leaching rate as a function of time. The ANS has standardized the Fick's law-based mathematical diffusion model as follows:

$$D_e = \pi [a_n / A_0 / (\Delta t)_n]^2 [V/S]^2 T_n \quad (1)$$

where a_n is the contaminant loss (mg) during the particular leaching period with subscript n ; A_0 is the initial amount of contaminant present in the specimen (mg); V is the specimen volume (cm^3); S is the surface area of specimen (cm^2); $(\Delta t)_n$ is the duration of the leaching period in seconds; T_n is the time that elapsed to the middle of the leaching period n (s) and D_e is the effective diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$).

The leachability index (LX), which is a parameter directly derived from the ANS 16.1 test results, is currently used by Environment Canada [21] as a performance criterion for the utilization and disposal of treated waste.

The LX is calculated using the diffusion coefficient obtained from Eq. (1). It is the average of the negative log of the effective diffusivity terms (expressed in $\text{cm}^2 \text{s}^{-1}$). Therefore, the leachability index is defined as follows:

$$LX = 1/m \sum_{n=1}^m [-\log(D_e)]_n \quad (2)$$

Where m is the total number of individual leaching periods. The relative mobility of different contaminants can be evaluated by this index, which varies from 5 ($D_e = 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, very mobile) to 15 ($D_e = 10^{-15} \text{ cm}^2 \text{ s}^{-1}$, immobile) [22].

The type of leaching mechanism that controls the release of metals can be determined based on the values of the slope of the logarithm of cumulative fraction release, $\log B_t$, versus the logarithm of time, $\log t$,

line [4]. If diffusion is the dominant mechanism, then theory suggests the following relationship:

$$\log B_t = 1/2 \log(t) + \log \left[U_{\max} d \sqrt{(D_e/\pi)} \right] \quad (3)$$

Where D_e is the effective diffusion coefficient in $\text{m}^2 \text{ s}^{-1}$ for component x ; B_t is the cumulative maximum release of the component in mg m^{-2} ; t is the contact time in seconds; U_{\max} is the maximum leachable quantity in mg kg^{-1} , and d is the bulk density of the product in kg m^{-3} .

When the slope is close to 1 (0.60–1.00), according to Nathwani and Phillips [21] the process is defined as dissolution. In that case, the dissolution of the material from the surface proceeds faster than the diffusion through the pore space of the soil matrix. If the slope is 0.5 (0.40–0.60), the release of heavy metals will be slow and diffusion will be the controlling mechanism. If the slope is less than 0.40 the release of metal will be probably due to surface wash-off.

Samples were prepared and leachate was collected and replaced according to the ANS 16.1 test.

In this study, the ANS 16.1 method was modified by including 0.014 M acetic acid (AA) pH 3.25 and humic acid (HA) solutions (20 mg TOC L^{-1}) as leachants. The objective was to mimic the worst possible conditions of the S/S waste disposed in the landfill environment.

TCLP toxicity characteristic leaching procedure

According to the USEPA protocol [23] two types of extraction solution were used. A 0.1 M acetic acid solution with a pH of 2.88 was used to extract S/S-treated samples due to the high alkalinity of the wastes. An extraction solution comprised of 0.1 M acetic acid and 0.0643 M NaOH with a pH of 4.93 was used for untreated waste. The samples were extracted at a liquid to solid (L/S) ratio of 20 for 18 h. After the extraction, the final pH of the leachate was measured and the liquid was separated from the solids by filtration through a 0.45 μm pore size membrane filter. This test was applied on every sample in triplicate and the $RSDs$ were below 5%.

DIN 3841-4-S4 German standard leaching test

DIN 3841-4 S4 [24], uses a grained sample with particle size smaller than 10 mm. Leaching is performed with deionised water at a 10:1 L/S ratio, and a 24 h testing period. After rotation, the final pH is measured, and the samples filtered through a 0.45 μm membrane filter.

