

## SULPHURIC ACID LEACHING OF LOW/MEDIUM GRADE MANGANESE ORES USING A NOVEL NITROGENOUS REDUCTANT- $\text{NH}_3\text{NH}_2\text{HSO}_4$

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(Received 06 August 2012; accepted 07 July 2013)

### Abstract

Low and medium grade land as well sea based manganese ores were used for manganese extraction in  $\text{H}_2\text{SO}_4$  -  $\text{NH}_3\text{NH}_2\text{HSO}_4$  (hydrazine sulphate) medium. For land based Mn ores, only Mn recovery is important but for sea nodules which contain substantial amounts of Co, Ni, and Cu, their recovery is equally important. In the present studies four samples used were: Indian ocean manganese nodules, medium and low grade Mn ores of Gujarat, and low grade Mn ore of Orissa, India. The Mn content of these ores varied from 15 to 39%. The objective of this work is to establish a reductant which can be used for leaching Mn from all types of ores. The optimum conditions established for nodules by varying parameters such as time, temperature, pulp density,  $\text{H}_2\text{SO}_4$  and  $\text{NH}_3\text{NH}_2\text{HSO}_4$  concentrations were: pulp density 10%, time 0.5h, temperature 110°C,  $\text{NH}_3\text{NH}_2\text{HSO}_4$  3.25 g/10g,  $\text{H}_2\text{SO}_4$  2.0% (v/v) for 96.9% Mn, 85.25% Cu, 92.58% Ni and 76.5% Co extractions. More than 92% Mn could be leached from different types of ores by varying amount of reductant and acid concentration at 35°C. Depending on Mn content 1.0 to 1.2 times stoichiometric amount of reductant and 1.5 to 1.8 times sulphuric acid were required for >92% Mn extraction.

**Keywords:** Leaching; Mn ores; Hydrazine sulphate; Sulphuric acid; Mn Nodules

### 1. Introduction

Manganese is the twelfth most abundant element in the earth's crust and in nature occurs most commonly as the minerals pyrolusite ( $\text{MnO}_2$ ) and rhodochrosite ( $\text{MnCO}_3$ ). The land based low and medium grade manganese ores usually contain silica or iron oxide as the major phases with minor amounts of Cu, Ni, Co, Zn etc. (<1%). Hydrometallurgical recovery of manganese from low/medium grade ores has gained importance as it provides an attractive way to utilize such ores to dissolve manganese as soluble sulphate, purify and use it either to produce manganese metal or battery grade manganese dioxide. Reducing agents and acids like coal [1], methanol-sulphuric acid solution [2,3], sulphuric acid and oxalic acid [4], ferrous sulphate [5,6], aqueous sulphur dioxide [7-13] sulphuric acid- hydrogen peroxide [14], non-aqueous dimethyl sulfoxide [15] etc. have been used for dissolution of manganese ores/oxides. A number of papers have also been published on leaching of manganiferous ores using organic reductants mainly carbohydrates like glucose [16-19], sucrose [20] and lactose [21] in combination with inorganic acids. Studies are also reported on use of saw dust [22, 23],

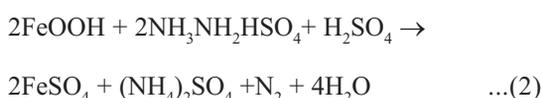
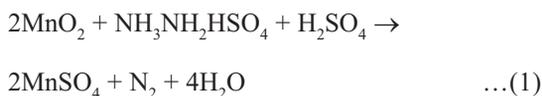
waste paper [24] and dried leaves [25] as the reductants for Mn extraction from manganese ores.

Besides the land based resources of manganese, deep sea nodules are considered as one the future resource of manganese along with Cu(II), Ni(II) and Co(II) [26]. In case of manganese nodules the major matrices for Mn and Fe are  $\delta\text{-MnO}_2$  and  $\alpha\text{-FeOOH}$  respectively but these are usually amorphous in nature. Similar to the land based manganese ores, it is essential to reduce  $\text{MnO}_2$  present in manganese nodules both for its dissolution as well as for the dissolution of other metal values associated with it. The various reductants used for dissolution of  $\text{MnO}_2$  associated with manganese nodules are similar to the ones used for land based ores and include charcoal [27], formic acid [28],  $\text{SO}_2$  [29-34], waste paper etc. [35]. The use of sulphur dioxide has environmental restrictions while the exact nature of oxidised products for organic reductants remains uncertain due to their partial oxidation during leaching. The present studies have been carried out with a view to test a new novel reductant, hydrazine sulphate for all types of manganese ores. This reductant was chosen as it is environmentally friendly due to the fact that its oxidation products are non hazardous.

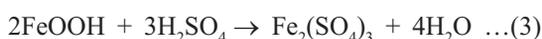
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## 2. Chemistry of Metal Oxide Dissolution

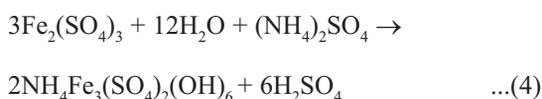
Manganese dioxide,  $MnO_2$  needs to be reduced for its dissolution. Goethite may give ferric sulphate or reduce to give ferrous sulphate in solution. The various reactions for dissolution of manganese and iron oxides in the presence of aqueous hydrazine sulphate in acid medium will be:



Goethite may partly dissolve as ferric sulphate



The Fe(III) present in the solution will precipitate as jarosite [34, 35] in the presence of ammonium sulphate as shown below :



## 3. Experimental

The bulk samples of manganese nodules, medium and low grade manganese ores were crushed, ground and sieved to obtain 100% passing through 150 mesh B.S.S. Weighed amount of each sample was acid digested and made into fixed volume for chemical analysis of Fe, Cu, Ni, Co etc., by atomic absorption spectrophotometer (AAS). Manganese analysis was carried out volumetrically by EDTA method [36].

