

CONCEPTUAL DESIGN FOR TREATMENT OF MINING AND METALLURGICAL WASTEWATERS WHICH CONTAINS ARSENIC AND ANTIMONY

Željko Kamberović¹, Marija Korać², Zoran Anđić³, Marija Štulović²,
Tihomir Kovačević², Aleksandar Vujović³, Ilija Ilić¹

¹University of Belgrade, Faculty of Technology and Metallurgy,
Belgrade, Serbia

²University of Belgrade, Innovation center of the Faculty of Technology and
Metallurgy, Belgrade, Serbia

³University of Belgrade, Innovation center of Chemical Faculty,
Belgrade, Serbia

Received 24.06.2012

Accepted 23.07.2012

Abstract

This paper presents a preliminary design for treatment of mining and metallurgical wastewaters (MMW) from the basin of antimony “Zajača“, which contains high concentrations of arsenic and antimony. MMW have been investigated in laboratory, due to large difference in concentrations of pollutants. Metallurgical wastewaters were treated using iron (II)-sulfate and lime milk used to adjust the pH value at 7. After chemical treatment of metallurgical wastewater and its joining with mining wastewater, residual amount of arsenic in water was below maximum allowed concentrations, while the concentration of antimony, remained above the maximum allowed value. The final phase of purification process was performed using ion exchange resin. After treatment of MMW, they can be used as technical water in the smelting process of secondary raw lead materials.

Key words: arsenic, antimony, mining and metallurgical wastewaters, ion exchange

Introduction

One of the sources of environmental pollution caused by metallurgy, in addition to emission of gases and dust and inadequate treatment and disposal of solid waste, is generating a wastewater with high metal content, without prior treatment. The huge amount of waste from smelter and mines containing heavy metals has been deposited on tailings during many years. Heavy metals, dissolved from historical tailings, as in the case of metallurgical-mining basin “Zajača“, can have negative influence on the environment. Therefore, it is necessary to make investments to improved technologies

and cleaner production as a preventive approach to protecting the environment and supporting the development of modern production process. This would provide savings of raw materials, auxiliary materials and energy while reducing operating costs and increasing profit [1].

Antimony smelter in Zajača, near city of Loznica, started working in 1897. and produced 126 t of antimony during the first year of operation. The capacity has increased to 8 t of antimony per 24 hours during 1938 [2]. Annual production was approximately 2000 t in the period between 1950 and 1980, with a maximum annual production of 2768 t, achieved in 1965 [1, 3]. After 1980, the production of antimony decreased to about 1000-2000 t per year, and was finally terminated in 1990. The production has been suspended due to low market price of antimony and low quality of available ore, especially due to high arsenic content [4]. About 84000 t of antimony regularly has been produced in "Zajača" during its existence, from 1897-1990 [3]. Today, refined lead from secondary raw materials (batteries) and lead-antimony alloys with the total volume of production of about 25000 t per year is being produced in "Zajača".

Recovery of antimony in the middle of 2012, was especially important considering that the expert group of European board has defined the list of 14 mineral raw, of key significance for European Union [5]. The list has been defined from the aspect of both possibility of primary production and the production of raw materials, and possibility of replacement by other raw materials, which production is not limited. In addition, the increasing demands for lead and lead-antimony alloys, as well as the permanent growth of market prices of these products, are in favor of recovering the production process.

By mixing of primary and secondary Sb and Pb raw materials treatment technologies, alkaline sodium will be generated as process waste, containing significant amount of antimony, arsenic, lead and other heavy metals which have been accumulated on the tailings during more than 100 years of antimony production, and during the production of lead from secondary raw materials in smelter "Zajača". These heavy metals, highly toxic, have been leached from tailings and reached the natural recipient, causing significant mortality of livestock. Impact on human health is not clearly perceived, but it exists.

Among all present heavy metals in MMW, arsenic and antimony are the most toxic and due to that fact, their compounds are considered to be pollutants of prime interest by the USEPA (*United States Environmental Protection Agency*) [6]. In addition, according to Knežević et al. [7] these metals are migratory, so dissolution from metallurgical and mine tailings can have negative influence on the environment and human health.

