Leachability and physical stability of solidified and stabilized pyrite cinder sludge from dye effluent treatment

Djurdja V. Kerkez[1], Milena R. Becelic-Tomin, Milena B. Dalmacija, Dragana D. Tomasevic, Srdjan D. Roncevic, Gordana V. Pucar, Bozo D. Dalmacija

University of Novi Sad, Faculty of Sciences, Department of Chemistry, Biochemistry and Environmental Protection, Novi Sad, Serbia

Abstract

The aim of this paper is to explore the possibilities of using solidification/stabilization (S/S) treatment for toxic sludge generated in dye effluent treatment, when pyrite cinder is used as catalytic iron source in the modified heterogeneous Fenton process. S/S treatment was performed by using different clay materials (kaolin, bentonite and native clay from the territory of Vojvodina) and fly ash in order to immobilize toxic metals and arsenic presented in sludge. For the evaluation of the extraction potential of toxic metals and the effectiveness of the S/S treatment applied, four single-step leaching tests were performed. Leaching test results indicated that all applied S/S treatments were effective in immobilizing toxic metals and arsenic presented in sludge. X-Ray diffraction analysis confirmed the formation of pozzolanic products, and compressive strength measurement proved the treatment efficacy. It can be concluded that the S/S technique has significant potential for solving the problem of hazardous industrial waste and its safe disposal.

Keywords: industrial waste, pyrite cinder, metal leaching, solidification/stabilization.

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Hazardous industrial wastes are an inevitable source of environmental pollution. Leachates from these wastes could contaminate potable water sources and affect human health. Poor waste management systems have been identified as one of the most important environmental problems in Serbia. One of the potential hazardous waste problem in Serbia is pyrite cinder generated in sulfuric acid production. About 500,000 t of pyrite cinders have been disposed in landfills in several locations in Serbia without any form of protection (www.ekoplan.gov.rs). The increasingly large dumps not only take up plenty of land, but most importantly, pose a serious threat to the environment. A high content of iron oxide of this type of waste, in the form of hematite and magnetite, is the basis for the research regarding the possibility of its use as a source of catalytic iron in the modified heterogeneous Fenton process in wastewater treatment, especially in dye effluent treatment [1–3]. If a waste material is the source of iron and a catalytic support in a heterogeneous Fenton process, on the one hand it can reduce the cost of the application of these processes, and on the other hand to enable the use of waste for the purpose of waste water treatment. After the utilization of this waste material in a heterogeneous Fenton process, generated sludge is mainly composed of the used pyrite cinder. As pyrite cinder also contains traces of toxic/hazardous heavy metals such as Cu, Zn, Pb, and As [4–7], generated sludge may be toxic and cannot be disposed directly without previous treatment. Stabilization and solidification (S/S) are characterized as the best available techniques for the treatment of hazardous and other waste types [8], and have been extensively used as the final treatment steps prior to the disposal of industrial wastes. Typically, the stabilization processes also involve some form of the physical solidification [9]. During S/S applications, the toxic constituents which are present in the waste are physically and chemically fixed [10]. In this way their mobility is significantly reduced, so their threat to the environment is minimized, and compliance with existing regulatory standards is ensured. By finding suitable S/S methods for a particular hazardous waste, we can achieve not only successful disposal of hazardous waste, but after proper modification, we can also provide a possibility for its next utilization in the building industry [9]. Clays and fly ash have widespread usage as low-cost binders. The pozzolanic nature of fly ash means it can be used in a variety of construction applications [11]. In Serbia, fly ash from power plants has the largest share in total waste produced (69%), but is put to very limited use. Quantifying the environmental impact of S/S materials in real environmental scenarios is crucial for selecting proper disposal and reuse alternatives and for certification of immobilization technologies. The performance of S/S treated wastes is gen-

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Correspondence: Dj.V. Kerkez, Department of Chemistry, Biochemistry and Environmental Protection, Faculty of Sciences, University of Novi Sad, Trg Dositeja Obradovica 3, 21000 Novi Sad, Serbia.

