

# Behavior of arsenic in hydrometallurgical zinc production and environmental impact

A.B. Peltekov<sup>1\*</sup>, B.S. Boyanov<sup>1</sup>, T.S. Markova<sup>2</sup>

<sup>1</sup>Paisii Hilendarski University of Plovdiv, Department of Chemical Technology, 24 Tsar Asen St., Plovdiv 4000, Bulgaria

<sup>2</sup>KCM SA, Asenovgradsko Shosse, Plovdiv 4009, Bulgaria

\*Corresponding author: e-mail: peltekov@uni-plovdiv.bg

The presence of arsenic in zinc sulphide concentrates is particularly harmful, because it creates problems in zinc electrolysis. The main source of arsenic in non-ferrous metallurgy is arsenopyrite (FeAsS). In oxidative roasting of zinc concentrates, FeAsS oxidizes to arsenic oxides (As<sub>2</sub>O<sub>3</sub>, As<sub>2</sub>O<sub>5</sub>). In this connection a natural FeAsS was examined, and also the distribution of arsenic in the products of the roasting process, the cycle of sulphuric acid obtaining and the leaching of zinc calcine were studied. The arsenic contamination of soils in the vicinity of non-ferrous metals smelter KCM SA, Plovdiv, Bulgaria as a result of zinc and lead productions has been studied.

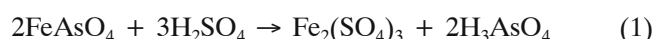
**Keywords:** arsenic, arsenopyrite, zinc concentrates, roasting, leaching.

## INTRODUCTION

Arsenopyrite (FeAsS) is the most common mineral of arsenic sulphides. The arsenic amount in the zinc concentrates varies within wide limits (0.001–0.88%)<sup>1</sup>. When the content of arsenic is high, a large part thereof is oxidized to As<sub>2</sub>O<sub>5</sub><sup>2</sup>. It reacts with hematite (obtained by the oxidation of pyrite), resulting in the formation of stable iron arsenate, which is non-volatile, and about 70–80% of the arsenic stays in the calcine. Monhemius and Swash<sup>3</sup> identify arsenic in the calcine as arsenate.

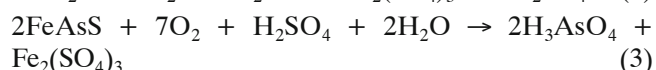
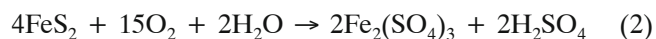
The remainder of the arsenic is oxidized to As<sub>2</sub>O<sub>3</sub><sup>4,5</sup>, which is volatile and is carried away by the roaster off-gas leaving the furnace for roasting in a fluidized bed (FBF)<sup>6</sup>. A part of the arsenic passes into the obtained acid in the sulphuric acid production<sup>7</sup>.

During the hydrometallurgical leaching of zinc calcine the iron arsenate is dissolved<sup>8,9</sup>:



The major reactions of sulphides and arsenides oxidation in an acid medium in the elevated temperature (190–230°C) and an oxygen over-pressure (350–700 kPa) involve total oxidation of the sulphidic sulphur to the sulphate form and of arsenic to the arsenate form<sup>10–12</sup>.

Oxidation reactions:



In practice, in order to remove arsenic from solutions of zinc production, the following process of precipitation of As<sup>5+</sup> with Fe<sup>3+</sup> is used:

Hydrolysis reaction:



Products obtained by precipitation of arsenic from industrial solutions, waste water and drinking water have been the subject of much research.

Swash and Monhemius<sup>13</sup> indicate five main factors that influence the stability of the obtained arsenates: type of arsenic containing species; crystallite/ particle size; hydration of the precipitated solids; presence of sulphate in the lattice, and Fe:As molar ratio.

The formation of the following products was established: scorodite<sup>11, 12, 14–17</sup>, arsenate-adsorbed ferrihydrite<sup>14</sup>, arsenate<sup>15, 16, 18</sup>, compounds belonging to the group of

hydrated ferric arsenate-sulphates<sup>19</sup>, „arsenic-bearing ferrihydrite“<sup>20</sup>, 4 types of arsenic-containing compounds: scorodite (150°C), type-1 arsenic bearing compound (225°C), type-2 arsenic bearing compound (200°C) and ferrihydrite (20°C), depending also on the ratio Fe:As and pH of solutions<sup>13</sup>.

The ratio between Fe and As in zinc sulphate solutions is very important, because the co-precipitation of arsenic is facilitated by a higher content of Fe in the solution during neutral leaching.

Purification of the zinc sulphate solution from arsenic is of great significance because arsenic leads to adverse effects during zinc electrowinning. Arsenic is more electropositive than zinc, and its presence in the electrolyte strongly reduces the coefficient of current efficiency. Hydrogen is released onto the impurity at lower overcurrent. Therefore, when arsenic ions are released on the zinc cathode, the detachment of hydrogen is increased.

On the other hand, when arsenic is released on the more electronegative zinc, it forms micro galvanic pairs and thus induces opposite dissolution of the zinc already detached on the cathode. On the reverse side of the zinc cathode sheet, holes characteristic of arsenic appear on the surface. For this reason, the arsenic content in the electrolyte is limited to 0.1 mg/dm<sup>3</sup>.

