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LEACHING OF HEAVY METALS FROM THE STEEL SLAG UNDER VARIABLE CONDITIONS

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ABSTRACT

Leaching of metals from steel slag in a systematic manner would lead to the recovery of the metals. Leaching studies are performed on the steel slag under the acidic, neutral and alkaline conditions. Effect of different conditions on the leaching of heavy metals such as Bi, Pd, Cr, Cu, Ni, Zn, As and Fe are analyzed from the steel slag set for the period for 7 days, 30 days and 50 days. The L/S ratio of 10 is used for all the studies. The leaching pattern has been discussed.The study on the steel slag shows that metals such as Cr, Fe, Ni, Zn and Pd leach out more under acidic conditions whereas metals such as Bi, Cu and As leach out more under alkaline conditions. Apart from As most of the metals were found to be leaching within the permissible limits. It is also found that the returns on the metal recovery is very less and is found to be very uneconomical.

Keywords: *Leaching, steel slag, acidic, alkaline.*

I. INTRODUCTION

Steel slag is a byproduct of the steel industry and has now found several applications [1]. Leaching of heavy metals from the steel slag would have the negative impact on the environment. Leaching of metals from steel slag in a systematic manner would lead to the recovery of the metals. Metals like La, Li, Co, V, Te, Ga, Se are called as the driving forces for the green technology [2]. It is suggested that metals like Fe, Ta, Au, Pb, Zn, Co, Ni Cr, Cu, Al, Nb and Ag can be recovered [3]. Most of the metals found in slag are categorized by European studies to fall under of EU 14 critical raw material list [2]. However, its low concentration in the solid waste makes the process of recovery or leaching uneconomical. Till date, Toxicity Characteristic Leaching Procedure, Batch leaching test and Column leaching test are used in most of the previously reported work. Their exist no accepted protocol for doing the leaching test on the steel slag [4]. Studies suggest, liquid to solid ratio of 10 to 30 with leaching time for 30 to 47 days for leaching [5], [6]. Rapid cooling of steel slag helps reducing the leaching of Ca, Fe, Al, Cr, Mo whereas leaching of V and Si is not found reduced [7].

The leaching of As, Cr, Se, Sb and V of alkaline waste such as steel slag is dependent on the redox state at which they occur in the solid. Generally they occur in oxyanionic metalloid. Studies has shown the compound of metals and the oxyanionic species like As^{III} and Cr^{III} and Cr^{IV}[8] . Studies furthers shows the order of leaching chemical components from converter steel slag as $CaO > SiO_2 > Al_2O_3$ and concludes that the leaching is due to intra-particle diffusion and can be best described by shrinking unreacted core model [9]. It is also found aged slag leaches less which is due to formation of new phases. The slag should be at least aged for 6 months of time as it drastically reduces the leachability of the slag [10]. Researchers also investigated the safe chemical composition of the slag wherein the leaching of Cr, Ba and V would be minimum by the analysis of seventy samples under standard leaching test. The results indicated that water to slag ratio is important for the leaching of those elements [11]. Gehlenite and kirschsteinite present in the slag helps resisting leaching [12]. Researchers also look for the sustainable wastewater technologies which are economical [13]. Increasing trend is observed for adoption technology [14]–[16]. Slag contain iron oxides which may even help in the adsorption of toxicants like Cu and Cr(iii) [17].

Elevated level of Cr(VI) is highly toxic to all forms of living organisms [18]. The researchers also proposed the new heap leaching method and predicted that Cr could leach up to 4-5 years for infiltration rate of 73,000 l/(y m^2) [19].However, due commercial use of Cr, its selective leaching has been tried by several researchers. Selective Cr leaching up to 46% was achieved by hydrometallurgical method at 1 M NaOH, 240 °C, 6 h, Mechanical Activation 30 min [20]. In another studies, NaOCl is applied as oxidation agent and NaOH as alkaline agent for the leaching of Cr from steel slag. The addition of $NaNO_3$ as an oxidant to the NaOH salt increased Cr leaching to 89% after roasting at 400 °C for 2 h [21]. Selective extraction of chromium from steel slag by NaOH added pellet roasting followed by water leaching could extract the Chromium up to 96%. The residues of slag can be safely disposed [22]. Selective leaching can even be tried in parallel with the treatment of phenol, ammonia and thiocyanate removal from the effluent, so that treatment of effluent is also done along with leaching [23]–[25]. Studies show that temperature controlled extraction with NaOH in the presence of NaOCl, followed by water leaching, $BaCrO_4$ is obtained as precipitate. The Cr recovery up to 99.9 % is obtained without alteration of mineralogy of slag. Decreasing leaching trend is observed for 10 years aged slag as compared with fresh slag for Ca, Cu, Mn, Pb, Ba, Fe whereas leaching was seen increased in V, Si, and Al [26]. Leaching of metals from blast furnace slag showed that L/S=10 with 20 % aqua regia showed increase in leaching of Ca and Mg whereas decrease in leaching was observed for Fe, Al, and Ti [27]. No literature on leaching of Fe, Ni, Cu, As and Bi is found. Leaching of Zn and Pb is mainly due to longer residence time and moderately higher temperature helping to be favorable [28]. Recovery of metal by bioprocess like fungi and bacteria are proving to be cost effective [29]. Innovative approach is however required for cost effective leaching as the steel slag produced from the industry is voluminous.