MWLP mine water leaching procedure

The aim of this method is to predict the leachability of heavy metals and trace elements from zinc leach residue and other industrial solids when in contact with acidic, metal bearing groundwater, such as acid mine drainage. The method, developed at the West Virginia

Water research Institute (WVWRI), involves the serial addition of acid mine water to an ash sample until all alkalinity has been exhausted by the acid water [25]. A 100 g sample placed in a 2 L of acid mine water was added. If mine water was not available, a 0.001 M H₂SO₄ solution was used. The bottle was agitated for 18 h at 30 rpm. At the end of the extraction, the leachates were filtered, and the sample was rinsed back into the container using 2 L of fresh leachant solution. The procedure was repeated until the pH of the leachate reaches that of the unreacted mine water (~3.5).

Microwave-assisted sequential extraction procedure (MWSE)

Raw mine tailing sample was characterized by performing sequential extraction MWSE as described by Jamali *et al.* (2009) [26]. Mean values were used and the RSDs ($n = 3$) were below 5%. The extractions were performed at ambient temperature and the optimization of the MW power and extraction time was carried out by carefully controlling the temperature of the extracting solutions, which did not exceed 50 °C, and the solutions were never brought to boiling. Blanks (containing reagent but no samples) were also taken through each complete procedure. Mileston, Stare E microwave (MW) was used for MW extraction and digestion.

RESULTS AND DISCUSSION

Chemical and mineral composition of fly ash and red mud, used as binders, are presented in Table 1. The main oxides of red mud used are Fe₂O₃, Al₂O₃, SiO₂ as well as significant amounts of Na₂O, TiO₂ and CaO indicating that they can be active in some pozzolanic processes leading to hydration products formation. Also, analysis of fly ash indicated that the content of CaO is rather high and that this fly ash belongs to class C and that has self-cementing characteristics lead to calcium aluminium and calcium silicate hydrate cementations product formation during pozzolanic reactions [27–29].

Pseudo-total metal content in the initial sample of mine tailing is showed in Table 2. If we compare the initial metal content with the limit values for waste classification, it could be seen that all three metals tested significantly exceeded limits according to the Directive for Solid waste disposal, EPA 658/09 [30], while the values for Pb (1313 mg/L) also exceeded the limit value according to the Waste classification guidelines (2009) [31]. These results indicate that examined

mine tailing represents hazardous waste that needs to be treated prior to disposal.

Table 2. Pseudo-total metal contenting the initial sample of mine tailing (mg/kg)

Metal	Value	Limit value ^a	Limit value ^b
Cu	406	60	-
Pb	1313	300	400
Zn	740	200	-

^aSolid waste disposal, EPA 658/09, 2009; ^bwaste classification guidelines, Part 1, Department of Environment, Climate Change and Water NSW, 2009

Sequential extraction of untreated sediment sample

The results obtained by performing sequential extraction on raw sludge sample are summarized in Figure 1. On the y-axis the percentages of extracted metals were presented in relation to the pseudo-total metal content. The following reduction of metal mobility can be observed in raw sludge sample: Pb > Zn > Cu.

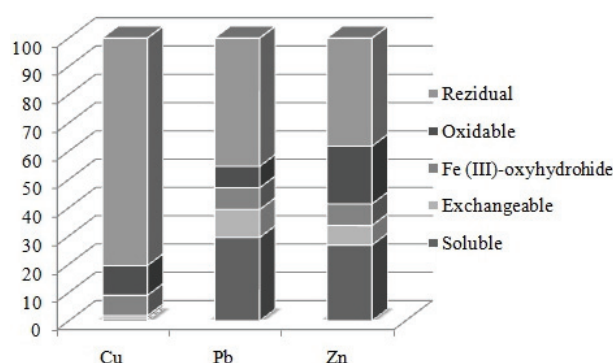


Figure 1. Distribution of Cu, Pb and Zn in sequential extraction fraction (%) of untreated sample of mine tailing.