Leaching experiments were carried out in a 250 mL glass reactor kept over a ceramic hot plate coupled with magnetic stirring system. The reactor was fitted with a reflux condenser and leaching studies at ambient temperature were carried out. Also, a few experiments ( $\geq 80^\circ C$ ) were carried out in a 300 mL closed reactor having provisions for temperature control, agitation, sampling and cooling. The

temperature could be maintained with in  $\pm 1^\circ C$ . Initially required amount of hydrazine sulphate was added to sulphuric acid solution of desired concentration. To that required amount of ore was added. This slurry was agitated in 250 mL glass reactor for leaching and in closed reactor for temperature variation ( $\geq 80^\circ C$ ) studies. Samples were collected at different intervals, immediately filtered and analysed for manganese volumetrically by EDTA method. The other metal ions such as Fe, Co, Ni and Cu were analysed using Perkin Elmer (Model AAnalyst 200) atomic absorption spectrophotometer after suitable dilutions of leach liquor. The X-ray diffraction (XRD) measurements were taken over a range of 20 to  $70^\circ$  using Phillips Powder Diffractometer Model PW 1830 with  $CoK_\alpha$  radiation at a scan speed of 1.2 $^\circ$ /min.

## 4. Results and Discussions

### 4.1 Chemical Analysis and Characterization

The chemical analysis of four samples taken up for the present study is shown in Table 1. In case of manganese nodules, though the major constituent is manganese, but due to high %ages of Cu, Ni and Co, the leaching behaviour of these metals was also studied. In leach solutions the iron extraction need to be minimized, therefore, the dissolution of iron was also monitored. For low and medium grade manganese ores, only Mn extraction and iron contamination were studied. The crystalline phases as identified from the XRD patterns are also given in Table 1. The manganese nodule was observed to be mainly amorphous in nature. The major crystalline phases associated with various manganese ore samples were pyrolusite, quartz/silica [23, 37].

### 4.2 Leaching Studies for Manganese Nodules

Leaching studies on manganese nodule were carried out by varying parameters such as leaching time, hydrazine concentration, sulphuric acid concentration, leaching temperature and pulp density. The results are briefly discussed in the following sections:

**Table 1.** Chemical Composition and Crystalline Phases of Various Ores used for Leaching

Sample	%Mn	%Fe	%Cu	%Ni	%Co	%Zn	%acid	XRD phases
Mn Nodule	27.37	7.3	0.92	0.96	0.11	0.08	16.5	amorphous
MMO-1 <sup>#</sup>	38.22	4.9	0.01	0.02	0.01	0.01	25.4	Pyrolusite, quartz
LMO-1*	29.5	3.37	0.037	0.06	0.06	0.01	34.82	Pyrolusite, quartz
LMO**	15.38	3.52	0.008	0.018	0.005	0.013	65.8	Pyrolusite, quartz

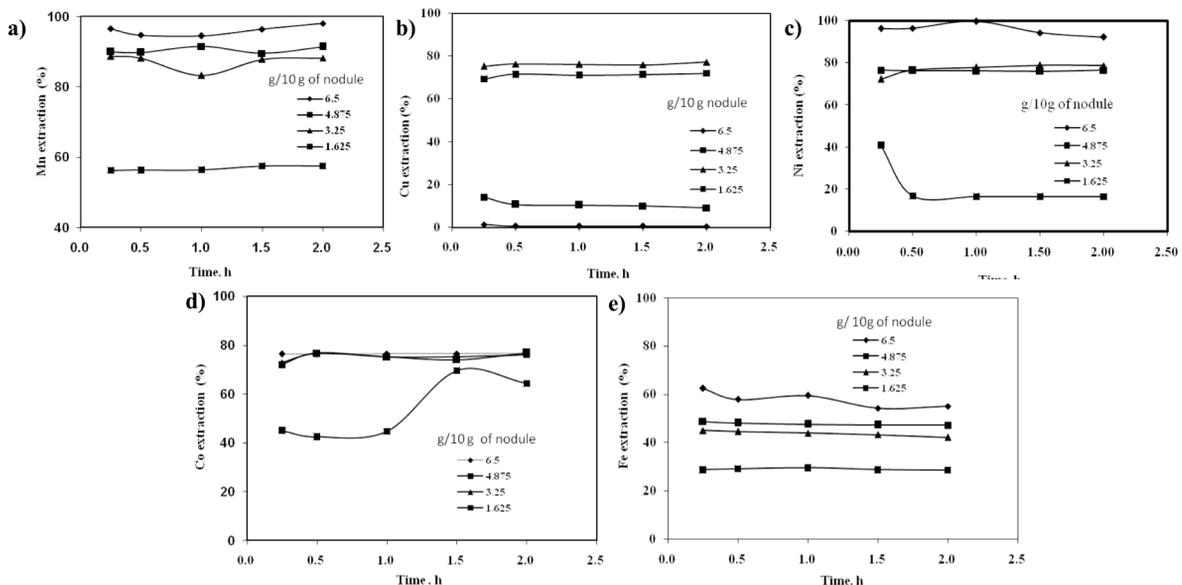
MMO-1<sup>#</sup> medium grade ore of GMDC, Gujarat, \*LMO-1 low grade Mn ore of GMDC, Gujarat, LMO-2\*\* low grade ore of Orissa

