HEAVY METAL ANALYSIS IN WASTE WATER SAMPLES FROM VALEA ŞESEI TAILING POND

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ABSTRACT. – Heavy metal analysis in waste water samples from Valea Şesei tailing pond. The mining of ore deposits and the processing and smelting of copper at Roşia Poieni have resulted in an increase of the toxic elements concentration within all components of the environment in the area. Valea Şesei tailing pond is a waste deposit for the Roşia Poieni open-pit and is the biggest tailing pond in Romania. In October 2009, we determined 8 heavy metals (Cd, Co, Cr, Cu, Fe, Mn, Ni and Zn) in 10 waste water samples. This water flows under the tailing dam, through the Valea Şesei stream, into the Arieş River, the water's pH varies between 3 and 4. The heavy metals concentration exceeds with orders of magnitude. In the stream the concentrations are much lower, but still exceed the admitted levels. The results show that the tailing pond is a pollution hot spot in the area affecting the environment.

Keywords: heavy metals, tailings, waste water, mining, environment

1. INTRODUCTION

Located in the Apuseni Mountain area, the biggest tailing pond in Romania is called Valea Şesei. Since 1986, it is used for tailings deposit from the Roşia Poieni ore, which is the biggest exploitation of copper ore in the country, and the second in Europe with over one billion tones ore, with 0.36% Cu (Milu et al, 2002). The geological structure is formed of a crystalline base at the intersection of 2 tectonic-magmatic alignments which correspond to 2 major dislocations oriented NW-SE between Roşia Montană-Corabia-Boteş and N-S on Roşia Poieni-Conţiu-Corabia-Arama direction. The volcanic edifice from Roşia Poieni area distinguishes by the presence of quartzite andesite (andesite of Poieni). This one is cut through by a volcanic body of amphibolites andesite (andesite of Fundoaia) (Duma, 1998). The mineralization is formed by chalcopyrite, pyrite, magnetite, bornite or molibdenite. Due to the exploitation, the Roşia Poieni landscape area has been modified by the transport of a big mass from a positive landscape form to a negative one and by the formations of dumps and tailing ponds. All of these changes induced intense erosion processes, landslides and earth falls, found in the zone's morphology through slopes precarious stability. Roşia Poieni mining zone includes 3 waste piles: Valea Cuibarului, Geamăna and Obârşia Muntari and 3 tailing ponds: Valea Ştefancei I, Valea Ştefancei II, Valea Şesei.

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Valea Şesei tailing pond is the main one, located on Geamăna village territory, where some of the buildings are still visible, being partially covered in tailings. The dam was build of rolled rock fill extracted from a nearby limestone quarry. The rolled rock fill contains limestone blocks and gravel. The dam is situated 1.2 km far from Şesei Valley and Arieş River confluence. The dam's height is 118 m, between 565 m and 683 m altitude (Duma, 1998), and the dam's inclination is 33º.

The geology under the tailing pond is based on 2 types: the east side is made of crystalline limestone and the west side is made of sedimentary rocks. The water circulation under the tailing pond is known to be at maximum 8 m, being affected by the acid water seepage. Valea Şesei tailing pond is situated in the valley with the same name, right affluent of Arieş River. Waste water from the tailing pond is acid due to origins from the waste piles, from flotation tailings and from rain. Near the sludge bed appeared sloughing phenomena as a result of phreatic level uplift, and landslides due to humidity excess. In dry periods, the wind remodels the sludge bed's surface involving dust. The surroundings vegetation is represented by beechwoods and coniferous forests, grasslands and shrubbery. The copper from the soil is absorbed by the plants, injuring them by reducing its respiration intensity and slaking the photosynthesis process, as well as lagging some microorganisms' activity.

