



## A solidification/stabilization process for wastewater treatment sludge from a primary copper smelter

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**Abstract:** Wastewater treatment sludge from a primary copper smelter is characterized as hazardous waste that requires treatment prior to disposal due to its significant contents of heavy metals and arsenic. The aim of the presented study was to investigate the feasibility and the effectiveness of a solidification/stabilization process of the sludge using fly ash and lime as binders. The effectiveness of the process was evaluated by Unconfined Compressive Strength (UCS) testing, leaching tests (EN 12457-4 and Toxicity Characteristic Leaching Procedure (TCLP)) and Acid Neutralization Capacity (ANC) tests. All the samples reached the target UCS value of 0.35 MPa. The calcium to silicon concentration ratio ( $c_{Ca}/c_{Si}$ ), determined by X-ray fluorescence analysis, was identified as main factor governing strength development. Inductively coupled plasma-optical emission spectrometry analyses of solutions after leaching tests showed excellent stabilization of Cu, Ni, Pb and Zn (above 99 %) and arsenic (above 90 %) in samples with high  $Ca(OH)_2$  content. Results of the ANC test indicated that the buffering capacity of solidified material linearly depended on Ca concentration in FA and lime. Samples with 20 % of binder having 50 % of FA and 50 % of lime met all the requirements for safe disposal.

**Keywords:** fly ash; lime; heavy metals; unconfined compressive strength; leaching tests.

### INTRODUCTION

Wastewaters produced during gas cleaning and cooling processes and electrolytic refining in the Copper Smelter RTB Bor in Serbia are currently discharged without previous treatment. These wastewaters, the amount of which occasionally have reached several hundred cubic meters per hour, represent a major environmental problem for the western Balkans and the Danube Basin.<sup>1</sup>

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The construction of a wastewater treatment (WWT) plant is planned during Bor Copper Smelter – Acid Plant Modernization Project in next few years. Generation of WWT sludge, bearing significant amount of heavy metals and arsenic, is estimated at  $11.2 \text{ t h}^{-1}$ .<sup>2</sup> This copper WWT sludge is characterized as hazardous waste in the Waste Catalogue (also adopted in Serbian law<sup>3</sup>) by the code 19 02 05\*, and must be chemically and physically treated prior to disposal in order to prevent secondary pollution. The aim of presented study was to investigate the feasibility and the effectiveness of a solidification/stabilization (S/S) process of future copper WWT sludge as an addendum to the ongoing project.

An S/S process is recognized as “the best demonstrated available technology” for treatment of industrial waste containing heavy metals.<sup>4,5</sup> It involves mixing a binding reagent with contaminated media or waste, changing the chemical and physical properties of hazardous materials to make it suitable for land disposal. Cement is the most frequently used binder for S/S treatment of hazardous waste.<sup>5</sup> In order to improve economic and environmental effects of the process, nowadays, cement is increasingly replaced by fly ash (FA), which is an excellent example of a cost effective utilization of a waste product.<sup>6</sup> In Serbia alone, about 5 million tons of ash is generated annually during coal combustion in thermal power plants.<sup>7</sup> Besides benefits in the use of waste materials such as FA, compared to other more expensive binders in S/S processes, FA increases the pH region for heavy metals immobilization and improves the mechanical properties of the treated waste.<sup>6</sup> In the S/S treatment of heavy metals- and arsenic-bearing waste, FA as a binder is usually used individually<sup>8,9</sup> or in mixtures with Portland cement and lime.<sup>4,10</sup>

The quality of an S/S process is determined by the compressive strength and leaching resistance of the treated material. Development of strength and immobilization of metal ions in waste primarily depend on the products of hydration reaction of pozzolanic components in FA ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$  and  $\text{Fe}_2\text{O}_3$ ).<sup>11</sup> The optimum amounts of pozzolans present in waste, or their addition, can lead to better mechanical properties of a material.<sup>12,13</sup> The hydration reaction is influenced by the nature and relative quantity of the waste.<sup>14</sup> It is generally believed that heavy metals ions present in the waste can affect the pozzolanic reaction by precipitation of insoluble Ca-heavy metals<sup>15</sup> and Ca-As<sup>16,17</sup> salts on the new formed hydrates. Precipitated salts can prevent further hydration and inhibit the development of the hydrated structure.<sup>18,19</sup>

The leaching behavior of stabilized waste is pH dependent and it is mainly controlled by the alkaline nature and acid buffering capacity of the S/S matrix. pH value of leachates should be within the range of the minimum solubility of the metals,<sup>20,21</sup> although Polat *et al.*<sup>22</sup> and Srivastava *et al.*<sup>23</sup> reported excellent stabilization behavior of FA over a wide pH range. For each individual waste stream, it is necessary to provide an integrated approach for the proper selection

of binder that would ensure stabilization of the pollutants and prevent their migration into the environment.