The results of sequential extraction are not in full agreement with the results of pseudo-total metal concentration in the mine tailing, which only confirms the opinion that the total metal concentration is not sufficient to define the real danger to the environment. Judging from the results of sequential extraction copper is at the highest percentage present in the fifth phase which is the environmentally least dangerous phase, and hence cannot be considered as full-threatening to the environment. Figure 2 shows that the most of Cu was bound in residual fraction (80%) and as such part of total Cu can be considered immobilized. This fraction represents the stable metal forms associated with anthropogenic or geogenic components,

Table 1. Chemical and mineral analysis of raw materials (%)

Material	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	TiO ₂	K ₂ O	Na ₂ O	SO ₃	Loss on ignition (LOI)
Fly ash	39.4	20.1	4.95	4.01	23.2	-	0.64	2.12	1.88	2.01
Red mud	9.04	19.62	48.97	-	4.12	5.21	-	5.68	-	6.23

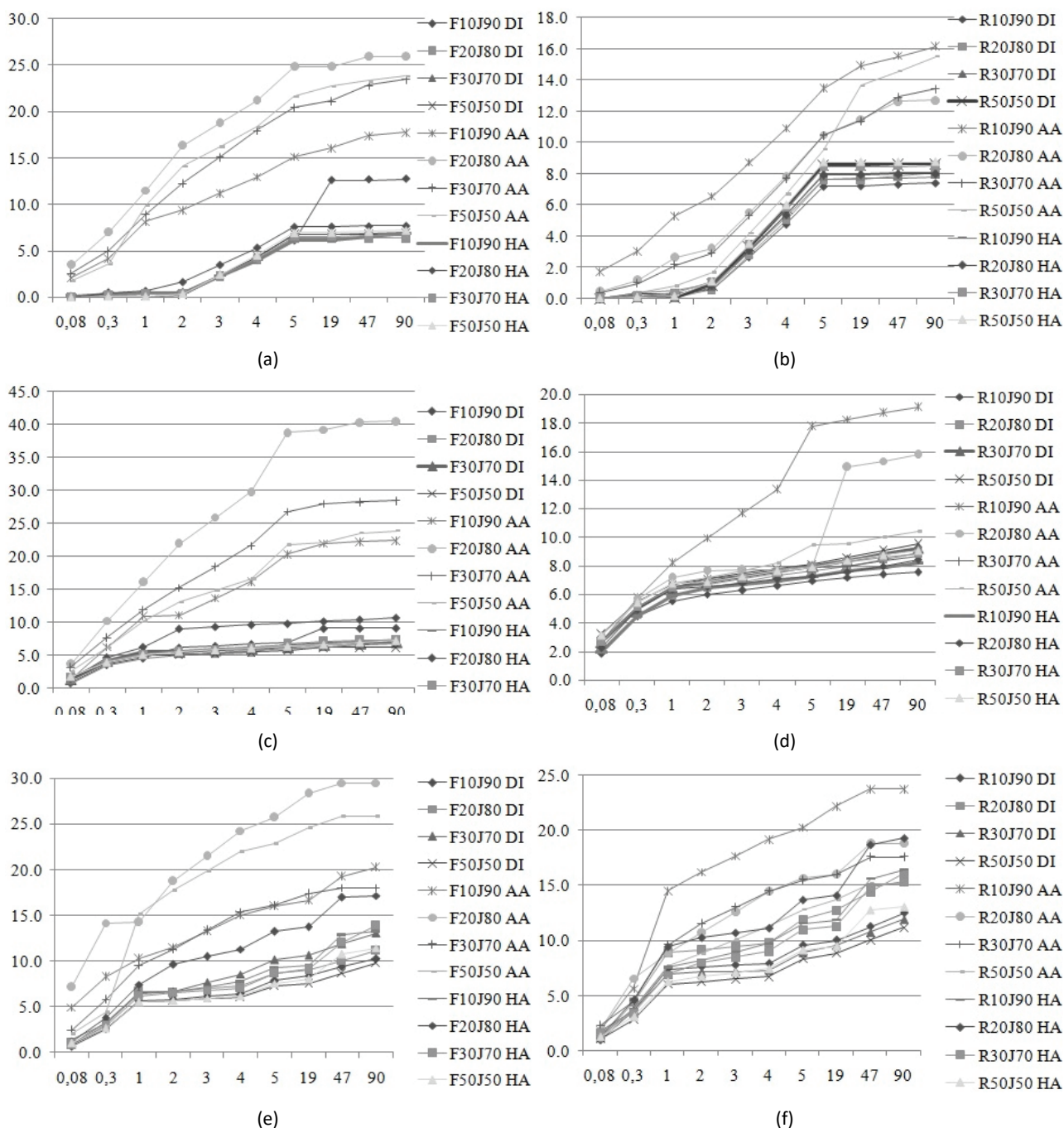


Figure 2. Total cumulative fraction (%) of mine tailing and: a) fly ash for Zn, b) red mud for Zn, c) fly ash for Pb, d) red mud for Pb, e) fly ash for Cu and f) red mud for Cu; leached in ANS 16.1 using deionized water (DI water), acetic acid (AA) pH 3.25, and humic acid (HA) 20 mg TOC L⁻¹ as leachates.

the influence of which on the ecological system is much smaller than the others under the majority of conditions. Percentages of Pb and Zn in this fraction are also high (45 and 38%, respectively), but on the other hand the percentages of these metals are also high in the first fraction (30 and 27%, respectively).

The first fraction is the most dangerous for the environment. Metals in exchangeable fraction can be

exchanged and are in equilibrium with the ionic content in water. This fraction is sensitive to pH variations.