In the processing of arsenic-containing sulphide zinc, copper and lead concentrates, there is a risk of contamination of the soil, water and atmosphere with arsenic<sup>21</sup>. According to the study of Materaa et al.<sup>22</sup> 90% of the arsenic in the soil is in the form of ferric arsenate (FeAsO<sub>4</sub>). Sheppard<sup>23</sup> reported that FeAsO<sub>4</sub> has high phytotoxicity, and the threshold level value (TLV) is below 40 mg kg<sup>-1</sup>.

In this context, the aim of the present study is to perform characterization of natural FeAsS using various methods. In industrial conditions in KCM SA, Plovdiv (Bulgaria) it is necessary to study the distribution of arsenic between the products of oxidative roasting of zinc concentrates, the products from zinc calcine leaching, as well as in the production of sulphuric acid in order to reduce the harmful effects of arsenic in zinc hydrometallurgy and the environment.

## EXPERIMENTAL

The chemical analysis of the samples was performed by inductively coupled plasma (ICP-OES) model iCAP 6300 from Thermo Scientific (England).

The X-ray diffraction analysis was carried out with an apparatus "TUR-M62" (Dresden, Germany) equipped with a computer-controlled HZG-4 goniometer with Co-K<sub>α</sub> radiation and Bragg-Brentano geometry. Data base (Powder Diffraction Files, Joint Committee on Powder Diffraction Standards, Philadelphia PA, USA, 1997) was used for the phase identification.

Mössbauer spectrum (MS) was obtained at room temperature with a Wissel electromechanical Mössbauer spectrometer (Wissenschaftliche Elektronik GmbH, Germany) working at a constant acceleration mode. A <sup>57</sup>Co/Cr (activity ≅ 45 mCi) source and an α-Fe foil standard were used. The experimentally obtained spectrum was treated using the least squares method. The parameters of hyperfine interaction such as isomer shift (IS), quadrupole splitting (QS) and effective internal magnetic field (H<sub>eff</sub>) as well as the line widths (FWHM) and the relative weight (G) of the partial components of the spectrum was determined.

Thermogravimetric and differential thermal analyses (TG-DTG-DTA) were performed on a Stanton Redcroft thermal analyzer STA 780 (England) in the temperature range 20–1100°C, with a heating rate of 10°C min<sup>-1</sup>, sample mass of 10.0 ± 0.3 mg. Zirconium melting pots of d = 4.5 mm were used and the purging gas was 100% air with a flow of 50 mL min<sup>-1</sup>.

Scanning electron microscope (SEM) Philips 515, digitized, with detectors for secondary electron image (SEI), accelerating voltage 30 kV, and magnification of 40 000 X was used to study the natural arsenopyrite.

## RESULTS AND DISCUSSION

### XRD analysis

The X-ray diffraction analysis (Fig. 1) shows the presence of a composite with a very high degree of crystallization.

A main phase FeAsS is identified. There is also a small amount of crystalline phase with possible inclusion of other elements. Most likely this is a phase As<sub>4</sub>S<sub>4</sub>, whose content is below 2%.

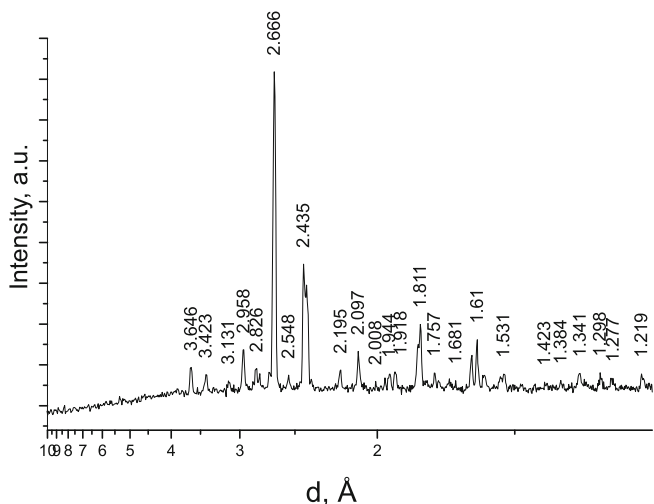
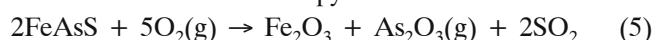


Figure 1. XRD analysis of FeAsS

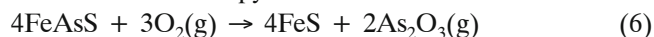
### DTA and TGA analysis

The performed DTA and TGA analysis (Fig. 2) show the presence of two exothermic effects at 511°C and 608°C.

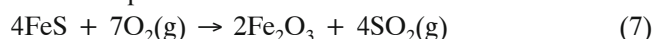
Based on data from literature and results from TG curve it can be concluded that the most likely mechanism of the oxidation of arsenopyrite is:



Some amount of pyrrhotite forms above 500°C:



The second smaller exothermic effect due to the oxidation process is:



Some amounts of FeAsO<sub>4</sub>, Fe<sub>3</sub>AsO<sub>7</sub> or unidentified Fe<sub>x</sub>As<sub>y</sub>O<sub>z</sub> probably occur because the loss of mass does not correspond to complete removal of arsenic and sulphur from arsenopyrite.