The presented study investigates the possibility of employment of an S/S process on the sludge from the WWT plant in the future modernized RTB Bor Copper Smelter – Acid Plant using FA and mixture of FA and lime as binders. Process optimization was achieved by varying content and composition of the binder. UCS Testing and the standardized leaching tests: EN 12457-4, TCLP and ANC tests were used to determine the effect of the binder on strength development and heavy metals/arsenic ion immobilization. The results provide a novel clarification of the effect of pozzolans on the quality of the S/S process.

#### EXPERIMENTAL

The experiments were conducted on synthesized sludge that chemically and physically corresponded to the future WWT sludge defined by the Modernization Project with 50.67 mass % water content and a density of 1.55 kg dm<sup>-3</sup>. Basic materials for the synthesis of WWT sludge were systematically collected dusts from the electro-filters of the reactor and converter in the Bor Copper Smelter. The synthesis of the sludge under laboratory conditions was described in detail previously.<sup>24</sup>

FA from the Bor heating plant, Serbia was used as the sole binder and in mixtures with commercial grade hydrated lime (“Nexe”, Jelen Do). The FA originated from the combustion of lignite coal from the Kolubara mines in Serbia. Due to conditions of storage and transport, the FA had to be dried at 105 °C for 24 h and sieved in order to obtain <100 µm fraction for the further experiments.

The chemical composition of the sludge, FA and lime, and the mineralogical composition of the sludge were determined by X-Ray fluorescence (XRF) and X-Ray diffraction (XRD) analyses, respectively. The pollution potentials of the sludge and FA were evaluated by EN 12457-4 and TCLP tests. These two leaching tests have both been adopted into Serbian Law<sup>3</sup> for the testing of the hazardous characteristics of waste and are described below.

In order to optimize the composition of the S/S mixture, eight series of experiments with different additions and compositions of binder were prepared. The compositions of the S/S mixtures are presented in Table I.

TABLE I. Compositions of the S/S mixtures, mass %

Sample	Binder composition		Sludge:binder
	FA	Lime	
S95F100	100	–	95:5
S90F100	100	–	90:10
S85F100	100	–	85:15
S80F100	100	–	80:20
S75F100	100	–	75:25
S80F90L10	90	10	80:20
S80F75L25	75	25	80:20
S80F50L50	50	50	80:20

The sludge, fly ash and lime were thoroughly mixed for 10 min with a mechanical mixer at room temperature to form a homogeneous paste. The paste was cast in two portions into

plastic molds dimensions  $5 \times 5 \times 5 \text{ cm}^3$  and vibrated in order to remove entrapped air and excess water. The specimens were cured according to the ASTM C109 Standard:<sup>25</sup> 24 h under wet towels to meet the requirement of 99 % moisture; after 3 days, the samples were removed from the mold and left to cure in air.

The UCS test provides basic information on material stabilization. According to the U.S. Environmental Protection Agency (USEPA), 0.35 MPa is the minimum compressive strength required for the safe disposal of stabilized waste.<sup>5</sup> The UCS values of the samples were determined after 7, 14 and 28 days of curing using a servo hydraulic testing machine type Instron 1332-retrofitted Fast track 8800 with a maximum load of 100 kN. The presented results are the mean measurements of three samples.

Leaching procedures allow the characterization of the environmental behavior of wastes and S/S products using the solubility and/or availability of pollutants as limits. TCLP<sup>26</sup> and EN 12457-4<sup>27</sup> are very common tests, standardized and accepted in the USA and the EU for evaluating the pollution potential of materials. The EN 12457-4 test was conducted after 28 days of curing to simulate long-term leaching processes at disposal sites. Distilled water was used as the extraction fluid at a liquid to solid (L/S) ratio of 10. Crushed samples (<10 mm, 100 g) were leached by rotating for 24 h in polyethylene bottles. TCLP tests, simulating the worst-case scenario, were conducted after curing the samples for 180 days. For this purpose, 50 g of ground samples (<10 mm) were placed in polyethylene bottle together with 1.0 dm<sup>3</sup> of extraction fluid (L/S 20). A solution of glacial acetic acid having a pH value of  $2.88 \pm 0.05$  was used as the extraction fluid. The mixture was agitated for  $18 \pm 2$  h. After the leaching tests, the solutions were filtered through a blue ribbon filter paper. The metal concentrations in the solutions were determined by atomic absorption spectroscopy (AAS) (after the EN 12457-4 test) and by inductively coupled plasma-optical emission spectrometry (ICP-OES) (after the TCLP test).

