J. Int. Environmental Application & Science, Vol. 11(1): 72-76 (2016)

Impact of Zinc's Cake in Groundwater Pollution

Milaim Sadiku[1], Ferat Shala[2,*], Selver Hoda[1], Ali Sadiku[3], Nushe Lajçi[1], Sadija Nikshiq Kadriu[1]

[1]*Faculty of Food Technology, University of Mitrovica, Mitrovicë, Kosovë;* [2]*Mechanical Engineering Faculty, University of Prishtina, Prishtinë, Kosovë;* [3]*Faculty of Geosiences, University of Mitrovica, Mitrovicë, KOSOVË*

Received January 10, 2016; Accepted March 18, 2016

Abstract: During the electrolytic extraction of zinc respectively during the freezes of neutral leaching of ZnO, there is created the allowance as waste that contains other metals such as lead, cadmium, arsenic, antimony and other metals but in the small amounts. It is estimated that the amount of allowance of zinc deposited is about 500 000 tons. Its impact on the environment is versatile, in air, ground, water and groundwater. In this paper is treated the impact of zinc's cake into groundwater. Basing on the obtained results by chemical analysis of groundwater adjacent to (near) the landfill as well as in its periphery, it results that the presence of heavy metals in these waters is much higher than the permitted limit values for drinking water by WHO. The presence of lead in groundwater near the landfill is 0.05 mg/L, while the WHO limit for drinking water is 0.01mg/L, zinc 565 mg/L whereas the WHO set no limit (here is no limit), while the concentration of cadmium is 1.66 mg/L, while the WHO limit for drinking water is 0.003 mg/L. The source of pollution of these waters is unknown, but since we are dealing with large quantities of this waste which has an economic value, then should be regarded the possibility of reprocessing primarily, drainage and cleaning of groundwater.

Keywords: *Cake of zinc, Pollution, Groundwater, Heavy Metals, Tailing.*

Introduction

The tailing of the zinc's cake is within Industrial Park of Mitrovica, and it lays in a surface of 10.2 hectare. The average altitude of the site is approx. 500m a.s.l. and the center of MIP has coordinates $42^o52'56.31''$ N and $20^o52'47.05''$ E (Final report, 2005). Adjacent of this tailing flow down Sitnica River and the impact of this tailing in the river is very high. Rain water and high water fluctuations of the river regularly saturate the ground of the waste site, resulting in highly contaminated water (e.g. by Zn, Pb, Cd, As, Cu) flowing back into the river. This contaminated water, aside from carrying pollutants far down the stream, heavily pollutes groundwater of the city of Mitrovica. This is of significance because the rudimentary infrastructure of the city still relies on non treated wells as the primary potable water source for its population (Sadiku *et al*., 2011). On the fig. 1, is given a view from zinc's cake. Zinc's cake contains 21- 25% of Zn, 2% of Pb, 0.15 % of Cd *etc*. According the present state of the landfill, and basing on the chemical analysis of air, water, groundwater and ground, and the blood analysis at a particular number of people, the negative impact of this landfill is very pronounced. The impact of zinc's cake is unavoidable.

Groundwater is that portion of subsurface water which occupies the part of the ground that is fully saturated and flows into a hole under pressure greater than atmospheric pressure. If water does not flow into a hole, where the pressure is that of the atmosphere, then the pressure in water is less than atmospheric pressure. Depths of groundwater vary greatly. Places exist where groundwater has not been reached at all (Bouwer, 1978).

The land disposal of municipal and industrial solid waste is another potential cause of groundwater contamination. Buried waste is subject to leaching by percolating rain water and surface water or by groundwater contact with the fill. The generated leach ate can contain high levels of BOD, COD, nitrate, chloride, alkalinity, trace elements, and even toxic constituents (in industrial waste landfill) that can degrade the quality of groundwater (Hughes *et al*, 1971; Zanoni, 1972). In addition, the biochemical decomposition of the organic matter in waste generates gases such as methane, carbon dioxide, ammonia, and hydrogen sulfide that can migrate through the unsaturated zone into adjacent terrains and cause potential hazards such as methane explosions (Flower, 1976; Mohsen, 1975). Stockpiles of

Corresponding: E-Mail: ferat.shala@uni-pr.edu; Tel: +37744158577

materials and waste tailings can also be a source of groundwater contamination. Precipitation falling on uncovered or unlined stockpiles or waste tailings causes leach ate generation and seepage into the ground. The leach ate can transport heavy metals, salts, and other inorganic and organic constituents as pollutants to groundwater. The landfill of the zinc's cake like an industrial tailing is course of underground water pollution with heavy metals and other accompanying metals.