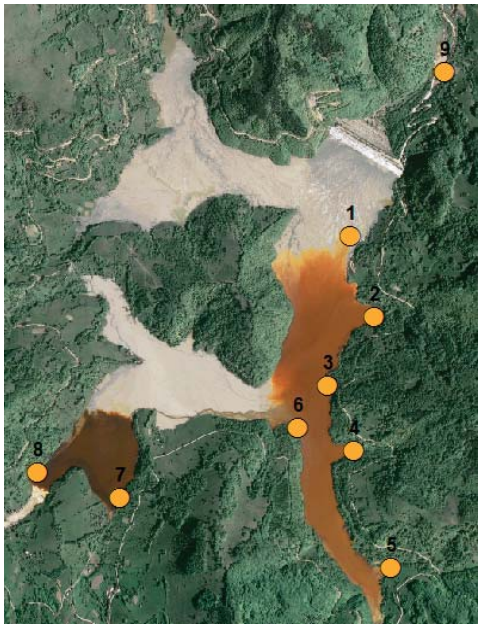

Fig. 1. ***Sampling points in Valea Şesei tailing pond***

2. MATERIALS AND METHODS

The waste water samples were collected in October 2009, when there was no activity at the mine. A number of 10 samples (figure 2) were taken from Valea Şesei tailing pond (samples P1A, P2A, P3A, P4A, P6A, P7A, and P8A), upstream (sample P5A), downstream (sample P9A) and before the confluence with the Arieş River (sample P10A). Each sample was acidified with muriatic acid, in order to get a pH lower than 2. The location of the samples is shown in figure 1.

Cd, Co, Cr, Cu, Fe, Mn, Ni and Zn were determined by inductively coupled plasma-optical emission spectrometry ICP-OES Optima 2100DV (Perkin-Elmer). Wavelengths were selected, to which were measured the atoms emissions.

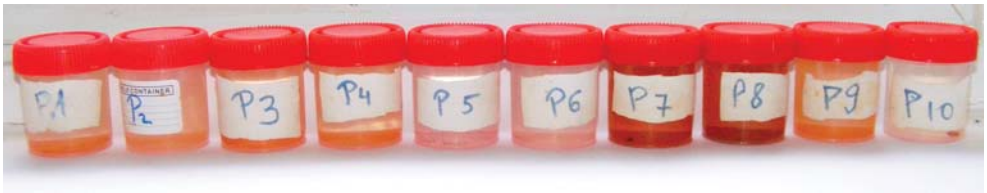

Fig. 2. ***Waste water samples taken from Valea Şesei tailing pond***

Spectrometer's operating parameters were set, as well as the size, concentrations of used standards and units. Standard's preparations were made of - 1000 ppm of standard solution (Merck, Darmstadt, Germany). Calibration curve was constructed using standards, calibration blank and standards (1.50, 100 ppm) were read. Each reported result was the average value of the three analyses. Determination of samples' pH was done with the device InoLab pH / Cond 720.

3. RESULTS AND DISCUSIONS

The comparisons between the samples taken according to heavy metal contamination are shown in table 1.

Table 1. ***Heavy metals concentration in waste water samples, from Valea Şesei tailing pond***

No.	Overview of the samples		Element concentration (mg/l)							
	Aspect (after agitation)	pH	Cd	Co	Cr	Cu	Fe	Mn	Ni	Zn
P1A	opalescent	1,25	4,85	20,78	0,39	1411,5	3689,5	1806	1,83	377
P2A	colorless with sediments traces	1,69	4,76	21,53	0,36	1570	4015,5	2045,5	1,80	436,8
P3A	colorless with sediments traces	1,55	4,66	20,26	0,36	1620,5	4575	2110,5	1,74	454,65
P4A	colorless with sediments traces	1,25	4,21	18,69	0,36	1527,5	4712,5	2235,5	1,65	430
P5A	colorless with sediments traces	1,24	-	0,08	-	0,28	6,89	2,99	-	0,13
P6A	colorless	0,80	0,04	1,06	-	22,54	327,6	82	-	20,81
P7A	slightly yellow	0,72	19,6	70,65	5,75	7699	14050	7083	7,54	2962,5
P8A	opalescent-yellow	0,84	17,06	62,56	5,25	6828	12380	6436	6,61	3052,5
P9A	colorless	0,80	3,85	19,35	0,40	1312,5	4832	2450,5	1,84	1389
P10A	colorless	0,83	2,33	11,40	0,32	663	1104,5	1381,5	0,99	305,8

Pb and Ag were below standard limits in all of the samples. In the table where is no value, means that the values were between limits. All underlined numbers are over the acceptable values, from Romanian Government Decision 352/2005 regarding wastewater discharge conditions into the aquatic environment.

The selected elements are associated with sulphide minerals in the Roşia Poieni area. Their concentrations within the tailing pond show a different distribution of elements than the samples outside of Valea Şesei. In this study the

highest contents of Cd, Co, Cr, Cu, Fe, Mn, Ni and Zn occur in the P7A and P8A (figure 3). The high acidity (figure 4) is caused by near surface oxidation of the sulphide fraction of the tailings. Fe, Ni, Cu, Co and SO_4^{2-} are released when pyrrhotite, pyrite, pentlandite and chalcopyrite are altered to iron hydroxides and oxides (Schwartz and Kgomanyane, 2007). The lowest heavy metals values are at the P5A sample, which is upstream of the tailing pond and P6A sample, where the tailings have settled and stream waster is over them.