## 4.2.1 Effect of Amount of Hydrazine Sulphate

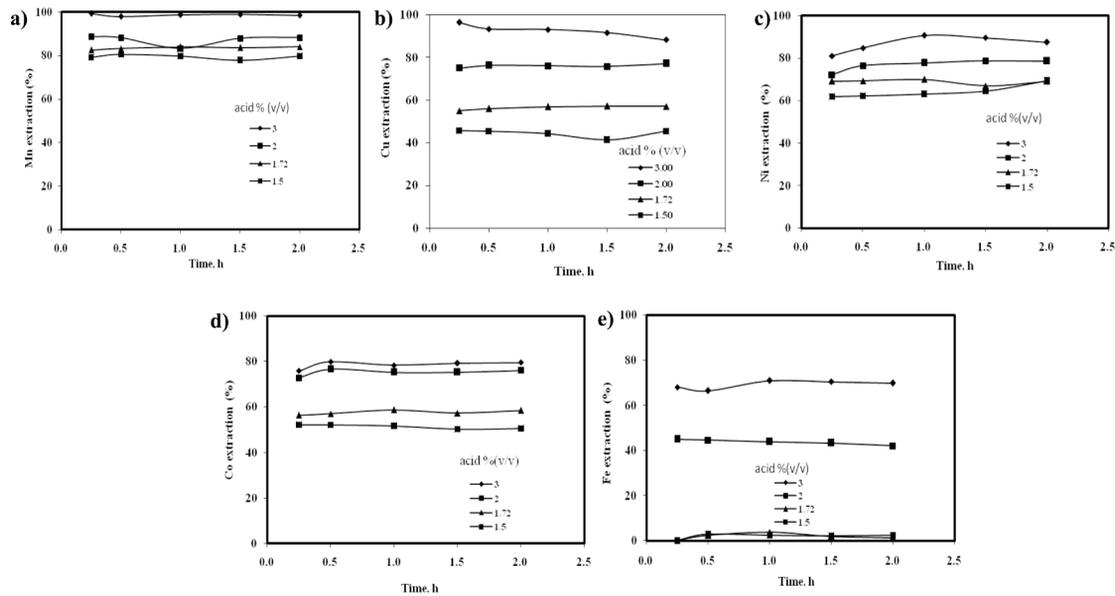
The effect of amount of hydrazine sulphate was studied while keeping rest of conditions as: pulp density 10% (wt/v),  $H_2SO_4$  2% (v/v), and temperature 35°C. The results are shown in Figs. 1a to 1e. With the increase in amount of reductant from 1.625g/10 g of nodule to 6.5g/10 g of nodule, % Mn extraction increased from 56.17 to 96.53% within fifteen minutes (Fig. 1a). Leaching time had no significant effect on manganese dissolution. In case of copper extraction, with the increase in amount of reductant extraction decreased from 69.3 to 1.3% within fifteen minutes (Fig. 1b). In this case also time of leaching had no significant role. The decrease in copper extraction could be due to more reducing environment at higher reductant concentration resulting in formation of cuprous sulphate which has low stability. The extraction remained more or less same from 15 minutes to two hours. Fig.1c shows that nickel extraction also exhibited similar trend as observed for manganese dissolution. With the increase in amount of reductant, % extraction of Ni increased and within 15 minutes 96.12 % nickel was extracted with the amount of hydrazine sulphate as 6.5 g/10g nodule. In this case too, time of leaching did not show any significant effect. Fig. 1d shows that cobalt extraction increased from 45.1 to 76.33% within fifteen minutes by increasing amount of reductant from 1.625g/10 g of nodule to 6.5g/10 g of nodule. Iron extraction also increased with the increase of amount of reductant (Fig. 1e). By using 6.5 g/10 g of reductant, within fifteen minutes 62.4% iron got dissolved.

4.2.2 Effect of  $H_2SO_4$  Concentration

The effect of acid concentration on metal extraction was studied while keeping the rest of parameters as: pulp density 10% (wt/v), hydrazine sulphate 3.25g/10g of nodule and temperature 35°C. The results are shown in Figures 2a to 2e. Percentage extraction of metal values increased with increase in acid concentration but the increase of leaching time from 15 minutes to 2 hours either did not have much influence on leaching efficiency or resulted in marginal increase as observed in case of Ni and Co. By keeping the acid concentration as 3% (v/v) the extractions of Mn, Cu, Ni and Co were 99.27, 96.53, 81.04, and 75.86% respectively. By keeping the amount of reductant less and increasing acid concentration copper extraction kept on increasing. With 1.5% acid Cu extraction was 45.67% which increased to 96.53% with 3% (v/v) sulphuric acid. By increasing acid concentration Cu extraction kept on increasing. With 1.5% acid Cu extraction was 45.67% which increased to 96.53% with 3% (v/v) sulphuric acid. It confirms that lower reductant amount and higher acid concentration favour copper dissolution. Iron contamination increased from 0.12% to 68.1% in fifteen minutes leaching time by increasing acid concentration from 1.5 to 3.0% (v/v). In the absence of  $H_2SO_4$  the recoveries of Co, Ni Cu, Mn, Zn and Fe were 2.5, 2.01, 6.83, 32.61, nil and 1.927% respectively confirming the need of sulphuric acid during leaching.



**Figure 1.** Effect of amount of hydrazine sulphate under the conditions: P.D 10% (wt/v),  $H_2SO_4$  2.0% (v/v), temp. 35°C on (a) % Mn extraction, (b) % Cu extraction, (c) % Ni extraction, (d) % Co extraction, and (e) % Fe extraction from manganese nodule.