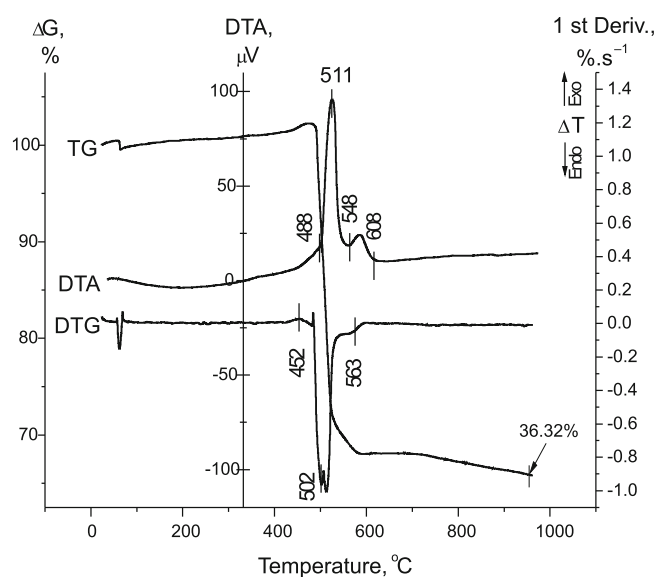


Figure 2. DTA, TGA and DTG analysis of natural FeAsS

### SEM study

We investigated the natural FeAsS which contains micro amounts of Si, K, Pb, O (Table 1) determined by SEM (Fig. 3a and Fig. 3b).

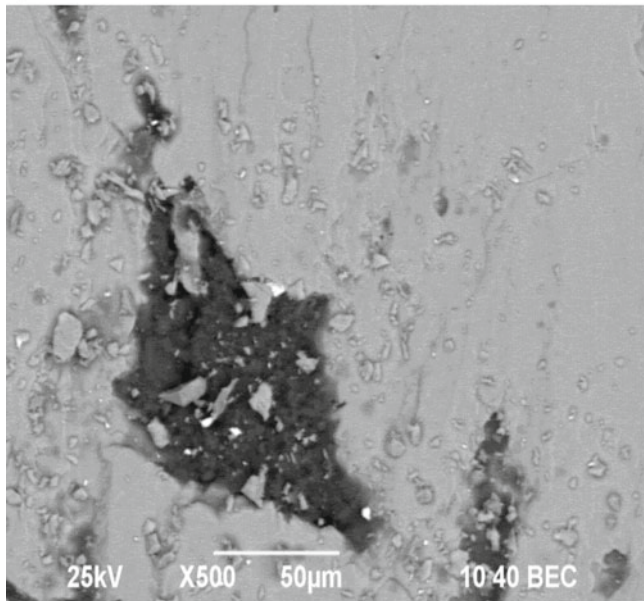
Table 1. Chemical phase composition of FeAsS determined by SEM

Phase	Containing
See x500 – Bright Phase	As, Fe, S
See x500 – Gray Phase – on dark spot	O, Al, Si, K, Fe
See x1000 – Gray Phase in Bright Particle	O, Al, Si, S, K, Fe, As, Pb

The Mössbauer study spectrum (Fig. 4) shows the presence of an independent paramagnetic doublet with hyperfine parameters, respectively: isomer shift (IS) = 0.26 mm/s, quadruple splitting (QS) = 1.06 mm/s, line width (FWHM) = 0.49 mm/s and a relative weight (G) = 100%.

These hyperfine parameters (Table 2) are typical for low-spin iron ions in the second oxidation and tetrahedron coordination, which is characteristic of the compound arsenopyrite.

a)



b)

