RECOVERY OF MANGANESE FROM STEEL SLAG AND DUST BY DIFFERENT TECHNOLOGIES

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ABSTRACT

This paper describes a few examples of the recovery of manganese from steel slag and dust by using different technologies based on acid leaching.

Reductive leaching in sulfuric acid (H_2SO_4) for recovery of manganese from electric arc furnace dust (EAFD) was represented. Recovery of manganese and iron was increased with increasing in the sulfuric acid concentration. By using different reductantcs such as oxalic acid and hydrogen peroxide were revealed a higher manganese recovery than the other reductants. The results were showed that leaching of manganese was accomplished at 0.31 mol/L oxalic acid concentration, 2 mol/L H_2SO_4, a liquid/solid ratio of 30/1 at 70 °C and with 90 min leaching time.

1. INTRODUCTION

Slags have been long considered as valuable by-products of steel industry. Some of the recycling alternatives used worldwide include cement incorporation, construction products, road base and sub-base aggregates, as well as additives used for soil improvement [1].

Slags are named based on the furnaces from which they are generated. Figure 1 shows a flow chart for the iron and steelmaking processes and the types of slag generated from each process [2, 3].

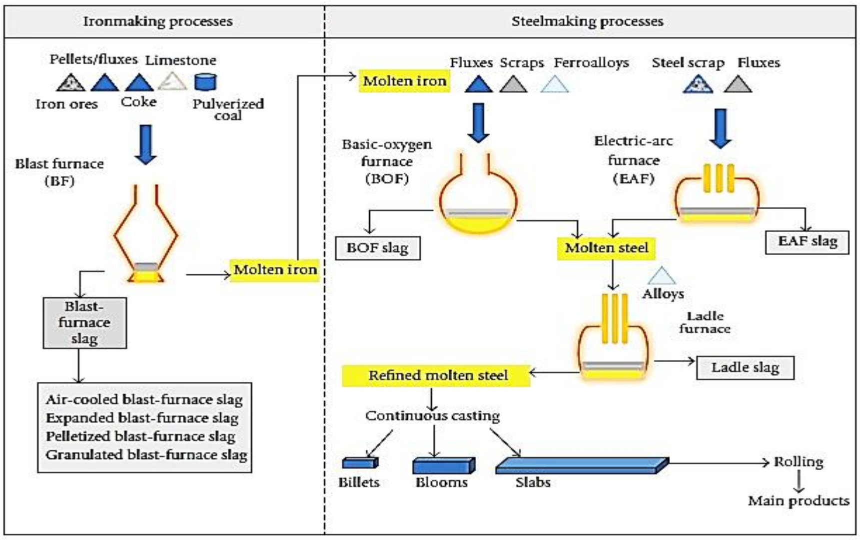

Figure 1. Flowchart of iron and steelmaking processes [2, 3]

Steel slags are slags that arised from BOF, EAF of steel production process, as the slag from secondary metallurgy steelmaking.

Globally annual steel slag production produced is at fifty millions ton and dumping it off is gradually becoming a major environmental issue [4].

The steelmaking industries in the US generate 10–15 million tons of steel slag every year [5].

According to EUROSLAG, the European Association of Slag Producers and Processors, the main use of steel slags are for road construction, cement incorporation and internal use for metallurgical purposes [6].

EAF dust (complex material consisting mostly of metal oxides) is formed under mini-mill steelmaking operations due to the high processing temperature (around 1600 ^{o}C). Certain metals such as Zn, Pb, Cd, Na, Mn and Fe are volatilized and oxidized, then condensed or mechanically carried over and finally collected as appeared as dust form.

It is estimated that the world-wide annual production of EAF dust is as high as 5 million tons, all of which must be treated / recycled or land filled [7].

2. CHEMICAL COMPOSITION OF STEEL SLAG AND DUST

Steelmaking slag (BOF or EAF) mainly consist of [8]:

- dicalciumsilicate (Ca_2SiO_4),
- dicalciumferrite ($Ca_2Fe_2O_5$) and
- wuestite ($(Fe_{1-x-y},Mg_x,M_{ny})O_z$).