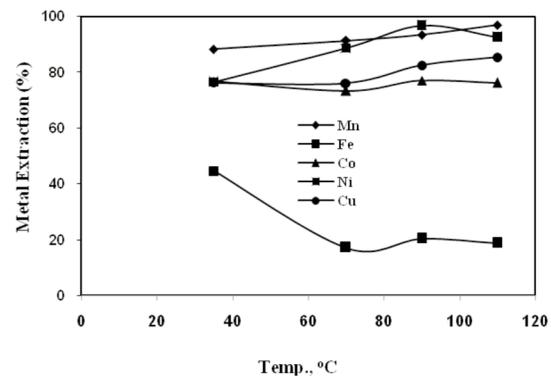
**Figure 2.** Effect of  $H_2SO_4$  concentration under the conditions: P.D 10%, hydrazine sulphate 3.25 g/10 g of nodule, temp.  $35^\circ C$  on (a) % Mn extraction, (b) % Cu extraction (c) % Ni extraction, (d) % Co extraction, and (e) % Fe extraction from manganese nodule.

#### 4.2.3 Effect of Temperature

The above results have confirmed that the % metal extraction does not depend on leaching time, hence effect of temperature ( $35-110^\circ C$ ) was studied by keeping the time as 30 minutes. The results are shown in Figure 3. With the increase of temperature from  $35$  to  $110^\circ C$ , in thirty minutes time, manganese, copper, and nickel dissolutions increased from 88.14 to 96.9%, 76.25 to 85.25%, and 76.4 to 92.5% respectively. Cobalt extraction remained as 76.5% in the studied range of temperature. In the same temperature range iron dissolution decreased from 44.62 to 17%.

#### 4.2.4 Effect of Pulp Density with Proportional Increase of Acid and Reductant

The effect of pulp density (wt/v) on extraction of manganese, copper, nickel and cobalt was studied at  $70^\circ C$  by varying the amount of nodules from 10g to 30g/100 mL. The acid concentrations and the amounts of reductant were increased proportionally. The results are given in Table 2. With the increase in pulp density % extraction of manganese was adversely affected but in case of other metals i.e., copper, nickel and cobalt, the % extraction increased till 20% solids and thereafter decreased. Iron contamination in the leach solution decreased from 17.1 to 1.0% with increase of % solids from 10 to 30%. To obtain good extraction of all the metal values only 10% pulp density need to be maintained.



**Figure 3.** Effect of temperature on % metal extraction from manganese nodule. Conditions: P.D 10%, hydrazine sulphate 3.25 g/10 g of nodule,  $H_2SO_4$  2% (v/v), time 30 min.

#### 4.2.5 Effect of Presence of Ammonium Sulphate

Iron contamination in the leach solution can be minimized by carrying out leaching in presence of ammonium sulphate to reject iron as jarosite [35, 36] as given by Eq(4). With a view to reduce the iron contamination, leaching experiments were carried out at different temperatures in presence of 100 g/L ammonium sulphate while keeping the rest of conditions as: pulp density 10% (wt/v),  $H_2SO_4$  2.0% (v/v), time half-an-hour, hydrazine sulphate 3.25 g/10g of nodule. The results given in Table 3 compare % metal extraction in presence and absence of ammonium sulphate. It is observed from Table 3 that

**Table 2.** Effect of Pulp Density on Extraction of Metal Values from Manganese Nodules temp. 70°C, time 30 min

%Metal	Pulp density, %(wt/v)			
	30	20	15	10
Extn.	acid 6% (v/v), (HS* 9.75g/10g nodule),	acid 4% (v/v), (HS 6.5 g/10g),	acid 3% (v/v) (HS 4.875g/10g)	acid 2% (v/v) (HS 3.25g/10g)
Mn	63.25	76.24	79.23	91.34
Co	73.22	81.17	97.86	93.75
Ni	88.58	87.85	92.58	79.08
Cu	76.03	88.28	92.2	79.08
Fe	17.05	18.07	1.89	1.01

\* HS hydrazine sulphate

in the presence of ammonium sulphate, iron dissolution had increased from ~17 to 30% at all temperatures. Percentage manganese extraction only marginally decreased whereas nickel and copper extractions were adversely affected due to presence of ammonium sulphate. The increase in iron dissolution may be due to reaction given by Eq (2) becoming more dominant resulting in its presence as Fe(II) in leach solution which does not form jarosite.

From the detailed studies carried out on leaching of manganese nodule the following observations are made: (i) manganese dissolution is not dependent on temperature, even at 35°C, most of it can be dissolved within half-an-hour (ii) for maximum extractions of copper, nickel and cobalt with minimum iron dissolution, temperature of 110°C is required (iii) presence of ammonium sulphate during leaching results in higher percentage dissolution of iron with lower extractions of other metal values (iv) pulp density (wt/v) more than 10% adversely affects manganese dissolution though good extractions of Cu, Ni and Co can be obtained even at 20% pulp density (v) metal dissolution depended on acid concentration and amount of reductant.

**Table 3.** Comparison of % Metal Extraction in Presence and Absence of Ammonium Sulphate. Conditions: P.D 10%, H<sub>2</sub>SO<sub>4</sub> 2% (v/v), time 30 min, HS 3.25g/10 g nodule

% Metal ion	Temperature, °C		
	110	90	70
%Fe	29.31(17.0)*	30.12(17.1)	29.89 (17.1)
%Mn	95.25 (96.9)	90.25 (94.3)	90.89 (94.1)
%Cu	72.74 (85.25)	71.53(82.45)	68.19 (76.0)
%Ni	79.46(97.8)	80.87(96.76)	78.12(88.57)
%Co	79.17 (76.9)	80.87(76.9)	78.12 (73.25)

\*values given in bracket refer to the % extraction in absence of ammonium sulphate under similar conditions.

