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Assessing the possibility of solidification and stabilization of pyrite cinder by using quicklime and fly ash

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Abstract

The aim of this study was to determine the possibility of using two low-cost binders, quicklime and fly ash for the solidification/stabilization (S/S) of pyrite cinder. Pyrite cinder, used in this study, represents a remnant from sulfuric acid production in fertilizer factory IHP "Prahovo" A.D. (Serbia), and has a very high toxic metal content. High contents and leachability of copper, lead and zinc make this waste material hazardous, representing an extraordinary risk to the environment. In order to determine the leaching behavior of the S/S mixtures, four single-step leaching tests were performed, each one having a different sort of leaching fluid (deionized water, inorganic and organic acidic solutions). X-ray diffraction (XRD), scanning electron microscope (SEM) and energy dispersive X-ray analyzer (EDS) were implemented to elucidate the mechanisms responsible for immobilization of Cu, Pb and Zn. Overall, the test results indicated that S/S treatment using both quicklime and fly ash was effective in immobilizing these metals, especially when there is a higher share of binder present. Treated waste can be safe for disposal and even considered for "controlled utilization". Furthermore, the use of fly ash for S/S treatment of pyrite cinder solves the disposal problems of two waste types, as it also represents a secondary industrial product.

Keywords: pyrite cinder, stabilization/solidification, metals, hazardous waste, fly ash, batch leaching test.

1. INTRODUCTION

Pyrite cinders are generated as a by-product of sulfuric acid industry. Annually, a large amount of sulfuric acid (more than hundred million tons) is produced worldwide (Tveit 2003), and in Serbia almost 500,000 tons. Pyrite cinders are mainly composed of iron oxides in the form of hematite and magnetite, and also contain traces of toxic/hazardous heavy metals such as Cu, Zn, Pb, and As (Álvarez-Valero, Sáez, Pérez-López, Delgado, & Nieto 2009; Vinals, Balart, & Roca 2002), which limit their usage in pig iron industry (Tugrul, Derun, & Piskin 2006; 2007). Furthermore, pyrite cinders are characterized by their fine size and can often lead to problems with dust in the surrounding area of the surface disposal site. In Serbia this waste is disposed on landfills without any form of

protection. The increasing dump not only occupies plenty of land, but the most important problem is that it puts a serious threat to the environment due to water pollution.

In this study, a stabilization/solidification (S/S) process was used in order to remediate pyrite cinder. Thus far, several studies have been carried out on pyrite cinders utilization and treatment (Alp, Deveci, Yazıcı, Türk, & Süngün 2009; He et al. 2010; Legodi & de Waal 2007; Liu & Zheng 2011; Querol et al. 2006; Tugrul et al. 2007; Vamerali, Bandiera, & Mosca 2011; Zheng & Liu 2011), but very few on using solidification and stabilization. S/S technology is widely applied to immobilize heavy metals in contaminated soils and sludges with various additives (Conner 1990; M. B. Dalmacija, Prica, Dalmacija, Roncevic, & Rajic 2010; Dermatas & Meng 2003; Jing, Meng,

& Korfiatis 2004; Moon & Dermatas 2007; Prica et al. 2012). Also, it is widely used for treatment of hazardous wastes that are mostly inorganic before their final disposal (Pereira, Rodríguez-Piñero, & Vale 2001) and it is viable for most metallic waste streams (Conner 1990). At the moment there is not enough data about S/S treatments of pyrite cinders. Conclusions obtained for soils cannot be fully extrapolated for this material.

During S/S applications, the toxic constituents which are present in 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. If established by the regulations, the stabilized wastes can be acceptable for landfill disposal or even used for construction purposes, such as road subgrade, backfill and base material. Quantifying the environmental impact of S/S materials in real environment scenarios is crucial for selecting proper disposal and reuse alternatives and for certification of immobilization technologies. The performance of S/S treated wastes is generally measured in terms of leaching tests (Jing et al. 2004). Batch leaching tests, with single extraction, are the preferred choice for regulatory assessment due to their simplicity, improved reproducibility, and shorter time requirements. The most often used leaching test, recommended by the USEPA, is the Toxicity Characteristic Leaching Procedure — TCLP test (USEPA, 2002b). The national regulations require that the concentrations of specific compounds in the TCLP leachate are compared to national regulatory values for examining toxicity characteristic of waste intended for disposal (Gazzete 2010). Also, the comparison with EPA regulatory levels (Hazardous Waste Identification 2005) was done. Synthetic Precipitation Leaching Procedure — SPLP tests were developed by the USEPA in order to assess metal mobility in wastes (USEPA 2002a). The SPLP is conducted in a similar fashion as the TCLP with the exception of the leaching fluid. SPLP leachate concentrations are commonly compared to the groundwater and drinking water quality standards (Erdem & Özverdi 2011). Here, the leached concentrations were compared to national standards for drinking water (Gazzete 1998) and with EU Directive 98/83/EC. The Waste Extraction Test — WET is used in California, US, in a similar manner as the TCLP (determination of whether a solid waste is a hazardous waste), and leached metal concentrations are compared with WET limit values (CCR 1998). One of the frequently used tests is also German Standard leaching test - DIN 3841-4 S4 stipulated by European Union Council as standard leaching test for determination of general characteristics of waste materials and sludge. Results of this test are interpreted using national regulation (Gazzete 2010; ?) and European waste disposal criteria regulated by Eu-