The ANC test provides information on the buffering (acid neutralization) capacity of S/S materials and thus their resistance to various environmental conditions at landfills. The ANC test was adapted from the Environment Canada procedure described by Stegemann and Cote.<sup>28</sup> The test consists of a series of batch extractions with increasing additions of nitric acid, ranging from distilled water to 2.0 M HNO<sub>3</sub> over 11 equal increments. The samples cured for 180 days were crushed, sieved to <125 μm and dried at 60 °C to constant weight. Samples of 3 g were placed in 50 cm<sup>3</sup> polyethylene bottles together with distilled water and 1 M HNO<sub>3</sub> to give an L/S ratio of 10 and the desired acid addition. The bottles were sealed and rotated for 48 h prior to centrifugation and measurement of the pH. Measured pH values were plotted against the equivalent mass of acid added per kg of dried material, eq. kg<sup>-1</sup>, for each individual mixture.

In order to determine the chemical composition of the S/S samples and its influence on the compressive strength and leaching resistance of the waste, XRF analysis was performed using a Niton XRF instrument.

The redox potential (*Eh*) and pH values of each filtrated solution after the leaching tests were measured. These data were used to determine ions species in aqueous solutions from *Eh*-pH diagrams. The *Eh*-pH diagrams were designed in the Outokumpu HSC Chemistry ver. 4 (HSC4) software package based on the concentrations of metals ions obtained by ICP-OES analysis of the solutions.

## RESULTS AND DISCUSSION

Chemical composition of the sludge, FA and lime, determined by XRF analysis, are presented in Table II. The metals in the sludge were in the form of sulfates and hydroxides and in FA in the form of oxides. By its chemical composition, the employed FA belonged to class F according to the ASTM C618 standard.<sup>29</sup> XRD Analysis of the sludge, Fig. 1, revealed that the main mineral phase was gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ).

TABLE II. Chemical composition of the sludge, FA and lime, mass %; n.d. – not detected

Element	Sludge	FA	Lime
Fe	13.38	8.02	0.02
Ca	12.49	10.68	54.09
S	10.81	2.14	0.12
Zn	5.15	0.02	n.d.
Cu	4.04	0.13	n.d.
Pb	0.86	0.03	n.d.
As	0.65	0.01	n.d.
K	0.12	0.56	n.d.
Mn	0.09	0.08	n.d.
Ni	0.08	0.01	n.d.
Se	0.02	n.d.	n.d.
Si	1.95	17.16	0.14
Al	n.d.	7.06	0.03
Sb	0.89	n.d.	n.d.

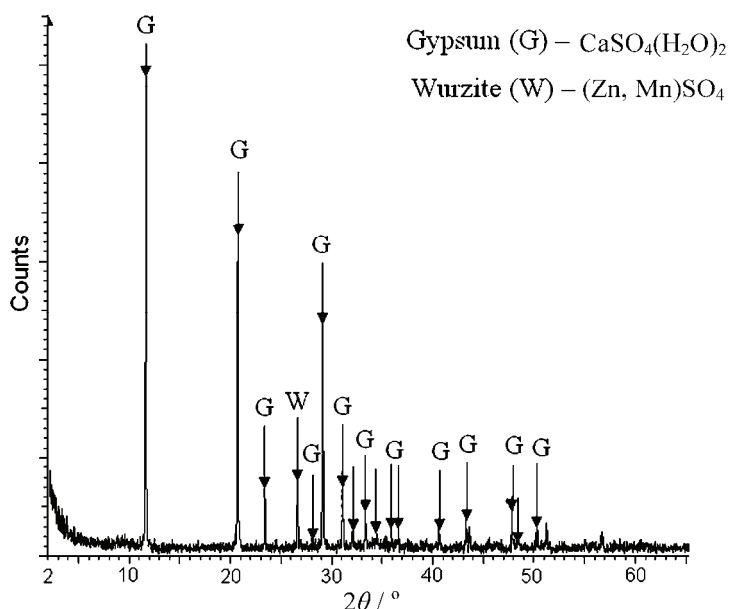


Fig. 1. XRD Analysis of the sludge.

The pollution potentials of the sludge and FA, evaluated by the EN 12457-4 and TCLP tests, are presented in Table III. The EN 12457-4 test showed leaching of Zn and Sb and the TCLP test showed leaching of Zn and Cu above the regulation limits.

TABLE III. Pollution potential of the sludge and FA compared with national legislative for non-hazardous waste

Metal	EN 12457-4, mg 100 g <sup>-1</sup> dried material			TCLP, mg dm <sup>-3</sup>		
	Sludge	FA	Limit	Sludge	FA	Limit
Fe	<0.1	<0.1	–	3.9	<0.1	–
Ca	604.2	638.9	–	951.4	1784.7	–
Zn	16.0	0.1	5	1232.6	0.05	250
Cu	<0.1	<0.1	5	26.2	<0.1	25
Pb	<0.3	<0.3	1	3.45	<0.3	5
As	0.14	<0.1	2	2.6	<0.1	5
Ni	0.42	<0.2	1	7.4	<0.2	20
Sb	0.27	<0.1	0.07	3.1	<0.1	15

The main metal constituents of the solidified material, as determined by XRF analysis and presented in Table IV, were Fe, Ca, Zn, Cu and Si, which were expected considering the nature of the sludge and FA.

