

## Leaching of Copper Secondary Wastes: Possible Soil Contaminants

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The United Nations Basel convention on the transboundary shipment of hazardous wastes was adopted to control the influx of hazardous materials being shipped from OECD countries to non-OECD countries. The ban allowed for developing countries to control the level of pollution and contamination prevailing in soils, water and the atmosphere. This study aims to look at the hazards posed by the secondary wastes industries, focusing in particular on copper slags, drosses and residues. To establish the levels of heavy metals becoming available in the environment, these wastes were extracted in different leach liquors. The results indicated that copper residue is more drastic toward soil and water contaminations. High amount of Cu from three different samples were leached, 39431.9, 7402.6 and 119301.6 µg/L, under physiological soil pH condition. Other heavy metals Pb and Zn were also calculated in concentration 10.1, 139.57 and 29.48 µg/L respectively. A significant improvement in morphology was also recorded from the scanning electron microscopic analysis.

**Key Words:** Basel Convention, Hazardous, Wastes, Slags, Drosses, Residues, Leaching, SEM.

### INTRODUCTION

A wide variety of pollutants is governed to the atmosphere by modern civilization through various anthropogenic activities such as industry, mining and transportation. Although trace levels of heavy metals are essential for living organisms, excess of these heavy metals is generally harmful to plants, animals and human health<sup>1</sup>. Contaminated soils with high levels of heavy metals are widely spread and concerns have been raised over the potential risks to humans, animals and agricultural crops. Humans and other animals can be exposed to heavy metals or chemicals through water, air, soils, dusts and their diets. These chemicals can enter the body by several different means such as ingestion, inhalation and skin contact<sup>2,3</sup>.

The copper dust, fly, dross, slag and residues during and after smelting processes represent a high potential risk of environmental contamination, depending particularly on the content and mobility of the metal contained<sup>4</sup>. The composition of residues of different origin show variations and thus exhibit different environmental and geochemical characteristics<sup>5,6</sup>. The release of contaminants from their sources mainly depends upon the pH and solution used for processing<sup>7</sup>.

Currently, contamination of soil in cultivated fields with toxic heavy metals such as at risk assessments are required to

be carried out under certain legislation<sup>8</sup> and are an estimation of the risk, which includes identifying the hazards, the magnitude of the effects and probability of an occurrence and an evaluation of it. This also includes quantifying the significance of the hazards and the consequences for persons and the environment effected. Trigger guide levels for metals have been set by the world health organization (WHO) and these values represent the acceptance level of concentration of metal in soils and waters, at which it presents no harm to humans, mammals and fauna. The trigger guide level for copper specified for the Basel convention<sup>9</sup> is 5 mg/L.

Cellular level by the formation of free radicals. Cellular injury by this type of mechanism is cadmium, copper, nickel and zinc has emerged as a new threat to agriculture<sup>10</sup>. Copper being one of the common heavy metals in industrial discharge of aeronautic, metal and metallurgy. Refinery industries shows toxic effects on plants and animals. Copper causes injury well documented for copper as well as other metals<sup>11</sup>. Laboratory estimation is, therefore, very important to understand the leaching behaviour and to identify the environmental risk represented by the residues of copper industry.

The aim of this study was to investigate the leaching behaviour of copper residues by aqueous solution at fixed pH. No doubt the residues and other form of residues is recycled

in smelting process but still it contain prominent amount of heavy metal that may cause serious contamination in soil and eventually in crops and living bodies<sup>12</sup>. This was studied by Kribek *et al.*<sup>13</sup> who recorded elevated concentrations of metals in the soils around smelters in the copper belt area and concluded that the dust fallout from process plant is one of the main source of contamination in this area. Sracek *et al.*<sup>14</sup> has also reported the changes in contaminant solubility after working on Zambian leaching plant wastes. Here in this study we have checked the leaching behaviour of copper secondary wastes with respect to the specific pH condition of soils *i.e.* pH 5.2. The comparative leachability were also comprehensively reviewed by Anjum *et al.*<sup>15</sup>. The main objective of the current study was to estimate the leaching concentration of heavy metals from different copper secondary wastes *i.e.* copper dross, copper slags and copper residue in different aqueous solutions conditions.