ropean Union (Council 2003), which are fully in accordance.

In this paper quicklime and fly ash were used as low-cost binders for S/S treatment. Lime is widely used as a stabilizing agent for acid mine soils and tailings (Davis, Eary, & Helgen 1999; Fernández-Caliani & Barba-Brioso 2010). It acts as a cementitious agent by producing highly alkaline conditions, in which silica and alumina go into solution and react with the available calcium to form pozzolanic products, increasing strength, impermeability and durability to chemical attack (Chrysochoou & Dermatas 2006). Owing to its pozzolanic nature, fly ash can be used in a variety of construction applications del Valle-Zermeño, Formosa, Chimenos, Martínez, and Fernández (2013). Namely, combustion of bituminous coal produces fly ash rich in calcium, with self-cementing characteristics, and the pozzolanic reactions lead to calcium aluminum and calcium silicate hydrate (CAH and CSH) cementations product formation. In addition, it has been reported that 26% of the total quantity of fly ash produced annually in the U.S. is used in construction materials (Moon & Dermatas 2007) but in Serbia, there is still very limited use of fly ash. Thus, fly ash can be used as an alternative material for stabilization with additional benefits, such as the reduced purchasing cost, and the minimization of fly ash disposal cost. Finally, by using fly ash as a stabilizing agent for pyrite cinder treatment – immobilization and disposal of different waste types is achieved.

The main study objectives can be summarized as follows: (1) assessment of the characteristics of pyrite cinder and evaluation of its environmental risk, (2) S/S treatment of pyrite cinder (with the addition of quicklime and fly ash), (3) evaluation of the effectiveness of S/S treatment by assessing the leaching potential and environmental impact based on the different leaching procedures, (4) investigation of S/S matrices binding mechanisms in the micro-scale by scanning electron microscopy equipped with energy dispersive X-ray spectrometer (SEM-EDS) and X-ray diffraction (XRD).

2. MATERIALS AND METHODS

2.1. Material collection and characterization

Pyrite cinder was obtained from IHP “Prahovo” A.D., Serbia, as a remnant in fertilizer production. Mineral composition was determined using X-ray diffraction (XRD) and X-ray fluorescence (XRF) analyzer (Bruker D4 Endeavor and Bruker S8 Tiger). The mineral composition was as follows: alite (2.21%), free lime (0%), periclase (0.09%), quartz (11.9%), anhydrite (0%), calcite (0.62%), mulite (2.30%), magnetite (4.69%), hematite (74.6%), thenardite (0.03%), rutile (0.89%), plagioclase (2.02%), K-feldspar (0.01%), cristobalite (0.12%),

gehlenite (0.48%), fly ash-amorph (0.01%). Quicklime used was commercial containing 99% of CaO. Carbon coal fly ash was provided from the Kolubara (Serbia) thermal power plant. Mineral composition of fly ash was also determined by using XRD-XRF analysis, and it was as follows: alite (0.17%), free lime (0.10%), periclase (0.26%), quartz (19.6%), anhydrite (0.60%), calcite (0.04%), mulite (10.6%), magnetite (0.87%), hematite (1.07%), thenardite (0.15%), rutile (0.48%), plagioclase (5.00%), K-feldspar (1.25%), cristobalite (0.95%), gehlenite (1.63%), fly ash-amorph (57.1%).

All materials were characterized in order to determine moisture content, loss on ignition, particle size distribution, Brunauer–Emmett–Teller (BET) specific surface area and micro-pore analysis ($V - t$ method). The contents of dry and organic matter (for pyrite cinder and fly ash) were determined by drying 5–10 g of sample at 105°C to a constant mass, and then heating to 550°C to determine the ignition loss according to the so-called NEN procedures of the Netherlands Normalization Institute (NNI): NEN 5754:1994. BET specific surface areas and micro-pore analysis of pyrite cinder, quicklime and fly ash were determined from the 77 K N₂ adsorption-desorption isotherms in a Quantachrome Autosorb iQ2.