### 4.3 Leaching Studies with Medium Grade Manganese ore (Gujarat), (MMO-1)

#### 4.3.1 Effect of Amount of Reductant

Effect of amount of reductant was studied by varying its amount from 4.5g to 6.0 g/10 g of ore while keeping rest of leaching conditions as: pulp density 10% (wt/v), temp. 35°C, acid concentration 3% (v/v). The results for manganese and iron dissolution are shown in Figures 4a and 4b respectively. The increase in amount of reductant from 4.5 to 5.5 g/10 g, resulted in increase of manganese dissolution from 80.25 to 92.9% in thirty minutes of leaching time and further increase in reductant amount had only marginal effect. Under these conditions iron dissolution was 38%.

#### 4.3.2 Effect of Sulphuric Acid Concentration

The results obtained on effect of sulphuric acid concentration in the range of 2.5 to 4.5% on manganese and iron extractions is shown in Figures 5a and 5b respectively. With the increase in acid concentration from 2.5 to 3.0% (v/v), manganese extraction increased from 75.2 to 92.9 % and further increase in acid concentration had very marginal effect. Iron dissolution kept on increasing with the increase of acid concentration from 2.5 to 4.5%. With H<sub>2</sub>SO<sub>4</sub> concentration of 2.5%, iron dissolution was only 21% but increased to 69.15 % when the acid concentration was increased to 4.5%.

#### 4.3.3 Effect of Temperature

Effect of variation of temperature in the range of 35 to 55°C on manganese and iron dissolution is shown in Figures 6a and 6b respectively. Manganese dissolution remains unaffected in the studied temperature range but iron dissolution decreased from 38.25% to 27.1 % with the increase in temperature from 35 to 55°C.

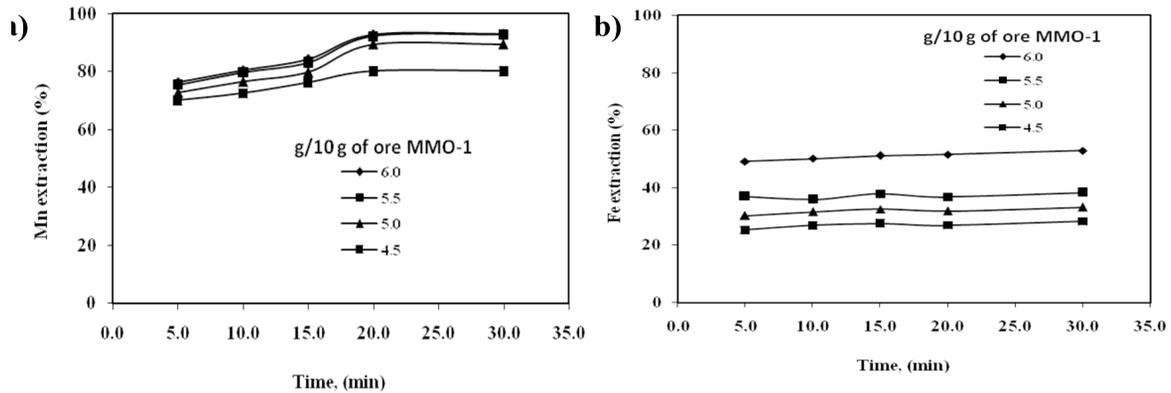


Figure 4. Effect of amount of hydrazine sulphate under the conditions: P.D 10% (wt/v),  $H_2SO_4$  3.0% (v/v), temp. 35°C. on (a) % Mn extraction, and (b) % Fe extraction from MMO-1.

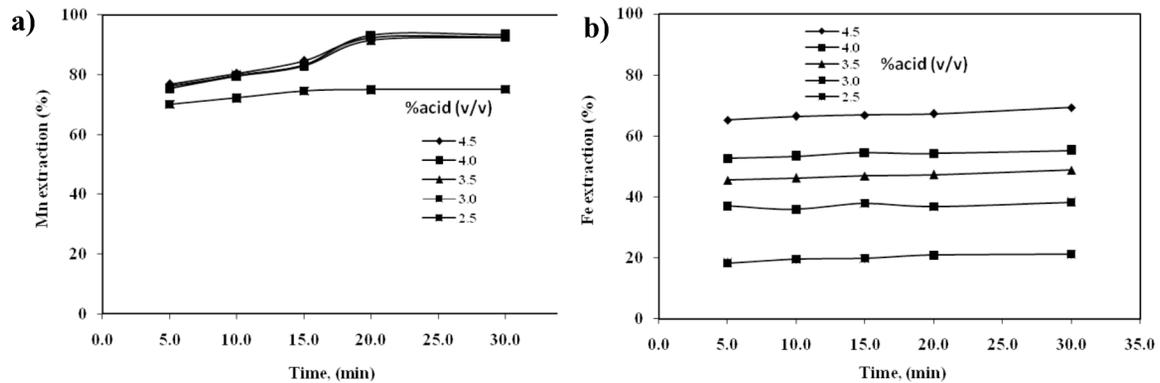


Figure 5. Effect of  $H_2SO_4$  concentration under the conditions: P.D 10%, hydrazine sulphate 5.5 g/10 g of MMO-1, temp. 35°C on (a) % Mn extraction, and (b) % Fe extraction from MMO-1.