The chemistry and mineralogy of slag / dust depend on material balance of feedstock and method of production. The main chemical constituents CaO, FeO and SiO_2 are given in Table 1 [9].

Table 1: Chemical composition of steel slags [9]

Chemical composition, [wt %]						
Slag type	**CaO**	**FeO**	**SiO_2**	**MgO**	**MnO**	**Al_2O_3**
BOF	47.9	26.3	12.2	0.8	0.3	1.2
EAF	24.4	34.4	15.4	2.9	5.6	12.2
Ladle	49.6	0.44	14.7	7.9	0.4	25.6

The chemical composition of EAF dust is given in Table 2. Generally, EAFD also contain many other metals as well, in the form of different oxides, ferrites, and silicates. Further constituents are alkali- and alkaline earth metal compounds as well as minor oxides of further heavy metals and silica [10, 11].

Table 2: Chemical composition of EAF dust [10]

Element	(%)	Element	(%)
Fe_T	36.19	CaO	5.70
FeO	5.62	ZnO	10.83
Fe_2O_3	44.88	SiO_2	6.57
Fe^0	0.4	Al_2O_3	1.5
PbO	1.04	Cl^-	2.93
Cr_2O_3	0.27	K_2O	1.34
MnO	2.12	Na_2O	2.25
MgO	1.84	Others	2.1
SO_3	1.45	Loss on ignition	9.12

3. THE POSSIBLE TECHNOLOGY OF MANGANESE RECOVERY FROM STEEL SLAG AND DUST

Some procedures for slag processing, are followed by:

- leaching process,
- a purification of the electrolyte by selective precipitation of other metals, extraction of the first valuable metal,
- dissolve separately each precipitate and
- extraction of the remaining valuable metals separately.

The steel slags must be properly conditioned (ground, heat treated or even partially reduced etc.) in order to liberate and make amenable the mineralogical phases to the chemical reagents (aqueous lixiviants). Then, if chosen and applied properly, they can dissolve selectively the designated components.

In this case, McIntosh and Baglin chose ammonium carbamate to leach manganous oxide selectively from the pre-treated silicon steel BOF slag according to the flowsheet shown in Figure 2 [12]. They were able to prove experimentally that manganese could be recovered from such type of steel slags with ammonium carbamate leaching up to 80 wt.% of Mn and 50 wt.% of Fe, where treatment of the slag in hydrogen prior to leaching enhanced manganese extraction. All in all, the process so developed was not profitable at that time and is so still today [12].

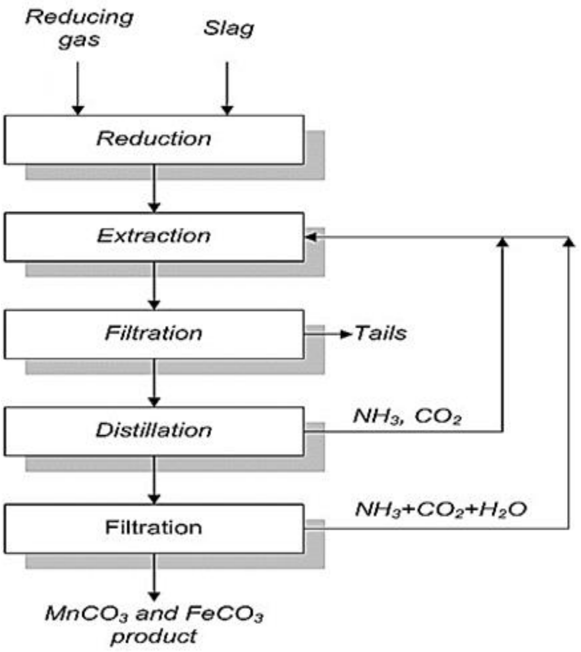

Figure 2: Simplified flowsheet of a proposed hydrometallurgical process to treat steelmaking slag for the recovery of manganese by-product metal [12]

Another method for recovering manganese from BOF steelmaking slags was included leaching with fluorosilicic acid (H_2SiF_6), where manganese and iron were extracted as soluble manganous and ferrous fluorosilicates. Best extraction and selectivity were achieved using a two-stage countercurrent leach. Sodium fluorosilicate (Na_2SiF_6) was precipitated from the pregnant liquor and recovered as a byproduct using sodium chloride. Manganese and iron were precipitated as hydroxide-carbonate salts with the addition of sodium carbonate to the treated liquor. Total recoveries for manganese and iron were 73 to 83 wt.% and 67 to 70 wt.% [13].

