Application of ICP-MS technique for analysis of heavy metals in LD slag fines

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Inductively coupled plasma-mass spectrometry (ICP-MS) is a powerful tool for analysing trace metals in environmental samples, industrial wastes and samples of biogenic nature. In the present study, this technique has been used to analyse the content of heavy metals in trace levels which specifically include elements like lead, cadmium, selenium and arsenic in LD slag fines. LD slag is the waste generated during the Linz–Donawitz steel making process or the basic oxygen furnace process. LD slag fines in the size range 0–6 mm are obtained after the recovery of metallic iron by means of physical separation in waste recycling plants, and are mostly recycled in sinter-making process. The non-metallic portion of LD slag fines is generally used as an aggregate in road construction, in acid mine drainage treatment and as an acidic soil conditioner. All these applications require a thorough analysis of trace and heavy metals as they can leach and penetrate into the soil and potentially contaminate it. The present study addresses this issue by analysing heavy metals in traces levels using ICP-MS. The analysis reveals that most of the heavy and hazardous elements are present in very low concentrations in the slag itself when compared with the EPA maximum allowed concentration in the leachate samples. However, the concentration of mercury in LD slag is more than the limit set by EPA in the leachate, and leachability of mercury needs to be studied further. The study also reveals that there are traces of platinum and palladium in the slag, indicating the requirement of future studies to understand their economic recovery.

Keywords: Heavy metals, LD slag, mass spectrometry, fires, steel making.

STEELMAKING slag generated during the basic oxygen furnace (BOF) process is known as LD slag or Linz–Donawitz slag. It is generated at an enormous rate and is highly basic in nature due to the presence of calcium silicate. As shown in Table 1, the unprocessed slag has a typical chemical composition.

From this data it can be seen that of the total iron content, 50% is metallic in nature, which is recovered by a waste recycling plant (WRP) with the help of different steps like screening and magnetic separation. The separation and recovery of this metallic portion in the WRP is represented in Figure 1, wherein the non-metallic portion which is –6 mm in size is separately piled[1]. The typical composition of this non-metallic slag or reject fine is generally about 47–52% CaO, 2–13% free lime, 12–19% Fe, 1.5–2% P, 1.5–2% Al_2O_3 and about 11–18% SiO_2. LD slag fines in the size range 0–6 mm are obtained after removal of metallic iron content through physical separation and are mostly recycled in sinter-making process.

Apart from recycling in the iron-making process, the slag has other uses such as replacement for aggregate in the road construction sector owing to its excellent mechanical properties[2–5]. According to the European Association of Slag Producers and Processors – EUROSLAG – the share of LD slag usage in the road construction industry is about 42% whereas it is 37% in case of the cement industry[6]. Slag is also used in agriculture for amendment of acidic soils and in acid mine drainage treatment[7].

The recycling process keeps adding metals like phosphorus, titanium, etc. into the iron metal, thus burdening the steelmaking process with extra cost. Also, even if the recycling processes are in place, substantial amount of LD slag fine is being dumped into landfills or amassed for a long period of time[8,9]. The LD slag fines stockpiled for a long time increase the pH of underground water due to its high alkaline nature[10]; the presence of calcium–alumina–silicate complexes is the main reason for this rise in pH[9]. Many hazardous elements will leach out if present in the slag, thus contaminating the underground system. Many researchers have reported about the hazardous nature of steel slags[11], thus raising questions on the landfilling of steel slag as well as on its recycling[12]. This scenario leads to the possibility of leaching out of soluble components of the slag matrix in the soil when exposed to different environmental conditions such as rainfall and moisture. In particular, the leaching of heavy metals is of interest owing to their significant impact on the environment.