Long exposure to arsenic and antimony causes increased risk of skin, lung, bladder and kidney cancer [8]. Also, exposing to arsenic can lead to nervous and cardiovascular system functional disorder. Arsenic can be transported through the pregnant women placenta and accumulate in the milk, affecting children's health. Antimony accumulates in the organs, especially in liver, kidneys and blood [9].

Several arsenic and antimony removal methods can be found: adsorption, coagulation, membrane separation, solvent extraction and electrochemical process, reverse osmosis, leaching as well as combination of these methods, suggested by many authors [10–18], but they are quite expensive. The most common method used for

treatment of industrial wastewater as well as drinking water is combining of adsorption and coagulation with addition of chemical agent to control the pH value.

Navarro et al. [11] have performed coagulation of arsenic and antimony from copper solution on active carbon. Separation of arsenic and antimony has been followed depending on the copper solution/active carbon ratio and temperature. They concluded that increasing of solution/active carbon ratio and decreasing of temperature have positive influence to antimony and arsenic separation.

Guo et al. have proven that the removal of antimony by coagulation method using Fe-coagulant is more efficient than using Al-coagulant [6]. NaHCO_3 has been added to the solution to maintain its moderate alkalinity, close to the natural water. In addition to antimony, the behavior of arsenic has also been followed and it has been observed that the Sb (V) was more difficult to remove than As (V), but the removal of Sb (III) was relatively better than As (III). The removal efficiency of different forms of As and Sb during coagulation process with Fe-coagulant in ambient pH was as follows: $\text{As (V)} > \text{Sb (III)} > \text{As (III)} > \text{Sb (V)}$.

Kang et al. [15] have prepared solutions of As (III), As (V), Sb (III) and Sb (V) by dissolution of As_2O_3 , $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$, Sb_2O_3 and KSb(OH)_6 in distilled water, respectively. The required pH values 3, 5, 7 and 10 have been adjusted by addition of NaOH and HNO_3 . The two types RO membranes were used. The removal of arsenic compounds significantly depend on pH value, especially As (III) compounds. Otherwise, pH value does not have significant influence on the removal of antimony compounds, until oxidation of Sb (III) to Sb (V).

Experimental

Laboratory examinations of wastewater beneath the metallurgical tailings "Zajača" and mine wastewater from processing of mineral raw materials which flows near the smelter, were carried out in order to produce purified water for its reuse as a technical water in the secondary lead smelting processes. The research has been carried out in the Laboratory for extractive metallurgy at the Faculty of Technology and Metallurgy, University of Belgrade. Design for treatment of MMW has been given based on the obtained results. Figure 1 shows the design flowsheet.

Due to large differences in the pollutants concentration in smelting and mining wastewater, purification process has been carried out as follows:

- Metallurgical wastewater, with a high pollutant content, has been treated by chemical process with iron (II)-sulfate and lime milk;
- Mining wastewater, with a low content of pollutants, has not been treated separately, but only as a part of the mixture with chemically purified metallurgical wastewater.

