

# Selective recovery of copper and zinc from mine dump waters of mining enterprises in precipitates

N N Orekhova<sup>1</sup>, G A Tarybaeva, D S Muravev

Mining Engineering and Transport Institute, Nosov Magnitogorsk State Technical University, Pr. Lenina, 38, Magnitogorsk, Russia

E-mail: n\_orehova@mail.ru

**Abstract.** The acid mine dump waters at mining companies that mining the copper and copper-zinc sulphide ore have the high concentrates of metals and classified in our view as the raw materials for selective recovery of metals in precipitates comparable in quality with concentrates of ores enrichment and suitable for further metallurgical processing. Authors have implemented three two-stage schemes for sequential extraction of copper and zinc: cementation-sulphide precipitation, galvanocoagulation- sulphide precipitation, precipitation-precipitation. Moreover, parameters of processes and quality of the obtained precipitates have described. The achieved copper recovery is 89% and 94% respectively with the application of cementation and galvanocoagulation, in sulphide precipitate exceeded 75%. Furthermore, the copper recovery from decoppering in precipitates amounted to more than 65%. Zinc-containing precipitates because of coprecipitation of iron, magnesium and calcium contain zinc from 14% to 28%, in two to three times less than the quality of conditioned zinc concentrates. The content of precipitates allows to apply them for additional charging to concentrates of enrichment or for the production of metals in metallurgical treatment. As a result of the studying the effect of reduced total salinity ( $S$ ) on mass fraction of zinc in precipitate ( $\beta$ ) with the constant concentration of zinc ( $C_{Zn}$ ), the changes in concentration with constant salinity and reduction in total salinity ( $S$ ) with constant ratio  $S/C_{Zn}$ , the following dependencies have obtained: ( $S$ ):  $(\frac{\partial \beta}{\partial C_{Zn}})_S > 0$ ,  $(\frac{\partial \beta}{\partial S})_{C_{Zn}} < 0$ , in the range of an index  $S$  from 4.5 to 90.0 g/L  $(\frac{\partial \beta}{\partial S})_{\frac{C_{Zn}}{S}} < 0$ , where  $(\frac{\partial x}{\partial y})_z$  is a partial derivative of  $x$  to  $y$ , whereas the value  $z$  is fixed.

## 1. Introduction

The acidification of mine and mine dump waters happens over time with increased concentrations of metals at mining plants that produce and process copper and copper-zinc sulphide ores. The key factor of forming the ionic composition of waters is the sulphide oxidation rate, the most moving of which are the minerals of copper, zinc and iron [1]. The concentrations of chalcophylic elements reach several grammes per litre in the mine dump waters of the Shemur and the Tarnier copper-zinc pyrite deposits that characterise the non-stationary period of sulphide oxidation. Characteristics of mine dump waters in 2012-13 are presented in Table 1.

These waters together with pit sump are guided to the treatment facilities. A treatment is carried out by reagent precipitation with the application of lime and sodium sulphide. The obtained precipitates the low content of copper (to 2%) and zinc (to 7%) and cannot be used in pyrometallurgical extraction.



**Table 1.** Characteristics of mine dump waters in 2012-2013.

Name of the ore deposit (type of water)	Average water flow (m <sup>3</sup> /h)	Concentration of ions (mg/L)				pH
		Cu <sup>2+</sup>	Zn <sup>2+</sup>	Fe <sub>total</sub>	Fe <sup>3+</sup>	
Tarnier (Copper-zinc mine's dump water)	6.02	402.5 – 2 082.0	2 156.0 – 8 680.0	4 075.0 – 9 334.0	1 652.1 – 2 952.2	2.2– 2.9
Shemur (Copper- mine's dump water)	0.45	626.4 – 2 940.0	43.1 – 300.0	3 126.0 – 16512.0	358.7 – 958.7	1.9– 2.4

To precipitate the copper from multicomponent solutions it is most often applied electrochemical methods, such as electrolysis [2,3] with the use of carbon as the cathode, cementation [4-6] and galvanocoagulation as its derivative [7]. Copper recovery reaches from 92 to 99% by these methods. It is proposed to use hydrolytic [8] and sulphide [9] precipitation with controlled pH range for the selective recovery of copper and zinc from acidic drainage waters. In most studies [2-4,7-9], the main controlled output parameter is the residual concentration of the polluting component. Moreover, little attention is given to the mass fraction of metal in precipitation and their phase content.