For characterizing pyrite cinder and fly ash in terms of metal leaching and establishing total metal content, TCLP test (USEPA, 2002b) and pseudo total trace metal contents (USEPA 3051a, 2007), were assessed on sample triplicate. The standard method and mean values were used. The relative standard deviations (% RSD) obtained ($n = 3$) were below 10%. Leached concentrations and metal content were determined by AAS (Perkin Elmer AAnalyst™ 700) according to the standard procedure (USEPA 2007b) USEPA (2007c). All the results are expressed with respect to material dry matter. All materials in contact with the leachant were pre-cleaned with HNO₃ and subsequently rinsed with deionized water.

2.2. Sample preparation

All materials were firstly dried at 105°C to the constant mass and then mixed in established proportions, in order to create stable and durable S/S matrices. Samples were designated by the capital letter (*P*: pyrite cinder, *L*: lime, *F*: fly ash) followed by a number indicating the percent weight of the given attribute. The content of each material was expressed as percentage of the total solids by weight. For the leaching tests, 10 types of samples (containing 30, 50, 80, 90 and 95 % of each binder) were prepared according to ASTM D1557-12e1 (2015). Samples were prepared in the form of monolithic cubes ((3 ± 0.1) × (3 ± 0.1) × (3 ± 0.1) cm) by compaction at optimum water content, defined as the water content at which

the sediment can be compacted to the maximum dry unit weight using modified compactive effort. Typically, cohesive soils and sediments at the optimum water content can be squeezed into a lump that barely sticks together when hand pressure is released, but will break cleanly into two sections when "bent" (Dalmacija et al., 2011). After 28 days, the monolithic samples were crushed and then subjected to the leaching experiments. Leached concentrations of metals were determined by AAS (Perkin Elmer AAnalyst™ 700) according to the standard procedure (USEPA 2007b; 2007c).

2.3. Single-extraction leaching tests

2.3.1. Toxicity Characteristic Leaching Procedure – TCLP test

According to the USEPA protocol (USEPA 2002b) a 0.1 M acetic acid solution with a pH of 2.88 was used to extract control sample and S/S-treated samples since the pH was above 5. The samples were extracted at a liquid to solid (L/S) ratio of 20 in capped polypropylene bottles on a rotary tumbler at 30 rpm 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.

2.3.2. Synthetic Precipitation Leaching Procedure – SPLP test

The SPLP test was performed in the same manner as the TCLP. The extraction fluid was made of two inorganic acids (nitric and sulfuric acid) to simulate acidic rainwater (pH 4.2). In a similar fashion as the TCLP, a 100-g sample of waste material was placed in a 2-liter extraction vessel and mixed with the extraction fluid. The mixture was rotated for 18 ± 2 h at 30 rpm. The leachate was then filtered through a 0.45 μm pore size membrane filter (USEPA 2002a). This test was applied on every sample in triplicate.

2.3.3. Waste Extraction Test – WET

The WET (CCR, 1998) is similar to the TCLP as it uses a buffered organic acid solution as the extraction fluid. This test used a pH buffered citrate acid solution with sodium hydroxide, a 10 : 1 L/S ratio, and a 48-h testing period. The WET extraction solution was prepared with a combination of 0.2 M citric acid solution and 4.0 N NaOH to pH 5.0 ± 0.1 . One liter of this solution was added to a 100-g sample and rotated for 48 h. After rotation, the final pH was measured, and the samples were filtered through a

0.45 μm pore size membrane filter. This test was applied on every sample in triplicate.

2.3.4. German standard leaching test – DIN 3841-4 S4

This test used a grained sample with particle size smaller than 10 mm. Leaching was performed with deionized water at a 10 : 1 L/S ratio, and a 24-h testing period. After rotation, the final pH is measured, and the samples were filtered through a 0.45 μm pore size membrane filter. This test was applied on every sample in triplicate.

2.4. Characterization of the specimen mixtures

To ascertain the mechanism of heavy metal immobilization and other micro structural properties, X-ray diffraction (XRD) and scanning electron microscope (SEM) analyses were performed on the prepared monolithic matrices of 28 days of age, before leaching tests. The monolithic matrices were crushed and dried, ground to powder and then subjected to XRD and SEM analyses. For the XRD data collection a Philips PW1710 automated X-ray powder diffractometer was used. SEM photographs of the samples were carried out on a Jeol, JSM-6460LV with INCA X sight program. Matrices with 70% of pyrite cinder and 30% of quicklime and fly ash were characterized.

