



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.

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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 H₂SO₄ (in the absence of K₂Cr₂O₇). The addition of 0.3 M K₂Cr₂O₇ 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 rec-

ommends 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% H₂SO₄ and 40% HNO₃ 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

iron and limestone is charged into the feed port at the top of the ISA-furnace. Smelting is carried out in a single continuous furnace consisting of a vertical cylindrical vessel at the top center of which there is a lance submerged into the slag for blowing oxygen enriched air. Up to 80% oxygen enriched air is used. The smelting process is autogenous and the temperature of the smelting zone lies in the range of 1180–1200 °C. The matte and slag are tapped simultaneously at the bottom of the furnace to a rotary holding furnace (RHF) maintained at ~1070–1100 °C where the slag and matte are separated. The slag is granulated by cold re-circulated water and disposed off. The matte is tapped and transferred to the Pierce-Smith converters for conversion to blister copper by blowing with air.

In this study, the rotary holding furnace (RHF) slag generated by the ISASMELT process corresponding to a wide range of concentrates (Table 1) was subjected to different leaching tests. First, the slag samples were subjected to the USEPA's toxicity characteristic leaching procedure (TCLP) tests and the leachate was analyzed for the various elements. Multiple extraction procedure as prescribed in the USEPA standard 1320 (extraction procedure toxicity test as specified in USEPA method 1310) was also carried out to ascertain the stability of slag and the mobility of heavy metals in the slag

under extreme conditions i.e., the highest concentration of each constituent that is likely to leach in a natural environment. In order to study the stability of slag over a prolonged period in a SO₂ bearing atmosphere, sulfuric acid leaching studies were also carried out as a function of pH and temperature on the as received as well as mechanically activated slag samples. The process of mechanical activation involves high-energy milling of the slag resulting in enhanced non-equilibrium stored energy. The stored energy in the material manifests in several forms such as enhanced surface area, increased point, line, surface and volume defects and sometimes in structural rearrangement. The stored energy is dissipated in the subsequent leaching process resulting in accelerated kinetics and a decrease in its activation energy. It has been observed earlier that the mechanical activation process can simulate the natural weathering process occurring on geological time scale with respect to oxidation and enhancement of surface area (Sasikumar et al., 2006). Leaching of activated slag samples is expected to yield results on the long-term stability as well as any change in the leachability of the heavy metals when weathering occurs. The advantages and limitations of the different leaching protocols adopted for the evaluation of the toxicity of solid wastes are summarized in Table 2.

Table 2
Advantages and limitations of the various testing protocols for toxicity characterization

Test method	Advantages	Limitations
Toxicity characteristic leaching procedure (TCLP)	Standardized method and enables comparison	May not be applicable for all leachants.
	Adopted by US Environmental Protection Agency and several others for classification of hazardous waste-TCLP limits for several elements prescribed Less time consuming	Toxicity limits for all heavy metals not specified May not be valid under extreme natural conditions Leaching at ambient temperature–temperature effects ignored
Multiple extraction procedure	Standardized method	Involves a minimum of 10 stages of leaching
	Adopted by US Environmental Protection Agency for determination of maximum leachability under extreme natural conditions (i.e., acid rain)	Time consuming Toxicity limits for all heavy metals not specified Leaching at ambient temperature–temperature effects ignored
Conventional leaching	Simple and fast method Allows variation of pH, temperature and pressure	Non-standard method–difficult to compare Toxicity limits for various elements undefined
Mechanical activation + conventional leaching	Can possibly simulate natural weathering occurring at geological time scale	Not validated
		Non-standard method

2. Materials and methods

2.1. Sampling and analysis

2.1.1. Sampling

Samples of the raw material (all the concentrates used during the period of study) and RHF slag were drawn on three successive days of a week over a 14-week period. It was ensured that the slag samples were drawn when there was no change in the raw material concentration (i.e., there was no change in the concentrates and the ratio of the different concentrates in the feed since a mixture of concentrates are used at any time to maintain a fixed Cu/S ratio) during the 3-day period. Slag samples drawn over the three successive days classified as a batch were thoroughly mixed several times and representative samples for the leaching experiments were drawn by coning and quartering.

