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Treatment of wastewater from new copper smelter RTB Bor

Copper mining and smelting complex (RTB) Bor in Serbia is one of the most important producers of copper and precious metals in Central Eastern Europe with active production since 1903. For many years, effluents from RTB Bor have been a major environmental problem for the western Balkans and the Danube Basin [1-3]. RTB Bor smelter and sulfuric acid plant modernization project includes reconstruction of an old existing wastewater treatment plant (WWTP). The old plant for weak acids neutralization was built in 1979, and was designed for the treatment of 15.300 kg/h of weak acid containing 98 kg/h of H_2SO_4, and 153 kg/h (1%) of suspended particles. The plant was put into operation in 1980. However, it stopped working soon after and has not been in function since then. In order to increase process efficiency and reduce environmental impact, off gas generated during smelting and converting processes in new copper smelter RTB Bor is now treated in wet scrubbers and cooling tower for wet gas cleaning. The result of this process is generation of wastewater from primary copper smelter that will be treated in the new/reconstructed WWTP. The task for a team from the Innovation Center of TMF was technical-technological solution for the reconstruction of WWTP with a new wastewater treatment process [4]. Waste streams that will be treated at the WWTP are (1) from the wet scrubber for purifying and cooling the off-gas generated during smelting process in Flesh furnace (FSF flow) and (2) from the wet scrubber for purifying and cooling the off-gas generated during converting process in Pierce- Smith Converter (PSC flow). Metals present in flue dust from smelting process, mainly in the form of oxides or sulfates, will be dissolved in wastewater during the wet gas cleaning. On the other hand, metals in flue dust from converting process, in sulfide or metallic form, will be present as suspended particles in wastewater [5]. The projected FSF and PSC effluent flows are very acidic, carrying a very high content of heavy metal particles and a significant amount of dissolved heavy metals, specifically Cu, Fe, Zn, Pb and As.

1 Introduction

Conventional methods for the removal of heavy metals from industrial wastewater generally include chemical precipitation process. Chemical precipitation is based on the conversion of the dissolved metals into insoluble compounds, such as hydroxides, sulfides and metal carbonates by using appropriate reagents. The usual method for removing dissolved metals from the wastewater is their precipitation in the form of hydroxide. Alkali addition raises pH value of a solution while dissolved metals form insoluble metal-hydroxides and precipitate from the solution. Wastewater treatment by metal hydroxide precipitation method is simple, easily applicable in the industry as an economically viable technology suitable for automatic control. The best available technique for the treatment of wastewater from a primary copper smelter is metal hydroxide precipitation by using hydrated lime [6]. This method is widely used due to low prices and high lime efficiency. The main disadvantage of this method is the formation of large quantities of wastewater treatment sludge [7].

Arsenic is commonly present in metallurgy of copper and gold. In these processes, arsenic is usually found as arsenite (As(III)) or arsenate (As(V)) inorganic oxyanions. Metallurgical wastewater, rich in arsenic, requires treatment prior to discharge or reuse as process water. The most often used methods for removal of arsenic from wastewater include (1) the use of lime and the precipitation of As in the form of a calcium(II)-arsenites ($Ca_3(AsO_3)_2$) and calcium (II)-arsenates ($Ca_3(AsO_4)_2$). This is the simplest and economically most cost-effective method, however, the resulting precipitate is unstable; (2) co-precipitation of As(V) with ferri ions is a practical and the most effective method for arsenic removal, particularly in the metallurgical industry in which large quantities of iron and arsenic are by-products of the processes; (3) Precipitation of As in the form of sulfides As_2S_3 is possible by introducing Na_2S, NaHS or H_2S into an acidic solution. The resulting sulfide is stable and relatively insoluble under acidic condition, however, extremely soluble in an alkaline environment; (4) the application of ion-exchange resins for removal of arsenic from a solution is area of intensive research.

The main residues from these processes are gypsum, metal hydroxides and sulfides in the form of wastewater treatment sludge (WWTS). WWTS, as a hazardous waste [8], requires chemical and physical treatment prior disposal in order to prevent secondary contamination of the environment. The solidification/stabilization process (S/S) is considered to be the best demonstrated available technology for the treatment of industrial waste containing heavy metals. It involves mixing of a contaminated media with a specific binder in order to convert hazardous constituents into less soluble, mobile or toxic forms by incorporating waste into a solidified matrix [9].The most frequently used binders are cement-based materials. However, in order to improve economic and environmental effects of the S/S process, nowadays, cement is increasingly replaced by pozzolanic waste materials such as fly ash (FA). Effectiveness of the S/S process is usually defined by compressive strength and leaching resistance of solidified products.