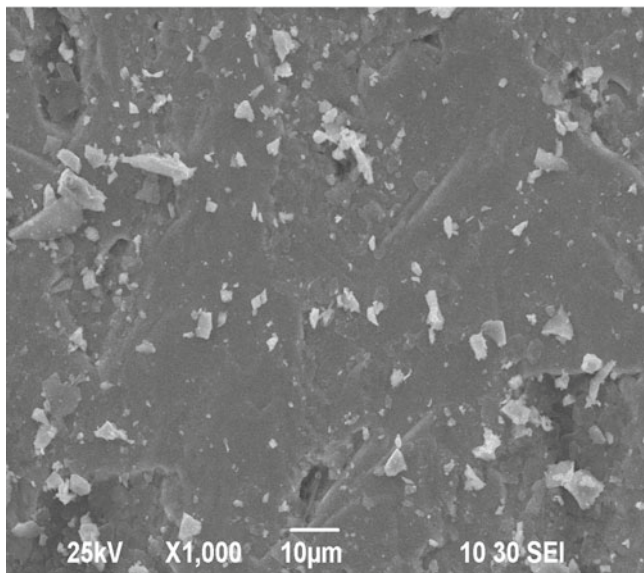


Figure 3. Image of surface of FeAsS taken by SEM

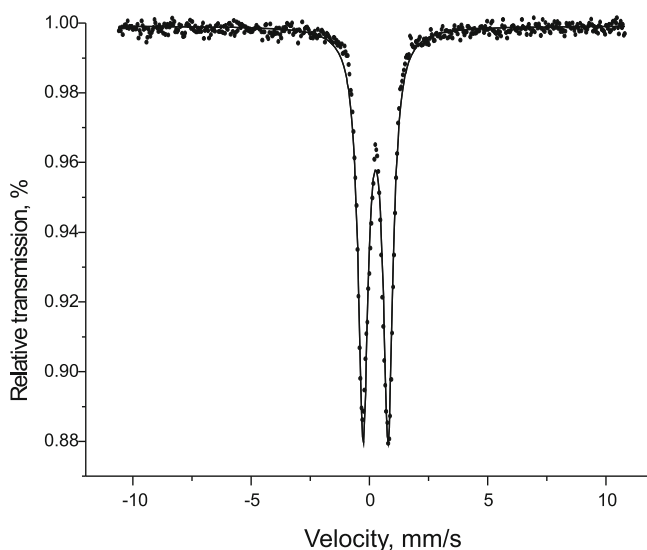


Figure 4. Mössbauer spectrum of FeAsS

Table 2. Hyperfine parameters of FeAsS

IS [mm/s]	QS [mm/s]	FWHM [mm/s]	G [%]	Referenses
0.26	1.06	0.49	100	our
0.26	2.10			24
0.24	1.12			25
0.25	0.69			
0.26	1.49			
0.17	1.61			26
0.13	1.04			
0.14	1.18			
0.30	1.15			27
0.34	1.05			28
0.35	1.12			
0.35	1.12			
0.34	1.05			29
0.35	1.07			
0.25	1.05			30
0.26	1.065			

## DISTRIBUTION OF ARSENIC IN ZINC HYDROMETALLURGY AND SULPHURIC ACID PRODUCTION

### Roasting of sulphide zinc concentrates in a fluidized bed

The scheme of the hydrometallurgical production of zinc using Waelz process for the processing of zinc cakes includes roasting of zinc concentrates as a first stage which is carried out under the following conditions: FBF (type "Lurgi" company, Germany)<sup>6</sup> surface 68 m<sup>2</sup>, temperature of fluidized bed 920–930°C, air flow 39 000 m<sup>3</sup>/h.

Sampling points (SP) for the determination of arsenic distribution in the roasting of zinc concentrates (Fig. 5) are: 1 – charge (SP 1); 2 – calcine by overflow threshold (SP 2); 3 – waste heat boiler (SP 3); 4 – cyclone (SP 4); 5 – electrostatic precipitator (SP 5); 6 – calcine by elevator (SP 6).

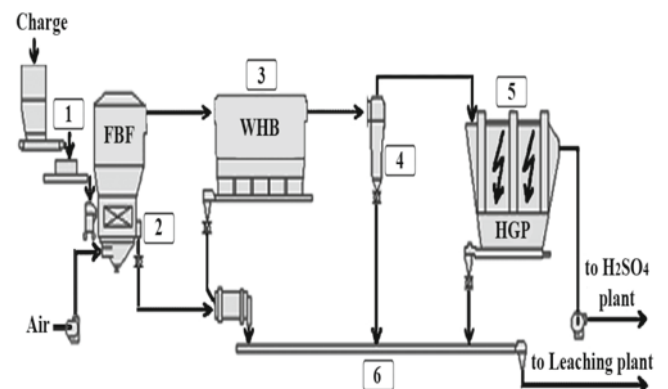


Figure 5. Zinc sulphide concentrates roasting

The results obtained (Table 3) show that arsenic is relatively evenly distributed between the calcine by overflow threshold and dust from roaster off-gas. This indicates that in the oxidative roasting the bulk of arsenic is oxidized to As<sub>2</sub>O<sub>5</sub>, which subsequently forms FeAsO<sub>4</sub> with Fe<sub>2</sub>O<sub>3</sub>.

Table 3. Arsenic content in SP from zinc sulphide concentrates roasting unit

Samples	Units	Values [%]
SP 1	Charge	0.064
SP 2	Calcine by overflow threshold	0.069
SP 3	Waste heat boiler	0.064
SP 4	Cyclone	0.075
SP 5	Electrostatic precipitator	0.15
SP 6	Calcine by elevator	0.075

Even if part of the arsenic is oxidized to volatile  $\text{As}_2\text{O}_3$ , there are good enough conditions on the way to the dry ESP for it to further oxidize to  $\text{As}_2\text{O}_5$ . In terms of receiving sulphuric acid clean of arsenic this is good, but the passage of nearly all arsenic in the calcine and dust is unfavorable for zinc production<sup>31</sup>.

### Leaching of zinc calcine and Waelz process

The zinc calcine leaching is carried out in a continuous two-hydrometallurgical circuit (neutral and acidic stage) with dilute sulphuric acid (60–70 g/L). In neutral cycle hydrolytic purification of As, Sb, Ge, Ga, In, Tl at 50–60°C is performed. The resulting zinc cake was processed by Waelz process. For this purpose, rotating tube furnaces with a diameter of 3 m and a length of 40 m are used. Waelz oxides are leached with a solution of sulphuric acid. The resulting solution of zinc sulphate is included in the main cycle or used to obtain crystalline  $\text{ZnSO}_4$ . The lead cake is processed in lead production.

Sampling points for the study of arsenic distribution at zinc calcine leaching and Waelz process (Fig. 6) are: 1 – calcine input (SP 1); 2 – first agitator (SP 2); 3 – last agitator (SP 3); 4 – solution by neutral thickener (SP 4); 5 – cake by neutral thickener (SP 5); 6 – waelz charge (SP 6); 7 – waelz oxides before roasting (SP 7); 8 – waelz oxides after roasting (SP 8); 9 – copper clinker (SP 9).