2.1.2. Analysis

The solid samples were digested in acid and neutralized using standard USEPA procedures. The chemical analysis of the digested samples and all leachate samples (generated from TCLP test, multiple extraction procedure tests, sulfuric acid leaching and leaching on mechanically activated samples) were carried out in an inductive coupled plasma-atomic absorption spectrophotometer (ICP-AAS) and flame atomic absorption spectrophotometer (FAAS). Flame atomic absorption spectrophotometry with prior calibration in the relevant composition range for each element (As, Bi, Cd, Cr, Cu, Zn, Pb, Ni and Fe) using E-Merck standards and standard procedures for the analysis of the leachate was adopted in all the leaching tests. A hydride generator kit was used along with FAAS for the analysis of arsenic. With the hydride generator kit, the sensitivity of arsenic detection improved to $2 \mu\text{g l}^{-1}$. The detection limits of other elements viz., Bi, Cd, Cr, Cu, Zn, Pb, Ni and Fe were 0.20, 0.005, 0.05, 0.003, 0.003, 0.01, 0.04 and 0.01 mg l^{-1} , respectively. An average of three replicate readings of analysis of the selected element was taken for interpretation of results. The chemical analysis of the leachate was carried out within 3 days of the leaching test. The analytical results measured by ICP-AAS and FAAS were in good agreement with each other for all the elements analyzed.

2.2. Characterization

The slag samples were characterized by XRD. The physical properties of the slag such as Moh's hardness, specific gravity as well as porosity were also measured.

The powder XRD patterns were recorded on a SIEMENS X-ray diffractometer (Model: D500) using Co K α radiation with Fe-filter at a scanning speed of $0.1^\circ/\text{min}$. The particle size distribution of the mechanically activated slag samples were measured using a laser particle size analyzer (CILAS-1180, France).

2.3. Slag leaching methodologies

2.3.1. Toxicity characteristic leaching procedure (TCLP)

TCLP tests on all the RHF slag samples were carried out using a TCLP apparatus supplied by Millipore Corporation (Model No. Y1320 RAHW). The test procedure as given by USEPA (method 1311) was adopted. The as received slag was in the particle size range of 0.1–3 mm. The as received slag was sieved in a 1 mm standard sieve and the <1 mm size fraction was used for the TCLP tests. The extraction fluid used was 5.7 ml glacial $\text{CH}_3\text{CH}_2\text{OOH}$ + 64.3 ml of 1 N NaOH diluted with reagent water to a volume of 1 liter. The pH of the extraction fluid measured with a calibrated pH meter was 4.93 ± 0.05 . The pH was measured for each TCLP experiment. The agitation apparatus, rotation speeds, extraction vessels and filtration devices were as recommended in USEPA 1311. A liquid/solid ratio of 19:1, a headspace of 20% and 16 h extraction time was used for the TCLP tests.

2.3.2. Multiple extraction procedure

Multiple extraction procedure (MEP) tests on the representative slag mixture corresponding to each batch were also carried out using the TCLP apparatus supplied by Millipore Corporation. The test procedure as given by USEPA (method 1320) was adopted. The as received slag of size <1 mm was used for the MEP tests. The flow chart giving the details of the multiple extraction procedure is given in Fig. 1.

Initially, slag samples were extracted according to the extraction procedure (EP) toxicity test (method 1310). Although the extraction procedure toxicity test (USEPA method 1310) is similar to the TCLP test (USEPA method 1311) minor differences in the leaching procedure such as in liquid to solid ratio exists. However, only USEPA method 1310 is recommended to be adopted prior to carrying out the multiple extraction procedure. The extraction fluid used was de-ionized water of pH 5. The pH of the extraction fluid was adjusted using 0.5 N acetic acid. The agitation apparatus, rotation speeds, extraction vessels and filtration devices were as recommended in USEPA 1310B. A liquid/solid ratio of 16:1 and 24 h extraction time was used for the EP toxicity tests.