Figure 1. A view of tailing of the zinc's cake

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The impact in the environment

Agricultural land along the banks of Sitnica River is endangered by risk of heavy metal contamination through deposition of contaminated dust and river floods. In case of the Roma community, living in shacks and make shift huts mostly along Ibër River, nutritional and hygiene factors have a critical impact in the level of contamination. In addition, many of these people do not have access to piped water, but rely on water from wells, which could be contaminated by heavy and toxic metals from the river water (Klitgaard; 2004). The environmental survey of Ministero Dell'ambiente and Università Di Siena recorded high concentrations of toxic heavy metals in soil within the region and confirmed absorption of these contaminants by agricultural plants grown in Sitnica and Ibër River valleys.

Methods

Within the framework of the groundwater sampling, one sample was taken from the piezometric number 3, P-3well. The sample in question is situated in north-western part of the MIP area between the River Sitnica and zinc's cake tailing.

Table 1. Groundwater field parameters

Parameter	P-3	DW-1	DW-2
(C°)	13.0	14.5	13.6
pH	6.30	8.25	8.65
ORP, mV	231	194	183
Diss. O_2, mg/L	0.26	6.50	2.18
Conductivity, μS/cm	2.85	885	783

Further two groundwater samples were taken from the private residential wells. In case of the samples DW-1 and DW-2 the present sampling device was used. The samples are taken in the neighborhood "2 Korriku" approximately 200m away from the landfill. In table 1 are appeared water parameters of underground water in five different samples. The methods that are used for chemical analyses are present in the Table 2.

Table 2. Oweview of the used laboratory methods – water samples

Parameter	**Testing methods**
Al, As, Ca, Cd, Co, Cr_{total}, Cu, Fe, Ga, Ge, K, Mg, Mn, Na, Ni, Pb, Sb, Tl, V, Zn	ISO 11885 - ICP spectrometry
Al, Pb, Zn	FAA - spectrometry
Cr^{6+}	CSN EN ISO 18412 - spetrophotometry
Soluble matters	CSN 757346 – gravimetric method
Unsoluble matters	CSN EN 872 – gravimetric method
Hg	AMA method
DOC	CSN EN 1484 - Combustion method
FNI	ISO 6439 - spectrophotometry
CN^{-}_{total}	Spectrophotometry
S^{2-}	ISO 13358 - spectrophotometry
PO_4^{3-}	CSN EN ISO 6878 - spectrophotometry
pH	ISO 10532 – electroanalytical method
Conductivity	CSN EN 27888 - electroanalytical method
$BNC_{8,3}$	CSN 757372 – titration method
$ANC_{4,5}$	CSN EN ISO 9963-1,2 – titration method

Results

According of the obtained chemical analysis of groundwater samples, Tables 3 and 4, which were obtained in three different countries, shows that the concentration of heavy metals in these waters exceed the allowed limit values for drinking water set by WHO. Allowed values for lead in water according to WHO is 0.01 mg/L (WHO, 2008) whereas in the first sample, P-1, is less than 0.05 mg/L, which however is a limited value. Same values for the concentration of Pb in groundwater are obtained for two other samples, DW-1 and DW-2. According to the WHO limit value for Cd in drinking water is

0.003 mg/L (WHO, 2008) whereas in P1 sample concentration of Cd is 1.66 mg/L, which is 553.33 times higher than the permissible value. Even in samples DW-1 and DW-2 concentration of Cd is lower but still above the allowed value, less se 0.04 mg/L. Concentration of Zn in water by WHO (WHO, 2008) allowed for drinking water there is no limit, in the presence of Zn sample P-1 is 565 mg/L. In two other samples, DW-1 and DW-2, the concentration of Zn is quite high 130 mg/L belongs of 80 mg/L. Meanwhile the concentration of other metals is under or in limit with permitted values.