A potential method to determine if the heavy metals can be removed by remediation techniques or predict removal efficiency is to determine speciation with selective extraction techniques [32]. Although Cu, Pb and Zn speciation in mine tailing were different, we applied the same remediation treatments because there are not enough data about the behaviour of

metals differently distributed in their mixture in mine tailing during their S/S treatment, and about the treatment efficiency in general. The main objective of every remediation procedure, dealing with several contaminants, is to carry out the treatment with the same agents, and thus achieve economic and environmental benefits.

ANS 16.1 test

Cumulative release of Pb, Cu and Zn After S/S treatment

The cumulative values of Pb, Cu and Zn leachability from the specimens treated with fly ash, and with red mud are presented in Figure 2.

With the increase in the proportion of fly ash in the mixture the percentage of leach metals decreases, regardless of the leaching solution. However, in the case of Zn, Cu and Pb the lowest percentage of leached metals were in the case of deionized water as a leaching solution (Figure 3). The most effective mixture was

the one with 50% fly ash with the lowest percentage of leach metals. This may be due to the formation of pozzolanic reaction products, such as CSH and CAH, capable of stabilizing metal cations [33]. Therefore, it is plausible to think that these pozzolanic reaction products contributed to Cu, Pb and Zn immobilization by sorption and/or chemical inclusion.

Fly ash contains 23.2% CaO by weight; thus, the addition of fly ash provides lime to calcium-deficient sediment samples. The significant immobilization of metals may be attributed to the inherent alkalinity of fly ash. On the surface of the fly ash the functional oxidized groups are present as SiO₂ and Al₂O₃. The surface of silica (SiO₂) has a high affinity towards metal ions. The central ion of silicates (Si⁴⁺) has a very strong affinity for electrons; therefore, the oxygen atoms that are bound to the silicon ions have a low basicity, making the silica surface acts as a weak acid. The oxygen atoms on the silica surface are free to react with