## EXPERIMENTAL

The present work focused on the leaching of industrial samples, such as copper dross, slag and residue using different leaching liquors which stimulate a variety of environmental conditions and scenarios. The leach liquors used were 0.5 M acetic acid, 0.01 M calcium chloride, 0.1 M hydrochloric acid/sodium chloride and 2 M nitric acid.

The samples of Cu secondary wastes used in this study are presented in Table-1.

TABLE-1  
Cu AND Zn SECONDARY MATERIALS PROVIDED  
BY COPPER INDUSTRY WASTE SAMPLES

Sample	Sample code	Supplier
Cu Dross	CD-1	Britannia refined metals (UK)
	CD-2	
	CD-3	
Cu Slags	CS-1	Huttenwerke Kayser, AG (Germany)
	CS-2	
	CS-3	
Cu Residues	Copper residue batch 1-4 (CR-B1-4)	A & H Knight Ltd. (UK)

**Acetic acid extraction:** Extraction with acetic acid was performed using modified version of the Canadian toxic characteristic leaching procedure (TCLP) with slight modification. In brief, 10 g of the sample was placed in a 250 mL stoppered conical flask to which 160 mL de-ionized water was added. The flask was shaken using a mechanical shaker (Griffin) at 50 rpm. After shaking the sample for 15 min, the pH of the solution was measured and adjusted at *ca.* 5.2 with the help of 0.5 M acetic acid. The sample was then shaken for 24 h with the pH being monitored after 1, 3 and 6 h with a final pH check after 22 h. However lower pH was adjusted to 5.2 by addition of de-ionized water. After 24 h the process was stopped and the solution filtered. The filtrate was transferred to a 250 mL volumetric flask and diluted it upto mark with de-ionized water slow filtration was overcome by extraction through centrifugation and filtrate was collected for further analysis.

**Calcium chloride extraction:** A single extraction with 0.01 M CaCl<sub>2</sub> has been proposed. In short, in a 250 mL conical

flask, 10 g of sample was placed to which 100 mL of 0.01 M CaCl<sub>2</sub> was added. The sample was shaken at orbital shaker for 2 h at 200 rpm after which the pH was noted. The solid and liquid fractions were separated by centrifugation and filtration. The filtrate then transferred to a 100 mL volumetric flask and added de-ionized water to make the volume 100 mL for further analysis.

**Hydrochloric acid extraction:** Acid based leaching was carried out by placing 0.5 g of sample into a 250 mL conical flask to which 100 mL of a mixture of 0.1 M hydrochloric acid and 0.1 M sodium chloride was added. The mixture was shaken for 1 h after which centrifugation and filtration was performed to separate the solid and liquid phases which used for further analysis.

**Nitric acid extraction:** This extraction was termed as aggressive extraction because of highly concentrated acid used. A sample of 10 g was added to 250 mL conical flask, followed by the addition of 100 mL 2 M nitric acid and the sample was shaken for 1 h. At the end of processing time, the mixture was centrifuged and filtered and the filtrate was transferred to a 100 mL volumetric flask. The volume of the filtrate was increased to 100 mL using de-ionized water for further analysis.

**Analysis of metal secondary waste:** The solution samples were analysed for Ni, Cu, Co and Fe using atomic absorption spectrophotometry. Sample solution was diluted by addition of 20 mL distilled water and the volume was made to 200 mL with distilled water and finally used for atomic absorption spectrophotometry analysis.

**Morphological analysis:** Such analysis of the copper industrial wastes before and after treatments were conducted by using the high tech facility like scanning electron microscopically technique following the methods described by Ajum *et al.*<sup>16</sup>.