3. RESULTS AND DISCUSSION

3.1. Characterization of the specimen mixtures

Results obtained from initial material characterization are presented in Table 1. Surface analysis indicates that there is a significant difference between BET surface areas of quicklime and fly ash. Fly ash has a considerably larger surface area, as well as double the micro-pore content, which can all contribute to metal encapsulation.

Table 1. Characteristic of pyrite cinder, quicklime and fly ash

| Parameter | Pyrite cinder | Quicklime | Fly ash |
|---|---------------|-----------|---------|
| Moisture content (%) | 0.481 | 0.302 | 0.210 |
| Loss on ignition (%) | 2.43 | – | 2.18 |
| BET (m ² g ⁻¹) | 7.01 | 3.15 | 10.9 |
| Micro-pore test (m ² g ⁻¹) | 2.86 | 0.938 | 6.90 |

In Table 2, TCLP results of untreated sample of pyrite cinder and fly ash are presented. Leached concentrations of Cu, Pb and Zn in pyrite cinder exceed national regulatory values for examining toxicity characteristic of waste intended for disposal. Also, leached concentration of lead

is greater than EPA regulatory levels for toxicity characteristic of waste which classifies it as hazardous. Leached metal concentrations of fly ash did not exceed any of the proposed limits.

Table 2. Leached concentrations of toxic metals after TCLP test of pyrite cinder and fly ash sample and their comparison with relevant standards

| Metals | Pyrite cinder | Fly ash | I | II |
|--------|-------------------|-----------------|-----|----|
| | mgL ⁻¹ | | | |
| Cd | 0.421 ± 0.0156 | 0.03 ± 0.002 | 1 | 1 |
| Cr | 2.16 ± 0.0324 | 2.27 ± 0.0245 | 5 | 5 |
| Cu | 211 ± 11.4 | 1.15 ± 0.0856 | 25 | – |
| Ni | 6.28 ± 0.132 | 6.26 ± 0.523 | 20 | – |
| Pb | 13.8 ± 0.538 | 0.0451 ± 0.0151 | 5 | 5 |
| Zn | 278 ± 19.2 | 2.43 ± 0.362 | 250 | – |

I – National regulations for examining toxicity characteristic of waste intended for disposal

II – EPA regulatory levels for toxicity characteristic of waste

TCLP results are in the accordance with the pseudototal metal content, which shows the highest share of copper, lead and zinc. Pyrite cinder contains 1492 ± 62.7 mgkg⁻¹ of Cu, 2130 ± 91.6 mgkg⁻¹ of Pb and 914 ± 28.3 mgkg⁻¹ of Zn.

3.2. Leaching tests

TCLP was specifically designed to mimic acidic conditions in a sanitary landfill and identify wastes that have potential to contaminate ground water. The results of the TCLP test on treated samples are presented in Fig. 1. The pH of the leachate after the test performance varied from 4.9–5.2 for samples with fly ash, and for samples with quick-

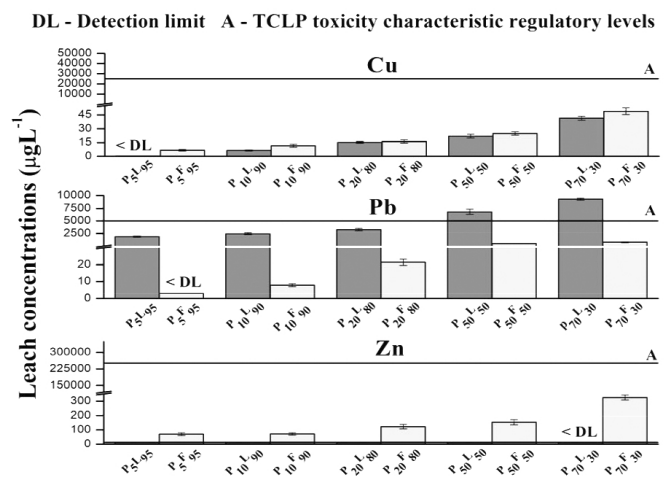


Figure 1. Leached concentrations of Cu, Pb and Zn in S/S specimens according to TCLP test

lime it varied from 11.8 to 12.1. None of the S/S samples

with the addition of fly ash exceeded 25 mg l^{-1} for Cu, 250 mg l^{-1} for Zn and 5 mg l^{-1} for Pb, which makes all specimens eligible for disposal. Addition of fly ash has an obvious positive effect on metal immobilization. All S/S samples with quicklime are satisfactory from the aspect of Cu and Zn. All zinc concentrations were under detection limit of $11 \mu\text{g l}^{-1}$. Lead was leached when matrices contained 50 and 70% percent of pyrite cinder, thus making the S/S matrices with 20, 10 and 5% of hazardous waste safe for disposal.