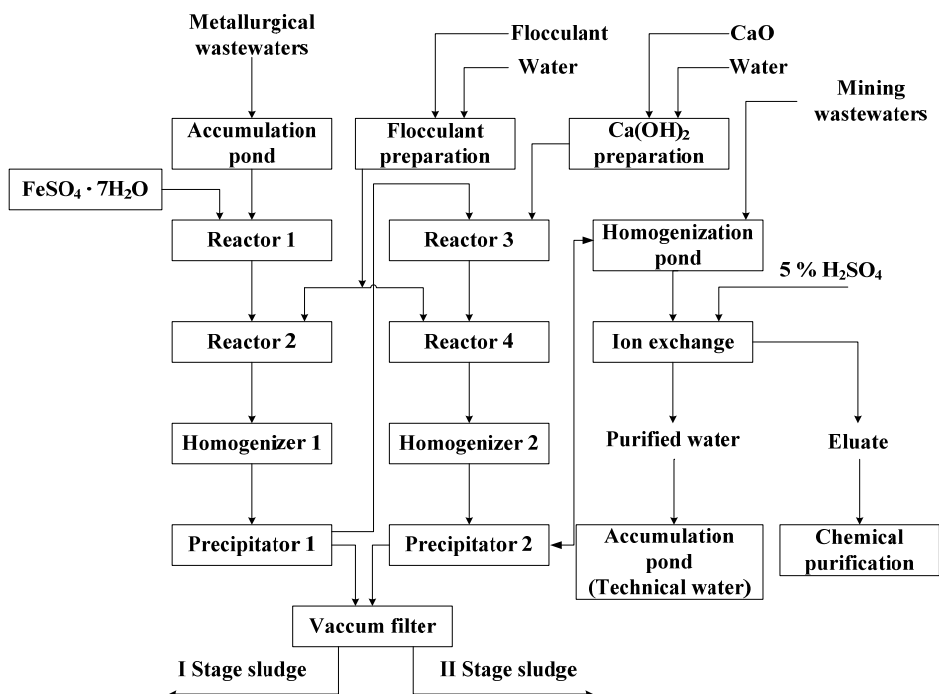


Figure 1. Design block scheme for purification process of MMW

After the metallurgical wastewater has been chemically treated, the same has been joined with mining wastewater. The mixture of MMW has been treated with an ion exchange in order to remove remaining amount of pollutants.

The chosen technological operations of purification of MMW are as follows: precipitation and neutralization, homogenization, flocculation and ion exchange.

Chemical treatment of smelting wastewater

Chemical precipitation of heavy metals from smelting wastewater has been carried out in two stages:

Stage I – Precipitation using iron (II)-sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) as a precipitation agent. Consumption of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was $2.0\text{--}2.5 \text{ g/dm}^3$ of wastewater, with constant stirring, 200 rpm, during 3-5 minutes. The anion polyelectrolyte (0.10 % „Superfloc”) was added as a flocculant, $2.0 \text{ cm}^3/\text{dm}^3$ of wastewater.

Stage II – Precipitation using suspension of lime milk, which also served as neutralization agent. Chemically treated wastewater was processed by suspension of lime milk, 3.3 g CaO in 100 cm³ of water. The volume of 10 cm³ of suspension is sufficient to neutralize 1 dm³ of water (pH 7) with simultaneous precipitation of Ni, Pb and Cd.

The suspension of lime milk was added during 3-5 minutes at constant stirring rate, then flocculant was added, same as Stage I, with intensive stirring for 3 minutes, then the slowly stirring for 10-15 minutes was performed.

Treatment of mixture of chemically treated smelting and mining water by ion exchange resin

After the chemical treatment, metallurgical wastewater has been joined with mining wastewater. In the next processing step the obtained mixture has been treated by ion exchange resin. „Lewatit“ TP 207 (LANXESS, Germany). Ion exchange resin is applicable to heavy metal ions extraction from wastewater, as well as from solution for toning in the presence of alkaline earth metals. This is weak macroporous cationic exchanger with gelatin iminodiacetate group for binding cations from weak acid or weak alkaline solutions.

During operation, ion exchange resin becomes saturated and ineffective in column and therefore needs to be regenerated after a certain period of time. In this case, the regeneration of ion exchange resin is carried out with 5 % H₂SO₄. After the flow of a certain amount of acid, the column needs to be leached using fresh water and then can be used in the process again. In order to prevent the leakage from the system to the natural recipient during regeneration process, there is need for another column which would accept and accumulate flows of wastewater until reconnected column goes back into the function. The separated eluate, desorbed from ion exchange resin, is chemically purified in order to achieve the precipitation of pollutants. Both the amounts of pollutants in the mixture of chemically treated MMW, and metal equivalent removed from mentioned mixture by ion exchange, have been calculated. In addition, the amount of precipitate obtained from both stages of purification process has been calculated, as well as the amount of pollutants.

Results and discussion

It was found that the variations in metallurgical wastewater flow points below tailings are 0.5-5.0 dm³/s, with an average value of 2.0 dm³/s, and for mining 1.0-2.0 dm³/s, average 1.6 dm³/s. The total flow of sMMW varies between 1.5 and 7.0 dm³/s, with an average value of 3.6 dm³/s.