The results for the distribution of As (Table 4) indicate that its content in the zinc calcine is below 0.08%, and this value is restrictive as the upper limit. Data for the following items present very well the hydrolysis purification to arsenic. The initial solution in the first agitator through continuous calcine leaching contains

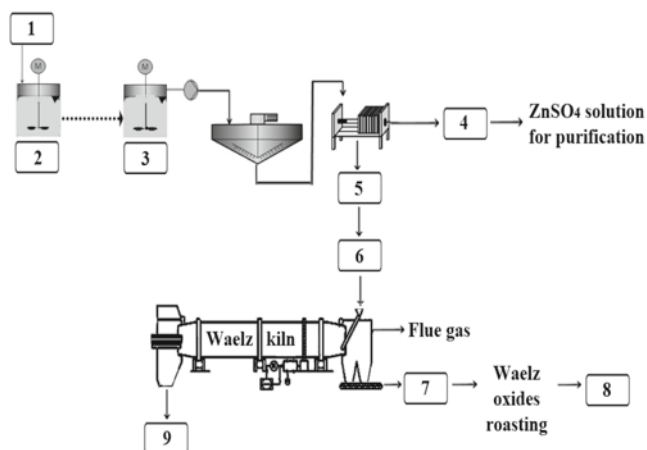


Figure 6. Zinc calcine leaching and Waelz process units

79 mg/L As, followed by oxidation of  $\text{Fe}^{2+}$  with  $\text{KMnO}_4$  and subsequent hydrolysis of  $\text{Fe}^{3+}$  to  $\text{Fe}(\text{OH})_3$  and coprecipitation of impurity ions of As, Sb, Ga, In, Tl and the like.

The arsenic content lowers to 0.3 mg/L, which is beneficial to the technology used and the subsequent zinc electroextraction.

The value of the arsenic content in the solution of neutral thickener (<0.05 mg/L) is significantly lower than the last agitator, which shows that the process of co-precipitation continues in the thickener. This is a very beneficial process because the low content of arsenic in the neutral solution of zinc sulphate will not adversely affect the electrolysis.

Table 4. Arsenic content in SP from zinc calcine leaching and Waelz process

Samples	Units	Values
SP 1	Calcine input	0.071%
SP 2	First agitator	79 mg/L
SP 3	Last agitator	0.3 mg/L
SP 4	Solution by neutral thickener	<0.05 mg/L
SP 5	Cake by neutral thickener	0.12%
SP 6	Waelz charge	0.18%
SP 7	Waelz oxides before roasting	0.095%
SP 8	Waelz oxides after roasting	0.082%
SP 9	Copper clinker	0.14%

Moreover, in the cementation of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  (also  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  in activated cementation) with zinc powder this low As content prevents the obtaining of highly toxic arsine ( $\text{AsH}_3$ ). The resulting filtration zinc cake has an arsenic content (0.18%) significantly higher than in the calcine. This is due to the smaller amount of cake as compared with the calcine and the substantial degree (over 98%) of hydrolysis purification of arsenic. In addition to the zinc cake there are also other raw materials in the charge for Waelz processing that contribute the content of arsenic to reach 0.18%.

On the basis of data from the Waelz process it can be concluded that arsenic is distributed between Waelz oxides and copper clinker. Reduction conditions likely contribute to a partial reduction of  $\text{As}^{5+}$  to  $\text{As}^{3+}$  and obtaining of the volatile  $\text{As}_2\text{O}_3$ .

Upon oxidative roasting of the resulting Waelz oxides in a tube furnace a very small decrease of the arsenic content is observed in the roasted oxides. This is further proof that under oxidizing conditions arsenic remains in the solid phase.

### Sulphuric acid production

The scheme for the sulphuric acid production is by the “Lurgi” company, Germany<sup>6</sup>. Sampling points in the production of sulphuric acid and gypsum (Fig. 7) are:

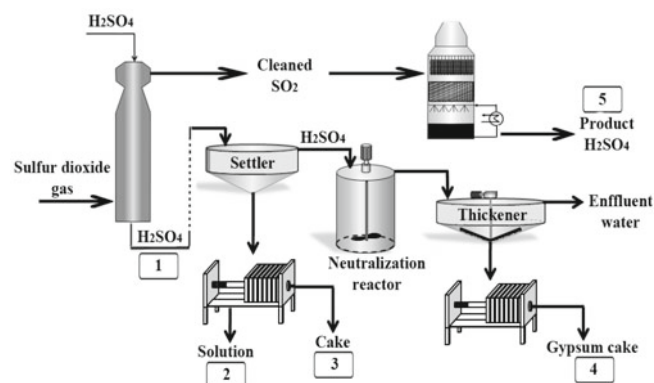


Figure 7. Sampling points of sulphuric acid production plant

1 – scrubber (SP 1); 2 – solution by filter press (SP 2); 3 – cake by filter press (SP 3); 4 – gypsum (SP 4); 5 –  $\text{H}_2\text{SO}_4$  product (SP 5). The results from the chemical analysis for arsenic are presented in Table 5.

Data from the chemical analysis show that the gases for production of sulphuric acid are further purified from arsenic in the scrubber.