## RESULTS AND DISCUSSION

The leaching trend of Cu, Pd, Fe and Zn were assessed in selected samples of Cu dross, slag and residues. Digestion and leaching of metals were carried out using standard procedures with slight modification. Liquid solution was prepared to determine the concentration of each metal through inductive coupled plasma and ion chromatography using a Dionex 2010i HPLC system.

**Copper dross samples:** Assessability of selected metals copper dross were performed by selecting three samples of copper dross, CD-1, CD-2 and CD-3. Four leaching liquid, CaCl<sub>2</sub>, CH<sub>3</sub>COOH, HNO<sub>3</sub> and HCl/NaCl were used to observe the leaching value of each metal. The leaching was performed at fixed pH 5.2, the pH range 3.7-7.0 is most favourable range to leach the metals from test samples and this pH range is specific to soil for cultivation<sup>2</sup>. Leaching with acetic acid depicted efficient and good leaching of Pb and Zn, 60.1 µg/L and 7.9 µg/L respectively from CD-1 sample but the amount of Cu leaching was very low. In contrast to acetic acid, HNO<sub>3</sub> appear promising liquor to leach Cu (39.8 µg/L) from similar sample. Out of other two liquors CaCl<sub>2</sub> and HCl/NaCl, CaCl<sub>2</sub> fail to leach any metal but HCl/NaCl showed minute leaching as shown in Table-2.

TABLE-2  
EXTRACTION OF HEAVY METALS FROM COPPER  
DROSS BY USING DIFFERENT LEACHING LIQUOR

Sample No.	Leach liquor	Concentration of metal leached ( $\mu\text{g/L}$ )			
		Cu	Pb	Fe	Zn
CD-1	CaCl <sub>2</sub>	-	6.1	-	-
CD-2		-	-	-	0.2
CD-3		-	7.0	-	2.3
CD-1	CH <sub>3</sub> COOH	0.1	60.1	-	7.9
CD-2		10.1	15.2	-	0.3
CD-3		-	43.4	-	11.8
CD-1	HNO <sub>3</sub>	39.8	-	10.6	4.9
CD-2		6.6	46.0	-	1.7
CD-3		4.7	-	-	-
CD-1	HCl / NaCl	1.1	10.3	-	1.9
CD-2		5.4	6.3	-	0.9
CD-3		-	-	-	2.43

**Copper slag sample:** Copper slag is a by-product of copper production from copper ore. During smelting, a molten pool of copper forms at the bottom of the furnace while a layer of impure metal, which is the slag, is drained off from the top. The copper slag is then quenched using industrial or sea water. Sometimes, it is left to cool by the air. For every ton of copper produced about 2.2 ton of slag is generated and it is recommended that about 10 % by mass can be used in concrete as building material. While working with copper slag samples, CS-1, CS-2 and CS-3, triplicate leaching process with four leaching liquors indicates that the CH<sub>3</sub>COOH highly efficient to leach lead (11.2-100.7  $\mu\text{g/L}$ ) from copper slag. However, HNO<sub>3</sub> is active liquor to leach Cu, 186.18, 311.40 and 340.46  $\mu\text{g/L}$  respectively, from all analyzed samples as shown in Table-3. Nitric acid has also showed well ability to leach Pd, 139.57  $\mu\text{g/L}$  from CS-2 and 126.33  $\mu\text{g/L}$  from CS-3 sample.