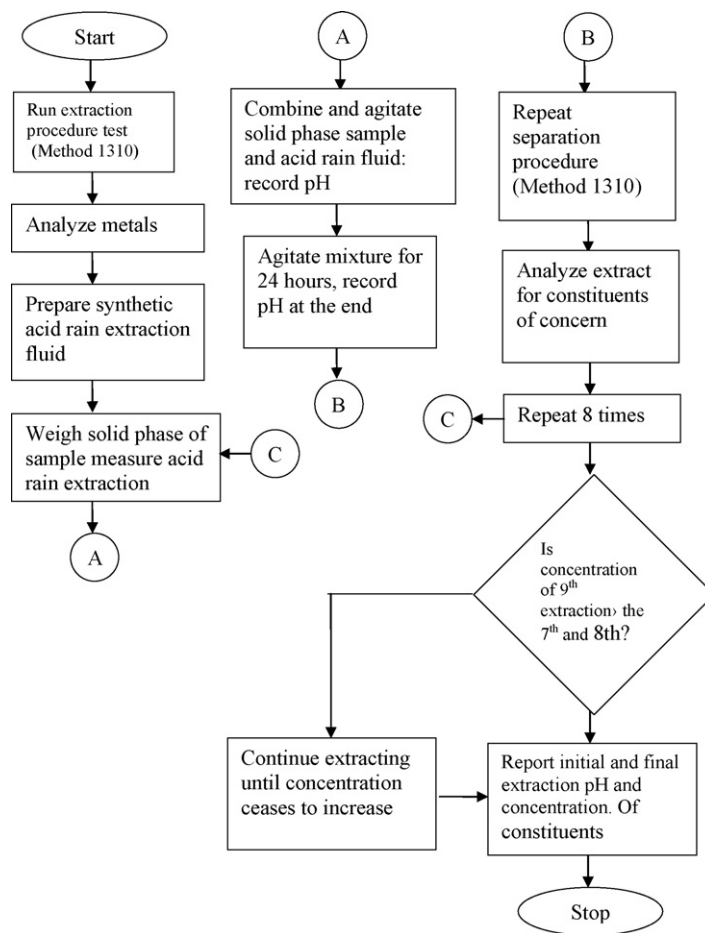


Fig. 1. Flowsheet of the multiple extraction procedure as per USEPA method 1320.

The solid portions of the samples that remained after the extraction as mentioned above (method 1310) were re-extracted nine times using a synthetic acid rain extraction fluid comprising of a mixture of 60 wt.% H_2SO_4 and 40 wt.% HNO_3 added to distilled de-ionized water and adjusted to pH of 3 (± 0.2). A liquid/solid ratio of 20:1 and 24 h extraction time was used for this multiple extraction procedure test carried out at ambient temperature. The pH was recorded at the end of the 24 h extraction period. After each extraction, the solid–liquid separation was carried out as given in USEPA method 1310. The extract was then analyzed for the various constituents (As, Bi, Cd, Cr, Cu, Zn, Pb, Ni and Fe). The chemical analysis was carried out within 3 days of the extraction test.

2.3.3. Sulfuric acid leaching of untreated slag as a function of pH

Conventional sulfuric acid leaching was carried out on the as received slag samples (of particle size <1 mm)

as a function of pH and temperature. pH was varied in the range of 5–7 and two temperatures (35 and 45 °C) were selected for the leaching experiments based on conditions attained in natural environments. Four 250 ml Pyrex glass reactors equipped with a thermometer, mechanical stirrer and a reflux condenser were used for leaching the slag samples. The reactors were heated simultaneously in a single water bath to maintain an isothermal condition. A resistance heated hot plate with temperature control and power regulation (Powerstat) was used to heat the reactors to the required temperature. A thermometer was fitted to one of the openings. The temperature during the leaching experiments could be controlled within ± 1 °C. To maintain uniform conditions during leaching, the ambient room temperature was maintained at 22 ± 2 °C. The leaching experiments were carried out with a solid/liquid ratio of 1:10. The reactors were filled with 100 ml of 0.1 M H_2SO_4 acid solution, adjusted to the required pH by titrating with NaOH, and after the stabilization of the

pH, 10 g of solid slag samples (taken from a homogenized lot) were added to each of the reactor. Stirring was carried out using a teflon-coated magnetic stirrer to keep the slag particles suspended in the leachant. The leaching experiments were carried out isothermally at each temperature for 4 h and about 7 ml of the solution from each reactor were withdrawn at time intervals of 1 h for the chemical analysis. The leach solutions were filtered and made up to 25 ml in a standard flask. Samples were drawn from the 25 ml aliquot and further diluted to an appropriate extent for the analysis of the heavy metals.