#### 4.4 Leaching Studies with Low Grade Manganese Ore of Gujarat (LMO-1)

Studies on medium grade manganese ore sample have shown that temperature has no effect on manganese dissolution though iron dissolution decreased to some extent. For low grade manganese ore samples studies were carried out only by varying amount of reductant and acid concentration.

##### 4.4.1 Effect of Amount of Reductant

Effect of amount of reductant was studied by varying its amount from 3.0 g to 4.5 g/10 g of ore while keeping rest of leaching conditions as: pulp density 10% (wt/v), temp. 35°C,  $H_2SO_4$  concentration 2.5% (v/v). By increasing the amount of reductant from 3.0 to 3.5 g/10g, manganese dissolution increased from 85.7 to 95.2% (Figure 7a) and further increase in its amount had no effect. Within 20 minutes of reaction time 95 % manganese could be extracted. Iron dissolution increased from 27.88 to 50.21% (Figure 7b) with the increase in amount of

hydrazine sulphate from 3.0 to 4.5 g/10 g of LMO-1 sample.

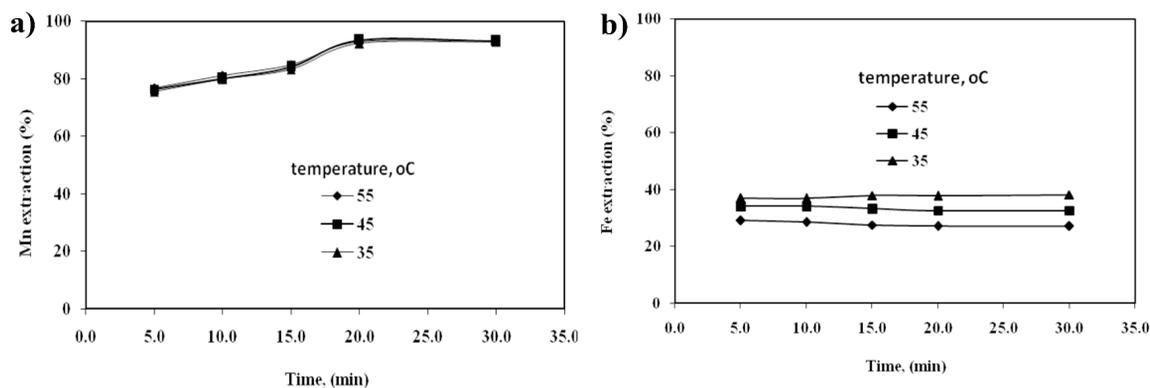
##### 4.4.2 Effect of Sulphuric Acid Concentration

Figures 8a and 8b show the effect of sulphuric acid concentration in the range of 2.0 to 4.0% on manganese and iron extractions respectively. With the increase in acid concentration from 2.0 to 2.5% (v/v), manganese extraction increased from 79.1 to 95% and further increase in acid concentration did not have any effect. Iron dissolution kept on increasing with the increase of acid concentration in the studied range. Iron dissolution was 65.25 % when acid concentration was increased to 4.0%.

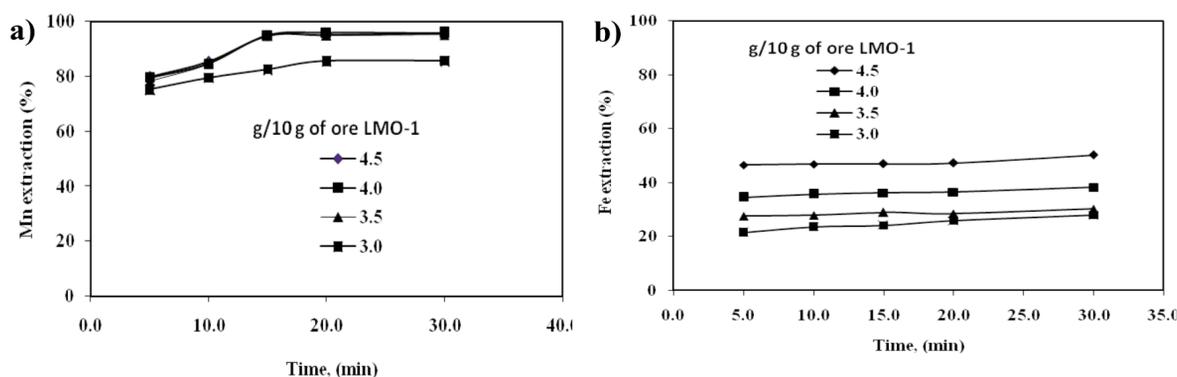
#### 4.5 Leaching Studies with Low Grade Manganese Ore of Orissa (LMO-2)