**Table 5.** Arsenic content in samples of sulfuric acid production unit

Samples	Units	Values
SP 1	Scrubber	0.42 mg/L
SP 2	Solution by filter press	0.93 mg/L
SP 3	Cake by filter press	0.077%
SP 4	Gypsum	<0.0005 %
SP 5	Production acid	<0.1 mg/L

Arsenic passes into the washing acid and is derived from this unit by the resulting cake and partly by technical gypsum. The sulphuric acid obtained has a very low arsenic content, which allows it to be used multilaterally, including in the production of fertilizers.

The characteristics of the natural FeAsS outlined herein and the study of arsenic distribution between products in zinc hydrometallurgy and sulphuric acid production contribute to optimal carrying out of technological processes. This helps prevent the harmful effects of arsenic in zinc electroextraction and obtain sulphuric acid containing minimal amounts of arsenic.

#### Monitoring of soil contamination with arsenic

The Non-ferrous Metals Smelter (KCM SA) is situated near Plovdiv (Bulgaria) and is the biggest producer of Zn, Pb, Cd, lead and zinc alloys in Central and Eastern Europe. The production activity at KCM SA started in 1961 with the inauguration of the zinc plant, and followed with the lead plant in 1963. Now the production list includes: zinc ingots, sulphuric acid, zinc sulphate "A" and "B", cadmium, refined lead, lead-copper matte, speiss, bismuth lead, DORE alloy, lead and zinc alloys, coin alloys, silver bars, gold, silver and gold wires<sup>32</sup>.

In the past KCM SA was a "hot" spot on the Bulgarian map in connection with the contamination of soil, air and water with aerosols, Pb, Cd, Zn, SO<sub>2</sub>, etc.

The main pollutants of soils in the region are lead, cadmium and zinc. This is due to the characteristics and specificity of the KCM SA metallurgical production – pyrometallurgical method of lead production and hydrometallurgical method of zinc production. Increased regulations regarding soil contamination with arsenic require monitoring with respect to this element too. In this regard, control of soil contamination with arsenic near KCM SA has started from 2012. The coordinates of the monitoring points are presented in Table 6.

**Table 6.** The location of the samples taking monitoring points for soil contamination

N	Latitude, N	Longitude, E
1	42°04'34.3	24°50'00.9
2	42°04'18.0	24°49'31.5
3	42°03'54.7	24°49'02.6
4	42°03'42.0	24°50'13.4
5	42°03'33.9	24°49'24.7
6	42°02'61.2	24°50'45.3
7	42°03'11.6	24°49'46.1
8	42°02'52.6	24°49'32.0
9	42°02'46.1	24°50'30.0
10	42°02'31.3	24°50'15.3
11	42°02'43.5	24°51'03.3
12	42°02'25.9	24°50'49.5
13	42°02'28.6	24°51'38.0
14	42°02'01.5	24°50'41.9
15	42°01'48.9	24°51'20.7

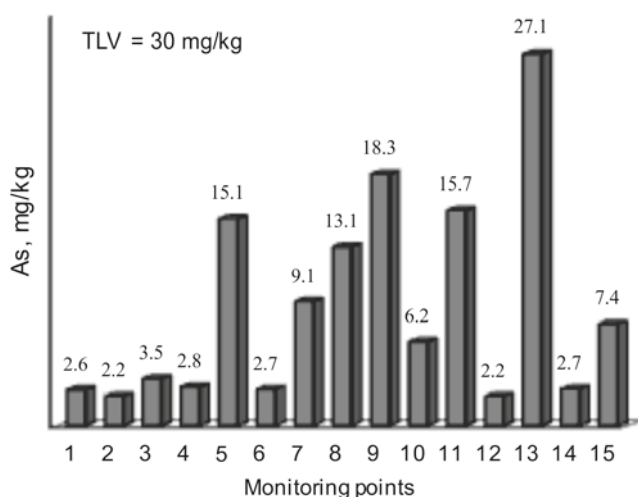
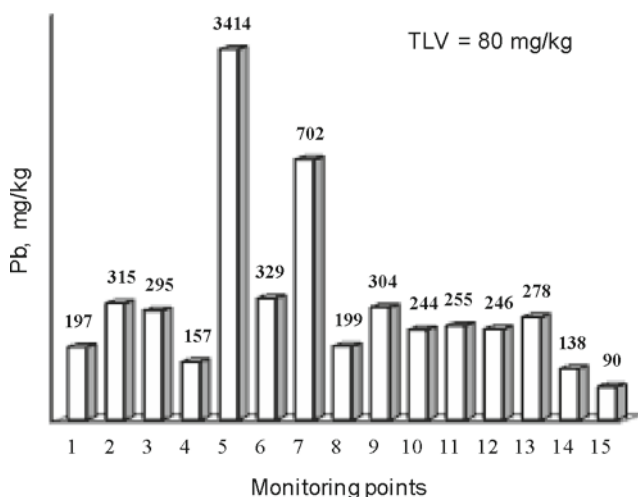
Based on the processing of the results of the chemical analysis of processed zinc and lead concentrates in KCM SA and the requirements for their charging the following conclusions were made:

1. In the processed zinc concentrates arsenic content varies between 0.001 and 0.88%. Due to the specific requirements for the content of arsenic in the solution for zinc electrowinning its content in the charge should not exceed 0.08%.