Laboratory studies showed that the main pollutants have been heavy metal ions leached from smelter tailings, primarily arsenic and antimony, which presence is the most significant (*Table 1*).

The measured weight of heavy metal ions in examined wastewater was approximately constant. This means that the concentration of heavy metals depends of the flow intensity. When the flow intensity is lower, the concentration of heavy metals is higher, and otherwise.

MMW is alkaline water and ionic forms of arsenic and antimony which may be found are as follows: As₃³⁻, AsS₂⁻, AsO₃³⁻; Sb₃³⁻, SbS₄³⁻, SbO₂⁻, SbS₂⁻.

Table 1. Concentration of elements in metallurgical and mining wastewater before treatment

| Elements | Metallurgical wastewaters (2.0 dm ³ /s) | | Mining wastewaters (1.6 dm ³ /s) | |
|----------|-------------------------------------------------------|-------|------------------------------------------------|------|
| | mg/dm ³ | mg/s | mg/dm ³ | mg/s |
| Sb | 15.65 | 31.30 | 0.18 | 0.29 |
| As | 29.83 | 59.66 | 0.08 | 0.13 |
| Cu | 0.085 | 0.17 | - | - |
| Pb | 1.05 | 2.10 | 0.053 | 0.08 |
| Zn | 0.085 | 0.17 | - | - |
| Ni | 0.07 | 0.14 | - | - |
| Fe | 0.055 | 0.11 | 0.10 | 0.16 |
| Cd | 0.08 | 0.16 | - | - |
| Na | 10.00 | 20.00 | - | - |

Tables 2 and 3 show the calculation of smelting-mining wastewater mixture after chemical treatment, as well as metals equivalent which should be removed by ion exchange.

Iron (II)-sulfate has been used for precipitation of arsenic and antimony from wastewater. A similar procedure for treatment of wastewaters which contain arsenic has been described by Lee et al [18]. Unlike the treatment shown in this paper, potassium (I)-ferrate (K₂FeO₄) has been used instead iron (II)-sulfate. Aside the role of coagulant, ferrate has also been used as an oxidant for converting arsenic from As (III) to As (V). As (V) obtained this way has been precipitated using iron in the form of Fe (III). Fe (III) has been obtained by reduction of iron from ferrate used for oxidation of arsenic. In this paper, arsenic is precipitated in the form of As (III). This is due to the fact that the iron in the iron (II)-sulfate has oxidation state (II), i.e. with no oxidizing properties, as can also be concluded from the fact that the sludge does not contain elemental iron.

Table 2. The calculation of wastewater mixture

| Mixture of MMW after chemical treatment (3.6 dm ³ /s) | | | |
|---------------------------------------------------------------------|-----------------------------------|------------------------|---------|
| Contents | Concentration g/m ³ | Atomic weight g/mol | Valence |
| Sb | 4.2 | 121.75 | III |
| As | 0.62 | 74.92 | III |
| Cu | 0.05 | 63.54 | II |
| Pb | 0.03 | 207.20 | II |
| Zn | 0.05 | 65.37 | II |
| Ni | 0.04 | 58.71 | II |
| Fe | 0.03 | 55.85 | III |
| Cd | 0.04 | 112.40 | II |

Table 3. Metals equivalent that should be removed

| Elements | Calculation | Metals equivalent, meq/dm ³ |
|----------|---------------|----------------------------------------|
| Sb | 4.20·3/121.75 | 0.1035 |
| As | 0.62·3/74.92 | 0.025 |
| Cu | 0.05·2/63.54 | 0.00157 |
| Pb | 0.30·2/207.19 | 0.00289 |
| Zn | 0.05·2/65.37 | 0.00153 |
| Ni | 0.04·2/58.71 | 0.00136 |
| Fe | 0.03·3/55.85 | 0.00161 |
| Cd | 0.04·2/12.40 | 0.00071 |
| Total | | 0.2509 |