This paper presents technical-technological solution for the reconstruction of WWTP within new copper smelter RTB Bor with a new wastewater treatment process [4]. The work includes simulation of the wastewater treatment process with determination of thermodynamic parameters of the process and amounts of necessary chemicals and generated WWTS. The simulation results were confirmed by experimental tests at the pilot plant level. The paper also proposes a treatment for the WWTS.

2 Materials and methods

2.1 Characteristics of wastewater from new copper smelter RTB Bor

Sample of wastewater (100 L) was taken from still operating old sulfuric acid plant within RTB Bor in October 2013. In order to obtain the projected composition of the wastewater from new copper smelter as joint FSF + PSC flow, the composition of the sample was corrected by adding: As_2O_3 (p.a) for As concentration adjustment; $CuSO_4$•$5H_2O$ (techn.grade), Cu (p.a) and CuS (p.a) for Cu adjustment; $FeSO_4$•$7H_2O$ (p.a.) for Fe_2+ adjustment; $Pb(CH_3COO)_2$ (p.a), PbO(p.a) and PbS (p.a) for Pb concentration adjustment; $ZnSO_4$•H_2O (techn.grade) and ZnS (p.a) for Zn concentration adjustment. Projected characteristics of wastewater generated in new copper smelter RTB Bor are listed in Table 1.

Table 1. Characteristics of copper smelter wastewater [4]

Parameter	Unit	Value
Temperature	T [ºC]	55
Volume	w [m^3/h]	8,66
Density	ρ [kg/m3^3]	1069
Solids content	[%wt]	1,36
Acid content (H_2SO_4)	c [g/L]	142,7
pH	-	-0,464
Dissolved metals	-	-
Cu	c [g/L]	0,53
Fe^{2+}	c [g/L]	0,38
Zn	c [g/L]	0,54
Pb	c [g/L]	0,45
As	c [g/L]	1,37

All experiments were performed on samples of wastewater with adjusted chemical composition.

2.2 Simulation of wastewater treatment process

Thermodynamic data for possible reactions during wastewater treatment process, as well as Eh-pH diagrams of the elements were obtained in Outcumpu's HSC Chemistry software package. The simulation was performed in SuperPro Designer software package. The input data for the simulation were projected characteristics of wastewater from new copper smelter RTB Bor, listed in Table 1, as well as stoichiometric quantities of reactants. The objective of the simulation was to evaluate the feasibility of the process and to determine the amount and composition of generated sludge and treated wastewater.

2.3 Wastewater treatment process at a pilot plant scale

Neutralization of acidic wastewater and precipitation of metals ions in the form of hydroxide were done by using 13% solution of hydrated lime, $Ca(OH)_2$ (commercial grade), in distilled water (lime milk). The treatment of 25 L of wastewater was performed in a detached boron silicate glass reactor with maximum volume of 80 L and controlled mixing, heating, pH regulation and feeding system for lime milk. Neutralization was performed by constant addition of lime milk with continuous monitoring of pH value and temperature of the suspension. After reaching the pH = 9,5, process was stopped and possible change of pH value was monitored for the next 30 minutes.

2.4 Solidification/stabilization treatment of obtained WWTS

WWTS generated during the treatment of wastewater at the pilot plant scale was subjected to S/S, in order to investigate the possibility of S/S treatment application on the WWTS. The WWTS and the binders with different composition were thoroughly mixed to obtain a homogeneous paste. Mixtures of fly ash (FA) and hydrated lime (HL) (FA : HL = 50 : 50); FA and portland cement (PC) (FA : PC = 90 : 10) and FA as the only additive were investigated as binders in the S/S process. WWTS to binder ratio was 4 and water to solid ratio was 0.4 in all mixtures. The paste was cast into plastic molds 5 × 5 × 5 cm dimensions and vibrated in order to remove entrapped air and excess water. Specimens were cured according to ASTM C109 standard [11]: 24 h under wet towels to meet the requirement of 99% moisture. After 3 days, samples were removed from the molds and left to cure in air. Quality of the S/S treatment was assessed by measuring unconfined compressive strength (UCS) of the solidificates and applying standard leaching test TCLP (toxicity characteristic leaching procedure) [12]. After 28 days of curing, the UCS of samples was measured using a servo hydraulic testing machine type INSTRON 1332-retrofitted Fast track 8800 with a maximum load of 100 kN. Results were the mean measurements of three samples. The TCLP test was conducted after 180 days of curing in order to determine the worst-case leaching scenario. A 50 g of grounded samples (<10 mm) were leached with glacial acetic acid solution (pH=2.88±0.05), L/S 20, by rotating bottles for 18 h.