E-mail: djurdja.kerkez@dh.uns.ac.rs

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erally measured in terms of leaching tests [12]. Batch leaching tests with a single extraction are the preferred choice for regulatory assessment due to their simplicity, improved reproducibility, and shorter time requirements. Serbian legislative also uses the Toxicity Characteristic Leaching Procedure — TCLP and DIN 3841-4 S4 complementary procedure for the evaluation of waste characteristics. Additionally, the Synthetic Precipitation Leaching Procedure — SPLP and Waste Extraction Test — WET leaching tests are also widely applied leaching tests for examining S/S efficacy, as they are also tests which mimic conditions in the field, contributing to a better risk assessment of the applied treatment [13]. The main objectives of this study can be summarized as follows: 1) assessing the characteristics of generated sludge from dye effluent treatment and evaluating its environmental risk (metal distribution according to sequential extraction and sample digestion), metal leaching according to TCLP and DIN 3841-4 S4 procedure); 2) S/S treatment of generated sludge with the addition of clays and fly ash; 3) defining metal distribution and evaluation of their environmental risk in selected S/S mixtures according to MWSE; 4) evaluation of the effectiveness of S/S treatment by assessing the leaching potential and environmental impact based on the different leaching procedures (TCLP, DIN 3841-4 S4, SPLP and WET procedure); (5) investigation of S/S matrices binding mechanisms by X-ray diffraction (XRD) and their potential usage by determining compressive strength.

MATERIALS AND METHODS

Used sludge was obtained after heterogeneous Fenton treatment of dye effluent, where pyrite cinder was used as catalytic iron source. For this treatment used pyrite cinder was obtained from IHP “Prahovo” A.D., Serbia. Class C coal fly ash was provided by the Kolubara (Serbia) thermal power plant. It is rich in calcium (> 20% CaO) with self-cementing properties, and therefore does not require addition of activator. Kaolin and bentonite are commercially purchased clays and native clay was sampled near brick works at site Potisje, Kanjiza near Krivaja river basin.

Initial sludge characterization and sample preparation

Raw sludge sample and selected S/S mixtures were characterized by performing sequential extraction as described in [14]. Milestone, Stare E microwave was used for digestion in order to determine pseudo total metal and As contact. Also initial TCLP and DIN 3841-4 S4 procedures were performed on raw sludge sample.

All materials were dried at 105 °C to constant mass and then mixed in established proportions, in order to create stable and durable S/S matrices. Samples were designated by capital letter (S: sludge, B: bentonite, K: kaolin, G: native clay and F: fly ash) followed by a number, indicating the percent weight of the given attribute. The content of each material was expressed as a percentage of the total solids weight. For the leaching tests, 6 types of samples (containing 5% of appropriate clay and 20 and 30% of fly ash) were prepared according to ASTM D1557-00 [15], with a detailed description of the sample preparation provided in [8]. After 28 days, the monolithic samples were crushed and then subjected to the leaching experiments and further characterization.

Leaching procedures

The Toxicity Characteristic Leaching Procedure – TCLP was performed according to the USEPA protocol [16]. The samples were extracted at a liquid to solid (L/S) ratio of 20:1 in capped polypropylene bottles on a rotary tumbler at 30 rpm for 18 h. The German standard leaching test – DIN 3841-4 S4 according to [17], 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. Waste Extraction Test – WET [18] uses a citrate acid solution pH buffered with sodium hydroxide, a 10:1 L/S ratio, and a 48-h testing period. The WET extraction solution is 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 is added to a 100-g sample and rotated for 48 h. The Synthetic Precipitation Leaching Procedure SPLP test is performed according to [19]. The extraction fluid is made of two inorganic acids (nitric and sulphuric acid) to simulate acidic rainwater (pH 4.2). In a similar fashion as the TCLP, a 100-g sample of waste material is placed in a 2-L extraction vessel and mixed with the extraction fluid. The mixture is rotated for 18± 2 h at 30 rpm. All tests were applied to every sample in triplicate. Mean values were used and the *RSD*s ($n = 3$) were below 5%.

Characterization on S/S mixtures

X-ray diffraction (XRD) was performed on the selected prepared monolithic matrices at 28 days of age, before the leaching tests. The monolithic matrices were crushed and dried, ground to powder and then subjected to XRD analysis (Philips PW1710 automated X-ray powder diffractometer was used).

Compressive strength was determined by using a penetrometer which measures the penetration resistance of undisturbed samples in kPa. The results are interpreted according to [11,20].