The SPLP test reproduces acid rain conditions and estimates metal mobility when wastes are disposed in an open area. Fig. 2 presents leaching concentrations after SPLP test. The pH of the leachate varied from 7.1–7.6 in the samples with fly ash, and in all the samples with

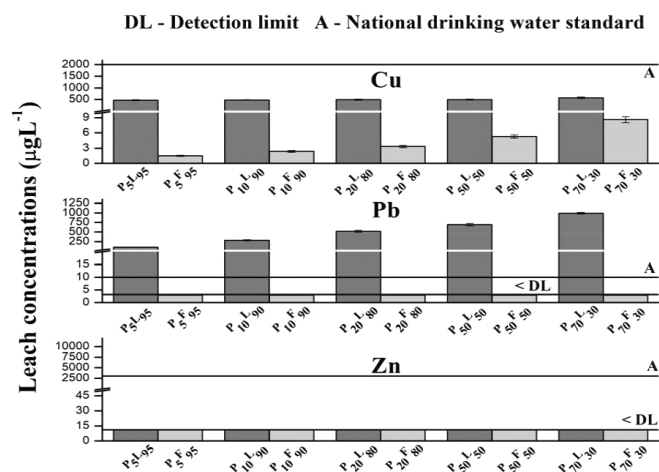


Figure 2. Leached concentrations of Cu, Pb and Zn in S/S specimens according to SPLP test

quicklime pH was around 12.6. Lower concentrations of metals were leached in SPLP than TCLP in most samples. This is consistent with literature (Janin, Blais, Mercier, & Drogui 2009; Townsend et al. 2004). Differences in metal leachability between TCLP and SPLP might result from several factors. Depending on the alkalinity of the waste tested, changes in the solution pH that occur during the 18 h of leaching may differ between SPLP and TCLP, and thus result in different amounts of metal leaching. Another factor is the complexation ability of the acid used in the leaching fluid, as TCLP uses acetic acid solution and SPLP uses the inorganic acids solution mixture. The anions resulting from organic acids such as citric or acetic acid can complex metals causing them to leach in greater concentrations (Townsend et al. 2004). SPLP is frequently used to assess the risk to groundwater posed by contaminated soils and in the risk assessment process for determining beneficial use of solid wastes. All S/S matrices complied with the regulations concerning Cu and Zn. Only S/S matrices with fly ash satisfied the regulations

concerning the leached concentrations of Pb (under detection limit), while specimens with quicklime exceeded those regulations, and thus should not be disposed to unlined landfills. Fig. 3 shows the results of WET test on treated samples. pH values of the leachant in samples

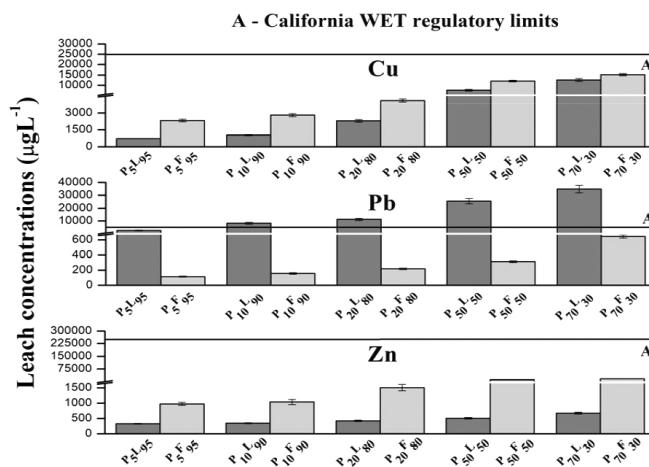


Figure 3. Leached concentrations of Cu, Pb and Zn in S/S specimens according to WET test