Lime milk has been used for neutralization, in order to achieve further precipitation of pollutants (Sb, Ni, Pb and Cd) at pH 7. pH value has a significant influence to the degree of removal of arsenic and antimony from wastewater. Degree of removal of Sb (III) and Sb (V), has been very low during the process of coagulation of antimony using iron (III)-chloride (FC), at pH 4. Degree of removal of antimony rises as pH value rises. The optimal pH value for Sb (V) removal is 4.5-5.5, while the pH values for high degree of removal of Sb (III) need to be between 4 and 10 [6]. Kang et al. have also noticed this very low dependence of removal of Sb (III) on pH value [13]. Examined wastewater from metallurgical-mining basin "Zajača" contains Sb (III), and according to previous authors, an optimal pH value for the removal of antimony has been achieved. Kang et al. have also shown that the degree of removal of As (V) was rapidly increasing at pH 7, which was confirmed in this paper.

A flocculant A-110 (Superfloc), polyacrylamide by structure, has been used for coagulation of precipitate from Stages I and II of the mentioned process. This flocculant has following advantages: effectiveness at very low concentration, applicability to a very wide range of pH values and good solubility in water.

Separated precipitate

It was experimentally found that in Stage I of purification, 0.75-0.80 kg of precipitate can be obtained from 1 m³ of metallurgical wastewater. Hydrate oxide of Fe, with impurities of As (2.5-4.7 %), Sb (0.18-1.8 %) and traces of Ni, Zn, Pb and Cd, is the major part of the separated precipitate.

After the precipitation with iron (II)-sulfate, which has been shown as very successful, the residual amount of arsenic in water was quite reduced, while the content of antimony, although greatly reduced, was still quite large. From this reason the mixture of MMW needs to be subsequently treated.

The precipitate from Stage I of purification process is dangerous to release due to the high content of arsenic and antimony. The separated precipitate could be treated with volatilizing roasting (separation antimony from roasting residue as volatile Sb₂O₃ which can be converted to raw antimony using the process of reduction melting) or could be used as a supplement to feedstock when arsenic rich concentrates are being treated. Solidification and stabilization (S/S) process is another way of treatment, which implies stabilization of arsenic and antimony in physical and chemical sense in tighter structure

and thereby preventing their emission into the environment. The obtained solidification products can be used as supplements for building materials, primarily for concrete.

In Stage II of purification, when a neutralization of solution using lime occurs, 0.85-0.90 kg of precipitate per 1 m³ of smelting wastewater is generated. An excess of iron and some other heavy metal ions as well as gypsum which is a result of neutralization of sulfate ion is precipitated during this stage. Separated precipitate is composed of gypsum contaminated with arsenic and antimony, but in very minor concentrations, so the treatment of this precipitate is not economically justified. Therefore, the precipitate is deposited to landfill, after using S/S process [19], which closes the circle of this metal.

Since the chemical deposition of arsenic and antimony from wastewater is only partial, an ion exchange is also taking place, resulting in no precipitation. Cations bind to the resin (instead of hydrogen), which is regenerated by occasional leaching using sulfuric acid. The obtained eluate, the carrier of heavy metal ions, is chemically treated, in order to precipitate pollutants.

Jessen and Münch [20] reported about using ion exchange resin in process of wastewater purification by BSB recycling company. After many purification operations including: precipitation, homogenization, neutralization, decantation etc, high concentration of heavy metals has remained. In order to reduce heavy metals content, ion exchange resin was employed. Due to residual amount of Ni, Cd and Zn, recirculation of wastewater was required, to reduce the concentration of mentioned pollutants over 90 %. Their results about content of As and Sb in water after treatment (0.01 mg/dm³ for As, 0.15 mg/dm³ for Sb) using the same type of resin is in accordance with presented results (Table 4). Using ion exchange resin in wastewater treatment plants, the content of heavy metals may be significantly reduced.

Table 4. Quality of treated water for technical reuse

| Elements | Achieved concentration, mg/dm ³ |
|----------|--------------------------------------------|
| As | < 0.05 |
| Sb | < 0.05 |
| Cu | < 0.01 |
| Pb | < 0.01 |
| Zn | < 0.01 |
| Ni | < 0.01 |
| Fe | < 0.50 |
| Cd | < 0.01 |

Table 5 shows the material balance of the predicted purification process. Balance is determined on a daily and annual level, based on adopted wastewater flow.