Pinto et al.[13] studied the effects of using LD slag as a limiting agent for pastures in Spain. The objective of their study was to understand the effect of LD slag on soil pH and exchangeable Ca and Mg, and its overall effect on the dairy population feeding on this fodder. It was observed that there were no detrimental effects on using LD slag as a limiting agent. Pinto and Gomes[8] carried out studies on leaching of heavy metals from slag. In this context, the objective of the present study was to determine the heavy metal composition of LD slag generated at Tata steel plant, Jamshedpur, Jharkhand, by using the inductively coupled plasma-mass spectrometry (ICP-MS) technique. This technique was chosen as we expected a

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Table 1. Typical chemistry of unprocessed LD lag

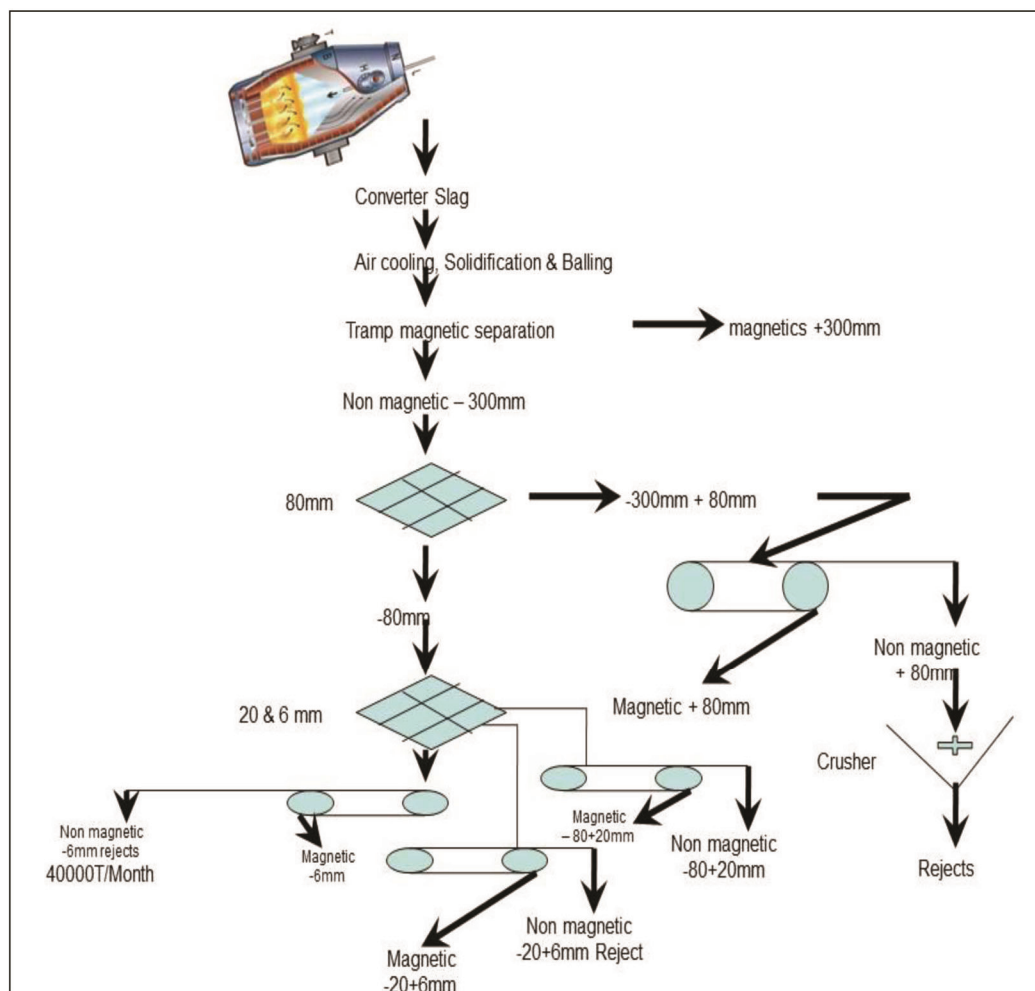| Parameters	Fe(T)	Fe(Met)	FeO	Fe_2O_3	CaO	SiO_2	P_2O_5	MgO	MnO	Al_2O_3	TiO_2	Na_2O	K_2O	C	S
Values (%)	31.57	14.36	16.81	5.97	42.87	10.6	2.16	3.36	0.36	0.96	0.89	0.03	0.005	0.88	0.15