Recently, the technological schemes of copper and zinc recovery from the water have developed with the application of hydrolytic precipitation methods [10], sulphide precipitation [11], cementation [6,12] and ionic flotation [13]. In accordance with the existing practice of the treatment of acidic mine dump waters [14] and theoretical research [1-4] in the area of copper and zinc recovery from acidic sulfate mine water [2-13], we have chosen such well-known processes as galvanocoagulation, cementation and sulphide precipitation for copper recovery and sulphide precipitation was chosen for zinc recovery.

According to the authors' opinion, the main issue in this paper is to determine the possibility of consistent recovery of copper and zinc-containing precipitates with the high content of metal at the realisation of three two-stage schemes: cementation-precipitation, galvanocoagulation-precipitation and precipitation-precipitation. Also, the searching for simple solutions is carried out to increase the content of zinc in a precipitate.

## 2. Experimental design

The experiments were carried out in a two-stage sequence. The first stage involved the precipitation of copper as a sulphide, cemented or ferrite precipitate. The second stage involved the precipitation of zinc as a sulphide.

### 2.1. Cementation method

The cementation is carried out in the flowing mode with the application of laboratory, cementation, the drum-type unit with a diameter of 20mm in rotary washing screen providing the continuous mixing of mine dump water with iron turnings. The ratio of the drum's length and width is 3:1 and the optimum rotation speed is calculated according to the following formulas [6]:

$$A_{\min} = 10.1/\sqrt{D} \quad A_{\max} = 19.7 \cdot \sqrt{D}, \quad (1)$$

where D is the diameter of the drum and equal to 35.7-69 rpm.

The actual rotation speed of the drum under load is 36 and 64 rpm, depending on the position of the transmission gears in the gearbox.

### 2.2. Galvanocoagulation method

The galvanocoagulation is carried out with the application of laboratory type drum galvanocoagulator with the drum. The size is 110x350 mm, the mass load of ferrum: carbon = 3:1, with the coarseness 5-10mm is 1200 g. The parameters of galvanocoagulation adopted from our experience on mine dump waters at mining enterprises of South Ural [15].

The experiments were conducted under dynamic conditions. Furthermore, the liquid phase and precipitates have been analysed, as well as charge before and after the contact with a solution.

To prevent accidental errors before each series of experiments, the galvanocoagulator was loaded with a new portion of the deoil charge of a known mass.

### 2.3. *Precipitation of the metals with sodium hydrosulphide*

The precipitation of the metals with sodium hydrosulphide was carried out in accordance with the results of studies described in [16]. The consumption of the sulphide reagent was taken as a percentage of the value of the stoichiometrical ratio for the reduction of Fe III to Fe (II) according to the reaction:  $\text{Fe}_2(\text{SO}_4)_3 + \text{NaHS} = 2\text{FeSO}_4 + \text{NaHSO}_4 + \text{S}$ , and the metal's full precipitation according to the reaction:  $\text{MeSO}_4 + \text{NaHS} = \text{MeS} + \text{NaHSO}_4$ , where Me stands for  $\text{Cu}^{2+}$  or  $\text{Zn}^{2+}$ . The conditioning with the reagent was performed in plastic containers with a working volume of 4 dm<sup>3</sup>. The contents were stirred for 5-15 minutes. Moreover, the treatment solution of sulphide reagent injected into the water mass closer to the reactor's bottom with constant mixing. The technical sodium hydrosulfide with the concentration of 31% was used as the precipitating reagent. The working solution with the concentration of 5% NaHS is produced by dilution of the 31% of concentration solution.