RESULTS AND DISCUSSION

The results obtained by performing sequential extraction on raw sludge sample as well as on selected S/S mixtures, are summarized in Fig. 1. On the *y*-axis the

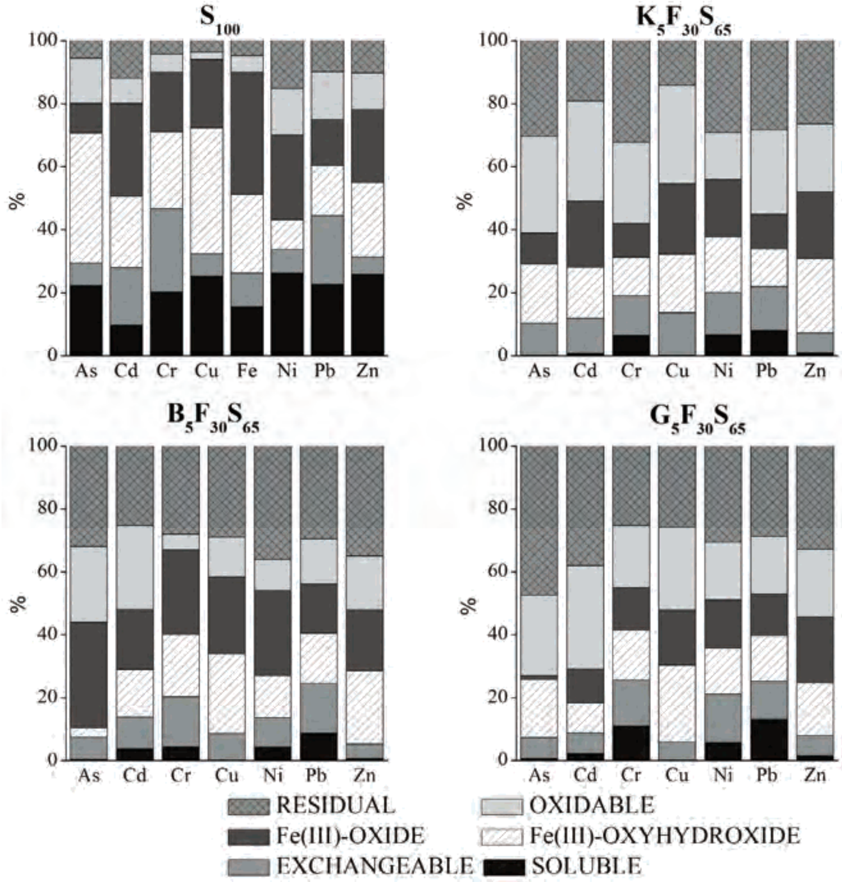


Figure 1. Metal distribution in raw sludge sample and selected S/S mixtures.

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: Cr >Pb> Ni > Cu > Zn > As > Cd > Fe. Percent of extracted, more mobile metals, in soluble and exchangeable fraction ranges from 47% for Zn to 28% for Pb and 26% for Fe in relation to total metal concentration.

In the raw sludge sample, as can be seen in Figure 1, all metals except iron and cadmium show a high risk to the environment, while iron, cadmium and arsenic show a moderate risk in terms of their content in soluble and exchangeable fraction [21,22]. Metals in these fractions are the most mobile and the most easily biologically accessible in the environment [2324]. The presence of metals in these phases increases the possibility of contamination of groundwater and surface water near the disposal site of such waste [25]. By comparing the results of the sequential extraction procedure of raw sludge sample and obtained S/S mixtures, a reduction of all metals and arsenic in soluble and exchangeable phase can be observed. There is almost no As, Zn and Cu present in soluble phase. All S/S mixtures represent moderate or low risk to the environment. Characterization results of raw sludge by using the TCLP and DIN 3841-4 S4 extraction test, normalized by national legislation in order to determine the nature of waste [26], are shown in Tables 1 and 2. Arsenic, copper, lead and zinc are leached in concentrations greater than allowed by the TCLP procedure, characterizing this waste as toxic, posing a risk to human health and the environment. Also arsenic, cadmium, copper, lead and zinc exceeded DIN 3841-4 S4 regulatory levels based on which raw sludge can be considered as hazardous waste.

The results of TCLP test on treated samples were presented in Table 1. This test is specifically designed to mimic the acidic conditions of the sanitary landfill, as well as to identify wastes that have the potential to contaminate groundwater. The leached concentrations of metals and arsenic from all mixtures are far below the limit values according to the Regulation on categories, testing and classification of waste [26]. Therefore, it can be concluded that these materials do not possess toxic properties and can be considered safe and non-hazardous for disposal.