Also, as the steel slag is now gaining the tag of commercial product and has several uses which are based on the physical and chemical properties of the steel slag. The leaching or recovery of metals from the steel slag would require the complete cost effective analysis taking into consideration the effect on the properties of the steel slag.

In the present leaching studies, steel slag is exposed to acidic, neutral and alkaline conditions. The acidic condition is maintained by 0.1 N Acetic acid Distilled water. The alkaline conditions were maintained by 0.1 N NaOH distilled water conditions. Under neutral conditions only distilled water is used. The experiments were set for the period for 7 days, 30 days and 50 days and Bi, Pd, Cr, Cu, Ni, Zn, As and Fe heavy metals were checked for the leachate analysis [30], [31].

II. MATERIALS AND METHODS

Steelmaking slag is collected form the slag dumping yard in Jamshedpur. Slag is screened for different particle sizes and dried at 150ºC for 24 hours and then kept in the desiccator for the further use. Steel slag of 150 micron size is used for the leaching studies. Slag composition is measured by WDXRF Spectrometer - Bruker S4 PIONEER. SEM images are obtained from Zeiss Model: V5:05 (SIGMA).EDS is used for elemental analysis. XRD is done using Rigaku Smartlab Guidance CuKa irradiation (1.54 Aº, 40 kV, 30 mA). ICP-MS used for leachate analysis is Agilent 7900.

Leaching studies are conducted on the slag of 150 micron which is air dried and then exposed to acidic, neutral and alkaline conditions. The acidic conditions is maintained under 0.1 N Acetic acid [32] and the alkaline conditions is maintained by 0.1 N NaOH. Under neutral conditions only distilled water is used. A container having flat bottom surface of 150 cm^2 was taken so that distilled water is in continues contact with the slag, as no agitation was provided during the leaching. 25 gm of slag with 250 mL of distilled water (L/S=10) is taken. The duration of leaching was kept for a period of 7 days, 30 days and 50 days. The liquid was separated from the slag for the leachate analysis is analyzed for heavy metals like Bi, Pd, Cr, Cu, Ni, Zn, As and Fe by ICP-MS [30], [31].

III. RESULTS AND ANALYSIS

Characterization of materials

The steel slag collected is a whitish dusty and the size of the grain varies from 0.75 microns to 4 mm in diameter. The steelmaking slag is characterized by sieve analysis.

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Table 1 shows the slag composition done by WDXRF Spectrometer - Bruker S4 PIONEER. Figure 2 shows the SEM images obtained from Zeiss Model: V5:05 (SIGMA) shows the porous nature of the steel slag which indicates that abundance of adsorption sites on its surface. The elements like O 46.05 %, Ca 34.29%, Si 5.2%, P 4.44 %, Fe 1.33 %, Al 0.23%, Mg 0.16%, S 0.14% are found in the steel slag. XRD of the slag shows the presence of oxides of Ca, Si, Mg, Fe and Al in the sample.The surface morphology of steel slag particle shows sharp edges, partly dense, and partly porous. According to the IUPAC, the material can be classified as mesoporous material. This is also confirmed by the studies done elsewhere [33].