3 Results and discussion

3.1 Simulation of wastewater treatment process

Eh-pH diagrams were made in order to determine the form of metals and arsenic present in untreated wastewater. Eh and pH values were measured on a semisynthetic sample which was obtained by adjusting the acidity and the chemical composition according to the projected joint FSF + PSC stream. The resulting diagrams for Cu, As, Zn and Pb are presented in Figure 1 together with the area of thermodynamic stability for the given conditions. Eh-pH diagrams for Cu, Zn and Pb shows that these metals are present in the form of ions M^{2+} (M = metal) in untreated wastewater. Under oxidizing conditions arsenic will be present as arsenate acid (H_3AsO_4), while under more reducing conditions As will be present in the form of meta-arsenite acid ($HAsO_2$).

Lime milk as 13% solution is used for neutralization of weak acid and metal hydroxides precipitation. Several mechanisms are analyzed for arsenic precipitation. It is expected that As would be precipitated in the form of a calcium(II) arsenates and calcium(II) meta-arsenites, as well as, by co-precipitation with Fe^{3+} ions forming iron(III) arsenates. For this mechanism addition of ferric sulfate as 46,6% solution is projected. Formation of scorodite in traces is also possible in the system. Expected reactions in the process of wastewater treatment, and their thermodynamic data (enthalpy (ΔH), entropy (ΔS), and Gibbs energy (ΔG)) at 50 ºC are presented in Table 2.

Thermodynamic data presented in Table 2 show that the primary reaction in the system is the reaction of $Fe(OH)_3$ precipitation, formation of $Ca(AsO_2)_2$ and acid neutralization. All reactions in the system are exothermic reaction except the reaction of As co-precipitation in the form of $FeAsO_4$.

Table 2. Possible reaction during wastewater treatment process [4]

Reaction	ΔH [kJ]	ΔS [J/K]	ΔG [kJ]
$H_2SO_4(ia) + Ca(OH)_2(s) = CaSO_4(s) + 2H_2O(aq)$	-105,297	171,098	-160,587
$CuSO_4(ia) + Ca(OH)_2(s) = CaSO_4(s) + Cu(OH)_2(s)$	-55,214	218,676	-125,879
$PbSO_4(ia) + Ca(OH)_2(s) = CaSO_4(s) + Pb(OH)_2(s)$	-53,271	88,356	-81,823
$ZnSO_4(ia) + Ca(OH)_2(s) = CaSO_4(s) + Zn(OH)_2(s)$	-24,903	214,455	-94,204
$2H_3AsO_4(aq) + 3Ca(OH)_2(s) = Ca_3(AsO_4)_2(s) + 6H_2O(aq)$	-58,606	10,991	-62,158
$2HAsO_2(aq) + Ca(OH)_2(s) = Ca(AsO_2)_2(s) + 2H_2O(aq)$	-183,390	-23,594	-175,766
$2H_3AsO_4(aq) + Fe_2(SO_4)_3(ia) = 2FeAsO_4(s) + 3H_2SO_4(ia)$	158,369	544,573	-17,610
$Fe_2(SO_4)_3(ia) + 3Ca(OH)_2(s) = 2Fe(OH)_3(s) + 3CaSO_4(s)$	-187,996	874,118	-470,467
$2H_3AsO_4(aq) + Fe_2(SO_4)_3(ia) + 2H_2O=2FeAsO_4×2H_2O(s) + 3H_2SO_4(ia)$	158,369	544,573	-17,610

