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Toxicity characterization and long-term stability studies on copper slag from the ISASMELT process

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Abstract

Detailed studies on the toxicity and long-term stability of copper slag of varying heavy metal concentration generated over a 14-week period in an Indian copper plant through the ISASMELT process was carried out using USEPA's toxicity characteristic leaching procedure (TCLP), multiple extraction procedure and sulfuric acid leaching of granulated and mechanically activated slag as a function of pH at two different temperatures. The TCLP, acid leaching and multiple extraction test results carried out on a large number of slag samples of varying compositions derived from the use of several copper concentrates indicate poor leachability of the heavy metals and assures long-term stability even in extreme atmospheres. Leaching tests on mechanically activated samples gives an idea of the resistance to leaching of the heavy metals even upon weathering. The multiple extraction leaching tests indicate that the heavy metals present in the slag are stable and are not likely to dissolve significantly even through repetitive leaching under acid rain in a natural environment. The highest concentration of all the elements is far below the prescribed limits in USEPA 40CFR Part 261.

Keywords: Copper slag; Acid leaching; TCLP; Heavy metals; Multiple extraction procedure

1. Introduction

Large amounts of copper slags are generated as waste worldwide during the copper smelting process. The world copper production is currently about 14.98 million tonnes (International Copper Study Group, 2005) and it is estimated that for every tonne of copper produced, about 2.2 tonnes of copper slag is generated as a waste (Gorai et al., 2003). Copper slags are suitable for a variety of applications such as for manufacture of cement, in aggregates, landfill, ballast, abrasives, roofing granules, glass, tiles, bituminous pavements, etc. The characteristics and utilization of copper slag have been recently reviewed (Gorai et al., 2003). However, the main concern in the large-scale use of copper slags is the apprehension of environmental hazard from the viewpoint of leaching of heavy metals from the slag and its long-term stability in extreme environmental conditions. Although copper slag does not feature in the hazardous waste category in schedule 1 of the hazardous waste management rules issued by the Ministry of Environment and Forests, India in 2003 (HWM-2003), it is not clear whether a concentration limit-based classification as given in schedule 2 of HWM-2003 will be applicable to copper slag.

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Table 1
Composition range of the concentrates and slags and their statistical variation used during the period of study

Element	Composition range of concentrates used (wt.%)	No. of concentrates	Composition range of slag studied (wt.%)	No. of slags studied	Toxicity limit as per schedule 2 of HWM-2003 (wt.%)
As	0.005–0.072	25	0.0031–0.0045	42	≤0.005
Bi	0.002–0.010	23	0.0010–0.0027	36	≤0.005
Cd	0.001–0.0041	23	0.0001–0.0029	38	≤0.005
Cr	0.0005–0.007	19	0.0014–0.0041	26	≤0.5
Mg	0.025–0.37	22	–	–	≤5
Mo	0.005–0.05	24	–	–	–
Ni	0.001–0.004	21	0.0007–0.0059	41	≤0.5
Pb	0.025–0.15	25	0.028–0.13	43	≤0.5
Se	0.002–0.020	24	–	–	≤0.005
S	25–37	25	0.43–0.95	43	–
Te	0.001–0.0085	19	–	–	≤0.005
Zn	0.02–0.8	25	0.10–0.40	36	≤2%

The concentration limits of toxicity for the various elements relevant to copper slag as given in schedule 2 of HWM-2003 are given in Table 1. Copper slag has been excluded from the listed hazardous waste category of United States Environmental Protection Agency (USEPA). However, its toxicity characterization under the characteristic hazardous waste category of USEPA has to be checked using the toxicity characteristic leaching procedure (TCLP). The leachability of various heavy metals from copper slag generated by various smelting processes in several countries has been reported in the literature (Altundogan et al., 2004; Johnson et al., 1982; Koren et al., 1995; Lagos and Luraschi, 1997; Lim and Chu, 2006; Queneau et al., 1991; Zain et al., 2004). Many of these investigators (Johnson et al., 1982; Koren et al., 1995; Lagos and Luraschi, 1997; Lim and Chu, 2006; Queneau et al., 1991; Zain et al., 2004) have adopted USEPA's toxicity characteristic leaching procedure (TCLP) test to study the leachability of the various heavy metals. The TCLP test employs buffered acetic acid (at a pH of 5) as the lixiviant. All these studies indicate very low-leachability of heavy metals under the conditions of the TCLP test. Altundogan et al. (2004) studied the sulfuric acid leaching behavior of copper converter slag in the presence and absence of dichromate. They reported significant dissolution of Co, Fe and Zn from the copper slag (66.6, 62.1 and 65.7%, respectively) in 1.0 M H_2SO_4 (in the absence of $K_2Cr_2O_7$). The addition of 0.3 M $K_2Cr_2O_7$ significantly enhanced the copper dissolution from slag but considerably decreased the Fe, Co and Zn extraction values. They have not investigated the leachability of the heavy metals in sulfuric acid. The environmental hazard of copper slag in the context of the Basel Convention has recently been discussed (Alter, 2005). Although the TCLP test is rigorous, US Environmental Protection Agency recommends the multiple extraction procedure (USEPA method 1320) to ascertain the stability and mobility of heavy metals under extreme natural conditions i.e., the highest concentration of each constituent that is likely to leach in a natural environment. This method employs several leaching cycles on the leach residue generated through the extraction procedure toxicity test using a lixiviant 60% H_2SO_4 and 40% HNO_3 and adjusted to a pH of 3.

The composition of the slag depends both on the smelting process as well as the composition of the copper concentrates used. Alter (2005) has statistically analyzed the chemical compositions of 28 copper slags from United States, Canada and Chile and found a large variation in the concentration of the heavy metals. Gorai et al. (2003) as well as Shen and Forssberg (2003) also reported considerable variation in the slag compositions from different countries (Turkey, Egypt, India, Czechoslovakia, Iran, Chile and US) adopting different types of copper smelters (INCO flash smelter, Mitsubishi flash smelter and reverberatory smelter). The objective of this study is to investigate the toxicity characteristics and long-term stability under extreme environmental and weathering conditions of the copper smelter slags being generated through the ISASMELT process at M/S Sterlite Copper in India. Slags of varying heavy metal concentration generated over a 14-week period were evaluated. A wide variety of copper concentrates (around 25) from several mines around the world (Australia, Brazil, Peru, Mexico and Chile) having a wide composition range of heavy metals have been used during this period (Table 1).

The ISASMELT process of MIM technologies, Australia has been adopted at M/S Sterlite Industries, Tuticorin, India. In this process, the charge comprising of copper concentrate mixed with quartz, coal/coke, pig