2.3.4. Mechanical activation of slag and leaching of activated samples

A Fritsch Pulverisette-5 planetary mill having agate bowl and balls (Fritsch GMBH, Germany) was employed for the mechanical activation of the slag samples. For the milling, balls of 20 mm diameter were used. The samples (about 40 g in each batch) were subjected to dry milling in ambient atmosphere. The ore to ball ratio in the bowl was maintained at 1:4 by weight for all the experiments. Milling was carried out at 200 rpm for all the batch experiments. No other additives were used during milling. The samples were activated in the planetary mill for 180 min. At the completion of milling, the contents of the bowl were thoroughly cleaned and dried before the next milling experiment.

The leaching conditions (pH, temperature and time) and the leaching procedure adopted for the mechanically milled slag samples was the same as that for the as received (unmilled) slag samples and given in the previous section.

3. Results and discussion

3.1. Physical and chemical characterization

As mentioned earlier, about 25 different copper concentrates were used during the period of study. The range of compositions of the concentrates used and the smelter slag generated during the period of study is summarized in Table 1. The slag was hard (~6 on Mohs scale), dense and black, glassy and shiny in appearance. Specific gravity and apparent porosity were measured to be 3.3 and 0.15%, respectively. Fourteen batches of slag samples (each batch corresponds to sample drawn on three consecutive days in a week wherein there was no change in raw material composition) with varying composition were tested for their leaching characteristics. For the sake of brevity, results from three batches representing different heavy metal compositions are only reported in this paper. The bulk chemical analysis of the copper slag used for the experiments and the corresponding average copper concentrate composition for the three batches of samples is given in Table 3. The representative XRD of the slag sample is shown in Fig. 2. The XRD of the slag shows that it is mostly amorphous in nature. Presence of low-intensity fayalite and magnetite peaks were also observed.

3.2. Leaching

3.2.1. Toxicity characteristic leaching procedure (TCLP)

The results of the TCLP tests on the copper smelted slag for the three selected batches are tabulated in

Table 3

Bulk chemical analysis of copper slag and the corresponding average copper concentrate composition for three batches of samples reported in the present study

Sl. no.	Concentrate composition (wt.%)			Slag composition (wt.%)		
	Batch 1	Batch 2	Batch 3	Batch 1	Batch 2	Batch 3
As	0.024	0.034	0.019	0.0037	0.0042	0.0031
Bi	0.007	0.0061	0.0045	0.0016	0.0024	0.0022
Cd	0.0014	0.0047	0.0012	0.00094	0.0020	0.0012
Cr	0.0045	0.0027	BDL	0.0059	0.0028	BDL
Cu	31.79	48.49	28.04	0.4	0.52	0.6300
Fe	26.07	27.85	26.79	52.2	48.9	43.46
Pb	0.0277	0.1389	0.0526	0.0323	0.1056	0.0699
Ni	0.0176	0.0089	0.0021	0.0053	0.0017	0.0013
Si	5.4746	7.256	8.318	37.78	32.72	33.62
S	30.28	30.97	28.789	0.53	0.82	0.7
Zn	0.1253	0.5180	0.2623	0.1687	0.138	0.1251

BDL = below detectable limit.

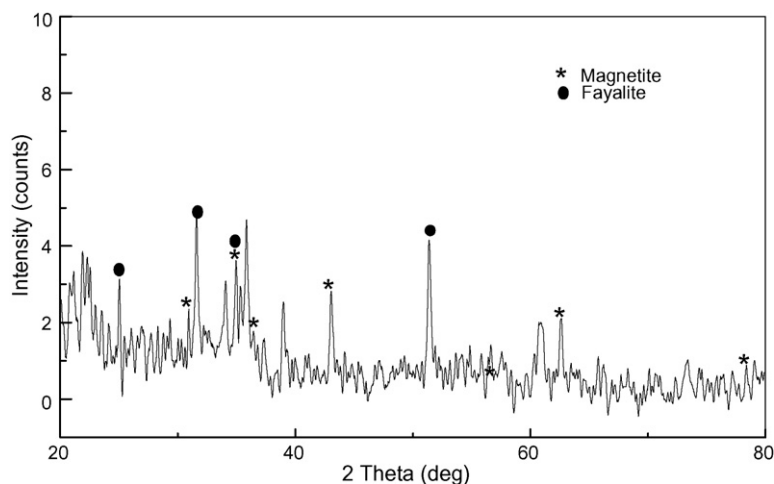


Fig. 2. X-ray diffractogram of the copper slag sample.