TABLE IV. Concentrations of metals in the solidified samples, *c* / mass %

Sample	Fe	Ca	Zn	Cu	Si	Pb	As	Ni	Mn
S95F100	13.06	10.06	5.61	4.60	2.71	0.90	0.69	0.08	0.08
S90F100	11.79	9.40	4.44	3.93	3.47	0.75	0.58	0.07	0.06
S85F100	12.03	8.59	4.07	3.67	4.23	0.69	0.53	0.05	0.07
S80F100	10.64	8.66	3.38	2.90	4.99	0.58	0.45	0.06	0.07
S75F100	11.53	10.74	3.23	2.80	5.75	0.57	0.44	0.05	0.07
S80F90L10	10.94	11.03	3.49	3.13	4.65	0.61	0.46	0.05	0.06
S80F75L25	10.06	13.03	3.77	3.18	4.14	0.61	0.50	0.05	0.06
S80F50L50	8.00	13.53	3.57	2.81	3.28	0.57	0.47	0.05	0.05

The results of the testing after 7, 14 and 28 days for systems of different compositions are given in Table V.

All samples, with a few exceptions for systems with a high lime content, exceeded the required value of 0.35 MPa for UCS even after 7 days of curing. In systems with FA as binder, the UCS increased with increasing binder content from 5 to 20 %, but decreased in the sample with 25 % of the binder. The reason for this was optimal water to solid ratio, which was considered to be between 0.6–0.4.<sup>5</sup> Water was introduced into the system within the sludge (50.67 mass % water content). Insufficient amount of water for the hydration reaction, below 0.4, as was the case was with 25 % added binder, resulted in a low value of UCS.

TABLE V. Results of UCS testing after 7, 14 and 28 days

Sample	UCS / MPa		
	7 <sup>th</sup> day	14 <sup>th</sup> day	28 <sup>th</sup> day
S95F100	0.40	0.45	0.57
S90F100	0.39	0.57	0.66
S85F100	0.40	0.66	0.78
S80F100	0.40	0.79	1.00
S75F100	0.40	0.58	0.84
S80F90L10	0.51	0.67	0.73
S80F75L25	0.35	0.47	0.64
S80F50L50	0.32	0.73	0.55

Addition of lime resulted in a decrease in the UCS after 28 days of curing. In the work performed by Antiohos and Tsimas, this was explained by insufficient silica present in the samples to react completely with the excess of hydrated lime.<sup>12</sup> The remaining unreacted  $\text{Ca}(\text{OH})_2$  exerted a negative affect on the strength development and possibly some durability properties.<sup>30</sup> The assumption about more than the optimum amount of  $\text{Ca}(\text{OH})_2$  for the pozzolanic reaction was confirmed by calculating the Ca to Si concentration ratio ( $c_{\text{Ca}}/c_{\text{Si}}$ ) in the samples determined by XRF analysis. This ratio provides information of the available pozzolans for the formation of cementitious phases in the waste. The correlation between the UCS, developed after 28 days of curing, and the corresponding  $c_{\text{Ca}}/c_{\text{Si}}$  ratio is presented in Fig. 2. An increase in the  $c_{\text{Ca}}/c_{\text{Si}}$  ratio in the system resulted in a reduction of the UCS due to higher amount of unreacted  $\text{Ca}(\text{OH})_2$ . The highest compressive strength was achieved for a  $c_{\text{Ca}}/c_{\text{Si}}$  ratio of 1.73 (sample S80F100), which was the lowest one. The ratios of the Ca concentration with the concentration of others elements were also analyzed but there was no agreement with the results of the UCS. This confirmed the major role of the silica concentration in governing the development of the UCS in waste samples.<sup>31</sup>

The results of leaching tests are presented in Table VI. After the EN 12457-4 test, the concentrations of Cu, Fe, Ni, Pb and Zn were below the detection limits for AAS analysis. Concentrations of As were in the range from 0.10 to 0.18 mg 100 g<sup>-1</sup> dried material, and Sb concentration from 0.10 to 0.29 mg 100 g<sup>-1</sup> dried material, Table VI. Variations in the results could be considered as errors of the measuring instrument due to the very low concentrations. Unlike EN 12457-4 test, the results of the TCLP tests, Table VI, showed the presence of heavy metals ions in the leachates due to the more aggressive leaching conditions. The addition of 25 % FA as binder resulted in reductions in the leaching by 84.5 % Cu, 73.4 % Ni, 90.7 % Pb and 87.9 % Zn compared to the untreated sludge (Table III). The addition of lime resulted even higher reductions in the leaching of heavy metals. For the sample with 50 % lime in the binder, the concentrations of Cu, Ni, Pb and Zn were reduced by 99.6, 99.7, 99.7 and 99.8 %, respectively. The concentrations

of As in the treated samples were very similar and the results evidenced no correlation between As leaching and FA/lime addition, although it was reduced by over 90 % compared to the leaching from the untreated sludge. The concentrations of Sb were below the detection limit for most samples.