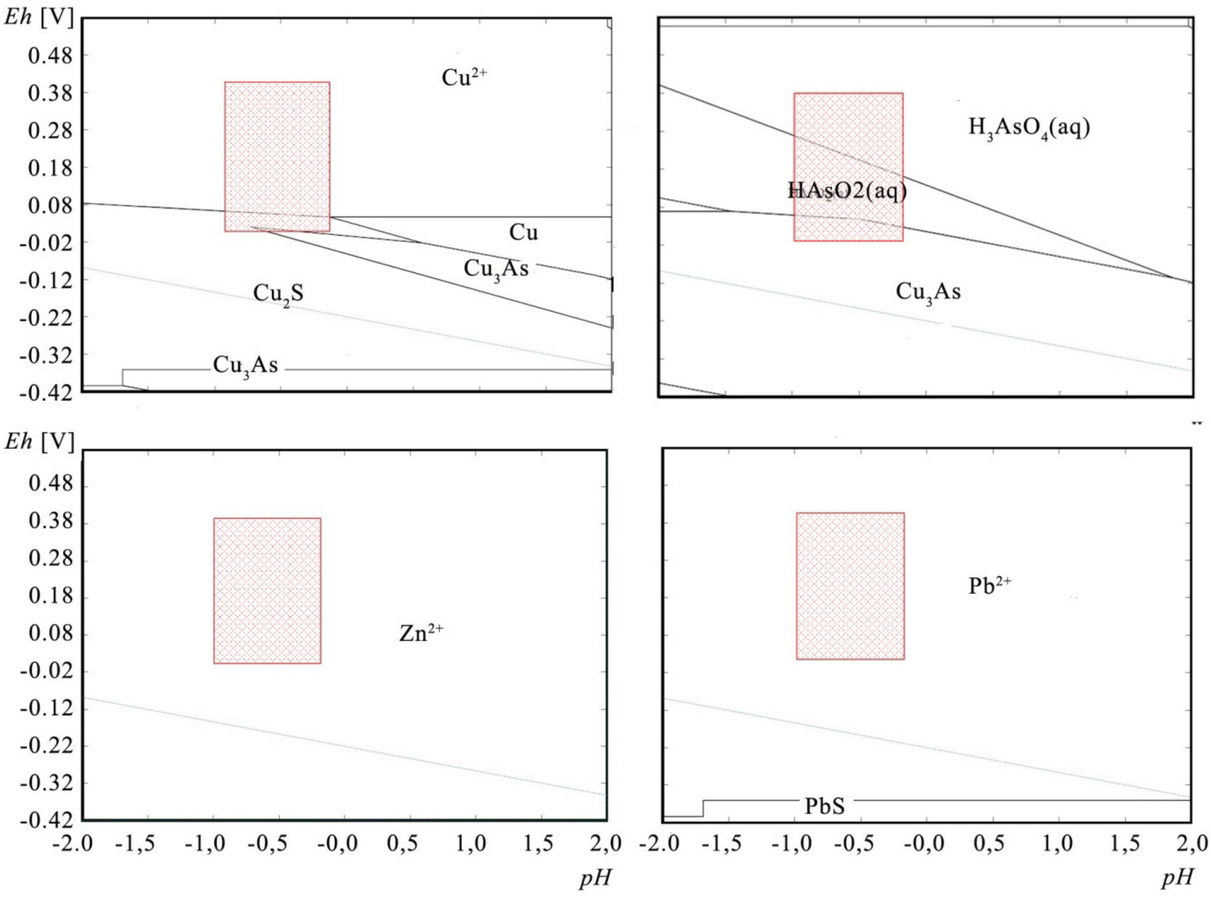

Figure 1: Eh-pH diagrams for Cu, As, Zn and Pb in untreated wastewater [4]

The scheme of wastewater treatment simulation with hydrated lime is presented in Fugure 2. The inflows into the system are two waste streams from FSF and PSC processes. These two steams are mixed and treated in four reactors. The characteristics of wastewater after the mixing of streams are as presented in Table 1. Lime milk is added to all four reactors: 50% of the projected flow of lime milk is added to the first reactor, 35% to the second, 14% to the third and 1% to the last one. In order to provide oxidative conditions, the solution of hydrogen peroxide is added into the first reactor. Ferric sulfate is added to the second (75% of projected flow) and third reactor (25% of projected flow) for co-precipitation of arsenic which is expected to start at pH 4,5 - 5,0 and to end at pH of 7. Complete acid neutralization, metal hydroxide precipitation and arsenic co-precipitation is expected at pH 9,5 - 10 in the fourth reactor. Treated wastewater is sent to a thickener, where the organic polymer is added as an agent for the coagulation/flocculation. The outflows from the thickener are overflow water and wastewater treatment sludge containing 25 - 30% solids. The quantities of input streams of wastewater and reactants, as well as characteristics of output streams, as the result of simulation are presented in Table 3 and 4, respectively.