Table 4 in comparison to the limits of TCLP concentration given in USEPA 40CFR Part 261 for classification as hazardous waste. It was observed that the TCLP test concentrations for the relevant elements (As, Cd, Cr, Pb and Ag) in all the slags are well below the TCLP limit. The TCLP test results confirm the earlier findings on the poor leachability of different elements from copper slag derived from the various smelting processes (Johnson et al., 1982; Koren et al., 1995; Lagos and Luraschi, 1997; Lim and Chu, 2006; Queneau et al., 1991; Zain et al., 2004).

3.2.2. Multiple extraction procedure tests

The results of the multiple extraction procedure tests on the three batches of slag samples collected during the study period are given in Tables 5–7 for the various elements (As, Bi, Cr, Cu, Zn, Pb, Ni and Fe). The results indicate that the concentrations of none of the constituent increases from seventh extraction to the ninth

extraction. The sum of the leachate concentrations over the nine extraction cycles yields the highest concentration of each constituent that is likely to leach in a natural environment. It is seen that the highest concentration of Cr, Cu, Zn, Pb, Ni, As and Bi that is likely to leach in a natural environment does not exceed 2, 5.5, 3.4, 1.2, 0.2 mg l⁻¹, 18 µg l⁻¹ and 2 mg l⁻¹, respectively which is within the TCLP limit for the relevant elements. The final pH values of each extraction are also tabulated in Tables 5–7.

3.2.3. Sulfuric acid leaching

The chemical analysis of the leachate of all the slag samples indicated that only Cu, Cr, Fe and Zn were present in detectable quantities in the leachate. The other elements, namely As, Cd, Pb, Bi, Sb and Ni were below the detectable limits of FAAS. The variation in the dissolution of Cu, Cr, Fe and Zn from the three-selected batch of slag samples is shown in Figs. 3–6 as a function

Table 4
Results of the TCLP tests on the slag samples (USEPA method 1311)

Sl. no.	Element	TCLP values (mg l ⁻¹)			Permissible limit (mg l ⁻¹), ref.: USEPA CFR40 Part 261
		1st batch	2nd batch	3rd batch	
1	Copper	2.0	2.20	2.98	–
2	Nickel	0.03	0.08	0.11	–
3	Chromium	0.12	0.15	BDL	5.0
4	Cadmium	0.01	0.01	0.02	1.0
5	Bismuth	BDL	0.18	0.02	–
6	Lead	BDL	0.10	0.14	5.0
7	Arsenic	0.03	0.04	0.07	5.0
8	Zinc	0.03	0.08	0.12	–

BDL = below detectable limit.

Table 5
Multiple extraction test results for the copper slag (1st batch) (USEPA method 1320)

Trial no.	Concentration (mg l ⁻¹), except As (μg l ⁻¹)								pH at the end of each extraction cycle
	Cr	Cu	Zn	Pb	Ni	Fe	As	Bi	
EP test	0.118	0.612	0.418	0.158	0.014	21.15	<2	<0.2	5.19
1	0.161	0.589	0.395	0.132	0.012	15.28	<2	<0.2	3.15
2	0.219	0.439	0.386	0.123	0.008	13.25	<2	<0.2	3.12
3	0.255	0.395	0.375	0.108	0.006	11.16	<2	<0.2	3.15
4	0.465	0.216	0.295	0.098	0.003	9.963	<2	<0.2	2.85
5	0.407	0.198	0.232	0.085	0.0	7.256	<2	<0.2	2.58
6	0.132	0.154	0.251	0.059	0.0	5.21	<2	<0.2	2.96
7	0.115	0.098	0.103	0.032	0.0	3.96	<2	<0.2	2.69
8	0.098	0.075	0.098	0.011	0.0	2.21	<2	<0.2	3.12
9	0.078	0.021	0.051	0.005	0.0	1.15	<2	<0.2	3.02
Total	2.048	2.797	2.604	0.811	0.043	90.59			

Initial pH value for MEP test: 3.0.