Figure 1. Unprocessed slag to processed LD reject fines in a waste recycling plant.
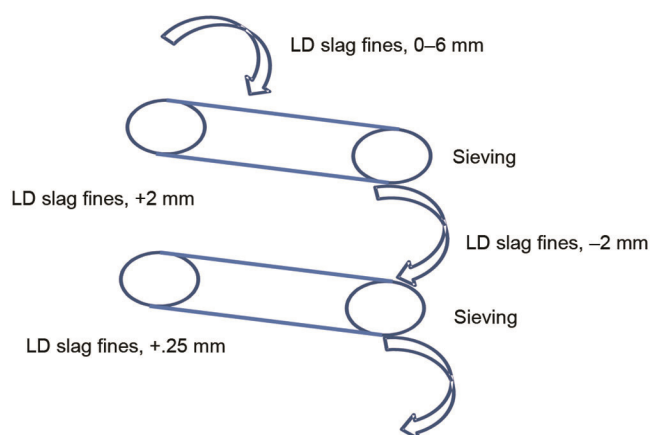

Figure 2. Process flow diagram of physical separation of 0–6 mm LD slag fines.

low range of analytical concentrations for different heavy metals and trace elements. Other elements were also quantified using ICP-optical emission spectrometer (OES), but these included only major elements (Table 1). The study also compared the obtained values in original LD slag itself with the maximum allowed concentration levels specified by the US Environmental Protection Agency (EPA) for leachate samples of various heavy and trace metals. It was found that the LD slag fines produced in the WRP during the metallic iron recovery were free from heavy and toxic elements.

LD slag fines left after the recovery of metallic iron were −6 mm in size. To study the trace and heavy elements in these fines, they were further subjected to physical separation by means of sieving to obtain three different sizes, viz. +10, +60 and −60 mesh respectively.

As shown in Figure 2, the process involves two steps of sieving, where +2.0, +0.25 and –0.25 mm LD slag fines are separated.

The LD slag fines were ground to fine powder in a clean pulveriser. Then 1 g of sample was taken in a teflon beaker and digested with 20 ml of aqua regia on a hot plate and cooled, filtered and made up to 100 ml with ultrapure water of resistivity 18.2 MΩ cm. All the glassware and polythene flasks used in the sample preparation and measurement were cleaned with nitric acid (2% v/v), rinsed with ultrapure water and dried. Since the samples were being tested for heavy and trace metals, they were digested in controlled atmosphere. Ultrapure acids (procured from E-Merck, India) were used for digestion of samples and blank test.

Tables 2 and 3 provide the analytical details of ICP-MS and ICP-OES respectively. The quantitative amounts of each analyte were determined using external calibra-

tion curves prepared from NIST traceable multi-element standard solutions and certified reference materials (CRMs) run under optimized instrument parameters (Tables 2 and 3).

In order to assess the concentration of heavy metals and trace elements properly, adopting a suitable sample dissolution method is important. The dissolution by an aqua regia extraction can lead to acceptable results, or a total dissolution by hydrofluoric acid is always necessary to establish total concentration and has been discussed by several researchers[14,15]. An assessment of different dissolution techniques has been done by Tsolakidou et al.[16], such as dissolution in open polytetrafluoroethylene (PTFE) vessels where HF was used for digestion with the second acid mainly HNO_3, H_2SO_4, or more commonly $HClO_4$. Another procedure was by dissolution (alkali fusion) involving the use of sodium carbonate, sodium hydroxide where determination of sodium is not possible, and finally using lithium metaborate as flux which is useful for the determination of all elements, including silicon in the major rock-forming silicates as well as several miscellaneous minerals associated with them. The main drawback of the dissolution system is that since the flux–sample ratio is kept high – 5 : 2 and 7 : 2 – the level of total dissolved solids in the resultant solution is high. This tends to clog the nebulizer. In the present study, we adopted an open digestion method as described below.