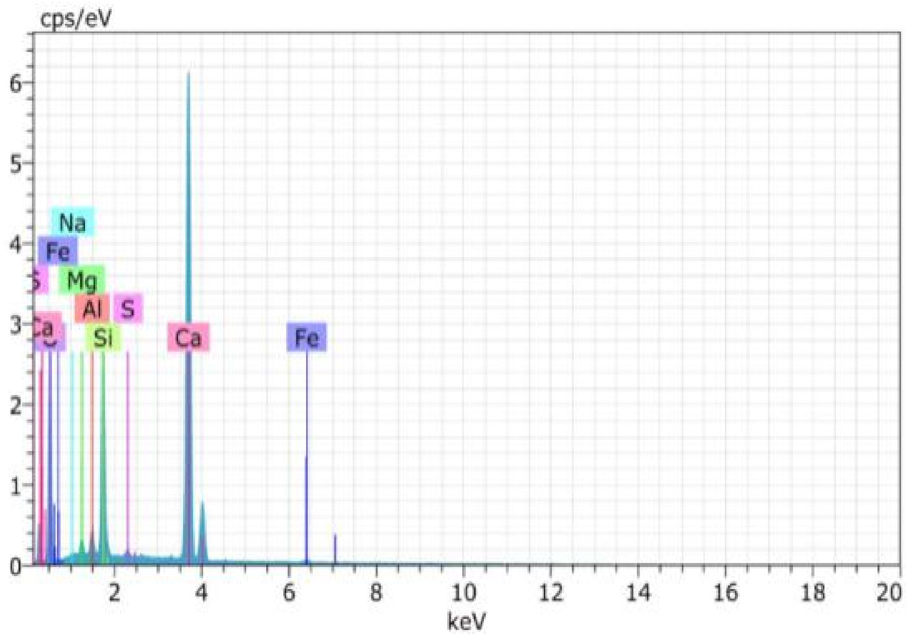

Figure 1: Presence of elements in steel Slag

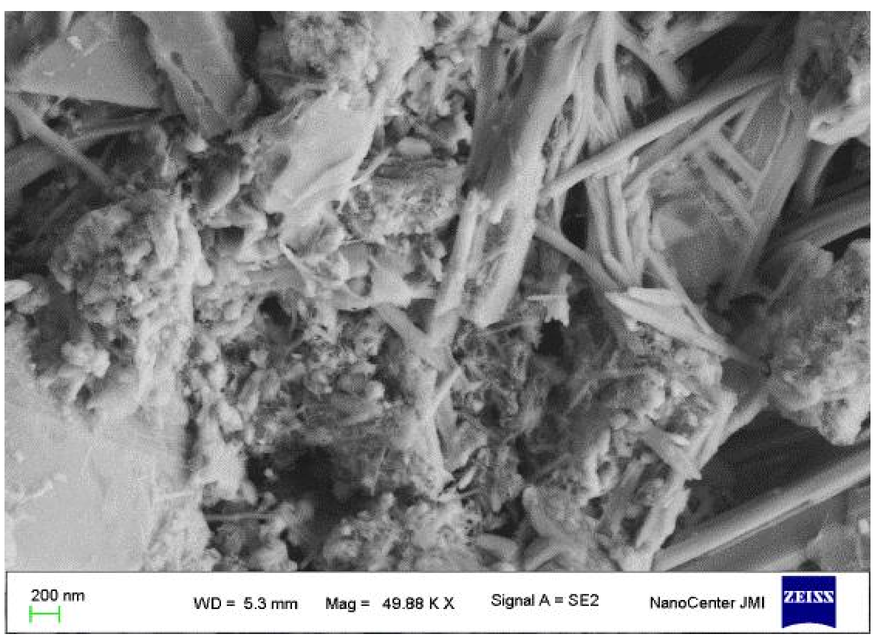

Figure 2: SEM of Steel Slag

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Sample	Steel Slag
CaO	46.21%
Fe_2O_3	14.89%
SiO_2	9.52%
MgO	2.51%
Al_2O_3	1.94%
P_2O_5	1.20%
TiO_2	0.56%
MnO	0.52%
Cr	0.07%
K_2O	0.02%
Na_2O	0.04%
Cl	0.01%
Cu, PPM	265.55
Nb,PPM	42.59
S, PPM	4835.20
Sr, PPM	201.72
V, PPM	370.60
Zr, PPM	13.02

Table 1: XRF of steel slag before and after treatment

Figure 3: Scale formation of the slag after 50 days of leaching

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A thin whitish layer as shown in Figure 3 was found on the slag after 50 days of leaching. The thin whitish layer is less in acidic medium. Table 2 shows the leaching of slag under acidic, alkaline and neutral conditions for 7, 30 and 50 days of contact time for the slag to leach under distilled water. Figure 4 shows Zn, Ni, Cu, Fe, Cr and Pd were the most leaching metals in acidic medium. The leaching of chromium increase as the pH and the time of leaching is increased. The maximum 8.47 ppb of chromium is achieved after 50 days of leaching. In alkaline conditions as shown in Figure 5 the metals like Cr, Cu, As and Bi were found leaching more. Both acidic and alkaline conditions favor the leaching of the iron from the slag, however, Iron is more leached in alkaline conditions. Maximum 67 ppb of iron is leached from the steel slag.