2. The content of arsenic in the lead concentrates is high and is in the range of 0.01 to 2.53%. The average content in the preparation charge is about 1%.

The main contribution in both atmosphere pollution with aerosols and soil pollution with heavy metals is due to lead production.

In this regard, a comparison of contamination with arsenic and lead in soil monitoring points from Table 6 (Fig. 8 and Fig. 9) was made.

**Figure 8.** Monitoring points for arsenic content in soils**Figure 9.** Monitoring points for lead content in soils

The results presented from the analysis of soil contamination with As indicate that it is below the TLV for all tested points.

With respect to the lead content at all points, it is greater than the TLV = 80 mg/kg. In points 5 and 7 lead contamination is significant and exceeds many times the TLV.

Compared to data from 2000, when soil monitoring began, the lead content has been kept within similar values. This indicates that the implementation of environmental projects in KCM SA for about 100 million USD has stopped further contamination of soil with lead. Similar results were also obtained for zinc and cadmium<sup>33</sup>.

A new plant for lead production (AUSMELT) for more than 105 million USD is currently being built. With this new project in addition to improving the technical and economic indices of lead production, the target is also significant reduction of environmental pollution.

## CONCLUSIONS

1. On the basis of this study it was found that in some zinc concentrates the content of arsenic (usually as FeAsS) often exceed acceptable values for the hydrometallurgical zinc production.

2. Natural FeAsS is characterized using XRD, DTA and TGA, Mössbauer spectroscopy, SEM.

3. A presence of iron as arsenates was established in the residue after oxidation of FeAsS, which created prerequisites arsenic to get into the solution, obtained by leaching of zinc calcine with sulphuric acid.

4. A suitable purification of zinc sulphate solutions from arsenic can solve this problem.

5. With the implementation of a new installation AUSMELT for lead production in 2014 a significant reduction in environmental contamination with lead, as well as Zn, Cd, As, SO<sub>2</sub>, etc., is expected.

## ACKNOWLEDGMENT

This study was conducted with financial help through the project NI13-HF-006 of Paisii Hilendarski Plovdiv University.

## LITERATURE CITED

1. Boyanov, B. & Peltekov, A. (2012). X-Ray, DTA and TGA analysis of zinc sulfide concentrates and study of their charging for roasting in fluidized bed furnace. *Bulgarian Chemical Communications* (44 Spec. Issue), 17–23.

2. Arias-Arce, V., Coronado-Falcón, R., Puente Santibáñez, L. & Lovera-Dávila, D. (2005). Refractory of gold concentrate. *Revista del Instituto de Investigación FIGMMG* (8) 5–16.

3. Monhemius, A.J. & Swash, P.M. (1999). The Removal and Stabilization of Arsenic from Copper Refining Circuits by Hydrothermal Processing. *J. Miner. Met. Mat. Soc.* 51 (9) 30–34.

4. Yuhu, L., Zhihong, L., Qihou, L., Zhongwei, Z., Zhiyong, L. & Zeng, L. (2011). Removal of arsenic from arsenate complex contained in secondary zinc oxide. *Hydrometallurgy* 108 (3–4), 165–170.

5. Shibayama, A., Takasaki, Y., William, T., Yamatodani, A., Higuchi, Y., Sinagawa, S. & Ono, E. (2010). Treatment of smelting residue for arsenic removal and recovery of copper using pyro-hydrometallurgical process. *J. Hazard. Mater.* (180), 1016–1023. DOI: 10.1016/j.jhazmat.2010.05.116.

6. Sander, U.F.H. (1984). Sulphur, sulphur dioxide, and sulphuric acid: An introduction to their industrial chemistry and technology. British Sulphur Corporation. Verlag Chemie International; English ed edition, p. 415. ISBN-10: 0902777645. ISBN-13: 978-0902777644.

7. Mutler, W. & Warren, G. (2009). Burning pyrites compared to sulphur. Sulphur and Sulphuric Acid Conference, 4–6 May 2009 (147–156). Johannesburg, South Africa.

8. Langmuir, D., Mahoney, J. & Rowson, J. (2006). Solubility products of amorphous ferric arsenate and crystalline scorodite (FeAsO<sub>4</sub> · 2H<sub>2</sub>O) and their application to arsenic behavior in buried tailings. *Geochim. Cosmochim. Acta.* (70) 2942–2956.

9. Zhu, Y. & Merkel, B.J. (2001). The Dissolution and Solubility of Scorodite, FeAsO<sub>4</sub> · 2H<sub>2</sub>O: Evaluation and Simulation with PHREEQC2. *Wiss. Mitt. Inst. für Geologie, TU Bergakademie Freiberg, Germany* (18) 1–12.

10. Fleming, C.A. (2009). Basic iron sulphate – a potential killer for pressure oxidation processing of refractory gold concentrates if not handled appropriately. *SGS Minerals Services, Technical paper -06*.

11. Papangelakis, V.G. & Demopoulos, G.P. (1990). Acid Pressure Oxidation of Arsenopyrite: Part I, Reaction Chemistry, *Can. Metallur. Q.* 29 (1) 1–12.

12. Papangelakis, V.G. & Demopoulos, G.P. (1990). Acid Pressure Oxidation of Arsenopyrite: Part II, Reaction Kinetics, *Can. Metallur. Q.* 29 (1) 13–20.