The main research methods of products have been selected as follows, chemical analysis for solutions, X-ray phase analysis and chemical analysis for dispersing sediments. The samples of sediments have been analysed at the Shimadzu XRD-6000 diffractometer, with a Cu anode and a graphite –monochromator. The sampling results were calculated with the Peter-Kalman method [17] with the application of coefficients taken from tabular data with maximum diffraction consistency. To determine the quantity of the X-ray amorphous component the addition technique was used. Three X-ray photograms were taken in the range of 24-30 degrees, then the average ratio of the reflection intensity for silicon (3,136 Å) and the intensity of maximum diffraction reflection on the X-rayogram of the sample is calculated. After that, the minor amount of silicon was again added to the sample and the whole photographing procedure was repeated.

## 3. Discussion

The results of experiments showed that the specific consumption of iron during the cementation of water from the «Tarnierskoe» deposit (4,7g of iron per gram of copper) is higher than the average consumption of iron according to the data of practical application of copper cementation (1.32-3.00 gFe/gCu) [7], which is most probably caused by the high content of Fe (III) in the mine dump water [4,11].

To reduce the iron consumption at acidifying the effluents to pH 2 for reduction of the precipitation process of hydroxides and basic iron sulphates. When the copper content in the initial mine water rises from 920 to 1250 mg/L (all other things being equal) we have seen a gradual increase in the rate of copper recovery from 88.6 to 93.1% which are linked to the shift in the concentration ratio of copper and zinc in favor of copper content. Mass fraction of copper in precipitate ranged from 17% to 23%.

The specific iron consumption at cementation of the copper from mine dump water of «Shemurskoe» deposit basically similar to the known range of iron consumption based on application practice data of copper cementation. When the copper content rises from 876.24 to 2 940.00 mg/L in the initial water with the relative concentrations of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Fe}^{3+}$  being equal, we have seen the decrease in the rate of recovery from 94.5% to 85.77%. The parameters of the cementation recovery of copper are given in Table 3. When you change the rotational speed of the drum, the iron consumption and copper recovery has hardly changed.

The ferrite precipitate obtained on the scheme of galvanocoagulation- precipitation from mine dump waters at the «Tarnierskoe» and «Shemurskoe» deposits, satisfying five components such as, weight content, recovery rate, selectivity, low iron consumption and low iron residual concentration in the drainage obtained at the rate of galvanocoagulator drum rotation of 12 rpm and the duration of Valvano coagulation to 6 minutes. The zinc-containing precipitate has obtained at the charge of NaHS, i.e. 125% on stoichiometry to precipitation of zinc. The values of the galvanocoagulation recovery are

given in Table 3. Specific consumption of iron is 4-5 times lower than with cementation (Table 3) and equal to 0.73-0.67 gFe/gCu.

The results obtained for mine waters with concentrations (mg/dm<sup>3</sup>) at «Tarnierskoe» deposit  $\text{Cu}^{2+} = 950.13$ ,  $\text{Zn}^{2+} = 6\,960.50$  and  $\text{Fe}^{3+} = 8\,899.67$  mg/L, and  $\text{Cu}^{2+} = 2\,091.0$ ,  $\text{Zn}^{2+} = 300.0$  and «Shemurskoe» deposit  $\text{Fe}^{3+} = 9\,800.83$  are presented in Tables 2-4.

Copper precipitation by sulphides is performed with acidification of the water before pH-rate of the selective extraction of 1.7–2.0. The consumption of concentrated sulfuric acid for waters with an initial pH range of 2.7 is 0.5-0.6 mL/L.