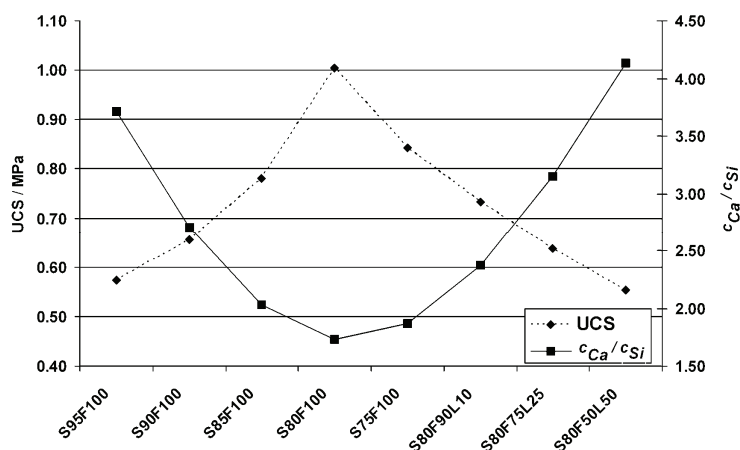


Fig. 2. UCS Values after 28 days and the corresponding Ca to Si concentration ratios ( $c_{Ca}/c_{Si}$ ) in the solidified samples, determined by XRF analysis.

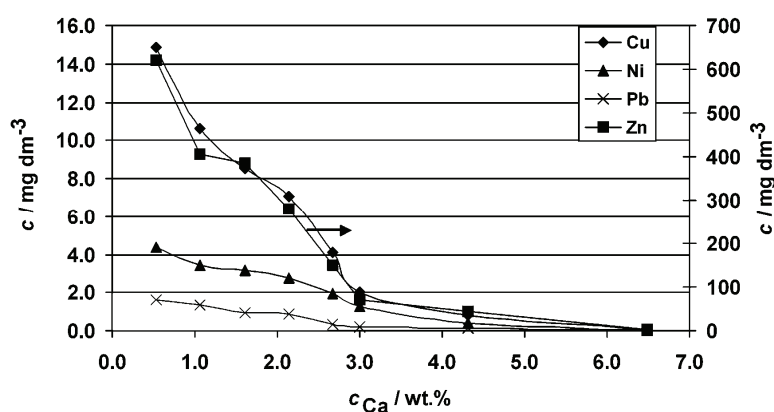
Although both tests are accepted in the National Law, the results of the EN 12457-4 and TCLP tests gave different toxicological characterization of the same waste. The Zn concentrations in the solutions after the EN 12457-4 tests were below  $0.1 \text{ mg } 100 \text{ g}^{-1}$  dried material for all samples and the S/S waste could be characterized as non-hazardous. However, according to the TCLP results, samples S95F100, S90F100, S85F100 and S80F100 had Zn leached concentrations above the concentration limits defining non-hazardous waste. The pH value of the extraction fluid was the main parameter governing the leaching of pollutants. The aggressive extraction fluid in the TCLP test can neutralize all alkalinity in an S/S sample and lead to much higher leaching of metals. The alkalinity of S/S waste samples depends on the content of CaO and  $\text{Ca}(\text{OH})_2$  derived from FA and lime. The Ca concentration in samples in the form of CaO and  $\text{Ca}(\text{OH})_2$  can be calculated according to FA and lime additions (Ca concentration in the binder). The influence of the alkalinity (presented as the Ca concentration in the binder,  $c_{Ca} / \text{mass } \%$ ) on heavy metals leaching during the TCLP tests is presented in Fig. 3. A larger amount of Ca in the form of CaO and  $\text{Ca}(\text{OH})_2$  in the samples resulted in a reduction of heavy metals leaching.