The results of DIN 3841-4 S4 test on treated samples were presented in Table 2. The majority of leached concentrations were lower than those obtained by the TCLP test, since this test uses deionized

Table 1. Leached metal and arsenic concentrations and limit values for metals according to TCLP procedure, 10^{-2} mg L^{-1}

Sample	Component						
	As	Cd	Cr	Cu	Ni	Pb	Zn
S100	516	42.1	216	9830	629	1380	27800
K5F20S75	15.6	3.30	6.80	1672	14.5	3.50	163
K5F30S65	11.8	1.20	5.50	991	9.20	0.200	145
B5F20S75	12.3	1.70	6.90	928	10.1	3.20	127
B5F30S65	1.02	1.60	2.90	798	4.60	0.20	104
G5F20S75	10.4	2.90	6.30	685	11.3	2.80	114
G5F30S65	8.60	2.20	3.60	684	6.20	2.30	112
Limit values	500	100	500	2500	2000	500	25000

Table 2. Leached metal and arsenic concentrations according to DIN 3841-4 S4 test (10^{-2} mg kg^{-1}); A– maximum allowed concentration of accepting waste as inert L/S = 10 (L/kg); B* – maximum allowed concentration of accepting waste as non-hazardous L/S = 10 L/kg [22]; *Z2 upper recommended value of usage[24]*

Sample	Component						
	As	Cd	Cr	Cu	Ni	Pb	Zn
S100	2610	543	83.2	18900	258	12200	32600
K5F20S75	75.1	17.7	5.40	26.3	7.70	73.7	71.8
K5F30S65	40.3	10.9	1.90	8.60	1.60	8.80	70.9
B5F20S75	96.2	5.50	1.50	7.40	3.40	12.2	66.1
B5F30S65	60.3	5.30	0.300	7.10	0.500	5.80	59.0
G5F20S75	124	9.00	1.40	7.80	12.2	27.7	81.1
G5F30S65	123	4.50	1.10	4.10	1.30	20.6	77.8
A*	50	4	50	200	40	50	400
B*	200–2500	100–500	1000–7000	5000–10000	1000–4000	1000–5000	5000–20000
LAGA Z2*	50	5	100	200	100	100	400

water as a leaching agent. These results were interpreted by using the national regulations for the testing and classification of waste [25], as well as by comparing it with the values prescribed by the European Union [27]. Only As and Cd were leached in significant concentrations, but even from the aspect of these metals all specimens represent non-hazardous waste. Also lead was leached above the limit value for inert waste only in the mixture containing 5% of kaolin and 20% of fly ash. From the aspect of LAGA criteria stipulated by German National Working Group on Waste [28], all specimens meet the set values from the aspect of Cr, Cu, Ni, Pb and Zn and can be further used.

Leached metal concentrations by WET test is generally demonstrated that there is a problem with the leaching of arsenic and copper in all S/S mixtures (Table 3), especially if there is a lower share of appropriate immobilization agents. Leached metal concentrations are higher than those obtained by TCLP test [29,30]. The test is conducted at L/S ratio of 1:10 whereas the ratio of the TCLP test is twice as higher.

Table 3. Leached metal and arsenic concentrations according to WET test, 10^{-2} mg L^{-1}; limit values for metals according to CCR regulative [14]

Sample	Component						
	As	Cd	Cr	Cu	Ni	Pb	Zn
K5F20S75	1027	9.30	74.5	5677	68.7	8.90	452
K5F30S65	900	8.70	58.7	4073	66.9	3.50	379
B5F20S75	882	8.20	72.1	4210	62.3	5.80	382
B5F30S65	637	8.10	45.1	2897	53.8	4.80	238
G5F20S75	977	9.00	65.1	3408	61.7	12.5	449
G5F30S65	721	8.60	49.7	3211	53.1	11.2	376
Limit values	500	100	500	2500	2000	500	25000

Also, citrate ion, as a multidentate ligand, used in WET test has the capacity to build a stable chelate with metals, which results in increased metal leaching [31]. Cd, Cr, Ni, Pb and Zn did not show a greater tendency for leaching, so from the aspect of these metals, the mixtures are considered to be adequately stabilized and solidified material. Arsenic is generally leached from S/S mixtures containing fly ash and clay which is consistent with similar studies [13]. Cu also leached above the permissible limits, but with the increase of fly ash share there was an obvious reduction of leaching.

