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Extraction of manganese from ferro-manganese slag

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ABSTRACT

In the present investigation an attempt has been made to recover manganese from ferro-manganese slag of ferro-alloy plant. Roasting and leaching are the techniques used to recover manganese. Roasting has been carried out by mixing the slag with CaO and $CaCO_3$ at 1200°C for 2 hours. The leaching of the roasted mass has been carried out in ferric chloride solution alone, as well as in presence of sucrose in ferric chloride solution. The optimum conditions have been established by varying the parameters like concentration of leaching agent, percent solids, particle size of the slag, temperature and time of leaching. It is possible to recover 87% of manganese from the ferro-manganese slag of 200# at a temperature of 80°C, 2 hours of leaching time and 5% solids in 0.154 M ferric chloride solution. It has been found that the presence of sucrose in ferric chloride solution enhances the rate and recovery of manganese from slag.

Keywords : *Ferro-manganese slag, Roasting, Leaching, Ferric-chloride, Sucrose, Manganese.*

INTRODUCTION

Manganese ore is an important raw material[1] for the production of various kinds of steels, ferro-alloys, cast iron etc. In steel industry manganese added in the form of ferro-manganese performs important functions[2] as a de-oxidiser and de-sulphuriser which are not as adequately performed by any other element. It also has higher affinity for sulphur and hence prevents the formation of iron sulphide. About half of the world production[3] of manganese ore is used in metallurgy of steel, alloy and foundry work. Among these, ferro-manganese industry is the single largest manganese ore based industry in India. India has

established itself a major manganese producing and exporting country. Indian ferro-manganese industry produce 2.2 lakh tonnes of ferro-manganese alloy per annum. India's consumption of ferro-manganese is much more than the world's average. The demand for ferro-manganese is directly linked with the production of steel. Yearly 4.75 lakh tonnes of high grade manganese ore is used for the production of ferro-manganese alloy. Incidental[4] to the production of ferro-manganese, the plants produce slag at the rate of about 750 to 850 Kg/tonne of liquid metal analysing about 18 to 19% MnO in flux practice and about 45 to 46% MnO in flux less practice. Every year nearly 0.62 lakh tonnes of manganese is lost in slag. This slag is being dumped at present as waste.

Minerals are non-replenishable commodity[5,6] and their demands are increasing with the availability and decreasing day by day imposing on the planners to look for better waste recovery and resource management and thus to extend the life of deposits/resources for future mankind. Therefore, keeping in view of the demand within the country and also for export it is found necessary to utilise the waste ferro-manganese slag for the recovery of manganese.

No detailed work has been done on the recovery of manganese from ferro-manganese slag. Reduction of ferro-manganese slag to manganese metal in rotary furnace has been reported[7,8]. In USA[9] manganese values have been recovered from ferro-manganese slag by chlorination, volatilization and condensation. In USSR[10] and India[11,12] the ferro-manganese slags have been processed by acid leaching and the manganese metal or its salt is then recovered from the leach liquor by electrolysis.

The aim of the present work is to obtain manganese values from the ferro-manganese slag by roasting with calcium compound and leaching with ferric chloride solution. The main constituents of slag are silicates of manganese, calcium and aluminium. Roasting of slag with CaO and $CaCO_3$ at reasonably high temperature converts insoluble $MnOSiO_2$ into soluble MnO. CaO combines with SiO_2 and displaces MnO from $MnOSiO_2$. -Lime has a melting point of 2570°C but when 50% of $CaCO_3$ is mixed with 50% lime, its melting point reduces to 1240°C.

$$MnOSiO_2 + CaO \rightarrow MnO + CaOSiO_2$$

EXPERIMENTAL

Material

The present study was carried out with ferro-manganese slag obtained from ferro-alloy plant of SMIORE Ltd., Vyasanakere, near Hospet. The slag was coarse in size, it was crushed, ground and screened to get different size fractions. The

chemical composition of the slag is shown in table-1. All the chemicals used in this investigations are of analytical reagent grade.

Table 1 : Chemical composition of slag

Constituents	%
MnO	30.10
SiO_2	29.56
CaO	15.70
Al_2O_3	20.4
FeO	0.68
Insolubles	3.56

Techniques

20 gms of powdered slag was mixed with 2.5 gms of CaO and 2.5 gms of $CaCO_3$ and roasted in a muffle furnace for 2 hours at 1200°C. Leaching of the roasted mass was carried out in a glass reactor fitted with condenser. Heating and agitation were done using a magnetic stirrer cum heater. In each experiment calculated amount of slag was leached with requisite quantity of ferric chloride solution. In all these experiments 0.1 ml of H_2SO_4 for 1 gm of sample was added to the leaching medium. After filtration and washing, the leach liquor was analysed for manganese.

In this investigation the effect of various parameters such as concentration of leaching agent (ferric chloride), percent solids, particle size of the slag, temperature of leaching and time of leaching on the extraction of manganese have been studied. Few leaching experiments having been carried out in presence of sucrose[13] in the leaching medium.

RESULTS AND DISCUSSION

Effect of Concentration of $FeCl_3$ Solution

In this set of experiments the concentration of ferric chloride solution was varied from 0.079 to 0.2080 M. The effect of concentration of ferric chloride on the extraction of manganese is shown in tables - 2&3 for 1 and 2 hours of leaching durations respectively for 10% solids at 30°C..

From tables 2 & 3 it is observed that, the extraction of manganese increased as the concentration of ferric chloride increases upto 0.154M and thereafter decreases. This decrease may be due to the reaction between ferric chloride and gangue material, which forms a semi solid product and causes hindrance to the leaching reaction.