The *Eh* and pH values of each filtrated solution after leaching were measured. These data were used for metal ions speciation in *Eh*-pH diagrams. Diagrams were realized in the HSC4 software package as combined diagrams in metal-Ca-



TABLE VI. Results of EN 12457-4 test, mg 100 g<sup>-1</sup> of dried material and TCLP test, mg dm<sup>-3</sup>

Test	As	Sb	Cu	Fe	Ni	Pb	Zn
S95F100							
EN 12457-4	0.11	0.12	<0.10	<0.10	<0.20	<0.30	<0.10
TCLP	0.12	<0.10	14.85	0.06	4.34	1.58	621.00
S90F100							
EN 12457-4	0.18	0.16	<0.10	<0.10	<0.20	<0.30	<0.10
TCLP	0.18	<0.10	10.60	0.03	3.46	1.34	405.70
S85F100							
EN 12457-4	0.17	0.19	<0.10	<0.10	<0.20	<0.30	<0.10
TCLP	0.33	<0.10	8.52	0.01	3.13	0.96	385.60
S80F100							
EN 12457-4	0.15	0.24	<0.10	<0.10	<0.20	<0.30	<0.10
TCLP	0.30	0.50	7.05	0.06	2.76	0.87	279.30
S75F100							
EN 12457-4	<0.10	0.29	<0.10	<0.10	<0.20	<0.30	<0.10
TCLP	0.19	0.20	4.07	0.01	1.97	0.32	148.90
S80F90L10							
EN 12457-4	<0.10	0.14	<0.10	<0.10	<0.20	<0.30	<0.10
TCLP	0.20	0.27	2.00	0.01	1.30	0.20	71.46
S80F75L25							
EN 12457-4	0.17	<0.10	<0.10	<0.10	<0.20	<0.30	<0.10
TCLP	0.25	<0.10	0.78	0.01	0.43	0.12	43.44
S80F50L50							
EN 12457-4	0.11	<0.10	<0.10	<0.10	<0.20	<0.30	<0.10
TCLP	0.20	<0.10	0.09	0.24	0.02	0.01	1.79

Fig. 3. Dependence of the concentrations of heavy metals,  $c$ , in solutions after leaching on the Ca concentration in the binder,  $c_{Ca}$ .

–S–H<sub>2</sub>O system based on different ion concentrations in the solutions after TCLP leaching. Zinc and arsenic were selected due to their very different behavior

during leaching: the As concentrations remained almost constant while the Zn concentrations were reduced by 99 % with the addition of lime. The *Eh*–pH diagram of As and Zn are shown in Fig. 4, combined with their concentrations in solution after leaching,  $c / \text{mg dm}^{-3}$ . Different additions and compositions of binder did not effect arsenic leaching. In all systems, As remained in the soluble form as  $\text{HAsO}_3^-$ . Concentrations of As were in the range from 0.1 to 0.3  $\text{mg dm}^{-3}$  in solutions after the TCLP leaching test of stabilized waste. The As concentration was ten times reduced compared to its concentration in solution of untreated sludge although in the same area of  $\text{HAsO}_3^-$ . This implies that, beside the formation of insoluble Ca–As salts, the binder effects the stabilization of As ions by increasing the pH value of the matrix and, possibly, by other physicochemical interactions. In contrast to arsenic, different amounts and composition of binder affected Zn leaching. The addition of FA caused an increase in the pH value of the material and zinc transformed from its soluble form into insoluble oxides. The Zn concentration in the S75F100 solution was reduced to below the regulation limits ( $200 \text{ mg dm}^{-3}$ ). Lime addition resulted in better Zn stabilization and in sample with 50 % of  $\text{Ca}(\text{OH})_2$  in binder (S80F50L50), zinc leaching was reduced by 99.8 %.