The prepared samples were tested for Pt, Pd, Se and Te; Table 4 presents the results.

It is evident from the table that trace elements like platinum and palladium are present in the non-metallic portion of LD slag fines of the mentioned sizes. Palladium is distributed evenly in all the sizes whereas platinum content is similar in –0.25 and +2.0 mm size LD slag fines, while +0.25 mm size fraction contains less amount of platinum. However, there is no evidence of selenium and tellurium in the slag samples.

The head sample was tested for different heavy and hazardous elements using both ICP-MS and ICP-OES; techniques and the results are presented in Table 5 and results of repeatability for ICP-OES and ICP-MS are provided in Tables 6 and 7 respectively.

Concentration of some toxic elements like arsenic, lead, cadmium and selenium in the LD slag fines was found to be less than that of EPA standards[17] for maximum allowed concentration in leachate samples (Table 8).

However, it was observed that the concentration of chromium in LD slag was very less as compared to that reported by Pinto and Gomes[8] and therefore its comparison to the values of leachate of the EPA allowed concentration will be definitely less and needs to be studied further. Also, chromium was present in the trivalent state and not the toxic hexavalent form, thus dismissing the related concerns. However, the concentration of mercury in LD slag was more than the limit set by EPA in the

Table 2. Optimized ICP-MS instrument operating parameters

	Value
Instrument parameters	
Model	Perkin-Elmer, DRC-e
RF power	1350 W
Plasma gas flow	15 l/min
Auxiliary gas flow	1.2 l/min
Nebulizer gas flow	0.88 l/min
Acquisition parameters	
Scanning mode	Peak hopping
AMU	50 ms
Integration mode/time	Cps/1000 ms
Detector dead time	70 ns
Acquisition time	20 s
Number of replicates	3
Curve type	Linear

Table 3. Optimized ICP-OES instrument operating parameters

Instrument parameters	Value
Model	Arcos Spectro, Germany
Plasma power	1400 W
Pump speed	30 rpm
Coolant flow	14 l/min
Auxiliary flow	1.0 l/min
Acquisition time	45 s
Number of replicates	3
Curve type	Linear

Table 4. Results of ICP-MS analysis for trace elements in LD slag

Sample description	Pt (ppm)	Pd (ppm)	Se (ppm)	Te (ppm)
LD slag, –0.25 mm	0.56	0.36	Tr	Tr
LD slag, +0.25 mm	0.02	0.36	Tr	Tr
LD slag, +2.0 mm	0.55	0.25	Tr	Tr

Table 5. Results of ICP-MS analysis for heavy and hazardous elements in LD slag

Element	B (ppm)	Cd (ppm)	Cu (ppm)	Ni (ppm)	Pb (ppm)	Cr (ppm)	As (ppm)	Hg (ppm)	Mo (ppm)	Be (ppm)	Co (ppm)
LD slag fines (0–6 mm)	71	1.00	132	43	2.1	355	0.6	2.5	53	33	94

Table 6. Repeatability in ICP-OES for heavy and hazardous elements in LD slag

Parameters	Repeat 1 (%)	Repeat 2 (%)	Average (%)
Sn	0.46	0.459	0.460
V	0.205	0.205	0.205
Sr	0.128	0.128	0.128
Cr	0.035	0.035	0.035

Table 7. Repeatability in ICP-MS for heavy and hazardous elements in LD slag

Parameters	Repeat 1 (ppm)	Repeat 2 (ppm)	Average (ppm)
Mo	53	52	53
Be	33	33	33
Co	94	94	94
Cd	1.00	0.99	1.0
Cu	132	131	132
Ni	43	42	43

Table 8. Comparison of EPA leachate standard values with concentration of certain toxic elements

Element	Concentration (mg/kg)	EPA maximum allowed concentration in leachate (mg/l)
Arsenic	0.6	5.0
Lead	2.1	5.0
Cadmium	1.0	1.0
Selenium	0.0	1.0
Chromium	355	5.0
Mercury	2.5	0.2