The results of the applied SPLP test on S/S mixture of sludge with chosen clays and fly ash are presented in Table 4. SPLP test reproduces the conditions of acid rain and is used to estimate the mobility of metals when the waste is disposed of in an inappropriate manner. It showed that in almost all S/S mixtures there is no increased metal leaching. With the increase of the mass fraction of immobilization agents in the mixtures, leaching of toxic metals and arsenic is reduced. Generally leach concentrations of metals according to SPLP test were lower than those obtained by TCLP test. This difference in leaching may be due to the different complexation abilities of acid used. TCLP test uses acetic acid, which binds metals strongly, causing them to leach in greater extent [30]. SPLP is also commonly used test for risk assessment of contaminated soil and waste onto surface and groundwater, as well as for the risk assessment process for useful use of solid waste. In this paper, the leach metal concentrations were compared with the emission limit values of waste water from surface waste disposal prescribed by the Regulation on limit values of pollutants in water and deadlines for achieving them [32].

The X-ray analysis indicated the formation of pozzolanic products after a period of 28 days (Fig. 2). Calcium silicate hydrate (CSH) and the calcium silicate hydroxide (CHS) were identified in all samples. Hematite, magnetite, pyrite and quartz, which are identified in all the S/S mixtures, originate from treated sludge. In general, formation of pozzolanic components, and the presence of calcite and gypsum, further confirms that these matrices have good potential to be used as construction materials [20,33].

The measurement results of compressive strength of tested S/S mixtures are shown in Figure3. According to the EPA [34], S/S materials with hardness greater than 0.35MPa shall be considered to have sufficient compressive strength. This minimum value is proposed in order to create a stable foundation for the disposal of these materials in landfills. In the UK, acceptable strength after 28 days is 0.7MPa, but the value of 0.35 is acceptable depending on the test sample [35].

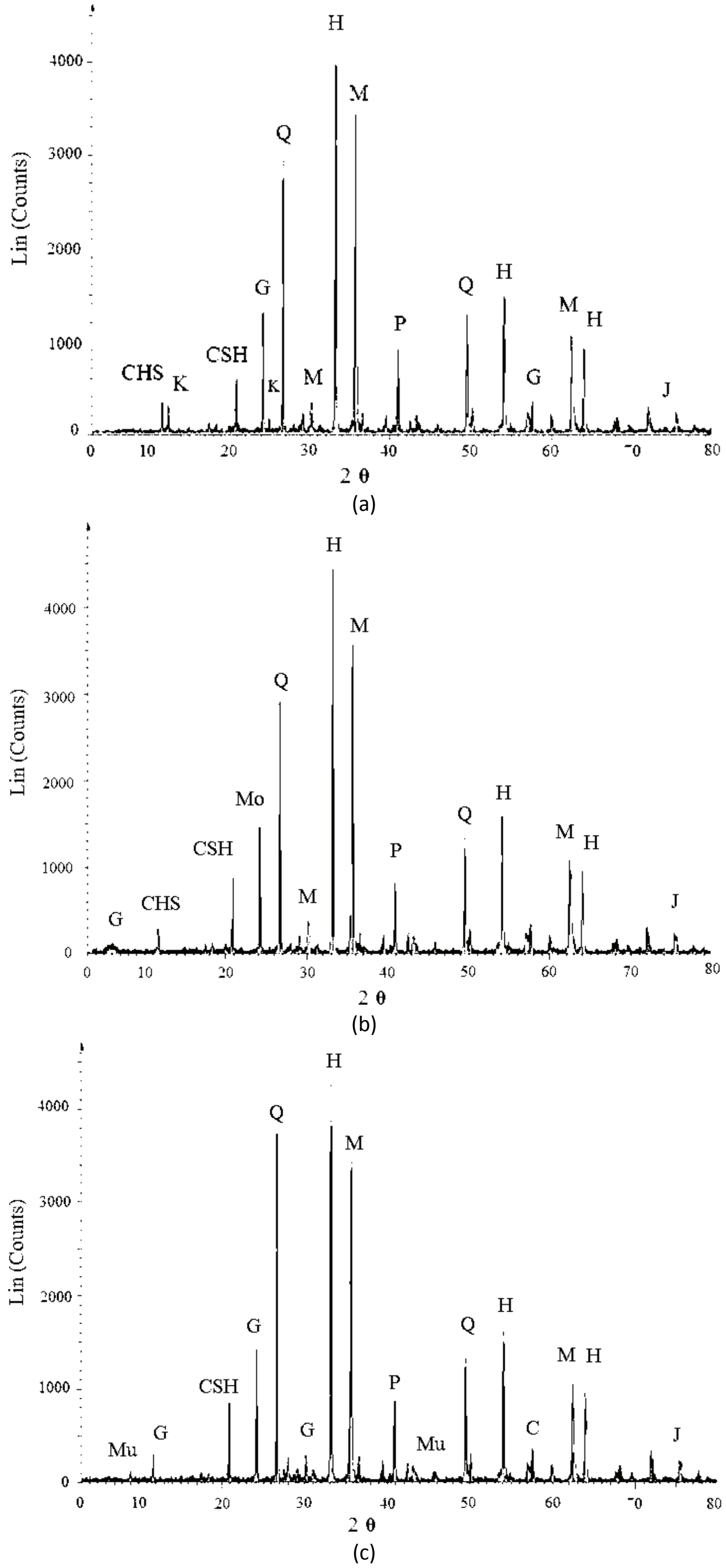
Studies have shown that the values of compressive strength for majority of stabilized and solidified wastes samples ranged from 0.06 to 19.9 MPa [36]. Compressive strength depends on the quality of pore structure and cementitious materials. This depends primarily on the type and quantity of the constituents which constitutes the pore structure (hydratation products) and pozzolanic reactions which take place in the S/S mixtures [37]. Overall, an increasing proportion of fly ash in the S/S mixtures proved to be negative in terms of compressive strength, but all obtained mixtures of clay and fly ash still can be used as a base for roads and bulk materials as they all exhibit compressive strength requirement of 0.35 MPa.