Acidic conditions are found to be favorable for the leaching of nickel from the steel slag. Maximum 13 ppb of the nickel is leached after 50 days. The copper leaches well in all pH conditions; however, maximum up to 5.03 ppb of copper is leached after 50 days. Maximum up to 18.28 and 83.13 ppb of zinc and arsenic leaching is achieved respectively. Palladium leaches more in acidic conditions whereas bismuth leaches more under alkaline conditions. Concentration of metals leaching in all figures is reported in ppb.

	Cr	Fe	Ni	Cu	Zn	As	Pd	Bi
7DAA	2.34	37.16	6.13	1.65	5.75	0.13	1.92	0
30DAA	3.89	46.18	8.33	3.11	16.18	0.14	3.27	0
50DAA	5.93	50.76	13.36	2.43	18.28	0.41	3.58	0
7DNAOH	2.24	4.66	0.94	3.48	0	52	0.14	0.93
30DNAOH	5.32	53.5	1.65	5.03	0	64.33	0.25	3.36
50DNAOH	8.39	67	1.75	4.03	0.95	83.13	1.6	3.63
7DDW	1.09	8.36	1.2	0.16	0	0.17	1.22	0.02
30DDW	7.83	4.76	1.55	2.27	0	0.52	1.26	0.05
50DDW	8.47	7.38	2.77	3.57	0	0.73	1.36	0.08

Table 2: Leaching of steel slag under different conditions

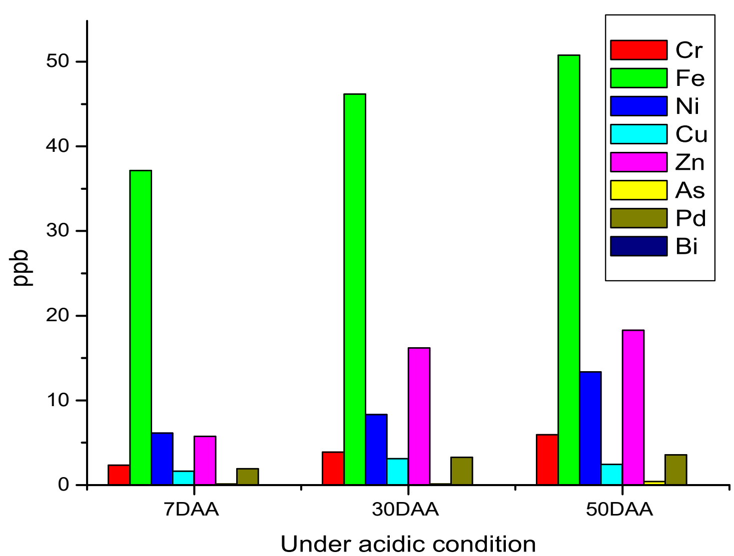

Figure 4: Leaching studies under acidic conditions

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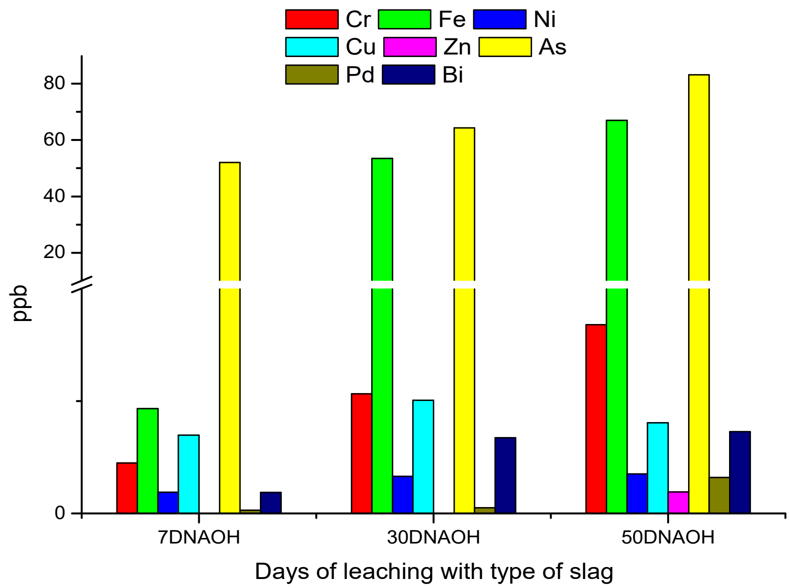