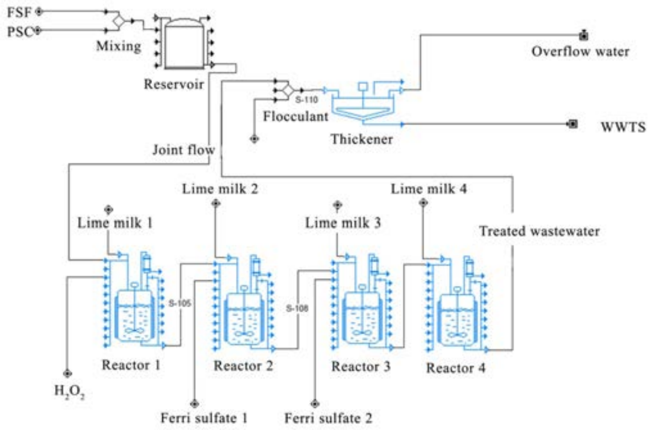

Figure 2: Scheme of wastewater treatment process with hydrated lime[4]

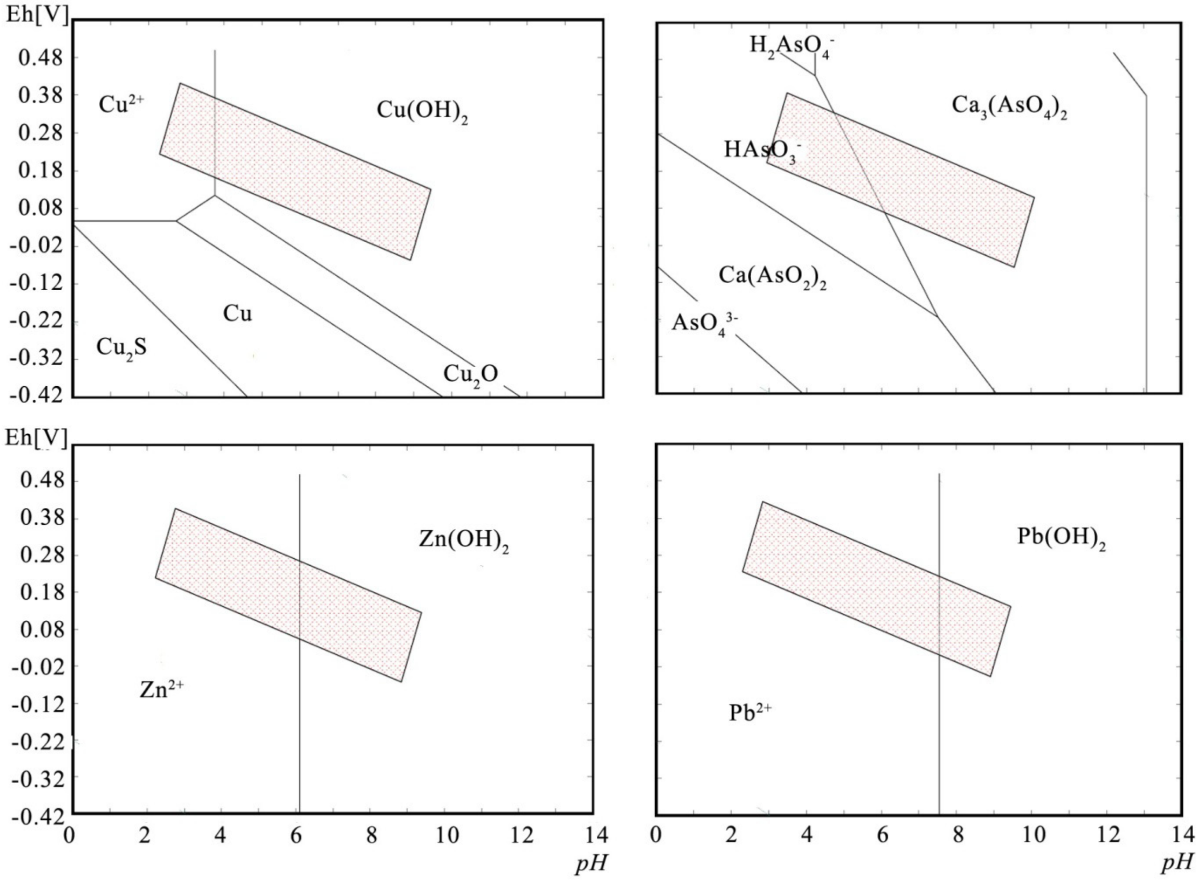

Figure 3: Eh-pH diagrams for Cu, As, Zn and Pb in treated wastewater [4]

Table 3. Quantities of simulation input streams

Input streams	Flow	Value
Wastewater	[m^3/h]	8,66
Hydrogen peroxide as 36% solution		
to the 1st reactor	[kg/h]	47,0
Lime milk as 13% solution		
to the 1st reactor	[kg/h]	4.340,7
to the 2nd reactor	[kg/h]	3.125,3
to the 3rd reactor	[kg/h]	347,2
to the 4th reactor	[kg/h]	86,8
Ferric sulfate as 46,6% solution		
to the 2nd reactor	[kg/h]	150,1
to the 3rd reactor	[kg/h]	50,0
Organic polymer as 0,15% solution		
to the thickener	[kg/h]	8,7

Table 4. Quantities of simulation output streams

Output streams	Flow	Value
Overflow water	[m^3/h]	7,21
WWTS	[kg/h]	10.281,6

Result of wastewater treatment process is generation of overflow water (7,21 m^3/h) and WWTS (10.281,6 kg/h) from the thickener. Eh-pH diagrams for the metals present in treated wastewater were done according to the projected amount of reactants and target pH value and presented in Figure 3.

Figure 3 shows that dissolved metals Cu, Zn and Pb will transform to hydroxides during the treatment, while As will be present as calcium(II) arsenate in treated wastewater. These elements will precipitate and form WWTS together with gypsum, as a result of acid neutralization. Chemical composition of WWTS, obtained by simulation, is given in Table 5. More than 75% of the sludge composition will be water, as a result of thickener operation performances. Main component of WWTS is gypsum together with metal hydroxides. WWTS will also include suspended particles of metal sulfides and metals in elemental form that remained undissolved in weak acid.