Table 6
Multiple extraction test results for the copper slag (2nd batch) (USEPA method 1320)

Trial no.	Concentration (mg l ⁻¹), except As (μg l ⁻¹)								pH at the end of each extraction cycle
	Cr	Cu	Zn	Pb	Ni	Fe	As	Bi	
EP test	0.122	0.595	0.405	0.132	0.038	24.819	<2	<0.2	4.89
1	0.115	0.515	0.325	0.063	0.029	23.392	<2	<0.2	2.87
2	0.105	0.428	0.218	0.058	0.03	24.021	<2	<0.2	2.74
3	0.101	0.405	0.196	0.04	0.021	22.167	<2	<0.2	2.84
4	0.103	0.285	0.158	0.028	0.018	21.325	<2	<0.2	3.05
5	0.085	0.187	0.125	0.03	0.015	20.325	<2	<0.2	3.02
6	0.068	0.153	0.113	0.025	0.012	18.553	<2	<0.2	2.79
7	0.059	0.137	0.052	0.012	0.005	18.623	<2	<0.2	3.02
8	0.038	0.105	0.047	0.004	0.0	14.228	<2	<0.2	2.56
9	0.014	0.088	0.021	0.0	0.0	5.21	<2	<0.2	2.98
Total	0.81	2.898	3.424	0.392	0.168	192.7			

Initial pH value for MEP test: 3.0.

Table 7
Multiple extraction test results for the copper slag (3rd batch) (USEPA method 1320)

Trial no.	Concentration (mg l ⁻¹), except As (μg l ⁻¹)							pH at the end of each extraction cycle
	Cu	Zn	Pb	Ni	Fe	As	Bi	
EP test	0.651	0.289	0.148	0.053	23.326	<2	<0.2	4.63
1	0.598	0.215	0.136	0.049	22.952	<2	<0.2	2.87
2	0.503	0.125	0.125	0.039	23.186	<2	<0.2	2.79
3	0.23	0.112	0.108	0.031	21.759	<2	<0.2	2.89
4	0.229	0.116	0.069	0.028	23.82	<2	<0.2	2.77
5	0.289	0.098	0.052	0.015	23.044	<2	<0.2	2.96
6	0.187	0.072	0.028	0.012	21.663	<2	<0.2	2.78
7	0.292	0.021	0.016	0.0	19.559	<2	<0.2	3.09
8	0.264	0.0	0.005	0.0	13.339	<2	<0.2	2.59
9	0.098	0.0	0.0	0.0	5.21	<2	<0.2	2.85
Total	3.341	1.048	0.687	0.227	197.9			

Initial pH value for MEP test: 3.0.

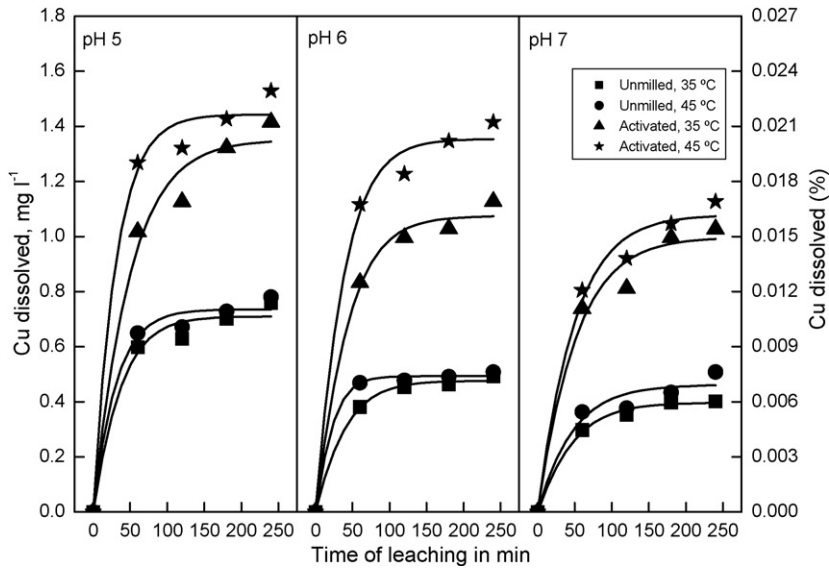


Fig. 3. Sulfuric acid leaching results for Cu in unmilled and activated state as a function of pH and temperature.