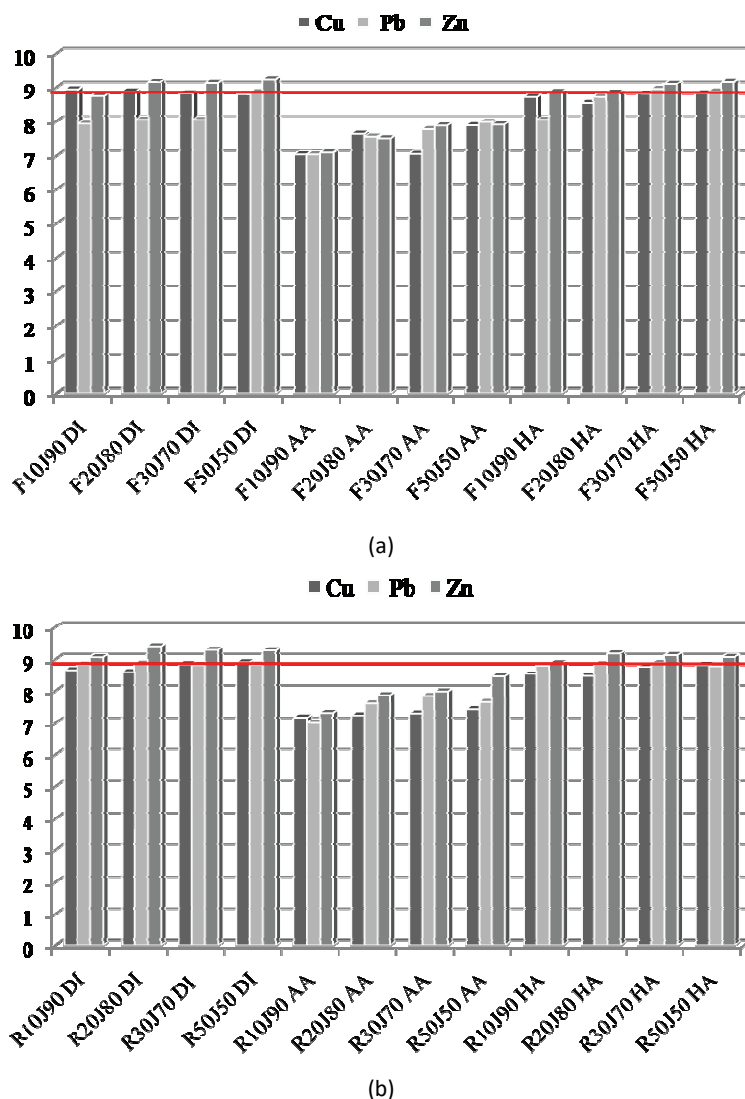


Figure 3. Mean leachability index (LX) for S/S mixtures with: a) fly ash, b) red mud.

water, forming surface silanol (SiOH) groups. The acidity of the silanol (SiOH) groups determines the dependence of the charge of the silica surface on pH. At low pH, a positively charged silica surface results, and at high pH values negatively charged surface prevails. Alumina and iron also show the same phenomenon of developing positive or negative charges depending on pH. The negative charge at an active site on the surface of the fly ash which allows metals (M^{2+}) and metal hydroxides ($M(OH)_2$) to be complexed at the surface [34].

Upon addition of red mud, Pb, Cu and Zn leachability was decreased (Figure 3). The percentages of Pb, Cu and Zn cumulatively leached with the AA solution at pH 3.25 are higher than those obtained using deionized water. In this study, the ANS 16.1 method has been modified using HA solution as a leachant. Being anionic polyelectrolytes, humic substances can react with heavy metal ions, radionuclides, and many other environmental pollutants. Even low concentration of humic substances may significantly influence both free and total metal concentrations, and thus play an important role in the binding and transport of metal ions in the environment. Therefore, the presence of humic substances can strongly influence the fate of metal ions, and potentially impact on the remediation. If we compare the results of using HA as a leachant (mimicking landfill conditions), we can see that the percentages of tested metals leached from all mixtures are lower than those obtained using AA solution.