Figure 5: leaching studies under alkaline conditions

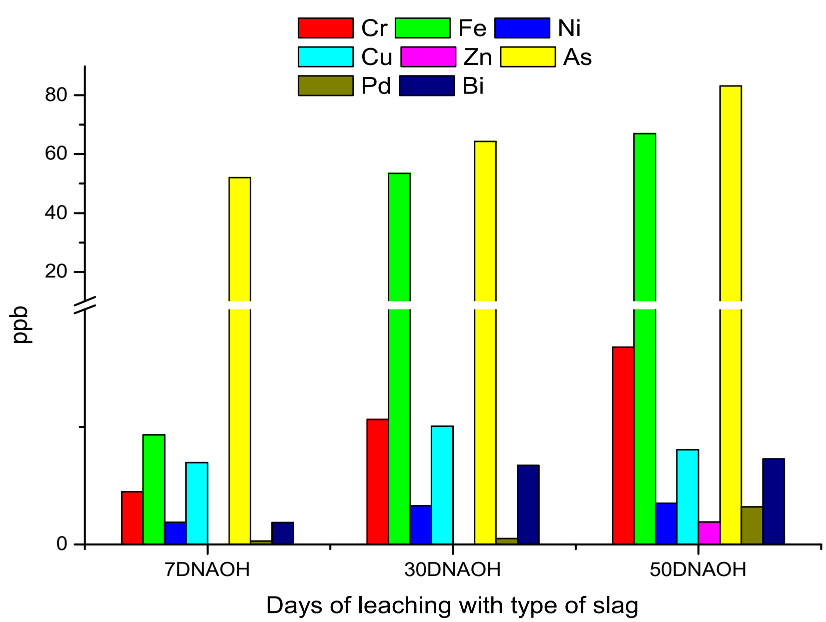

Figure 6: Leaching studies under neutral conditions

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Figure 6 shows that As and Fe leach most in neutral condition. The above study on the filtrate under leaching studies reveals that Cu, Fe and As are prominent metal leaching under alkaline conditions [34]. Leaching was not observed for As under acidic and neutral conditions but are found leaching under alkaline conditions. Bi also did not leach under acidic conditions but was found leaching under alkaline conditions. Ni, Pd and Zn leached more under acidic conditions. The concentration of Cr do not exceed the permissible limits (Cr < 0.05 mg/L) of the Indian standards (second revision IS 10500) for the 50 days leaching test. Leaching of Ni and Fe is also found within the permissible limits (Ni <0.02 mg/L and Fe < 0.3 mg/L) under acidic and alkaline conditions. Leaching of Zn and Cu is also found to be under permissible limits (Zn < 5 mg/L and Cu < 0.05 mg/L). However, leaching of As exceeds beyond permissible limits (As < 0.05 mg/L) [35]. Overall it can be stated that steelmaking slag is non-toxic.

Returns from the recovery

Metal recovery from the solid waste is required to be seen in terms of return on investment. Table 3 shows the value generation from the metal recovery. The prices quoted are taken from the website of 'Sigma' for the pure metal wherever possible. It can be seen that, if one kg of steel slag is processed and pure metals are extracted under the conditions where the maximum of the leaching is observed in the above experiments, the value of all metals recovered is just Rs 1.06 per kg i.e. Rs 1000 per ton. This shows that returns are very less. This return does not include the purification of the metal, transportation of slag, Manpower cost. Also, significantly, steel slag has got its potential use as cementitious material. So any change in the physiochemical properties would have the large impact in terms of final disposal of steel slag. In view of the above, it seems to be uneconomical to recover the metals from the steel slag.

Metals	Price*/mg	Metals recovered mg/kg	Total (Indian Rupees)
Cr	0.74	0.1	0.07
Fe	0.03	0.56	0.02
As	1.05	0.7	0.74
Pd	3.44	0.04	0.14
NI	0.72	0.051	0.04
Bi	0.04	0.036	0.00
Zn	0.01	0.16	0.00
Cu	1.49	0.04	0.06
		Total	1.06

Table 3: Returns from metal recovery

* https://www.sigmaaldrich.com

IV. CONCLUSION

Leaching studies are performed on the steel slag. The study on the steel slag shows that metals such as Cr, Fe, Ni, Zn and Pd leach out more under acidic conditions whereas metals such as Bi, Cu and As leach out more under alkaline conditions. Apart from As most of the metals were found to be leaching within the permissible limits. It is also found that the returns on the metal recovery is very less and is found to be very uneconomical.

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