with fly ash after the testing period varied between 5.8–6.7, and in samples with quicklime were 12.1–12.4. Concentrations of Cu, Pb and Zn were below WET limit values for all matrices containing fly ash. Specimens with quicklime are also in compliance with WET standards concerning Cu and Zn concentrations. From the aspect of Pb, only the sample with 5% of pyrite cinder and 95% of quicklime is acceptable. The WET extracted higher concentrations of metals than TCLP in all samples. This is consistent with literature (Townsend, Dubey, Tolaymat, & Solo-Gabriele 2005; Townsend et al. 2004). TCLP was conducted at a 20 : 1 liquid-to-solid ratio and WET was carried out at 10 : 1 liquid to solid ratio; TCLP was two time more diluted compared to WET and in general higher leachate concentrations were observed at lower liquid-to-solid ratio (Townsend et al. 2004). The greater element concentrations observed in the WET leachates relative to the TCLP leachates most likely result, however, from citrate's propensity to chelate metals. Other leaching studies support this conclusion (Hooper et al. 1998; Townsend et al. 2004). Citric acid has multidentate ligands while acetic acid has monodentate ligands, and in general, complexes with monodentate ligands are less stable than those with multidentate ligands (Stumm & Morgan 1996). Greater share of quicklime and fly ash in samples resulted in metal leachability reduction. In Fig. 4 the results of DIN 3841-4 S4 test are presented. Great majority of leached concentrations are lower than those in TCLP test, as this test uses deionized water as a leachant. pH values of the leachant, in S/S samples containing fly ash, after the testing period

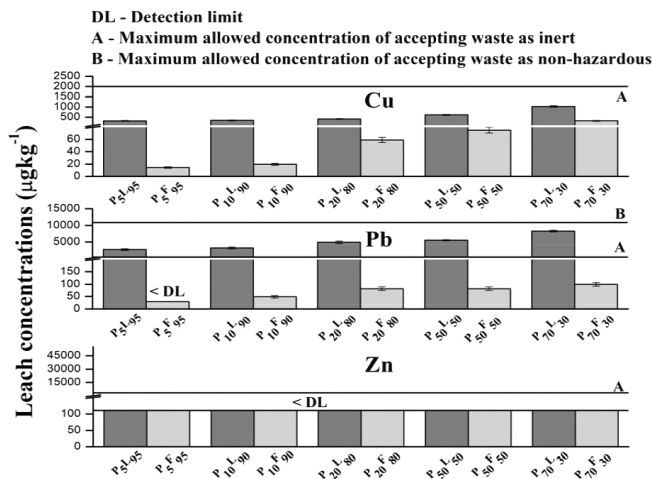


Figure 4. Leached concentrations of Cu, Pb and Zn in S/S specimens according to DIN 3841-4

was finished varied between 8.3–10.0, and in all samples with quicklime pH was around 12.2.

Results are interpreted using national regulation for testing parameters of waste and leached liquids for inert, non-hazardous and hazardous waste landfills, as well as with European waste disposal criteria regulated by European Union. Concerning this regulations all S/S matrices with quicklime can be classified as inert waste from the aspect of leached concentrations of copper and zinc. Lead concentrations in the leachant exceeded this value, and despite that, it represents non-hazardous waste. S/S specimens with fly ash represent the inert waste in aspect of all leached metals. Overall, in S/S samples with quicklime there is an evident lead leaching compared to other two metals, which can be due to high alkalinity of the leachant $\text{pH} > 12$, where Pb forms soluble hydroxide anion complexes and leaches out (Brewster & Passmore 1994; Jing et al. 2004; Quina, Bordado, & Quinta-Ferreira 2009). Copper and zinc hydroxides are less soluble and at a given pH value they are mostly present in solid oxides and hydroxides (Hage, Van Weert, & Schuiling 1998; Ortiz-Aparicio et al. 2007; Thompson & Kaye 2011). S/S specimens containing fly ash showed very modest metal leaching, proving that this binder is a great immobilizing agent for toxic metals.

Generally, the decrease in the mobility of metals in mixtures can be explained by the occurrence of a pozzolanic reactions between minerals present in pyrite cinder, calcium from lime, calcium and minerals from fly ash (as secondary binding material) and water. In this way, compounds with cement properties such as calcium silicate hydrated gel and calcium aluminate hydrate are obtained (Maubec, Deneele, & Ouvrard 2017). These pozzolanic reactions form a solid, water-resistant gel that has the ability to immobilize trace elements.

3.3. Microstructural characterization of solidified/stabilized sediment matrices

XRD and SEM studies of the matrices were done in order to elucidate the microscopic structures and morphology of surfaces. X-ray diffraction analyses of all mixtures indicated that pozzolanic product formation did take place within the 28-day curing period (Fig. 5). Calcium silicate hydrate (CSH) and calcium hydroxide silicate (CHS) were identified. Some excess lime was also identified, indicating that pozzolanic reactions were definitely not over by the end of the 28-day period. Also, calcium aluminum sulfate hydroxide hydrate products (CAH or ettringite) were confirmed in S/S matrices with quicklime. Overall, pozzolanic product formation, as well as the presence of calcite, gypsum and portlandite, further confirm that these matrices have a possibility to be used in construction materials (Erdem & Özverdi 2011) Patel and Pandey (2012). Fig. 6 shows the morphology of the different S/S matrices at 28 days of age. SEM of hardened S/S matrices reveals a dense microstructure with normal hydration products, calcium silicate hydrate (gel-like flocks) and calcium hydroxide (fibrous-like crystals). Needle-like ettringite is mostly present in S/S specimen with quicklime Dermatas and Meng (2003); Leist, Casey, and Caridi (2003). Formation of ettringite crystals can contribute to swelling and deterioration of the S/S matrices, as well as the increase in matrix porosity that can consequently lead to metal leaching (Kundu & Gupta 2008).