Projected amounts of reactants and products of wastewater treatment process, obtained by simulation are tested during the experiments at pilot plant scale.

3.2 Experiments on pilot plant scale

The sample of wastewater (25 L) is directly treated with 13% solution of lime milk to achieve pH≈9,5. The process temperature increased from 31,9 °C at the beginning to 38,8 °C at the end of the treatment due to exothermic effect of the neutralization reaction. The pH value of the suspension after the completion of the neutralization was 9,69. The amount of lime milk consumed for complete neutralization was 10,34 kg. The density of the obtained suspension was 1,157 kg/dm^3. The phase separation was performed after the constant pH value had been achieved. The amount of overflow water was 8 L. The mass of filter cake obtained in vacuum filtration was 2,72 kg after drying for 24 h at 105 °C. Moisture content prior to drying was 64,5%. The density of the filter cake was 380 kg/m^3.

Table 5. Chemical composition of WWTS [4]

WWTS	Flow [kg/h]	[%]
$Ca(OH)_2$	1,08	0,01
$CaSO_4{\cdot}2H_2O$	2.384,06	23,19
Cu	6,45	0,06
$Cu(OH)_2$	6,49	0,06
Cu_2S	33,14	0,32
$Fe(OH)_2$	11,41	0,11
$FeAsO_4$	32,98	0,32
$Fe(OH)_3$	31,74	0,31
Pb	0,42	0,00
$Pb(OH)_2$	14,86	0,14
PbO	1,69	0,02
PbS	7,08	0,07
SiO_2	0,33	0,00
H2O	7.719,71	75,08
$Zn(OH)_2$	12,89	0,13
ZnS	0,37	0,00

Chemical composition of treated wastewater as overflow from thickener compared with characteristics of untreated wastewater from primary copper smelter is given in Table 6. It can be seen that removal of over 99% of investigated metals (Cu, Fe, Zn, Pb and As) has been achieved by applying described wastewater treatment process.