In figure 1 the results of copper recovery from the dump water of a copper and zinc deposit with a  $\text{NaHSO}_4$  consumption in the range from 95% to 135% of the corresponding stoichiometrical ratio value have shown that it is not possible entirely to separate copper from zinc. More than 5.49% of zinc is precipitated with a copper recovery of 65%. The predominance of zinc several times over copper in mine dump water necessitates the mass fraction of zinc in precipitate at the level of the mass fraction of copper. The increase in consumption of the sodium sulphide precipitator to over 115% of the stoichiometrical ratio one leads to the precipitation of Fe (II) and zinc in quantities exceeding that of copper. The optimal consumption was taken to be 115% of the relevant level of stoichiometrical ratio. The parameters of recovery of  $\text{Cu}^{2+}$  from /mine dump water are presented in Tables 2-4.

**Table 2.** The results of copper recovery by cementation and the recovery of zinc by the sulphide precipitation.

Process	Specific weight in precipitate, g/L	Mass fraction of metal in precipitate, (%)			Recovery rate (%)		Specific consumption of iron	
		Cu <sup>2+</sup>	Zn <sup>2+</sup>	Fe <sub>total</sub>	Cu <sup>2+</sup>	Zn	(g/L)	(g <sub>Fe</sub> /g <sub>Cu</sub> )
Copper-zinc mine dump water								
Cementation	4.53	18.64	1.05	7.89	88.84	0.68	3.90	4.70
Zinc precipitation	30.80	0.34	14.32	15.00	10.62	63.03	-	-
Copper mine dump water								
Cementation	8.26	24.12	0.49	13.53	95.63	13.55	4.30	2.10

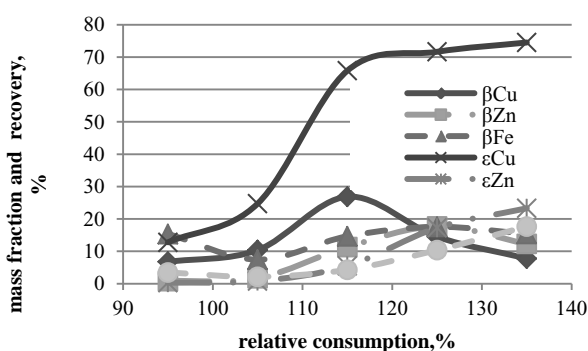
**Table 3.** The results of copper recovery by galvanocoagulation and zinc by the sulphide precipitation.

Process	Specific weight in precipitate, g/L	Mass fraction of metal in precipitate, (%)			Recovery rate (%)			Specific consumption of iron	
		Cu	Zn	Fe	Cu <sup>2+</sup>	Zn <sup>2+</sup>	Fe <sub>total</sub>	(g/L)(g <sub>Fe</sub> /g <sub>Cu</sub> )	
Copper-zinc mine dump water									
Galvanocoagulation	6.69	16.73	0.83	14.42	94.40	0.90	9.71	0.75	0.67
Zinc precipitation	17.22	0.37	21.75	12.98	4.90	63.10	24.8	-	-
Copper mine dump water									
Galvanocoagulation	15.84	17.67	0.56	18.42	95.20	29.33	29.78	0.61	0.73

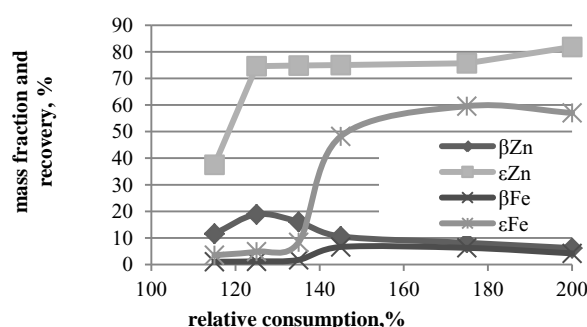
The results of zinc recovery from decoppered mine water with a consumption of  $\text{NaHSO}_4$  in the stoichiometrical ratio in the range of 115-200% which are presented in Figure 2, showed that an increase in the consumption more than 135% leads to an explosive precipitation of iron and the decrease in zinc weight content in the sediment. According to the results of experiments, the optimum consumption of the precipitator adopted to be 125% of the stoichiometrical ratio value. The obtained values of selective sulphide precipitation of  $\text{Zn}^{2+}$  are presented in Table 4.