13. Swash, P.M. & Monhemius, A.J. (1994). Hydrothermal precipitation from aqueous solutions containing iron (III), arsenate and sulphate. International Symposium “Hydrometallurgy '94” 11–15 July 1994, Cambridge, England, 177–190.

14. Jia, Y.F., Demopoulos, G.P., Chen, N., Cutler, J.N. & Jiang, D.T. (2003). Preparation, characterization and solubilities of adsorbed and co-precipitated iron (III)-arsenate solids (Conference Paper). Proceedings of the TMS Fall Extraction and Processing Conference 2 (2003) 1923–1935, Hydrometallurgy 2003: Proceedings of the 5th International Symposium, 24–27 August 2003, Vancouver, Canada, Code 62514.

15. Dutrizac, J.E., Jambor, J.L. & Chen, T.T. (1987). Behaviour of Arsenic During Jarosite Precipitation: Reactions at 150 degree C and the Mechanism of Arsenic Precipitation. *Can. Metallur. Q.* 26 (2) 103–115.

16. Dutrizac, J.E. & Jambor, J.L. (1987). Behaviour of Arsenic During Jarosite Precipitation: Arsenic Precipitation at 97 degree C from Sulphate or Chloride Media. *Can. Metallur. Q.* 26 (2) 91–101.

17. Filippou, D. & Demopoulos, G.P. (1997). Arsenic immobilization by controlled scorodite precipitation (Review). *JOM* 49 (1–2), 52–55.

18. De Klerk, R. J., Jia, Y., Daenzer, R., Gomez, M.A. & Demopoulos, G.P. (2012). Continuous circuit coprecipitation of arsenic(V) with ferric iron by lime neutralization: Process parameter effects on arsenic removal and precipitate quality. *Hydrometallurgy* 111–112 (1), 65–72.

19. Ugarte, F.J.G. & Monhemius, A.J. (1992). Characterisation of high – temperature arsenic – containing residues from hydrometallurgical processes. *Hydrometallurgy* 30 (1–3), 69–86.

20. Jia, Y., Demopoulos, G.P., Chen, N. & Cutler, J. (2005). Coprecipitation of As(V) with Fe(III) in sulfate media: Solubility and speciation of arsenic (Conference Paper). TMS Annual Meeting, San Francisco, United States, 13–17 February, 137–148, Code 65371.

21. Azcue, J.M., Mudroch, A., Rosa & F., Hall, G.E.M., (1994). Effects of abandoned gold mine tailings on the arsenic concentrations in water and sediments of Jake of Clubs Lakes, B.C. *Environ. Technol.* 15 (7), 669–678. DOI: 10.1080/09593339409385472.

22. Matera, V., Le Hecho, I., Laboudigue, A., Thomas, P., Tellier, S. & Astruc, M. 2003. A methodological approach for the identification of arsenic bearing phases in polluted soils. *Environ. Pollut.* 126, 51–64.

23. Sheppard, S.C. (1992). Summary of phytotoxic levels of soil arsenic. *Water Air Soil Pollut.* (64) 539–550.

24. Yoshida, Y. & Langouche, G. (2013). *Mössbauer spectroscopy – Tutorial Book*, Spinger – Verlag Berlin Heidelberg.

25. Bindi, L., Moëlo, Y., Lèone, P. & Suchaud, M. (2012). Stoichiometric arsenopyrite, FeAsS, from La Roche – Balue Quarry, Loire – Atlantique, France: Crystal structure and Mössbauer study, *Can. Mineral.* 50 (2) 471–479.

26. Constantinescu, Ș., Udubasa, S.S., Popescu-Pogrion, N., Mercioniu, I. & Udubasa, G.A. (2011). Complex investigations of the iron and gold inclusions in inerals species at nanosize scale. *Rom. J. Phys.* 56 (5–6), 708–718.

27. Darby Dyar, M., Agresti, D.G., Schaefer, M.W., Grant, C.A. & Sklute, E.C. (2006). Mössbauer Spectroscopy of Earth and Planetary Materials, *Annu. Rev. Earth Planet.* (34) 83–125.

28. Baláž, P. & Lipka, J. (2000). Mössbauer spectroscopy of sulphidic minerals. *Acta Montan. Slov. Roč.*, 5 (2), 105–112.

29. Kjekshus, A. & Nichol森, D.G. (1971). The significance of Back – Bonding in compounds with pyrite, marcasite and arsenopyrite Type structures. *Acta Chem. Scandin.*, (25) 866–876.

30. Imbert, P., Gerard, A. & Wintenberger, M. (1963). Etude des sulfure arseniosulfure et arseniuret de fer naturels par effect Mosbauer, *Comp. Rend.* (256), 4391–4393.

31. Friedrich, B., Krüger, J. & Bernal, G.M. (2002). Alternative solution purification in the hydrometallurgical zinc production. *Sav. Inzen. Metalurg. Jugoslav.* 85–101.

32. <http://www.kcm.bg>

33. Boyanov, B.S., Kehayov, Y.I. & Ivanov, K.I. (2012). Monitoring of soil contamination in vicinity of lead-zinc smelter KCM SA, Bulgaria, Proceedings – 2012 International Conference on Biomedical Engineering and Biotechnology, iCBEB 2012, art. No. 6245135, 385–388.