On 2θ of 9, 29 an 49,8 small peaks of tobermorite can be presented. Tobermorite represents a crystalline C–S–H phase ($\text{Ca}_{4.5}\text{Si}_6\text{O}_{16}(\text{OH})\cdot 5\text{H}_2\text{O}$). The layered structure is built up of sheets of Ca polyhedral linked through non-bridging oxygens to chains of silicate tetrahedral on both sides. Tobermorite is also closely related to the structure of amorphous C–S–H phases. In general, three different modes of heavy metal interaction with 11 Å tobermorite can be envisaged as surface complexation, uptake in the interlayer and incorporation (Vespa, Dähn, & Wieland 2014). Both S/S matrices represent systems suitable for the entrapment of heavy metals.

Table 3. Element percentages and ratios of solidified/stabilized (S/S) matrices P70L30 – 70% of pyrite cinder and 30% of quicklime, P70F30 – 70% of pyrite cinder and 30% of fly ash, using energy dispersive X-ray analysis (EDS)

| Specimen | Element (wt %) | | | | | | |
|----------|----------------|------|------|------|------|------|------|
| | O | Mg | Al | Si | K | Ca | Fe |
| P70L30 | 41.4 | 1.28 | 6.49 | 10.4 | 1.23 | 31.4 | 7.83 |
| P70F30 | 46.2 | 2.72 | 8.22 | 12.3 | 1.42 | 8.63 | 20.5 |

Fig. 6a shows raw pyrite cinder sample and it can be noticed that it represents a morphologically uniform material with slight random agglomeration. The presence of

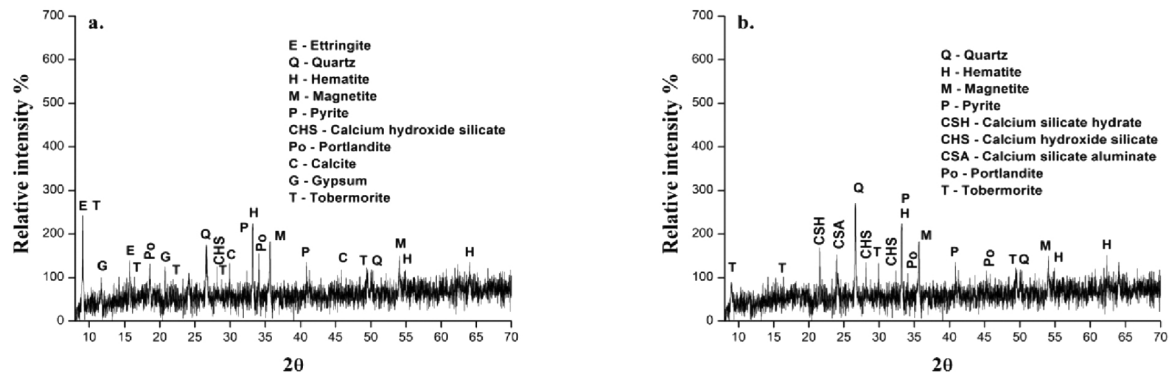


Figure 5. X - ray diffraction (XRD) of the specimens mixtures with (a) P70L30 – 70% of pyrite cinder and 30% of quicklime, (b) P70F30 – 70% of pyrite cinder and 30% of fly ash