**Table 4.** The results of copper and zinc recovery by the sulphide precipitation

Process	Specific weight in precipitate, g/L	Mass fraction of metal in precipitate, (%)			Recovery rate (%)		
		Cu	Zn	Fe	Cu <sup>2+</sup>	Zn <sup>2+</sup>	Fe <sub>total</sub>
Copper-zinc mine dump water							
Precipitation of copper	5.01	14.25	7.23	7.50	75.15	5.82	4.43
Precipitation of zinc	14.50	1.60	28.29	16.70	24.41	65.95	28.51
Copper mine dump water							
Precipitation of copper	6.20	28.67	0.46	4.57	86.39	9.75	2.94



**Figure 1.** Influence of NaHS consumption on the parameters of recovery of Cu<sup>2+</sup>, Zn<sup>2+</sup> and Fe<sub>total</sub> from mine dump water ( $\beta$  is a mass fraction of metal in the precipitate;  $\epsilon$  is a rate of recovery of metal in precipitate).



**Figure 2.** Influence of NaHS consumption on the parameters of recovery of Zn<sup>2+</sup> and Fe<sub>total</sub> from decoppered mine dump water ( $\beta$  is a mass fraction of metal in the precipitate;  $\epsilon$  is a rate of recovery of metal in precipitate).

Precipitates obtained by sulphide precipitation contain from 14% to 28% of zinc, that two, three times less than the quality of certified enrichment concentrates. Therefore, we have analyzed the influence of the following factors on mass fraction of zinc in precipitate ( $\beta$ ): the decrease in salt content (S) with constant concentration of zinc ( $C_{Zn}$ ), the change of zinc concentration with constant salinity and decrease in total salinity (S) with constant ratio of S/CZn. These experiments were carried out with simulated mine dump water of copper-zinc deposit and the following concentrations of components g/L: Ca<sup>2+</sup> - 4.26, Mg<sup>2+</sup> - 7.00, Na<sup>+</sup> - 0.0081, K<sup>+</sup> - 0.00096, Al<sup>3+</sup> - 1.754, Mn<sup>2+</sup> - 0.348, Fe<sup>2+</sup> - 7.86, Cu<sup>2+</sup> - 0.0152, Zn<sup>2+</sup> - 6.7, NH<sub>4</sub><sup>+</sup> - 0.0105, Cl<sup>-</sup> - 0.425, SO<sub>4</sub><sup>2-</sup> - 102.48, NO<sub>2</sub><sup>-</sup> - 0.00122, NO<sub>3</sub><sup>-</sup> - 0.00295, pH - 2.4.

It was not able to achieve in the simulated water the same calcium concentration as in the mine dump water. The concentration of calcium in the water was limited by ion product of calcium sulphate Ca<sup>2+</sup> - 0.466 g/L. The mass fraction in precipitates of the base experiment with the NaHS flocculent's consumption of 100% amounted to 34.2%, as well as extraction amounted to 68.27%.

In the first case, the mass fraction of zinc in precipitate gradually grows with the decrease of the indicator S. The extraction of zinc from solution and mass fraction of zinc precipitate increases with decreased total salinity. The mass fraction of zinc increases by one and half times and accounts for 49% with the reduction of indicator S in 10 times. The extraction increases by 11.2%.