A recovery of 98% of manganese was achieved for an ore containing 12.2% manganese, using hydrogen peroxide (H_2O_2) as the reductant [14]:

$$MnO_2 + H_2O_2 + 2H^+ \rightarrow Mn^{2+} + 2H_2O + O_2 \quad \Delta E^0=0.549\ V \quad ...(1)$$

More than 98% of manganese was extracted from low-grade manganese ore using oxalic acid ($C_2H_2O_4$) as the reductant according to the following reaction [15]:

$$MnO_2 + C_2H_2O_4 + 2H^+ \rightarrow Mn^{2+} + 2H_2O + 2CO_2 \quad ...(2)$$

To recover manganese from EAF dust few methods are found in literature. Reductive leaching is an alternative and environmentally friendly hydrometallurgical process for EAFD dissolution.

Thus, in this work was emphasized method of manganese extraction from electric arc furnace dust by leaching in sulfuric acid solution in the presence of different reductants: hydrogen peroxide and oxalic acid.

The chemical composition of the sample was 24.64% Mn, 10.08% Fe, 6.47% Si, 5.87% Ca, 2.83% Al, 0.34% Mg, 0.16% Ti, 0.05% Pb, 0.04% Zn, 0.01% Cu and > 0.01% Ni. The major phases in the sample were manganese dioxide (MnO_2), silica (SiO_2), iron oxide (FeO) and calcium oxide (CaO).

The effect of H_2SO_4 concentration on the simultaneous leaching of manganese and iron in the absence of any reducing agent is shown in Figure 3.

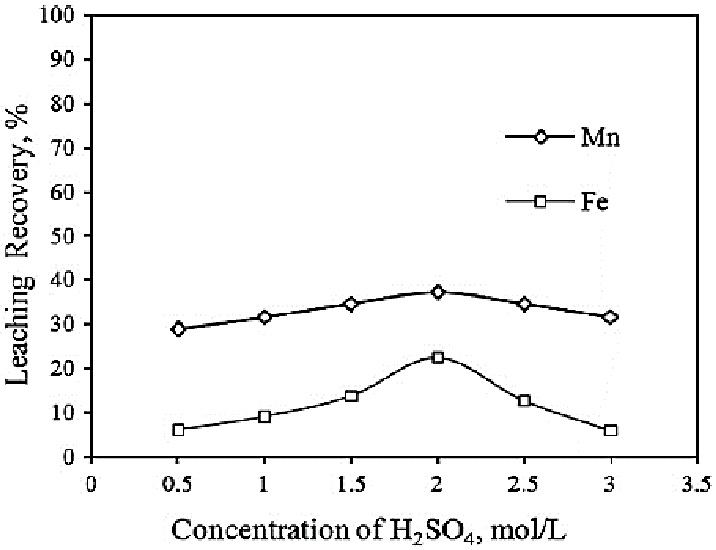

Figure 3: Effect of H_2SO_4 concentration on the leaching of manganese in the absence of reductants: temperature 70 °C, leaching time 90 min, S:L 1:10 [16].

The effect of temperature on the recovery of manganese and iron in the presence of oxalic acid (0.31 mol/L) and H_2O_2 (0.65 mol/L), as well as effect of liquid/solid ratio are illustrated in Figure 4 and Figure 5.