##### 4.5.1 Effect of Amount of Reductant

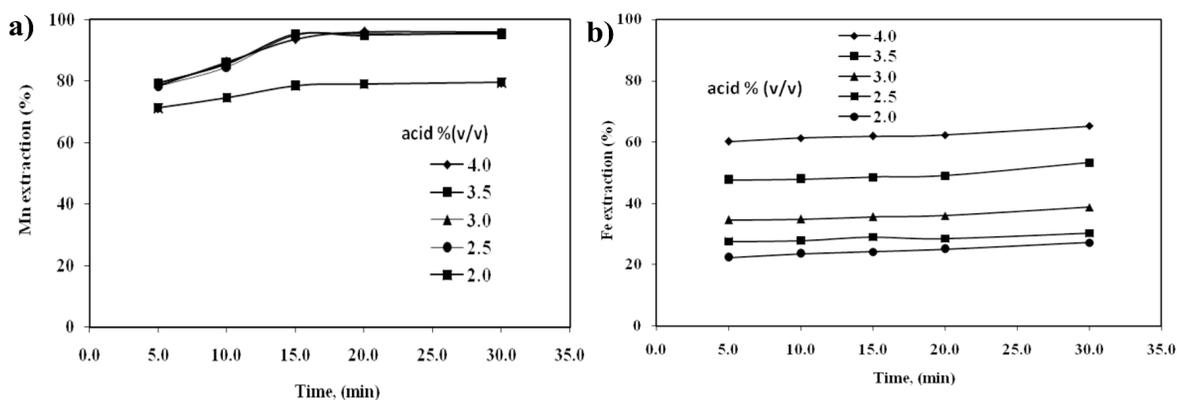
Effect of amount of reductant was studied by varying its amount from 0.5 to 2.0 g/10 g of ore while keeping rest of leaching conditions as: pulp density



**Figure 6.** Effect of temperature under the conditions: P.D 10%,  $H_2SO_4$  3.0% (v/v), hydrazine sulphate 5.5 g/10 g on (a) % Mn extraction, and (b) % Fe extraction from MMO-1.



**Figure 7.** Effect of amount of hydrazine sulphate under the conditions: P.D 10% (wt/v),  $H_2SO_4$  2.5% (v/v), temp. 35°C on (a) % Mn extraction, and (b) % Fe extraction from LMO-1.



**Figure 8.** Effect of  $H_2SO_4$  concentration under the conditions: P.D 10% (wt/v), hydrazine sulphate 3.5% (wt/v), temp. 35°C on (a) % Mn extraction, and (b) % Fe extraction from LMO-1.

10% (wt/v), temp. 35°C,  $H_2SO_4$  concentration 1.0% (v/v). It is observed that with the increase in amount of reductant from 0.5 to 2.0 g/10g, manganese dissolution increased from 81.6 to 98.9% within 20 minutes of reaction time (Figure 9a). Iron dissolution increased from 30.2 to 50.25% (Figure 9b) with the

increase in amount of hydrazine sulphate from 0.5 to 2.0 g/10 g of LMO-2 sample.

#### 4.5.2 Effect of Sulphuric Acid Concentration

Effect of sulphuric acid concentration in the range

of 0.5 to 2.0 % on manganese and iron extractions is shown in Figs 10a and 10b respectively. With the increase in acid concentration from 0.5 to 1.0% (v/v), manganese extraction increased from 90.2 to 98.9 %. Iron dissolution was 18.25% but increased to 68.55 % when the acid concentration was increased to 2.0 %.

#### 4.6 Comparison of Optimum Conditions of Various Ores

A comparison of experimental conditions for achieving maximum extractions of metal values from manganese nodule and different types of manganese ores is presented in Table 4a. The results show that by leaching the medium and low grade manganese ores at 35°C, >92% manganese extraction can be achieved irrespective of grade of ores. In case of manganese nodule, taking in view of other valuable metals i.e., copper, nickel and cobalt, leaching need to be done at a higher temperature of 110°C. Table 4b compares the theoretical requirements of reductant and acid for manganese extraction as per the reaction given by Eq.(1) with experimentally used values for best

extractions in the present study. The reductant requirement varied between 1.0 to 1.2 times stoichiometric whereas acid requirement varied from 1.5 to ~1.8 times stoichiometric requirement. Higher requirement of acid is due to part dissolution of iron. This is first time that a reductant which works efficiently at 35°C for almost complete dissolution of manganese from variety of ores is being reported.

The major impurity for manganese ore leach solutions will be iron (though iron extraction varies from 18.76 to 50.25% for different ores as given in Table 4a, but its concentration will be 1.36, 1.87, 1.02 and 1.77 g/L for manganese nodule, MMO-1, LMO-1 and LMO-2 samples respectively) with small amounts of Cu(II), Ni(II), Co(II) and Zn(II) which need to be removed and not recovered [23, 25]. In case of manganese nodule, the leach solution is to be processed for recovery of copper, nickel and cobalt along with manganese. The leach solutions obtained can be first treated for iron removal by pH adjustment using lime slurry. The iron free solution can be treated with sodium sulphide to precipitate Cu(II), Ni(II), Co(II) and Zn(II) as bulk sulphides for disposal or

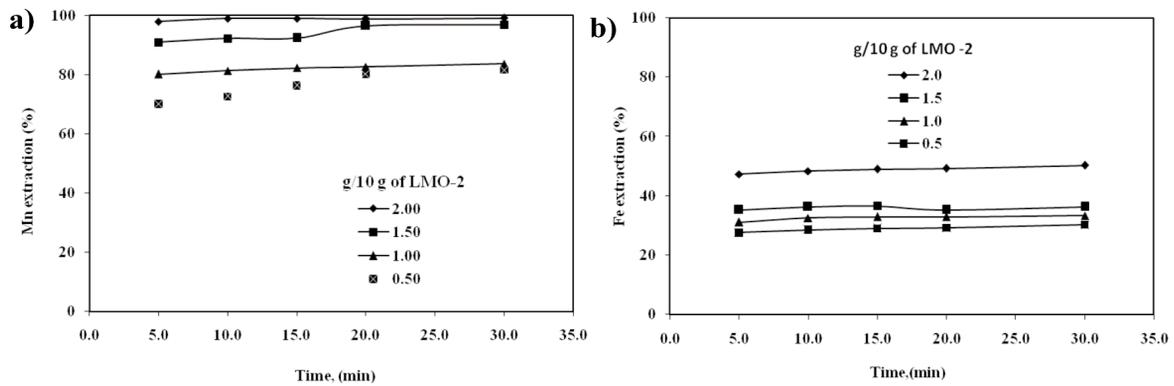


Figure 9. Effect of amount of hydrazine sulphate under the conditions: P.D 10% (wt/v), H<sub>2</sub>SO<sub>4</sub> 1.0% (v/v), temp. 35°C on (a) % Mn extraction, and (b) % Fe extraction from LMO-2.