Table 5. Material balance

| Raw materials | Daily | Annual |
|------------------------------------------|-------|--------|
| Metallurgical wastewater, m ³ | 173 | 63145 |
| Mining wastewater, m ³ | 140 | 51100 |
| FeSO ₄ ·7H ₂ O, t | 0.43 | 157 |
| Flocculant, kg | 0.72 | 263 |
| CaO, t | 0.06 | 22 |
| H ₂ SO ₄ , kg | 1.97 | 720 |
| Rinse water | 0.06 | 22 |
| Arsenic, kg | 4.5 | 1642 |
| Antimony, kg | 1.1 | 401 |

Since the content of arsenic is much higher than that of antimony, processing can be performed on arsenic and antimony-based alloys required as required by the market.

Figure 2 shows the conceptual design for treatment of wastewater points below metallurgical tailings, as well as mining wastewater obtained from technological processes in mines „Zajača“ which flows near smelter. Implementation of the chosen wastewater treatment provides protection of surrounding natural recipients from contamination, meaning that the treated water is collected into the accumulation pond and returned into the smelting process as the technical water.

Design solution is selected according to identified best available technique (BAT) for wastewater treatment.

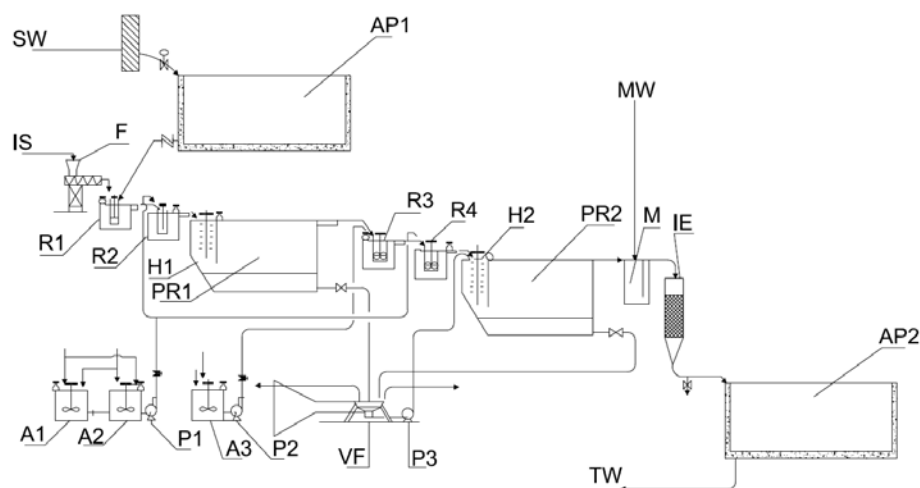


Figure 2. Conceptual design for treatment of smelting-mining wastewater:
 AP1, AP2-Accumulation pond, SW-Smelting wastewater, IS-Iron (II)-sulfate,
 MW-Mining wastewater, F-Feedstock, R1, R2, R3, R4-Reactors,
 H1, H2-Homogenizers, A1, A2, A3-Agitators, P1, P2, P3, P4-Pumps,
 PR1, PR2-Precipitators, VF-Vacuum filter, M-Mixer, IE-Ion exchange, TW-Technical
 water

Conclusion

A combination of precipitation (precipitation using iron (II)-sulfate and lime milk, flocculation) and ion exchange methods has proven to be very successful from the point of a removal of heavy metal ions from wastewater of smelter and mines „Zajača“. Using precipitation and flocculation processes, heavy metals can be converted into the forms that can be easily removed from the wastewater and their traces can be removed by ion exchange. The optimal pH value for complete separation of heavy metals from wastewater is 7. Water which may be reused as the technical water for secondary lead smelting process is obtained by applying the described treatment. Assumption is that water obtained after chemical treatment may be used as technical for operations in smelter, without further treatment with ion exchange resin. In case that water balance shows excess of finally purified water, the same may be released from accumulation pond if it is economically justifiable.