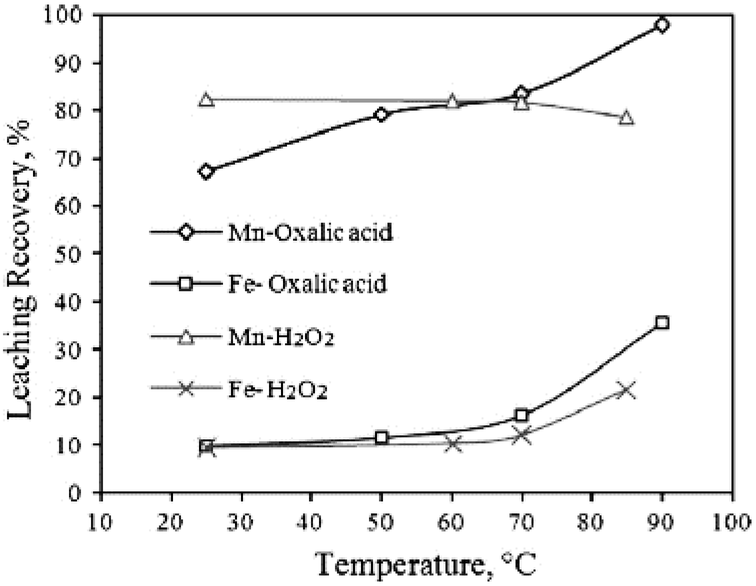

Figure 4: Effect of temperature on the recovery of manganese and iron; oxalic acid concentration 0.31 mol/L, H_2O_2 concentration 0.65 mol/L, H_2SO_4 concentration 2 mol/L, time 90 min, S:L 1:10 [16].

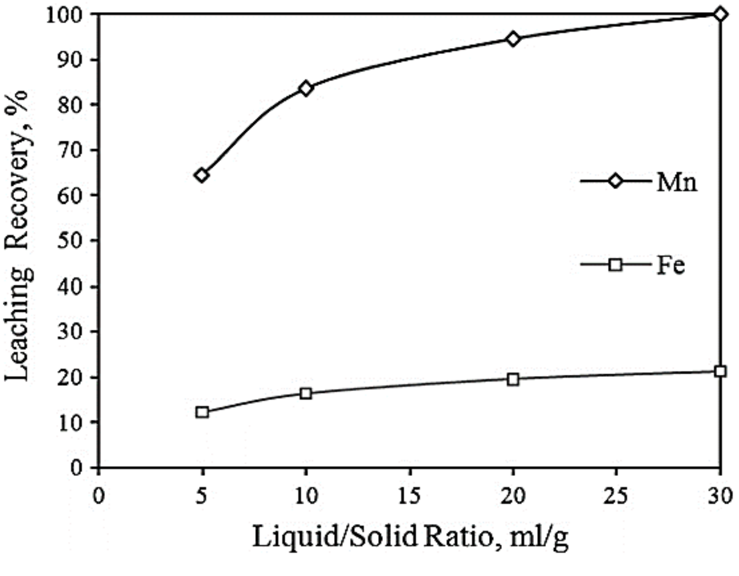

Figure 5: Effect of liquid/solid ratio upon the leaching recovery of manganese; oxalic acid concentration 0.31 mol/L, H_2SO_4 concentration 2 mol/L, time 90 min, temperature 70 °C [16].

4. CONCLUSION

Because of facts that some methods of recovery manganese were not profitable (e.g. ammonium carbamate leaching) and that can be applied for some steelmaking slags but not others, their use is required if strategically necessary.

Another alternative method of manganese extraction from EAF dust, emphasized in this work, was performed by leaching in sulfuric acid solution without or with the addition different reductants. Leaching of manganese was not complete in the absence of reducing reagents. By increasing the sulfuric acid concentration from 0.5 to 2 mol/L increased the recovery of manganese from and for iron, so 2 mol/L was taken as the optimal condition for the manganese leaching. In the presence of oxalic acid leaching recovery of manganese increased and in this system, oxalic acid and hydrogen peroxide act almost similar. Complete leaching of manganese was achieved at 0.31 mol/L oxalic acid concentration, 2 mol/L H_2SO_4, a liquid/solid ratio of 30/1 at 70 °C and with 90 min leaching time.

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