Table 9. Validation of results using multi-element standard solution

Merck, CRM IV	Certified value (ppm)	Working value (ppm)	Observed value (ppm)	Recovery (%)
Ba	1000	100	105	105
Sr	1004	100	103	103
Ni	1006	101	98	97
Co	1005	101	92	91
B	1000	100	104	104
Cd	1004	100	99	99
Cu	1005	101	103	102
Cr	1004	100	100	99
Cr	1004	1000	1010	101

Table 10. Validation with Bureau of analysed samples (certified reference material (CRMs))

BAS, CRM	Parameters	Certified values (ppm)	Observed values (ppm)	Recovery (%)
681-1	Ni	160	156	98
681-1	Pb*	72	67	93
681-1	Co*	80	81	101
681-1	As*	139	135	97
683-1	V	257	250	97
683-1	Cr	180	178	99

*Reference values.

leachate. Therefore, the leaching effect of mercury needs to be studied in detail.

The results obtained for heavy metals and other trace elements were validated using the solutions of certified reference materials prepared under similar conditions along with the samples (Tables 9 and 10).

The present study has revealed some interesting facts which need to be considered during the reuse of LD slag. ICP-MS analysis has shown that most of the heavy and hazardous elements are present in very low concentration in the slag itself, compared to EPA maximum allowed concentration in the leachate samples. However, the effect of mercury has to be studied further using toxicity characteristic leachate procedure to ascertain whether or not it will leach out beyond the maximum permissible concentration.

LD slag fine can be used as a liming agent after grinding to a suitable particle size for acidic soils. As the study reveals, it contains heavy metal concentration within the limit set by regulatory authorities and government agencies; other trace elements can be useful as plant micronutrients. Detailed study on the optimum quantity to be applied for agricultural purposes needs to be undertaken with the help of agricultural universities across India.

This study also reveals that there are traces of platinum and palladium in the slag, indicating that the economic recovery of these elements needs to be considered further as a future activity.

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Preparation of nanosized bioapatite by cryogenic grinding from sintered scales of silver carp *Hypophthalmichthys molitrix* (Cuvier and Valenciennes)

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The present study is based on the processing of bioapatite (BAp) of sintered fish scales, i.e. heat treated fish scales at 900°C, by the cryogenic grinding technique. It shows that BAp formed by cryogenic grinding of sintered fish scales became purer and nanosized. Earlier studies had reported that nanosized bioapatite increases the resorbability and bioactivity for tissue replacement and regeneration like bones and dental tissues of human beings. Energy dispersive X-ray spectroscopy of sintered fish scale BAp confirmed the presence of tetracalcium phosphate with Ca/P ratio of 1.97. Field emission scanning electron microscopy and dynamic light scattering (DLS) showed microsized particles. The sintered fish scales when cryoground showed the formation of nanosized particles as revealed by transmission electron microscopy and DLS. The Fourier transform infrared spectroscopy results of sintered and cryoground BAp had similar functional groups, but cryoground BAp showed greater purity.

Keywords: Bioapatite, biogenic source, cryogenic grinding, fish scales, sintering.

RECENT years have witnessed exponential research growth in the area of nanoscience and nanotechnology and their bio-applications. Nanoparticles have the ability to partially dissolve during fibre attachment; so they can be used as a novel implant component. It is believed that nanosized bioapatite (BAp), isolated or prepared from biogenic sources, is most appropriate for tissue replacement and regeneration. It exhibits enhanced resorbability and much higher bioactivity than micron-sized or synthetic hydroxyapatite (HAp)[1].

Fish biowaste, such as scales which are dumped as waste due to their unexplored commercial value, contains several types of calcium salts[2]. These fish scales can be used to isolate hydroxyapatite or bioapatite to be exploited in the research and development of useful biomaterials in the field of bone implantation, fabrication and fixation.

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