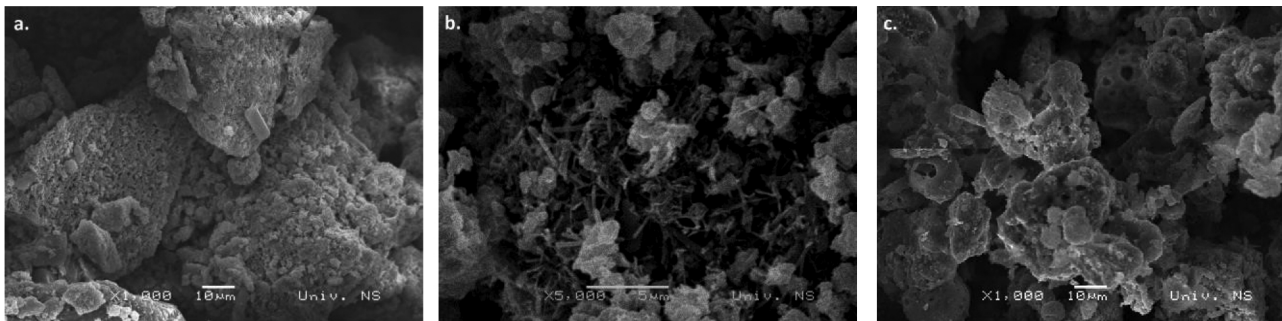


Figure 6. SEM photographs of native pyrite cinder sample and solidified/stabilized (S/S) matrices: (a) pyrite cinder, (b) P70L30 – 70% of pyrite cinder and 30% of quicklime, (c) P70F30 – 70% of pyrite cinder and 30% of fly ash

cavities and the cross-linking pattern of aggregated particles in the pyrite cinder and lime matrix was observed over a 28-day drying period (Fig. 6b). This indicates short-term reactions of lime consumption and possible unavailability of sufficient lime to conduct the pozzolanic reaction to produce cement compounds, creating free space and causing less bonding between particles (Jha & Sivapullaiah 2016). Thin Portland hexagonal crystals have the ability to fill microscopic pores in S/S mixtures. With a longer time period, texture homogeneity will be even better established with the development of many fibrous compounds leading to the formation of a densely packed and compacted structure, with the presence of small white spots, which reflect the consumption of the cement gel of the amorphous structure and particle bonding. The unreacted cement particles were present in the CHS gel, which was also confirmed by XRD analysis (calcite + CHS).

After 28 days, spherical structures characteristic of fly ash are observed, as well as irregularly shaped particles indicating the presence of quartz (Fig. 6c). After 28 days, rhombic quartz crystals are highly presented, and after a longer time period, the quartz particles will be more and more covered with thin, interwoven strips of illite. The presence of illite particles helps to preserve porosity by covering potential quartz nucleation sites (Wang, Han, &

Mu 2018). The figure also suggests the crucial role of fly ash in the growth of hydration products thus creating sticky CSH gel composites. Table 3 shows the EDS data of different S/S matrices. Based on the results, the high yield of silicate and calcium may participate in the formation of calcium silicate hydrate (CSH) and calcium hydroxide silicate (CHS) gel.

Also with aluminate, calcium aluminate hydrates (CAH) or ettringite, and calcium silicate aluminate (CSA) can be formed. This is in a good correlation with literature data (Guo, Shi, & Dick 2010).

Sorption potential of metals on CSH is supposed to be controlled by an important characteristic of CSH. The fact that CSH has a very high specific surface area with irregular hydrogen bonding can facilitate sorption of both water and other alien ions such as metal ions. This was in agreement with results of the XRD pattern.

4. CONCLUSIONS

The assessment of the pyrite cinder, based on the pseudo-total content of metals, as well as the initial TCLP testing showed that this waste can be considered hazardous from the aspect of Cu, Pb and Zn content. The S/S treatment applied, using quicklime and fly ash, appeared to be efficient in the remediation of pyrite cinder containing these

three metals. The single extraction tests TCLP, SPLP, WET and DIN 3841-4 S4 were applied to evaluate the extraction potential of Cu, Pb and Zn. The results showed that in all S/S samples containing fly ash, a very limited leaching of all three metals occurred. Leaching of Cu and Zn in all S/S specimens with quicklime is also very moderate. Only Pb turned out to be problematic, due to high pH of the leachant, causing Pb to form soluble hydroxide anion complexes. Also, evidently higher BET surface and micro-pore content of fly ash, as well as the lack of excessive ettringite formation specimens containing this binder, contribute to better compaction and metal fixation, compared to specimens with quicklime. XRD and SEM analyses confirmed the formation of pozzolonic compounds in all S/S samples, such as CSH, CHS, CSA, ettringite (CAH) etc. The addition of each binder caused a decrease in metal leachability. S/S materials are viable for safe disposal and can be considered as acceptable for "controlled utilization". This may justify the application of the already-expensive remediation procedures, especially when it comes to treating a material containing a mixture of pollutants. In addition, this kind of waste treatment is advantageous from an economic point of view, because in this way hazardous wastes are immobilized and stabilized using low-cost binders. Additional advantage when using a fly ash as immobilizing agent in S/S treatment of pyrite cinder, is managing the disposal of two waste types. These results represent a promising technology in the field of green remediation.

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All authors confirm that there are no financial problems that may lead to a conflict of interest.

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