The mass fraction of zinc in the precipitate is decreased with fixed total salinity and decrease in concentration of zinc. The decrease in the mass fraction of zinc in precipitate from 34.2 to 17.6% is observed with the decrease in concentration of zinc in 4 times. The mass fraction of zinc in the precipitate is increased before dilution by 20 times with precipitation of zinc from dilute multicomponent model solutions. Further dilution leads to the decrease in the mass fraction of zinc in

a precipitate. For example, the mass fraction of zinc is 42,2 % with the dilution by 20 times ( $S = 4,5$  g/L), however, the mass fraction of zinc is 30,1 % with the dilution by 30 times ( $S = 3,0$  g/L). The obtained patterns may be represented in the following way):  $(\frac{\partial \beta}{\partial c_{Zn}})_S > 0$ ,  $(\frac{\partial \beta}{\partial S})_{c_{Zn}} < 0$ , in the range of an index  $S$  from 4.5 to 90.0 g/L  $(\frac{\partial \beta}{\partial S})_{c_{Zn}} < 0$ , where  $(\frac{\partial x}{\partial y})_z$  is a partial derivative of  $x$  to  $y$ , whereas the value  $z$  is fixed.

The above results proved that quality indicators of zinc-containing products obtained by metal extraction from mine dump waters with sulphide precipitation may be increased by diluting the initial solution. As shown by the X-ray phase analysis, precipitates formed in the process of sulphide precipitation contain sulphide and sulphate phases of copper and zinc, elemental sulphur, and sulphates of calcium and magnesium that are presented in Table 5.

The precipitation of calcium and magnesium sulphates in the range of copper and zinc-selective recovery parameters resulted from the high concentration calcium and magnesium in the water and its saturation with sulphur derivatives as a result of sulphide injection.

**Table 5.** Semi-quantitative phase analysis of precipitates

Phase with mass fraction more than 1%		Copper precipitate	Zin precipitate
Name	Formula	Content, %	
		Cu=14,25; Zn=7,23; Fe=7,50; S=35,4	Cu=1,6; Zn=28,2; Fe=16,7; S=20,45
Sulfur	$S^0$	17	5,5
Poitevinite	$(Cu,Fe)SO_4 \cdot H_2O$ ; Cu:Fe $\approx$ 1:1	4	-
Covellite	$CuS$	11	-
Gunningite	$Zn_{0,75} Mn^{2+}_{0,25} (SO_4) \cdot (H_2O)$	26	15
Rozenite	$FeSO_4 \cdot 4H_2O$	14	14
Greigite	$Fe_3S_4$	4	8
Kieserite	$Mg[SO_4] \cdot H_2O$	11	-
Gypsum	$CaSO_4 \cdot 2H_2O$	5	7
Blinde	$ZnS$	-	14
Bianchite	$FeZn_2[SO_4]_3 \cdot 18H_2O$	-	3
Boyleite	$(Zn,Mg)SO_4 \cdot 4H_2O$	-	2
Unrecrystallization phase		5	20

#### 4. Conclusion

The processing stage of acid mine dump waters for selective recovery of zinc and copper from them in precipitates is possible with the use of any of three two-step schemes: cementation-precipitation, galvanocoagulation-precipitation, precipitation-precipitation.

Obtaining the copper precipitates with high copper content is not a difficult task. Selectivity of copper recovery from the solution is provided by the position of copper in electrochemical series and it's the fact that ion product for copper sulphide is less than for zinc or ferric sulphides. The most difficult task is to obtain zinc-containing precipitate with the high content of zinc in the process of sulphide precipitation. The higher content of zinc in precipitates (28 – 29 %) is obtained by sulphide precipitation with reagent consumption equal to 125% of the stoichiometrical ratio after preliminary copper precipitation from the water by hydrosulphide with consumption equal to 115% of the stoichiometrical ratio.

The phase composition of the precipitate indicates coprecipitation of calcium, magnesium and aluminium with obtaining of substances that can crystallise forming a joint crystalline grid, while mixed crystals are obtained. The reduction of total salt content by dilution of decoppered mine dump water happening because of the decrease in coprecipitation and increase in the content of zinc in precipitates. Moreover, for mine dump waters of copper-zinc deposits, the obtained dependence of the zinc content in precipitates on the dilution is exponential. The highest content of zinc has obtained with decreased total salinity to 4.5 g/L.

