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Recovery of Manganese from Ferromanganese Slag

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ABSTRACT

Selective acid leaching of manganese from ferromanganese slag (Garividi, Vizianagram Dt.,) using hydrochloric and sulphuric acid media was attempted. Rate of leaching in both acids was found to be 1st order kinetics. Extraction of Mn (II) by Dibutyl phosphoric acid (HDBP) dissolved in xylene from both the acid media has been carried out. Effect of concentrations of metal and HDBP on the extraction has been studied. Attempts were also made to strip manganese from the organic phase with 1.0M H_2SO_4. The extracted species was also identified.

High Lights

- Acid leaching of manganese from ferromanganese slag has been carried out.
- Solvent extraction of manganese (II) by HDBP has been studied.
- The role of pH, acid, metal ion, HDBP etc., is essential to follow the process.
- Extraction mechanism has been discussed.

Keywords: Leaching, Ferromanganese slag, Extraction, Dibutyl phosphoric acid (HDBP).

INTRODUCTION

Hydrometallurgical treatments are generally adopted to treat low-grade ores at less than 100 degree centigrade [1]. This technique has been successfully applied in recent times for the extraction of Manganese, copper, cobalt, iron, nickel and chromium from chrome slag [2-4].

Manganese is a grey white metal resembling iron, but harder and very brittle. One of the prominent metals among non-ferrous. It improves the qualities of steel such as strength, hardness, stiffness and wears resistance [5]. It is a used in the production of ferro manganese, dry cell technology, chemical industry and manufacture of glass and ceramics [6, 7]. Due to its prominence, extraction of manganese from all possible sources needs considerable attention. Large amounts of manganese pass into slag as manganese oxide along with oxides of calcium, manganese, iron, silicon and aluminium from blast furnace during the production of ferro manganese [8]. Leaching is employed as pre-treatment of process to facilitate the recovery of metal values by selective dissolution in a suitable leachant to get the metal values.

Earlier workers could extract manganese from various reagents [9-11]. The present communication describes our studies on leaching of manganese from Ferro manganese slag followed by extraction using HDBP were dissolved in xylene.

MATERIALS AND METHODS

A stock solution of manganese (II) was prepared by dissolving an accurate quantity (3.08g) of manganese sulphate monohydrate in 1L double distilled water which was contained 1 g L^{-1} of manganese (II) ion. The ferro manganese slag obtained from Ferro Alloys Corporation (Garividi, Vizianagram Dt.,) was ground, clarified and analysed for particle diameter. The slag of suitably required size was taken in a 250 mL and was leached with concentrated sulphuric and hydrochloric acid media to follow the kinetics of leaching of manganese. Slag contains manganese along with other metals such as calcium, magnesium, iron, silicon and aluminium in oxide form. Metal concentrations were analysed using Atomic absorption spectrophotometer type AAS-SVL Spectronics-model 205.

Extraction Procedure: An attempt was also made to study the selective extraction of these metals using acidic l extractants like dibutyl phosphoric acid (HDBP). An aliquot (10ml) of manganese of appropriate concentration and sulphuric or hydrochloric acid were equilibrated with an equal volume of HDBP ($2.5X10^{-2}$ M) was shaken for 15 min. The two phases were allowed to settle and were separated. Manganese (II) from the organic phase was stripped with 10 mL of 1.0M H_2SO_4 and was estimated with AAS. The equilibrium metal concentration in the organic phase was determined by taking the difference in the initial and the equilibrium manganese (II) concentrations in the aqueous phase.

RESULTS AND DISCUSSION

Acid leaching: It is observed that in sulphuric acid leaching the rate of dissolution follows 1st order kinetics under chemical conditions. On the other hand the order of reaction with hydrochloric acid is found to be half ordered indicating the acid concentration. The activation energies of chemical reactions are found to be around 5000 in sulphuric and 4000 in hydrochloric acid solutions respectively. This indicates the rate of leaching is more temperature sensitive in both the acid solutions. It is observed that the chemical control conditions exist above stirring speed of 200 rpm. Diffusion control conditions exist in all cases. Mixed conditions exist in 200-400 rpm. Rate of leaching under chemical control conditions for different metals in the slag as per the following equations:

$$MnO + HX \text{ -----> } MnX_2 + H_2O$$

$$FeO + 2HX \text{ -----> } FeX_2 + H_2O$$

$$CaO + 2HX \text{ -----> } CaX_2 + H_2O$$

$$MgO + 2HX \text{ -----> } MgX_2 + H_2O$$

Where, X = chloride or sulphate ion of the respective acid.

The results obtained on the effect of acid concentration on the extraction of manganese (II) by HDBP are given in table 1. From sulphuric acid media, extraction efficiency was found to increase gradually with increasing pH up to 4.8 and thereafter remained constant in the pH range 4.8-7.0. Maximum value at pH 5.0 followed by decrease in efficiency in case of hydrochloric acid solutions is noticed (Table 1).