of time of leaching, temperature and pH, respectively. The leachate concentration as well as the percent of the element leached is depicted in the figures. As expected, the extent of dissolution of Cu, Fe and Zn increases as a function of time and temperature and decreases with increase in pH. For, Cr, although the extent of dissolution increased with temperature, it showed no significant variation with pH in the range 5–7. Chromium exists as Cr^{6+} in this pH range (Rodriguez-pinero et al., 1998). However, it is observed that the concentration of these

elements in the leachate as well as the percent extraction is extremely low. The maximum extraction of all elements was below 0.05% of the initial concentration.

3.2.4. Leaching of activated slag as a function of pH

The representative particle sizes i.e., D_{10} , D_{50} and D_{90} of the mechanically activated slag were about 0.3, 2 and 15 μm , respectively (i.e., a mean particle size of 2 μm). The process of mechanical activation under ambient conditions can result in oxidation, phase transforma-

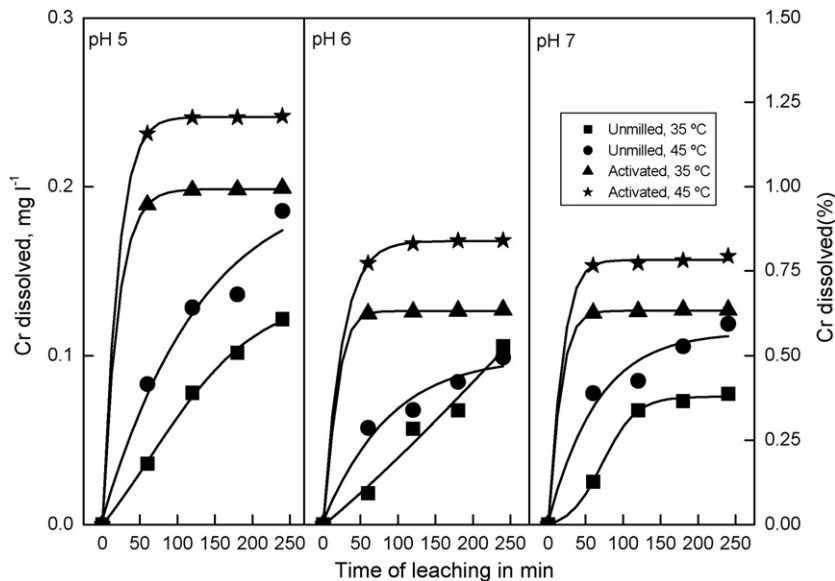


Fig. 4. Sulfuric acid leaching results for Cr in unmilled and activated state as a function of pH and temperature.

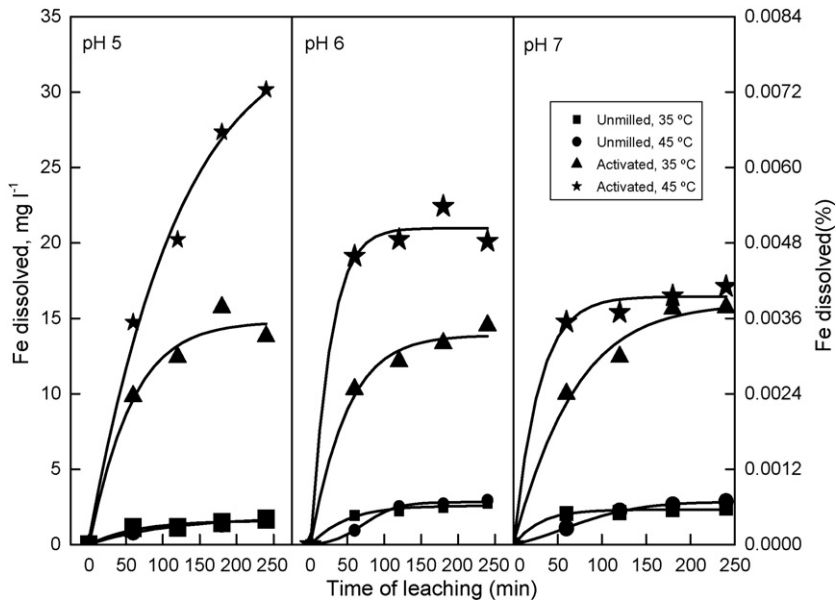


Fig. 5. Sulfuric acid leaching results for Fe in unmilled and activated state as a function of pH and temperature.