CONCLUSIONS

The assessment of the sludge, generated in dye effluent treatment, based on the sequential extraction, as well as the initial TCLP and DIN 3841-4 S4 testing, showed that this waste can be considered as hazardous due to high metal and As content. The S/S treatment applied, using tree different clays and fly ash, appeared to be effective in the remediation of sludge from dye effluent treatment when using pyrite cinder as catalytic iron source. Sequential extraction indicated that after the treatment there was a significant change in metal and As distribution. Namely, after the S/S treatment, metal content in soluble and exchangeable phase decreased and consequently the environmental risk was

Table 4. Leached metal and arsenic concentrations according to SPLP test, 10^{-2} mg L^{-1}; emission limit values for waste water from surface waste disposal [28]

Sample	Component						
	As	Cd	Cr	Cu	Ni	Pb	Zn
K5F20S75	9.10	2.10	0.500	3.20	1.10	2.70	42.2
K5F30S65	5.50	0.500	0.100	1.80	0.400	2.00	25.7
B5F20S75	3.70	2.00	0.400	15.5	1.10	2.50	75.5
B5F30S65	1.80	0.900	0.100	2.50	0.900	1.30	56.1
G5F20S75	11.9	1.50	2.50	2.80	1.90	6.80	314
G5F30S65	7.80	1.40	0.100	2.70	0.200	1.20	116
Limit values	10	10	50	50	100	50	200



(a)

(b)

(c)

Figure 2. X-Ray diffraction analysis (XRD) applied on S/S mixtures with: a) 5% kaolinite and 30% of fly ash, b) 5% bentonite and 30% of fly ash and c) 5% native clay and 30% of fly ash; the identified chemical species are following: H – hematite, M – magnetite, P – pyrite, Q – quartz, C – calcite, G – gypsum, CSH – calcium silicate hydrate, CHS – calcium hydroxide silicate, J – jarosite, Mo – montmorilonite, K-kaolinite and Mu-muscovite.