Table 6. Characteristics of untreated and treated wastewater

Parameter	Unit	Untreated wastewater	Treated wastewater
Volume	w [m^3/h]	8,66	7,21
Solids content	[%wt]	1,36	< 0,1
pH	-	-0,464	9,7
Dissolved metals	-	-	-
Cu	c [mg/L]	530	0,01
Fe^{2+}	c [mg/L]	380	0,014
Zn	c [mg/L]	540	0,025
Pb	c [mg/L]	450	< 0,03
As	c [mg/L]	1370	4,0

Table 7. Chemical composition of WWTS

Metal	c [mg/kg]
As	12.200
Ba	1,7
Cd	89
Cr	2,4
Cu	5.700
Ni	2,9
Pb	2.730
Sb	8,3
Zn	15.100

3.3 S/S process of WWTS

Results of UCS and TCLP test of solidified samples F (FA as the only additive), L50 (FA:HL = 50:50) and C10 (FA:PC = 90:10) are shown in Figure 4 and 5, respectively.

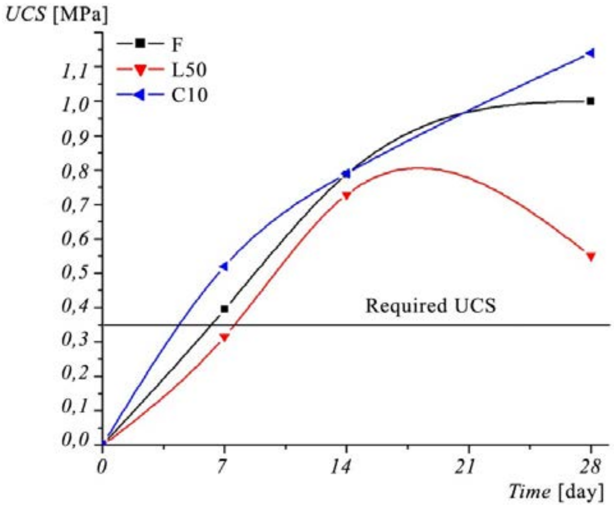

Figure 4: UCS of solidified samples of WWTS after S/S process

Addition of PC to FA had positive effect on development of UCS, in contrast to HL addition which resulted in reduction of UCS after 14 days of curing. Nevertheless, all of three samples had UCS higher than 0.35 MPa required for the safe disposal of stabilized waste [13].

TCLP test of WWTS showed that concentration of leached Cu and Zn are higher than limit for non-hazardous waste [8] which confirmed its characterization as hazardous waste. After S/S process with FA as the only additive, Cu concentration decreased below the limit, while Zn concentration remained high. Addition of PC to FA as the agent for S/S process, reduced concentration of all investigated metals (Cu, Pb, As, Zn) below the limit for non-hazardous waste, while addition of HL had even greater effect. TCLP test of L10 sample showed concentration of Cu, Zn and Pb below detection limit for those metals, and concentration of As well below the limit for non-hazardous waste. Stabilization of more than 99% of heavy metals and 90% of arsenic has been achieved in the system with the HL addition [10].