Red mud can be efficient in the adsorption of heavy metals. Because of its high pH, red mud can be used as an adsorbent for surface precipitation and adsorption of heavy metals. Red mud also has a strong binding capacity for heavy metals [35,36] because its finely grained particles have a high surface/volume and high charge/mass ratios.

The controlling leaching mechanism

The controlling leaching mechanisms can be evaluated using the diffusion model developed by de Groot and van der Sloot [6].

The type of leaching mechanism that controls the release of metals can be determined based on the values of the slope of the logarithm of cumulative fraction release, $\log B_t$, vs. the logarithm of time, $\log t$, line, represented by Eq. (3).

The controlling leaching mechanisms were evaluated using the described diffusion model for the case of leaching with deionized water (Table 3).

Generally, the slope values obtained indicate that Pb, Cu and Zn release from treated samples was mainly controlled by diffusion. The slope values for most mixtures were in the range from 0.40 to 0.60. Exceptions are the mixtures of mine tailing and low content of both immobilization agents (F10J90, F20J80, R10J90 and R20J80) where slope values were slightly lower than 0.4, and on the basis of these values it can be concluded that the dominant mechanism for leaching was surface wash-off.

Table 3. Regression analysis results for Pb, Cu and Zn release

Sample	Pb		Cu		Zn	
	Slope	R^2	Slope	R^2	Slope	R^2
F10J90 DI	0.37	0.97	0.39	0.98	0.58	0.99
F20J80 DI	0.41	0.97	0.37	0.97	0.61	0.97
F30J70 DI	0.40	0.99	0.40	0.99	0.59	0.98
F50J50 DI	0.42	0.98	0.41	0.99	0.60	0.99
R10J90 DI	0.39	0.97	0.36	0.99	0.62	0.99
R20J80 DI	0.39	0.97	0.38	0.98	0.62	0.98
R30J70 DI	0.42	0.99	0.40	0.99	0.60	0.97
R50J50 DI	0.40	0.98	0.40	0.98	0.58	0.98

Effectiveness of S/S Treatment

Diffusion coefficients (D_e) for treated samples, computed by Eq. (1), are listed in Table 4. As can be seen from the table, the diffusion coefficients for Pb in treated samples ranged from 10^{-7} to 10^{-8} $cm^2 s^{-1}$ (low mobility), for Cu from 10^{-8} to 10^{-10} $cm^2 s^{-1}$ (low mobility) and for Zn from 10^{-8} to 10^{-9} $cm^2 s^{-1}$ (low mobility). The mobility for all three tested metal was higher when

Table 4. Mean effective diffusion coefficient D_e ($cm^2 s^{-1}$)

S/S mixture	Metal								
	Pb			Cu			Zn		
	DI	AA	HA	DI	AA	HA	DI	AA	HA
F10J90	2.7E-08	1.7E-07	2.2E-08	4.8E-08	1.6E-07	4.1E-08	1.1E-08	1.2E-07	1.1E-08
F20J80	2.1E-08	5.7E-07	4.7E-08	5.6E-08	4.1E-07	6.8E-08	9.2E-09	4.5E-07	1.4E-08
F30J70	2.1E-08	3.3E-07	2.5E-08	3.1E-08	1.7E-07	3.3E-08	1.1E-09	2.2E-07	1.9E-08
F50J50	3.1E-08	2.9E-07	2.9E-08	2.2E-08	3.4E-07	3.1E-08	1.7E-09	2.4E-07	1.4E-08
R10J90	3.3E-08	1.3E-07	3.5E-08	3.5E-10	2.2E-07	6.4E-08	1.4E-09	7.9E-08	1.7E-08
R20J80	3.0E-08	3.9E-08	3.1E-08	7.6E-10	1.1E-07	7.4E-08	1.2E-09	3.5E-08	1.4E-09
R30J70	3.3E-08	3.2E-08	2.9E-08	1.6E-09	1.1E-07	3.8E-08	1.3E-09	3.1E-08	1.3E-09
R50J50	3.2E-08	4.8E-08	3.5E-08	1.7E-09	8.1E-08	3.1E-08	1.3E-09	2.7E-08	1.7E-09

leaching was carried out with the AA and HA solutions. This finding is in agreement with the results of cumulative release of the three metal ions from the S/S-treated mixtures.