Table 3. Results of laboratory analyses – groundwater from well P-3

Parameter	Unit	Results	Parameter	Unit	Results
Al	mg/L	0.09	Soluble matters	mg/L	3 800
Cd	mg/L	1.66	Unsoluble matters	mg/L	106
Co	mg/L	0.02	S^{2-}	mg/L	< 0.01
Cr_{total}	mg/L	< 0.05	NO_3^-	mg/L	7.59
Cr (VI)	mg/L	0.01	SO_4^{2-}	mg/L	2 700
Cu	mg/L	< 0.02	PO_4^{3-}	mg/L	< 0.03
Hg	mg/L	< 0.001	HCO_3^-	mg/L	58.0
Ni	mg/L	1.31	CO_2 free	mg/L	796
Pb	mg/L	< 0.05	DOC	mg/L	4.4
Sb	mg/L	< 0.005	Ca	mg/L	577
Tl	mg/L	< 0.03	K	mg/L	4.97
V	mg/L	< 0.01	Na	mg/L	76.8
Zn	mg/L	565	Mg	mg/L	101
Fe	mg/L	0.11	Mn	mg/L	4.39

Table 4. Results of laboratory analyses-groundwater from private residential wells

Parameter	Unit	Sample				Parameter	Unit	Sample			
		DW-1	DW-2	DW-3	DW-4			DW-1	DW-2	DW-3	DW-4
Al	mg/L	< 0.05	< 0.05	< 0.05	< 0.05	Soluble Matters	mg/L	-	-	-	604
Cd	mg/L	< 0.004	< 0.004	< 0.004	< 0.004	Un soluble Matters	mg/L	< 10	< 10	< 10	31
Co	mg/L	< 0.02	< 0.02	< 0.02	< 0.02	S^{2-}	mg/L	-	-	-	< 0.01
Cr_{total}	mg/L	< 0.05	< 0.05	< 0.05	< 0.05	NO_3^-	mg/L	-	-	-	41.2
Cr (VI)	mg/L	< 0.01	< 0.01	< 0.01	< 0.01	SO_4^{2-}	mg/L	-	-	-	146
Cu	mg/L	< 0.02	< 0.02	< 0.02	< 0.02	PO_4^{3-}	mg/L	-	-	-	0.27
Hg	mg/L	< 0.001	< 0.001	< 0.001	< 0.001	HCO_3^-	mg/L	-	-	-	314
Ni	mg/L	< 0.03	< 0.03	< 0.03	< 0.03	CO_2 free	mg/L	-	-	-	48.8
Pb	mg/L	< 0.05	< 0.05	< 0.05	< 0.05	DOC	mg/L	-	-	-	4.8
Sb	mg/L	< 0.005	< 0.005	< 0.005	< 0.005	Ca	mg/L	-	-	-	106
Tl	mg/L	< 0.03	< 0.03	< 0.03	< 0.03	K	mg/L	-	-	-	5.76
V	mg/L	< 0.01	< 0.01	< 0.01	< 0.01	Na	mg/L	-	-	-	30.8
Zn	mg/L	0.11	0.15	0.13	0.08	Mg	mg/L	-	-	-	25.1
Fe	mg/L	-	-	-	0.19	Mn	mg/L	-	-	-	< 0.02

Conclusion

Basing on the obtained results. we notice that the concentration of heavy metals is much higher than the permitted limit values for drinking water set by WHO, in particular, heavy metal concentration is high in sample sides. Since the adjacent landfill of sample sides (place where the samples are taken) P-1 respectively Sitnica River flows, the impact of these waters in the river water pollution Sitnica is incontestable, that the chemical analysis shown, which made Sitnica River water. These waters also have an indirectly effect on human health, as residents from the neighborhood "2 Korriku" samples were taken from DW-1 and DW-2, will water (wells) use for washing and irrigation of their gardens. This waste contains up to 23% Zn as well as other metals, therefore, this residue has an economic value, then the first step have to be undertaken in the reprocessing of this waste, where the whole will move away and become rehabilitation of the surface area extends landfill. In case that such a thing would not be relatively quickly accomplished, as well as material resources are lacking, then should be the drainage of the landfill where collected water will be drainage from the landfill which would be subject to further purification process. Thereafter, in the last phase should be cleaning of the groundwater.

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