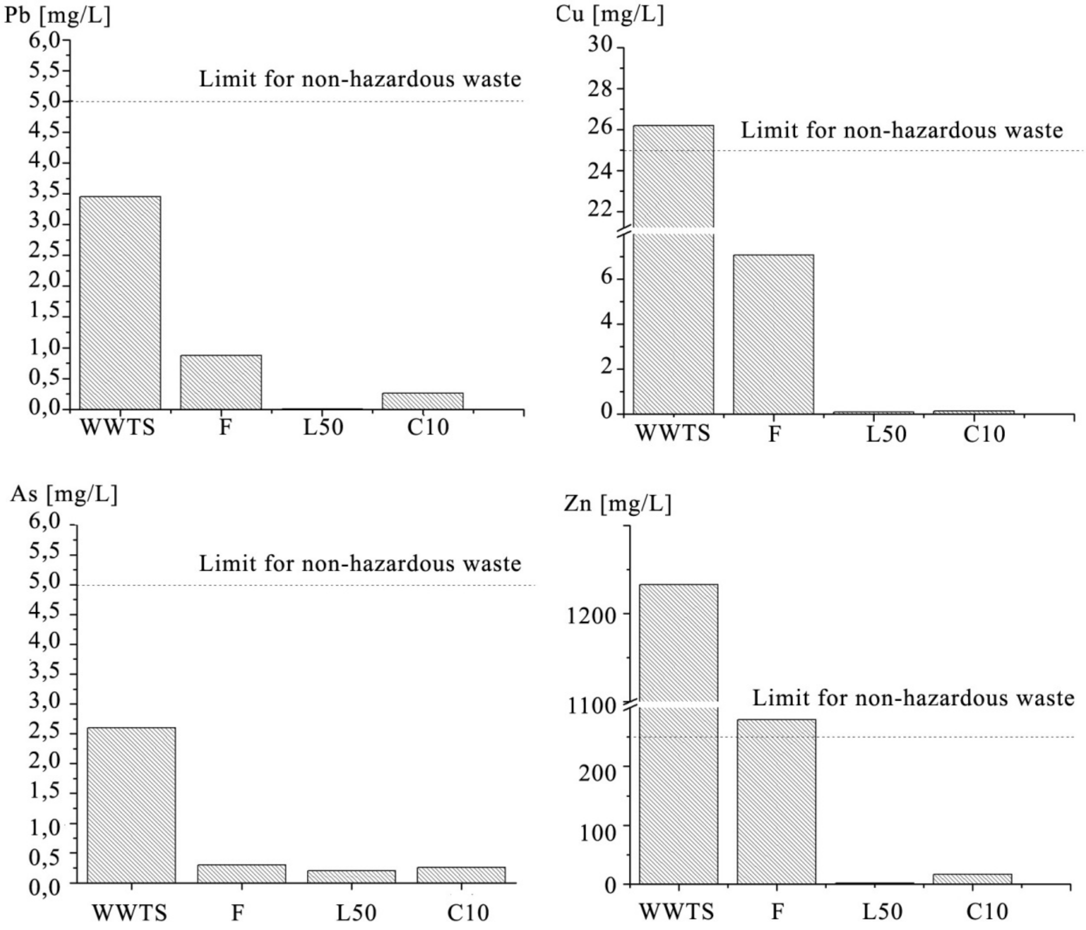

Figure 5: Results of TSCL test of WWTS and solidified samples after S/S process

4 Conclusions

RTB Bor smelter and sulfuric acid plant modernization project includes reconstruction of an old existing WWTP. The projected FSF and PSC effluent flows that will be treated in the WWTP, are very acidic, carrying a very high content of heavy metal particles and a significant amount of dissolved heavy metals, specifically Cu, Fe, Zn, Pb and As. Eh-pH diagrams for Cu, Zn and Pb shows that these metals are present in the form of ions M^{2+} (M = metal) in untreated wastewater. Under oxidizing conditions arsenic will be present as arsenate acid (H_3AsO_4), while under more reducing conditions As will be present in the form of meta-arsenite acid ($HAsO_2$). Lime milk and solution of ferric sulfate are used for acid neutralization, metal hydroxides precipitation and arsenic co-precipitation. Results of wastewater treatment simulation are amount and composition of treated wastewater and WWTS. Projected amounts of reactants and products of wastewater treatment process, obtained by simulation are tested by the experiments at pilot plant scale. Result show that removal of over 99% of investigated metals (Cu, Fe, Zn, Pb and As) has been achieved by applying described wastewater treatment process. The WWTS is considered to be hazardous waste due to high amount of pollutants and requires chemical and physical treatment prior to disposal. Stabilization of more than 99% of heavy metals and 90% of arsenic has been achieved in the system with the FA and HL addition by proposed S/S treatment.

Abbreviations

FA – Fly ash
FSF - Flesh smelting furnace
HL - hydrated lime
PC - portland cement
PSC - Pierce- Smith Converter
RTB - Copper mining and smelting complex
S/S – Solidification/stabilization
TCLP - toxicity characteristic leaching procedure
UCS - unconfined compressive strength
WWTP - wastewater treatment plant
WWTS - wastewater treatment sludge

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