Table 2 : Effect of concentration of $FeCl_3$ solution (Time 1 hr)

Sl. No.	Concentration of $FeCl_3$ (Molar)	% Mn extraction			
		-80#	-100#	-150#	-200#
1.	0.0769	28.07	34.05	40.69	45.79
2.	0.1232	36.79	37.35	44.60	48.02
3.	0.1540	37.59	38.60	47.62	52.07
4.	0.2080	-	-	-	-

Table 3 : Effect of concentration of $FeCl_3$ solution (Time 2 hr)

Sl. No.	Concentration of $FeCl_3$ (Molar)	% Mn extraction			
		-80#	-100#	-150#	-200#
1.	0.1232	38.33	48.81	53.87	66.98
2.	0.1540	42.89	51.97	56.97	74.32

Effect of Percent Solids

To find out the effect of the percent solids on the extraction of manganese the percent solids were varied from 5 to 15% and results have been tabulated in tables-4&5 for 1 and 2 hours of leaching time respectively.

It is seen from tables 4&5 that a maximum recovery of manganese of 76.26% can be obtained when there is only 5% solids with 2 hours of leaching time and 30°C leaching temperature and recovery decreases as percent solids increases.

Effect of Particle Size

The effect of particle size of the slag on the extraction of manganese has been studied by varying the particle size from -80 to -200#. The results are given in tables 2 to 5.

It is clear from tables 2 to 5 that as there is decrease in particle size of the slag there is an increase in the recovery of manganese. This is obvious because decrease in size of particle increases the surface area. As the surface area increases large amount of solid is exposed to the reaction medium and hence the recovery.

Effect of Temperature and Time

Several leaching experiments have been done at different temperatures ranging from 30 to 80°C for -150 and -200# size material to study the effect of temperature on the extraction of manganese. In these experiments even the time

of leaching and percent solids have also been varied from 1 to 3 hours and 5 to 10% solids respectively and the effect of time on leaching of manganese has been studied maintaining $FeCl_3$ concentration at 0.154M for all experiments.. The results are given in table-6.

Tables 4 : Effect of percent solids (Time 1 hr)

Sl. No.	% Solids	% Mn extraction			
		-80#	-100#	-150#	-200#
1.	5	39.30	51.35	53.50	61.31
2.	10	37.59	38.60	47.62	52.07
3.	15	17.48	24.33	28.37	31.69

Tables 5: Effect of percent solids (Time 2 hr)

Sl. No.	% Solids	% Mn extraction			
		-80#	-100#	-150#	-200#
1.	5	54.54	62.59	66.25	76.26
2.	10	42.89	51.90	56.97	74.32
3.	15	23.16	26.86	34.58	44.87

The results given in table-6 indicate that, increase in temperature increases the recovery of manganese. This may be due to the increase in activation energy of the reaction. A maximum of 87.1% manganese can be recovered from -200# size slag at a temperature of 80°C and 2 hours of leaching time. Comparing the recovery of manganese at 5 and 10% solids, there is a little difference between the two, but the reagent consumption is double in case of 5% solids.

It is also observed from table-6 that, as the time of leaching increases the percent extraction of manganese increases upto hours of leaching time, further increase in leaching time resulted in a little increase in percent recovery of manganese, i.e. saturation of reaction takes place. This may be due to -

i) Reaction takes place very fast within a short interval of time by dissolving most of the manganese into a solution.

ii) Rest of the manganese may not be dissolved, because it may still be present in the form of silicates of manganese.

Effect of Sucrose in Leaching Medium

Some leaching experiments have been carried out in presence of sucrose (1 gm/100 ml) in leaching medium at different temperatures and leaching durations for -200# material at 10% solids and using 0.154M $FeCl_3$ solution to find out the effect of sucrose on the recovery of manganese. The results obtained are given in table 7.

Table 6 : Effect of temperature and time

Sl.	% solids	Time in Hrs	Temp °C	% Mn extraction	
				150#	-200#
1	5	1	30	53.50	61.31
2	5	1	60	56.91	64.34
3	5	1	80	61.68	68.50
4	5	2	30	66.25	76.26
5	5	2	60	70.50	80.12
6	5	2	80	73.87	87.10
7	5	3	30	67.56	79.43
8	5	3	60	73.43	82.02
9	5	3	80	78.20	87.40
10	10	1	30	47.62	52.07
11	10	1	60	51.91	54.38
12	10	1	80	59.65	66.08
13	10	2	30	56.97	74.32
14	10	2	60	65.34	77.95
15	10	2	80	72.34	81.91
16	10	3	30	66.08	77.48
17	10	3	60	69.34	79.70
18	10	3	80	77.96	82.10

Table 7 : Effect of sucrose in leaching medium

Sl. No.	Temp°C	% Mn Extraction		
		1 hour	2 hours	3 hours
1	30	68.36	76.28	79.54
2	60	71.73	78.46	82.70
3	80	86.00	88.46	88.52

The results indicate that it is possible to extract 88% manganese contained in the slag at 80°C in just 2 hours of leaching time. This shows that the presence of sucrose in ferric chloride medium has not only increased the recovery but also enhanced the rate of recovery.

CONCLUSION

Ferro-manganese slag is amenable to ferric chloride leaching. Roasting of slag with calcium prior to leaching is essential in order to convert manganese into soluble form. It is possible to recover over 82% manganese in 2 hours of leaching at 80°C using 0.1540 M ferric chloride solution from the slag of -200# size with 5-10% solids. The presence of sucrose in ferric chloride solution has been found to increase the rate and amount of manganese recovery into the solutions. It is ascertained that 86% of manganese can be recovered in just 1 hour in presence of sucrose.

This liquor containing manganese can be used to prepare electrolytic manganese dioxide/manganese metal. The ferro-manganese slag can be thus utilised for these purposes saving valuable manganese ore for metallurgical purposes.

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