The effectiveness of stabilisation treatments using various agents was assessed by determining the *LX* values (Eq. (2)). All the applied treatments of mine tailing with DI and HA leachate solutions were effective in Zn immobilization because *LX* values for treated samples are higher than 9, and all of them can be considered acceptable for “controlled utilization” (Fig. 3). As for lead and copper, when the leachability test was performed with all three leachability solution the *LX* value were lower than 9, which mean that the treatments employed may be considered efficient, but only if the treated waste are about to be disposed of in segregated or sanitary landfills.

TCLP, MWLP, DIN leaching test

The TCLP [23] was specifically designed to mimic acidic conditions in a sanitary landfill and identify wastes that have the potential to contaminate ground water. The results of the TCLP on treated samples are presented in Table 5.

Table 5. Leaching of metals according to TCLP test (mg/L); LV – limit values for metals according to TCLP procedure

S/S mixture	Cu	Pb	Zn
F10J90	1.05	1.54	9.92
F20J80	0.50	1.43	4.28
F30J70	0.56	1.37	9.47
F50J50	0.53	1.63	7.81
R10J90	0.40	2.57	7.98
R20J80	0.93	1.85	9.40
R30J70	0.36	1.18	2.84
R50J50	1.16	1.07	0.72
LV	5	5	50

None of the S/S samples with the addition of fly ash exceeded 25 mg/L for Cu, 250 mg/L for Zn and 5 mg/L for Pb, which means that all the samples are eligible for disposal. The addition of fly ash has an obvious positive effect on metal immobilization. All S/S samples with red mud are satisfactory from the aspect of all three tested metals.

MWLP [25] test is useful in predicting long-term leaching characteristics of heavy metals from industrial waste when they come in contact with acid drainage at the site of waste disposal in the long term period. It is expected that MWLP test provides more precise simulation of the conditions in the area of the mine tailings treatment than TCLP.

Table 6 shows the testing results of the S/S process efficiency using different agents applying MWLP test.

From the test results it can be seen that all three tested metals do not exceed the limit values for leaching from treated mine tailing. This means that mine tailing treated with fly ash and red mud represents a non-hazardous waste according MWLP test.

Table 6. Leaching of metals according to MWLP test (mg/L); LV – limit values for metals according to TCLP procedure

S/S mixture	Cu	Pb	Zn
F10J90	1.03	2.02	12.2
F20J80	0.66	2.36	11.1
F30J70	0.63	2.46	11.2
F50J50	0.31	1.76	7.93
R10J90	0.37	1.11	9.40
R20J80	<DL	0.64	2.37
R30J70	<DL	0.58	<DL
R50J50	<DL	0.96	0.94
LV	25	5	50

Table 7 presents the results of the DIN 3841-4 S4 test [24]. A great majority of leached concentrations are lower than those in the TCLP, as this test uses deionised water as a leachant.

Table 7. The amount of leached metal (mg/kg) from the S/S samples according to DIN 38414-4 test

S/S mixture	Metal			pH
	Cu	Pb	Zn	
F10J90	0.23	2.67	3.59	7.3-8
F20J80	0.18	4.19	3.28	
F30J70	0.21	4.02	2.78	
F50J50	0.15	2.43	2.96	
R10J90	0.12	1.46	2.66	
R20J80	0.55	4.01	7.50	
R30J70	0.17	2.86	2.86	
R50J50	0.41	1.66	2.81	
Value LAGA Z2 ^a	2	1	4	7-12.5
A ^b	2	0.5	4	
B ^c	50	10	50	≥6

^aUpper recommended value of use; ^bmaximum allowed concentration for accepting waste as inert, *L/S* = 10 L/kg; ^cmax allowed concentration for accepting waste as non-hazardous, *L/S* = 10 L/kg