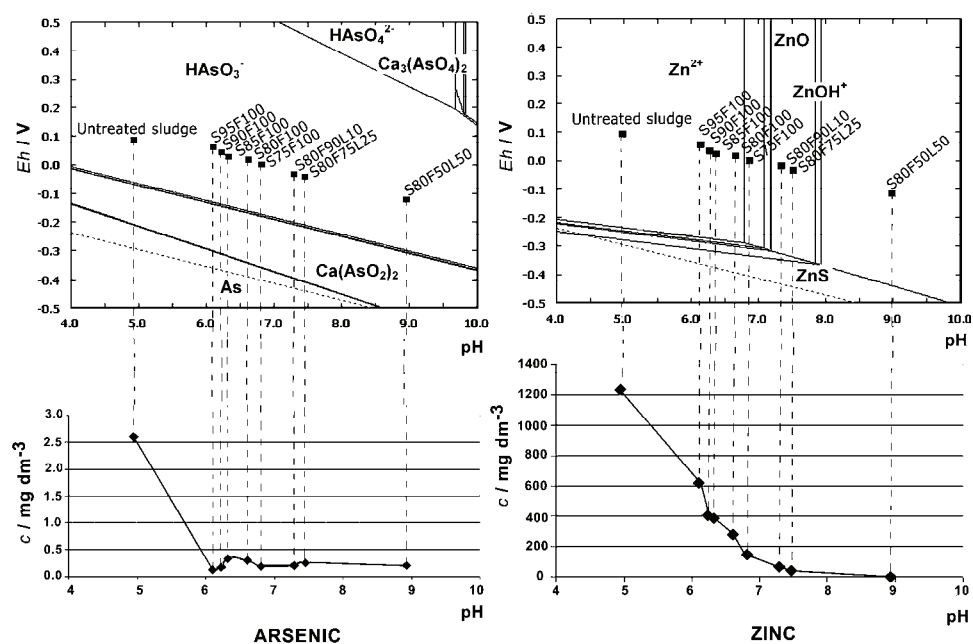


Fig. 4. *Eh*–pH diagrams of As and Zn for the systems metal–Ca–S–H<sub>2</sub>O at 25 °C with their concentration in solution after leaching,  $c$ .

The ANC test was conducted for determining the buffering capacity of the S/S samples. Since the S/S process is pH-dependent, sufficient acid neutralizing capacity is necessary to stabilize the heavy metals. The ANC test results presented in Fig. 5 show the pH value of leachates as a function of added equivalents of nitric acid per kilogram of dried sample, ANC in eq. kg<sup>-1</sup>. These figures are known as titration curves and a plateau at a defined pH describes the waste buffer capacity. A material has a larger buffering capacity if it can neutralize more equivalents of acid.

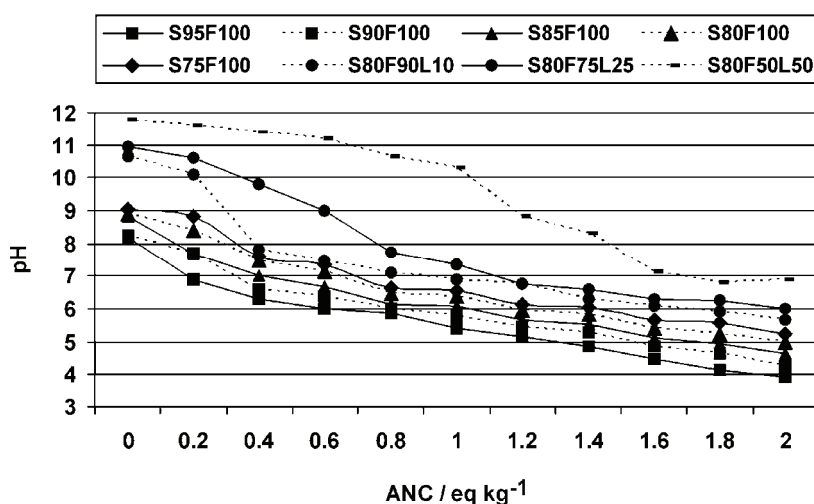


Fig. 5. ANC Test results.

Samples with FA as binder had initial pH values between 8 and 9, and a lower decrease at around pH 6. The reason for this was, primarily, the presence of gypsum and other sulfates with a buffering capacity around pH 5–6,<sup>32</sup> and a significant content of iron and zinc in the WWT sludge having a buffering capacity also around pH 5–6.<sup>33</sup> The amount of acid that a stabilized material could neutralize (at pH 7) increased with the amount of FA in the samples, from 5 to 25 %. The samples with added lime had greater buffering capacities. The acid neutralization capacity, ANC, depends on the amount of alkaline reagents in the S/S waste, while pozzolanic agents have negative effects on the buffering capacity with nitric acid, due to the substitution of basic reagents by acidic oxides.<sup>34</sup> In addition, alkalis in FA are combined in the glassy phase and the amorphous silica in FA might react with the alkalis rendering them less available.<sup>21</sup> In the literature, the ANC was found to be a function of the calcium containing compounds in the binder,<sup>35,36</sup> which was also confirmed in present study. Buffering capacity of stabilized waste (at pH 7) linearly depended on the concentration of calcium in the FA and lime (Ca concentration in binder,  $c_{Ca}$  / mass %), Fig. 6.

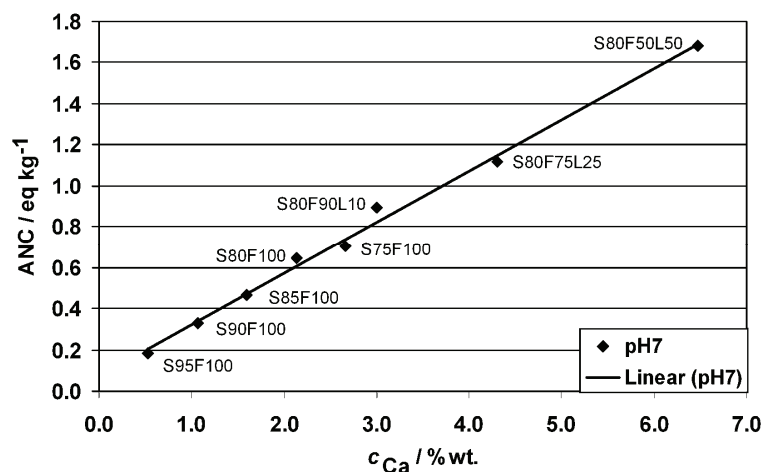


Fig. 6. ANC at pH 7 as a function of the Ca concentration in the binder,  $c_{Ca}$ .