References

- [1] N. Radović, Ž. Kamberović, D. Panias, Cleaner metallurgical industry in Serbia: a road to the sustainable development, *Chemical Industry & Chemical Engineering Quarterly*, 15, 1, p. 1-4, 2009
- [2] Lj. Popović, *Antimony of Yugoslavia*, Publisher „Zenit“, Beograd, 1995 (in Serbian)
- [3] B. Nikolić, P. Bogdanović, A hundred years of metallurgical production of antimony in Serbia, *Tehnika - RGM*, Beograd, 2001 (in Serbian)
- [4] R.Ž. Vračar, Theory and practice of obtaining of non-ferrous metals, Association of Metallurgical Engineers of Serbia, 2010 (in Serbian)
- [5] European Commission, Report lists 14 critical mineral raw materials, MEMO/10/263, Brussels, 17 June 2010
- [6] X. Guo, Z. Wu, M. He, Removal of antimony(V) and antimony(III) from drinking water by coagulation-flocculation-sedimentation (CFS), *Water Research*, 43, p. 4327-4335, 2009
- [7] M. Knežević, M. Korać, Ž. Kamberović, M. Ristić, Possibility of secondary lead slag stabilization in concrete with presence of selected additives, *Journal of Metallurgy MjOM*, 16, 3, p. 195-204, 2010 October, 2007
- [8] World Health Organization, Environmental Health Criteria 224, Arsenic and arsenic compounds, Effects on human health, second edition, 2001
- [9] REDOIL (Resisting Environmental Destruction on Indigenous Lands), ACAT (Alaska Community Action on Toxics), Mining and Toxic Metals
- [10] N. Khalid, S. Ahmad, A. Toheed, J. Ahmed, Potential of rice husks for antimony removal, *Applied Radiation and Isotopes*, 52, p. 31-38, 2000
- [11] P. Navarro, F.J. Alguacil, Adsorption of antimony and arsenic from a copper electrorefining solution onto activated carbon, *Hydrometallurgy*, 66, 1-3, p. 101-105, 2002
- [12] M.D.S. Erosa, W.H. Höll, Removal of selenium and antimony species from aqueous solution by means of a weakly basic ion exchanger, Combined and Hybrid Adsorbents, NATO security through Science Series, p. 287-292, 2006
- [13] M. Kang, T. Karnei, Y. Magara, Comparing polyaluminum chloride and ferric chloride for antimony removal, *Water Research*, 37, 17, p. 4171-4179, 2003

- [14] L.Y. Chen, Engineering case and research of antimony oxide production wastewater treatment, *Hunan Nonferrous Metal*, 2a, 2, p. 29-31, 2005
- [15] M. Kang, M. Kawasaki, S. Tamada, T. Karnei, Y. Magara, Effects of pH on the removal of arsenic and antimony using reverse osmosis membranes, *Desalination*, 131, 1-3, p. 293-298, 2000
- [16] S.M. Saleh, S.A. Said, M.S. El-Sharawi, Extraction and recovery of Au, Sb and Sn from electrorefined solid waste, *Analitica Chemica Acta*, 436, 1, p. 69-77, 2001
- [17] A.S. Koparal, R. Özgür, ÜB. Ögütveren, H. Bergmann, Antimony removal from model acid solutions by electrodeposition, *Separation and Purification Technology*, 37, 2, p. 107-116, 2004
- [18] Y. Lee, I. H. Um, J. Yoon, Arsenic (III) oxidation by iron (VI) (Ferrate) and subsequent removal of arsenic by iron (III) coagulation, *Environment Science and Technology*, 37, p. 5750 – 5756, 2003
- [19] C. Sullivan, M. Tyrer, C.R. Cheeseman, N.J.D. Graham, Disposal of water treatment wastes containing arsenic - A review, *Science of the Total Environment* 408 (2010) 1770–1778
- [20] Stefan Jessen and Andreas Münch, Zwei Jahre Erfahrung mit Ionenaustauschern in der Abwasserbehandlung bei der BSB Recycling GmbH, *Erzmetall – World of Metallurgy*, p. 27-31, 2012