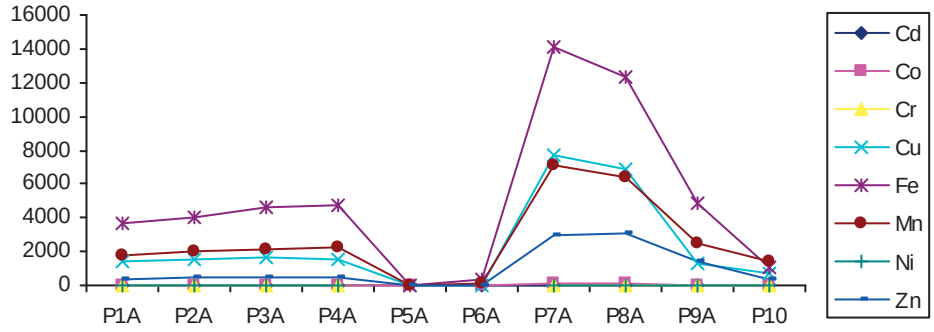

Fig. 3. ***Chart representation of the heavy metals distribution***

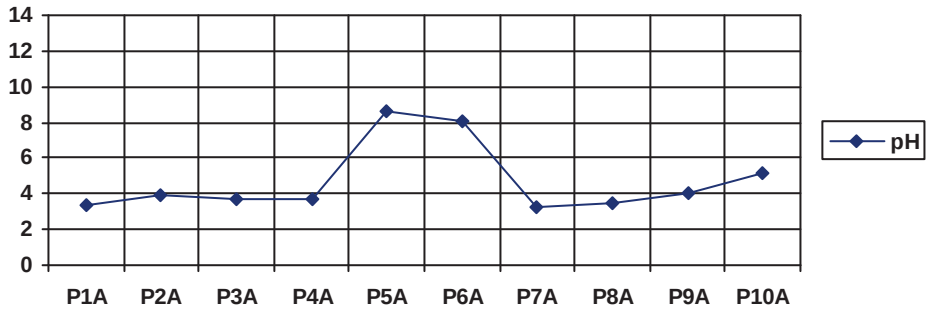

Fig. 4. ***Samples' pH before the acidification***

Seepage water from tailings mixes with mine water after being discharged into the Arieş River. The result has a pH of 4.03 (sample 9) under the tailing dam and a pH of 5.16 (sample 10) near the influx into the Arieş River, which flows into the Mureş River, Tisa and finally arrives to the Danube River. Both values are under limit of Government Decision 352/2005 (6.5-8.5).

Samples P1A, P2A, P3A and P4A are in a more homogenous area, where values of trace element and pH are very similar. Sample P5A was taken outside the tailing pond, in a stream that flows into the sludge bed. Due to the sedimentation process, in sample P6A the water is not so contaminated and the pH is slightly alkaline (8.59). Samples P7A and P8A however, are highly contaminated through

the leakage from waste piles, where it started the bacterial leaching phenomena (figure 5). The situation is exacerbated by the fact that this section is bordered by gardens, courtyards (figure 6).

Fig. 5. ***Valea Şesei tailing pond***

Fig. 6. ***Houses near the tailing pond***

The trace elements in the tailings waste water are above all level of allowable concentrations. The pH increases gradually, and the resulting dilution of heavy metals, in the stream before flow to Arieş River, is greatly reduced, but the values still exceed the permissible levels.

CONCLUSIONS

The toxic metal-rich leachates are an important environmental problem in metal mining regions worldwide. In those areas where tailings are located near or within communities, this issue becomes not just an environmental problem, but a matter of public health concern.

Using the water samples of a relatively big scale in study area, an estimation of eight heavy metal concentrations in Valea Şesei tailing pond and downstream were tested. Most of the samples have heavy metals concentration over the admitted level, with higher values in samples 7 and 8 due to the leakage from waste piles.

The heavy metals concentrations exceed with orders of magnitude. In the stream the concentrations are much lower, but still exceed the admitted levels. The results show that the tailing pond is highly polluted, being a threat for the Arieş River and the surrounding environment.

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