TABLE-3  
EXTRACTION OF HEAVY METALS FROM COPPER  
SLAG BY USING DIFFERENT LEACHING LIQUORS

Sample No.	Leach liquor	Concentration of metal leached ( $\mu\text{g/L}$ )			
		Cu	Pb	Ni	Zn
CS-1	CaCl <sub>2</sub>	-	-	-	-
CS-2		-	11.5	-	0.2
CS-3		-	-	-	-
CS-1	CH <sub>3</sub> COOH	6.8	100.7	0.8	0.5
CS-2		4.6	34.8	-	2.2
CS-3		4.2	11.2	-	1.8
CS-1	HNO <sub>3</sub>	186.18	-	-	36.16
CS-2		311.40	139.57	-	29.48
CS-3		340.46	126.33	-	54.40
CS-1	HCl/NaCl	1.1	61.2	-	3.5
CS-2		1.8	13.5	0.5	0.8
CS-3		1.1	28.2	-	0.2

Calcium chloride indicated passive nature to leach these metals. Inter sample comparison showed that sample CS-3 bear comparatively more Cu than any one other. Variation in concentrations of copper and other metals surely is the function of raw ore used to extract pure copper as shown. Other metals like Ni, Mn were also detected but in trace amounts.

**Leaching of copper residues:** Residues of different origin vary in composition and thus exhibit different geochemical and environmental characteristics<sup>3,4</sup>. Copper residues consist

of mainly three form met, fines and mattes. All types of samples were tested to assess the concentration of copper and other metals in residues. All residue samples were obtained from A & H Knight Ltd. (UK) in four different batches.

**Copper residue batch 1 (CR-B1):** The samples within each batch were either one or two of mets, fines or mattes. The first batch, CR-B1, contained two samples mets and fines. Each of which, was extracted with acetic acid, nitric acid and HCl/NaCl. The acid saline solution extracted high concentrations of Cu and Zn *i.e.* 39,431.9  $\mu\text{g/L}$  and 7,402.6  $\mu\text{g/L}$  respectively. With the nitric acid extraction, unexpectedly small amounts of metals were extracted from each of the two mets and fines samples. Anyhow, nitric acid leaching process showed high concentration of Cu and Zn in fines than those in the mets. This trend was also observed under acetic acid leach conditions where a large proportion of Zn approximately 125.2  $\mu\text{g/L}$  was observed in mets than in fines (Fig. 1).

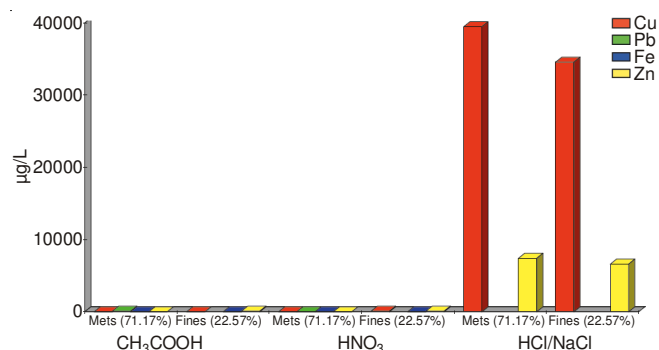


Fig. 1. Leaching of heavy metals from copper residue batch 1 samples under different conditions

**Copper residue batch 2 (CR-B2):** The second batch of copper residues (CR-B2) contained three samples of mets, mets-1, mets-2 and mets-3, with 9.53, 8.13 and 18.65 % concentration regarding copper respectively. In this batch sample nitric acid leached actively Cu and to some extent Zn. The leached concentration of Cu from each sample of mets, 26503.6, 53582.7 and 119301.6  $\mu\text{g/L}$  respectively, were noted. The high concentration of copper; leached from sample mets3 can be attributed the higher percentage of copper in it as compared to other two samples. Other metals Zn and Fe were also detected in prominent amount when leaching was performed with HNO<sub>3</sub> as compared to other leached solvents as shown in Fig. 2. Anyhow acetic acid looking promising solution for leaching Pd from copper residue.