Table 1. Variation of acidity with extraction efficiency

S. No.	Acid [M]	Mn (% E) H_2SO_4	Mn (% E) HCl
1	1.0	79.42	68.92
2	2.0	80.86	76.86
3	3.0	82.98	80.25
4	3.5	87.75	82.37
5	4.0	90.25	85.58
6	4.5	93.54	88.54
7	4.8	94.30	89.80
8	5.0	95.62	90.65
9	6.0	96.03	88.82
10	7.0	96.03	85.06

The equilibrium studies on extraction of metal values indicate that 0.025M HDBP dissolved in xylene can extract manganese at pH 4.8. In view of leaching of other metals along with manganese, studies were undertaken under the experimental conditions. It was also observed that extraction of those metals was negligible or lowest under this pH conditions.

Composition of extracted species: In the extraction isotherm method [12] at constant concentration of HDBP the mole ratio [Mn(II)] vs. [Metal complex] in the extracted species is 1.0 indicates the formation of a single extracted species.

Extractant variation: In the distribution ratio method [13] log-log plot of K_d vs. [HDBP] gave straight line with a slope of two (sulphuric acid media) which indicates that the mole ratio [[HDBP]/[Metal complex] in the extracted species is 2.09 (Figure 1).

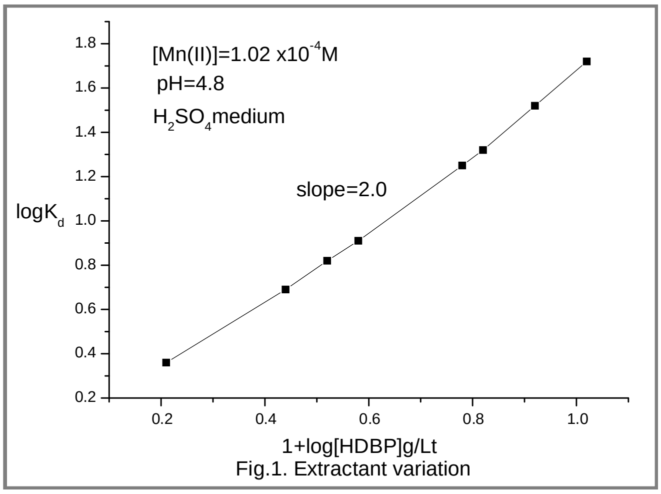

Figure 1. Distribution ratio method.

The results obtained on the equilibrium studies of extraction of manganese using reagent HDBP indicates that the above stoichiometric equation holds well. Hence the following ion-exchange reaction mechanism has been proposed.

$$Mn^{2+} + 2HX == MnX_2 + 2H^+,$$

Where, HX is HDBP

Effect of diverse ions: Manganese (II) was extracted in presence of large number of diverse ions (Table 2). The tolerance limit was set as the amount of foreign ion causing ± 1.8 % error in recovery. When 55µg of was taken in the presence of 200 µg of anions they were tolerated in the ratio of 1:6.

The 290 µg of alkali metals with 50 µg of manganese (II) were tolerated in the ratio of 1:5 while the elements belonging to main group were tolerated in the ratio of 1:4 but transition metals were tolerated in similar ratio of 1:2.

On the other hand it was observed that ions like phosphate and cations like aluminum(III), chromium(III), copper(II), magnesium(II), molybdenum(VI), nickel(II) and vanadium(V) and anions (bromide etc.) were not tolerated in any ratio (Table 2) to show interference in the extraction.

Table 2. Separation of Manganese (II) from a binary mixture (Mn= 50 µg)

[HDBP] = 2.5 x 10^{-2} M (From H_2SO_4 medium)

Foreign ions	Amount tolerated (µg)	Ratio
Na^+, Cs^+, Sr^{2+}	290	1:5
Sb^{3+}, Sn^{4+}, Bi^{3+}, As^{3+} and Ti^+	245	1:4
Pd^{2+}, Co^{2+} and Pb^{2+}	205	1:3
Zn^{2+} and Cd^{2+}	110	1:2
K^+ and Zr^{4+}	55	1:1
Al^{3+}, Mg^{2+}, V^{5+}, Cr^{3+}, MoO_4^{2-} and Ni^{2+}	0	Interfere
Br^-, CH_3COO^-, PO_4^{3-}, NO_3^- $C_2O_4^{2-}$ and $S_2O_3^{2-}$	0	Interfere

APPLICATION

Leaching of manganese from Ferro manganese slag from sulphuric and hydrochloric acid media carried in the present studies followed by extraction using HDBP was successfully applied. It can be observed that manganese can be selectively extracted in presence of other metals and impurities with accuracy.

CONCLUSION

Leaching rate of dissolution follows 1^{st} order kinetics under chemical conditions in both the acid media employed in the study. The results obtained on the extraction of manganese from sulphuric acid media using HDBP as extractant indicates that the above stoichiometric equation holds good.

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