Mixtures, for which the concentrations of metals are above LAGA22-values [37], defined by the German National Working Group on Waste, can be used but they must be properly deposited or subjected to additional treatment in order to reduce the release of pollutants. Table 7 shows that, in terms of the leached metal concentrations, all S/S mixtures can be considered as inert, except from the aspect of Pb. The same results were obtained regarding the criteria for depositing prescribed by the European Union

(2003/33/EC) [38], while the S/S mixtures from the aspect of Pb can be considered as non-hazardous.

CONCLUSION

This work focuses on studying different factors influencing the process of metal leaching from mine tailings stabilized with fly ash and red mud. Based on these results it can be concluded that the fly ash and red mud can be effectively used for the immobilization of metals in the mine tailings.

The assessment of the mine tailing, based on the pseudo-total content of metals, showed that this waste can be considered as hazardous due to the Cu, Pb and Zn content. The same treatment was applied despite of the fact that the results at the beginning of the experiment gave different distribution and availability of metals. Also, it was shown that stabilization is effective regardless of the oxidation state of lead, copper and zinc. The single extraction tests TCLP, DIN 3841-4 S4 and MWLP were applied to evaluate the extraction potential of Cu, Pb and Zn in S/S matrices. The results showed that all S/S samples can be considered as non-hazardous. Based on the *LX* values and diffusion coefficient and results it appeared that the distribution of metals in the starting mine tailing did not influence the efficiency of treatment.

It can be concluded that the solidification/stabilization technique has significant potential in terms of solving problem with tailings from mine "Sase" (Bosnia and Herzegovina) and, at the same time, problems of huge quantities of fly ash and red mud. Obtained S/S mixtures can be undergo by "controlled utilization" or safely disposed at the sanitary landfill. Since fly ash and red mud are itself considered wastes, their use to treat contaminated media would be, at the same time, a cost-effective method of its disposal and mitigating possible negative environmental effects, through proper engineering control.

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IZVOD**ZELENA REMIDIJACIJA JALoviŠTA RUDNIKA POMOĆU NEORGANSKIH AGENASA**

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Uvećavanje količine otpadnog materijala iz industrijskih aktivnosti u različitim procesima postaje sve urgentniji problem budućnosti. U radu je prikazan problem jalovišta rudnika "Sase" (Republika Srpska, Bosna i Hercegovina) sa visokim sadržajem metala (Pb, Cu i Zn). Deponija ove jalovine predstavlja potencijalnu opasnost za vode u blizini ove lokacije. Izabran proces remedijacije je bio stabilizacija/solidifikacija (S/S). Neorganski agensi koji se koriste u ovom radu su leteći pepeo i crveni mulj koji predstavljaju srednji industrijski otpad generisan na lokacijama relativno blizu rudnika. Zbog toga, njihova primjena može da se koristi kao primjer održivog rješenja regionalnog problema životne sredine. Dalja istraživanja odnose se na uticaj različitih faktora na izluživanje metala iz stabilizovane/solidifikovane jalovine korišćenjem navedenih imobilizacionih agenasa. Učinak imobilizacije istraživanja je korišćenjem nekoliko testova izluživanja: ANS 16.1, TCLP, DIN i MWLP. Rezultati su pokazali da se svi S/S uzorci mogu smatrati neopasnim otpadom, kao i sve koncentracije izluženih metala prema utvrđenim kriterijumima. Ovi rezultati će dodatno omogućiti modeliranje ponašanja metala tokom dugotrajnog izluživanja od tretirane jalovine rudnika. Podaci su od neprocjenjive vrijednosti u smislu ekonomskog i ekološki prihvatljivog upravljanja jalovištom rudnika.

Ključne reči: Lebeći pepeo • Crveni mulj
• Jalovište rudnika • Stabilizacija/solidifikacija • Zelena remedijacija