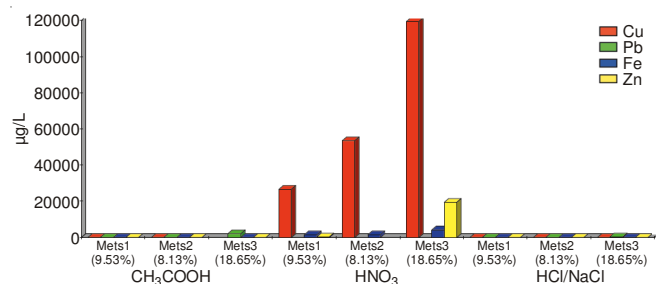


Fig. 2. Leaching of heavy metals from copper residue batch 2 samples under different conditions



**Copper residue batch 3 (CR-B3):** Sample used in third batch of copper residues were consisted of only fines of copper residues, fines-1, fines-2 and fines-3. Acetic acid, as usual, showed moderate leaching behaviour as compared to HCl/NaCl and particularly HNO<sub>3</sub> as shown in Fig. 3. Since HCl/NaCl leaching showed large amounts of Fe extraction form all three samples. Lead was found to be leached in samples 2 and 3 whereby fines-2 contained 183.6 µg/L and fines-3 contained 144.6 µg/L. Zinc was present in all three samples with the highest concentration contained in fines-2. The only prominent extraction was achieved through HNO<sub>3</sub>. The amount of copper extracted by HNO<sub>3</sub> was as high as 171,025.9 µg/L but it was still less than extracted amount of Zn that was 2157502 µg/L from sample fines-2. All other samples contained less amount of Cu and Zn, this may be due to the use of different ores of Cu as raw material having different salts.

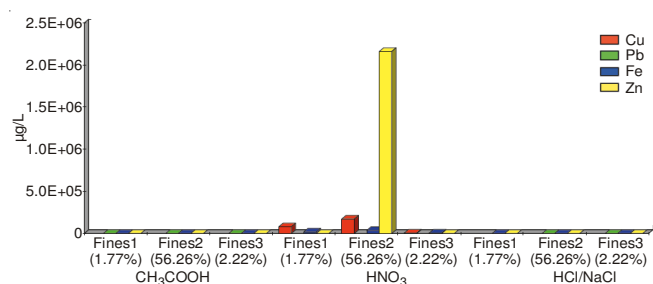


Fig. 3. Leaching of heavy metals from copper residue batch 3 samples under different conditions

**Copper residue batch 4 (CR-B4):** The final batch of copper residues obtained from A & H Knight Ltd. (UK) consisted of two samples, matte sample of 25.10 % composition and a fines sample which had a composition of 89.19 %. Copper was found to be extracted only with the acetic acid in minute quantity. The only metal that was found in high concentration as compared to Cu was Zn and to less extent Fe, extracted with the help of HNO<sub>3</sub> (Fig. 4). The concentration of Cu leached was low in terms of trigger guide level. A significant improvement in morphology was also recorded from the scanning electron microscopic analysis. The data related to scanning electron microscopy presented in the Fig. 5 before and after the treatment showing a remarkable change in the morphological structure of the sample.

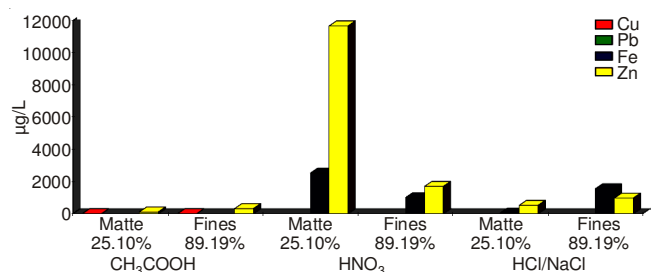


Fig. 4. Leaching of heavy metals from copper residue batch 4 samples under different conditions

## Conclusion

The leachability of primary copper particularly and some other metals from industrial wastes has been determined under various conditions that simulate environmental situations including