tions, increased surface area, structural defects, strain and changes in the surface characteristics resulting in enhanced dissolution during leaching (Balaz et al., 2000) (Tkacova and Balaz, 1996). With respect to oxidation and enhancement of surface area, it may be expected that the mechanical activation process at ambient conditions can simulate the natural weathering/alteration process occurring on a geological time scale (Sasikumar et al.,

2006). For the activated slag samples also, the chemical analysis of the leachate indicated that only Cu, Cr, Fe and Zn were leached to any detectable extent. The results on the activated slag samples are also depicted in Figs. 3–6 for Cu, Cr, Fe and Zn, respectively as a function of leaching time, temperature and pH. The dissolution behavior is similar to that observed for the unmilled samples. It is observed that although the dissolution of all the ele-

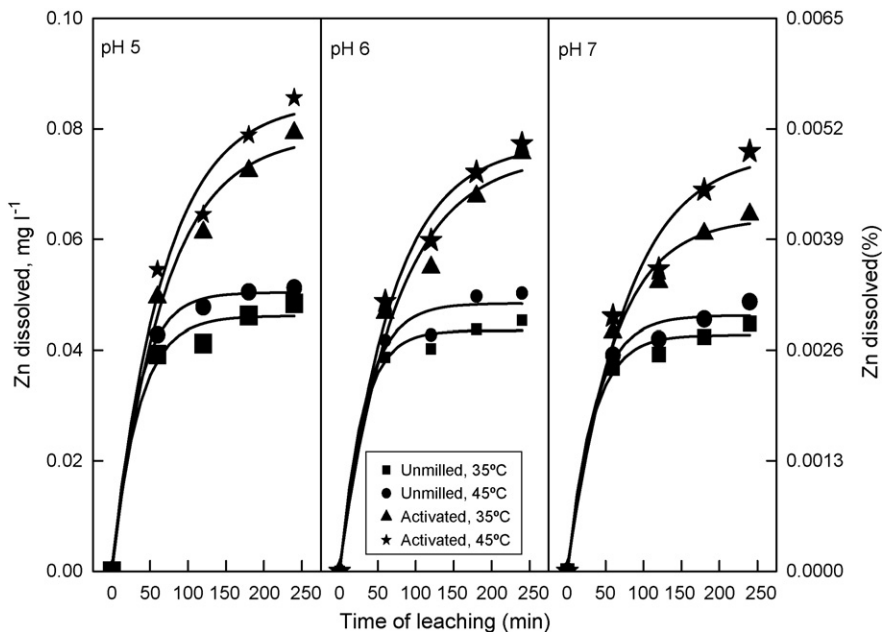


Fig. 6. Sulfuric acid leaching results for Zn in unmilled and activated state as a function of pH and temperature.

ments is higher for the activated samples than for the unmilled samples, they are still very low and likely to be non-toxic.

4. Conclusion

The TCLP, multiple extraction procedure test and sulfuric acid leaching results indicate that the heavy metals present in the slag are very stable and have poor leachability. The TCLP test values are far below the prescribed limits in USEPA 40CFR Part 261. The multiple extraction leaching tests indicate that the heavy metals present in the slag are highly stable and are not likely to dissolve significantly even through repetitive leaching under acid rain in a natural environment. The highest concentration of the elements extracted by the multiple extraction procedure is below the prescribed limits in USEPA 40CFR Part 261 for the elements covered under this standard. The poor leachability of the activated sample also indicates long-term stability of this slag and that weathering is not likely to activate the slag. Since all the leaching tests, i.e., TCLP, multiple extraction tests and conventional acid leaching of as received and activated slag samples indicate poor leachability of the heavy metals and assures long-term stability, it is suggested that the slag is safe to be considered for use in a wide variety of applications such as for Portland cement, building materials such as tiles and bituminous pavement constructions. The slag samples are non-toxic and pose no environmental hazard.

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