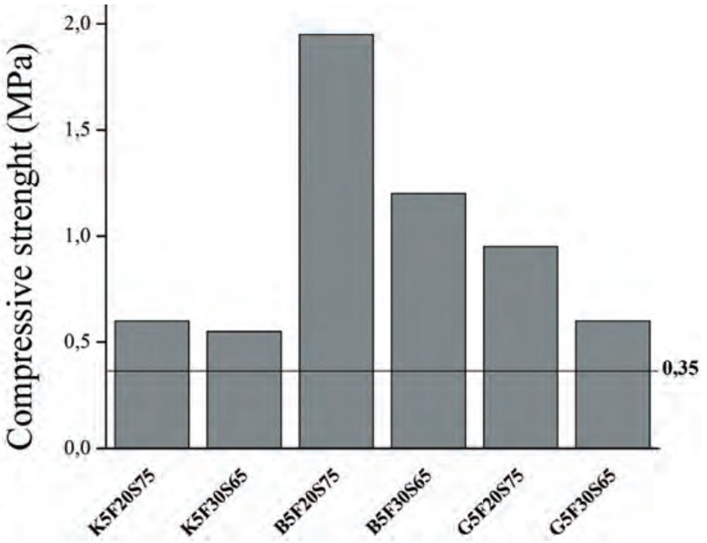


Figure 3. Compressive strength (MPa) of obtained S/S mixtures after 28 days.

reduced. The single-step leaching tests TCLP, DIN 3841-4 S4, WET and SPLP were applied to evaluate the extraction potential of metals and As in S/S matrices. The results showed that in all S/S samples very limited leaching occurred, and leached metal and As concentrations are in majority of cases below the proposed regulatory limits. XRD analyses confirmed the formation of pozzolonic compounds in all S/S samples. From the aspect of compressive strength analysis, produced S/S materials are viable for safe disposal and can also be considered as acceptable for "controlled utilization". This may justify the application of such already-expensive remediation procedures, especially when it comes to treating materials 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 industrial wastes are immobilized and stabilized using low-cost binders. An additional adventage of using fly ash as an immobilizing agent in the S/S treatment of this kind of sludge is the simultaneous disposal of two waste types. These results represent a promising technology in the field of green remediation.

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IZVOD

IZLUŽIVANJE I FIZIČKA STABILNOST SOLIDIFIKOVANOG I STABILIZOVANOG MULJA PIRITNE IZGORETINE KOJI POTIČE IZ TRETMANA EFLUENATA KOJI SADRŽE BOJE

Djurdja V. Kerkez, Milena R. Bečelić-Tomin, Milena B. Dalmacija, Dragana D. Tomaševic, Srdjan D. Rončević, Gordana V. Pucar, Božo D. Dalmacija

Univerzitet u Novom Sadu, Prirodno–matematički fakultet, Departman za hemiju, biohemiju i zaštitu životne sredine, Novi Sad, Srbija

(Naučni rad)

Ovaj rad se bavi istraživanjem mogućnosti korišćenja solidifikacije/stabilizacije (S/S) u tretmanu toksičnog mulja nastalog u tretmanu obojenih efluenata, kada je piritna izgoretina korišćena kao izvor katalitičkog gvožđa u modofokovanom heterogenom Fenton procesu. S/S tretman je izveden uz korišćenje različitih glina (kaolin, bentonit, lokalna glina sa teritorije Vojvodine) i letećeg pepela u cilju imobilizacije toksičnih metala i arsena prisutnih u mulju. Za procenu potencijala ekstrakcije toksičnih metala i arsena, kao i za efektivnost primenjenog S/S tretmana, izvedena su četiri testa izluživanja u jednom koraku. Svaki test koristi različito sredstvo za izluživanje kako bi se oponašali realni uslovi u životnoj sredini. Generalno, sekvencijalna ekstrakcija S/S smeša pokazala je smanjenje sadržaja metala i arsena u rastvornoj i izmenjivoj fazi u poređenju sa uzorkom sirovog mulja. Rezultati testova izluživanja ukazuju da je primenjeni S/S tretman bio efikasan u imobilizaciji toksičnih metala i arsena prisutnih u mulju. Takođe, X-ray difrakciona analiza potvrdila je formiranje pozolaničkih proizvoda, a merenja pritisne čvrstoće potvrdila su efikasnost tretmana. Stoga može se zaključiti da S/S tehnika ima značajan potencijal pri rešavanju problema opasnog industrijskog otpada i njegovog bezbednog odlaganja.

Ključne reči: Industrijski otpad • Piritna izgoretina • Izluživanje metala • Solidifikacija/stabilizacija