Stegemann and Cote proposed that the S/S product should have an ANC greater than 1 eq. kg<sup>-1</sup> before reaching pH 9 in order to be disposed at a segregated landfill.<sup>37</sup> Only sample S80F50L50 met this condition. The reasons why the other samples did not fulfill this condition were primarily the chemical composition of the WWT sludge and the use of FA as the main binder.

#### CONCLUSIONS

In the presented study, it was observed that solidification and stabilization of WWT sludge from a Copper Smelter bearing high amounts of heavy metals and arsenic was possible using FA in mixtures with lime. All samples with different addition and composition of binder had UCS above the required 0.35 MPa after 28 days of curing. The  $c_{Ca}/c_{Si}$  ratio was found to be the main factor governing strength development. With addition of lime, there was not enough silica present in waste to react with the surplus of Ca(OH)<sub>2</sub>. Unreacted Ca(OH)<sub>2</sub> caused a decrease in the UCS values. In the leachates after the EN 12457-4 test, the concentration of Zn and Ni were under 0.1 and 0.2 mg 100 g<sup>-1</sup> dried material, respectively. Different additions and compositions of binder had no influence on the leaching As and Sb. On the other hand, the results of the TCLP tests revealed stabilization of Cu, Ni, Pb and Zn by over 99 % and As by over 90 % with addition of 50 % of lime to the FA. Heavy metals leaching was reduced with increasing calcium concentration in the form of CaO and Ca(OH)<sub>2</sub> (Ca concentration in binder), probably due to the formation of insoluble Ca-heavy metals salts and by increasing the pH value of the waste. The difference in the extraction fluids employed in the EN 12457-4 and TCLP leaching tests resulted in different toxicity characterization of the same waste. Acid neutralization (buffering) capacity, ANC, of waste increased with addition of FA and more with the addition of lime.

The results showed a linear dependence of the buffering capacity on the Ca concentration in the form of CaO and Ca(OH)<sub>2</sub>. However, only the sample with 50 % of lime added to the FA had an ANC value above required one. The reasons for this were the high gypsum and heavy metals concentrations in the WWT sludge and employment of FA as the binding agent. Sample with optimal addition of 20 % of binder containing 50 % of lime mixed with FA met all the requirements for safe disposal. Although the addition of lime to FA decreased the UCS, it was necessary for a better stabilization of the heavy metals and an increase in ANC value. Results of conducted tests indicate that the optimum amount of pozzolans present in the material could lead to the successful solidification/stabilization of WWT sludge bearing high amounts of heavy metals and arsenic.

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#### ИЗВОД

#### ПРОЦЕС СОЛИДИФИКАЦИЈЕ/СТАБИЛИЗАЦИЈЕ ЗА ТРЕТМАН ОТПАДНИХ ВОДА МУЉА ИЗ ПРИМАРНЕ ТОПИОНИЦЕ БАКРА

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Муљ који настаје третманом отпадне воде из примарне топинице бакра представља опасан отпад који се мора третирати пре одлагања услед високог садржаја тешких метала и арсена. Циљ презентованог рада је испитивање изводљивости и ефикасности процеса солидификације/стабилизације овог муља коришћењем летећег пепела и хидратисаног креча као агенса за стабилизацију. Ефикасност процеса се одређивала мерењем притисне чврстоће (УЦС) солидификата, тестовима лужења (EN 12457-4 и *Toxicity Characteristic Leaching Procedure* (TCLP)) и тестом капацитета за неутрализацију киселине (ANC test). Сви испитивани узорци су имали притисну чврстоћу изнад захтеваних 0,35 МПа. Однос концентрација калцијума и силицијума ( $c_{Ca}/c_{Si}$ ) у узорцима, одређен рендгенско–флуоресцентном анализом, је идентификован као главни фактор развоја притисне чврстоће. Оптичка емисиона спектрометријска анализа са индуковано спрегнутом плазмом раствора након тестова лужења је показала одличну стабилизацију Cu, Ni, Pb и Zn (изнад 99 %) и арсена (изнад 90 %) у узорцима са високим садржајем Ca(OH)<sub>2</sub>. Резултати ANC теста указују на то да пуферски капацитет солидификованог материјала линеарно зависи од концентрације Ca у летећем пепелу и кречу. Узорак са 20 % везива састава 50 % летећи пепео и 50 % хидратисани креч испуњава све захтеване услове да буде безбедно одложен.

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