## Acknowledgements

This research was financially supported by the Ministry of Science and Education of Russian Federation (State assignment № 2014/80).

## References

- [1] Blowes D W, Ptacek C J, Jambor J L, Weisner C G 2003 The geochemistry of acid mine drainage *Treatise on geochemistry* **9** 149-04
- [2] Hatfield T L, Kleven T L, Pierce D T 1996 Electrochemical remediation of metal-bearing wastewaters Part I: Copper removal from simulated mine drainage waters *Journal of Applied Electrochemistry* **26** (6) 567–74
- [3] Gorgievski M, Božić D, Stanković V, Bogdanović G 2009 Copper electrowinning from acid mine drainage: A case study from the closed mine “Cerovo” *Journal of Hazardous Materials* **170** (2) 716-21
- [4] Chanturia V A, Shadrunkova I V, Medyanik N L, Mishurina O A 2010 Electric flotation extraction of manganese from hydromineral wastes at yellow copper deposits in the South Ural *Journal of Mining Science* **46** (3) 311-16 (in Russian)
- [5] Alkatsev M I 1981 *Cementation processes in nonferrous metallurgy* (Moscow: Metallurgy) (in Russian)
- [6] Halezov B D, Vatolin N A, Makurin Yu N and Bykov N A 2005 Research of extraction of copper in drum cementator *Russian Journal Min. Inform. Anal. Bull* **3** 302-11 (in Russian)
- [7] Solozhenkin P et al 2001 The effect of microgalvano pairs in waste-water treatment. New Developments in Mineral Processing *Proc. of the 9th Balkan Mineral Processing Congress* (Istanbul: Turkey) pp 11-13
- [8] Balintova M, Petrlikova A 2011 Study of pH influence on selective precipitation of heavy metals from acid mine drainage *Chemical Engineering Transactions* **25** 1-6
- [9] Sampaio R M, Timmers R A, Xu Y, Keesman K J, Lens P N 2009 Selective precipitation of Cu from Zn in a pS controlled continuously stirred tank reactor *Journal of Hazardous Materials* **165** (1-3) 256-65
- [10] Shidlovskaya I P, Maltsev G I and Naboichenko S S 2005 Determination of optimal conditions for the deposition of metal hydroxide impurities in wastewater treatment *Russian Journal Non-Ferrous Metals* **6** 14-17 (in Russian)
- [11] Khalezov B D 2009 *Research and Development of a Process for Heap Leaching of Copper and Copper-Zinc*, Dissertation, Institute of Metallurgy, Ural Division, Russian Academy of Sciences of Yekaterinburg (in Russian)
- [12] Medianik N, Chanturia V, Shadrunkova I 2012 Quantum chemical method of the selection of a collecting agent and its use in the process of the floatation extraction of cationic zinc and copper (II) from mine water *Russian Journal of Mining Science* **1** 155-65 (in Russian)
- [13] Global Acid Rock Drainage Guide (GARD Guide) INAP: The International Network for Acid Prevention. [http://www.gardguide.com/index.php?title=Main\\_Page](http://www.gardguide.com/index.php?title=Main_Page). Accessed 28 September 2013
- [14] Chanturia V, Shadrunkova I, Orekhova N and Chalkova N 2011 Process for recovery of zinc from mine and mine dump water *Russian Journal of Ore Beneficiation* **1** 35-9 (in Russian)
- [15] Shadrunkova I V, Orekhova N N 2015 A process for advanced recycling of water originating from mining operations, with metal recovery *Mine Water Environment Journal* **34** (4) 478–84
- [16] Khalezov B D, Nezhivikh V A, Ovchinnikova L A 2005 Semiindustrial trials of zinc recovery by a sodium hydrosulphide from a liquors of heap leaching *Russian Journal of Min. Inform. Anal. Bull.* **4** 278-79
- [17] Peter E, Kalman A 1964 Quantitative X-ray analysis of crystalline multicomponent systems *Acta Chimica Hungarica* **41** 413–22