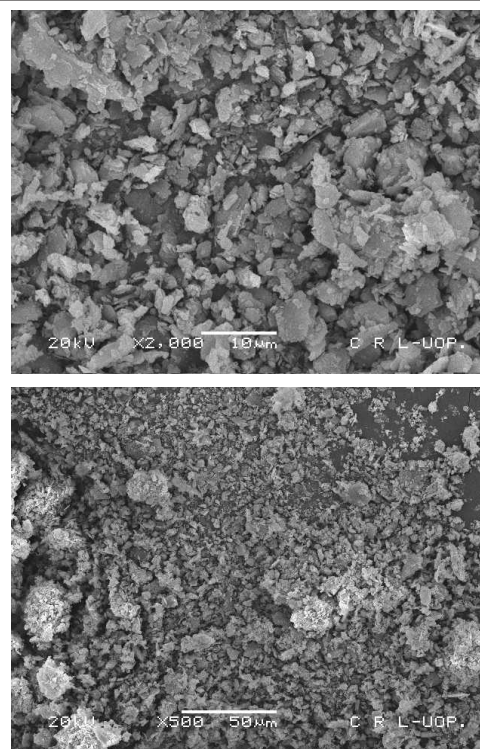


Fig. 5. Scanning electron microscopic analysis of the copper industrial waste copper slag by HCl/NaCl extraction liquor before and after the treatment

acidic and biological activity in landfill and gastric fluids. The leaching studies provide information on the bioavailability of copper and other secondary metals *e.g.* Fe, Pb and Zn in various acidic aqueous solutions. The leaching pattern of secondary metals pointed to a serious environmental threat that may become serious during rainy season in copper belt. These results may also use to estimate possible metal contamination and to take effective step to retard metal contamination under different acidic or basic conditions by the use of different Cu- and/or Fe-bearing sulphates and oxides. A significant changes in morphology were recorded before and after chemical leaching by scanning electron microscopic analysis.

## REFERENCES

- L. Jarup, *Br. Med. Bull.*, **68**, 167 (2003).
- V. Martina, E. Vojtech, H. Jiri, A. Thomas and K. Bohdan, *Appl. Geochem.*, **26**, S263 (2011).
- V. Ettler, O. Sebek, T. Grygar, M. Klementova, P. Bezducka and H. Slavikova, *Environ. Sci. Technol.*, **42**, 7878 (2008).
- G.S. Ohmsen, *J. Waste Manage. Assoc.*, **51**, 1443 (2001).
- T. Astrup, J.J. Dijkstra, R.N.J. Comans, H.A. van der Sloot and T.H. Christensen, *Environ. Sci. Technol.*, **40**, 3551 (2006).
- V.Z. Lukas, R. Josh, K. Tim, M. Graham and M. Steven, *Sci. Total Environ.*, **329**, 29 (2004).
- D.J. Spurgeon and S.P. Hopkin, *Appl. Soil Ecol.*, **11**, 227 (1999).
- A. Cox and T. Sheales, *Aust. Commod.*, **3**, 3 (1996).
- H. Alter, *Resour. Conserv. Recycl.*, **43**, 353 (2005).
- D. Singh, K. Nath and K.Y. Sharma, *J. Environ. Biol.*, **28**, 409 (2007).
- X. Shi, S.N. Dalal and S.K. Kasprzak, *Biochem. Biophys. Acta*, **302**, 294 (1993).
- J. Ross and D. de Vries, Mufulira Smelter Upgrade Project - "Industry" Smelting on the Zambian Copperbelt. Mopani Copper Mines PLC Int. Rep., Kitwe, Zambia (2005).
- B. Kríbek, V. Majer, F. Veselovsky' and I. Nyambe, *J. Geochem. Explor.*, **104**, 69 (2010).
- O. Sracek, F. Veselovsky, B. Kríbek, J. Malec and J. Jehlicka, *Appl. Geochem.*, **25**, 1815 (2010).
- F. Anjum, M. Shahid and A. Akcil, *Hydrometallurgy*, **117-118**, 1 (2012).
- F. Anjum, H.N. Bhatti, M. Asgher and M. Shahid, *Appl. Clay Sci.*, **47**, 356 (2010).