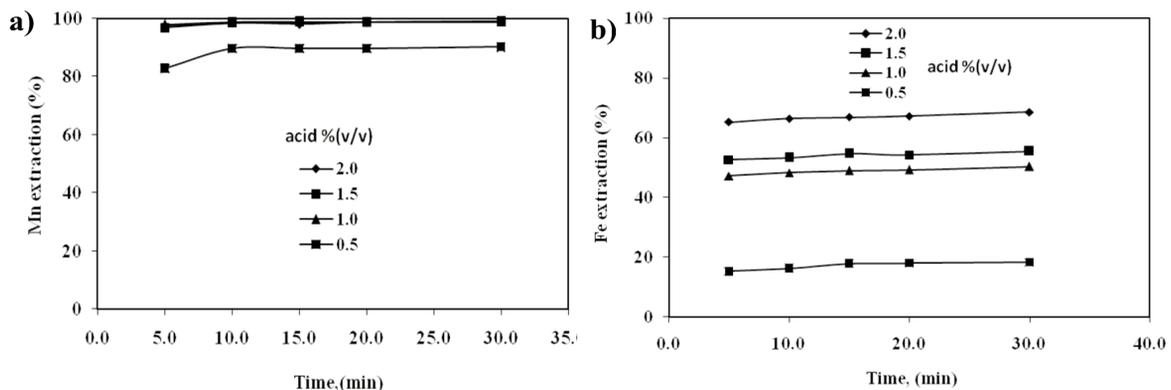


Figure 10. Effect of H<sub>2</sub>SO<sub>4</sub> concentration under the conditions: P.D 10% (wt/v), hydrazine sulphate 2.0% (wt/v), temp. 35°C on (a) % Mn extraction, and (b) % Fe extraction from LMO-2.

**Table 4a.** Comparison of Optimum Conditions for Various Grades of Ores

Sample	% Metal extraction					Conditions			
	Mn	Fe	Cu	Ni	Co	time, min	temp, °C	HS	acid
								(g/10g of ore)	(v/v)
Mn Nodule	96.93	18.76	85.25	92.58	76.58	30	110	3.25	2
MMO-1 <sup>#</sup>	92.88	38.25	-	-	-	30	35	5.5	3
LMO-1*	95.2	30.27	-	-	-	30	35	3.5	2.5
LMO-2**	98.9	50.25	-	-	-	30	35	2	1

MMO-1<sup>#</sup> medium grade ore of GMDC, Gujarat, LMO-1\* low grade ore of GMDC, Gujarat, LMO-2 low grade Mn ore of Orissa.

**Table 4b.** Comparison of Stoichiometric Amount of Reductant and Acid used under Optimum Conditions of Mn extraction (stoichiometry calculated for hydrazine sulphate and sulphuric acid as given by Eqn (1)).

Sample	Stoichiometric requirement		times stoichiometric amount used	
	HS*	acid	HS	acid
	g/10g of ore % (v/v)			
Mn Nodule	3.24	1.32	1	1.5
MMO-1	4.52	1.85	1.2	1.62
LMO-1	3.49	1.43	1	1.78
LMO-2	1.82	0.73	1.1	1.37

\* HS hydrazine sulphate

metal recovery. The purified leach solution can be used for manganese sulphate production [25].

The present studies have confirmed the technical feasibility of using hydrazine sulphate in sulphuric acid medium as a reductant for the dissolution of manganese from low and medium grade ores at 35°C. The studies have also shown good extractions of Cu, Ni, Co and Mn from manganese nodules at 110°C. Further studies are essential to generate data for downstream processing of the leach solutions to obtain saleable products as well as by products. The techno economic feasibility of the entire process can be worked out after pilot plant testing and obtaining material, energy and water balance.

#### 4. Conclusions

Sulphuric acid leaching studies were carried out for extraction of manganese and other valuable metals from low and medium grade land as well sea based manganese ores in the presence of hydrazine sulphate

as the reductant. In the present studies four samples used were: (i) Indian ocean manganese nodules (ii) medium grade manganese ore of Gujarat, (iii) low grade manganese ore of Gujarat and (iv) low grade manganese ore of Orissa. The manganese content of these ores varied from 15 to 39%. In case of manganese nodules conditions were established for extraction of Cu, Ni, Co along with Mn by varying experimental parameters which included time, temperature, pulp density, acid and reductant concentrations. The optimum conditions established for manganese nodule for maximum metal extractions were: pulp density 10%(wt/v), time 30 min, temperature 110°C, amount of hydrazine sulphate 3.25 g/ 10 g of nodule, sulphuric acid 2.0% (v/v). Under these conditions the recoveries were: 96.9% Mn, 85.25% Cu, 92.58% Ni and 76.5% Co. with Fe extraction of 18.76%. 92 to 98% Mn recovery from different types of medium and low grade manganese ores could be obtained at 35°C by varying amount of reductant and acid concentration. Depending on the manganese content of the ore 1.0 to 1.2 times stoichiometric amounts of reductant and 1.5 to 1.8 times sulphuric acid were required to achieve >92% Mn extraction. A simple single stage room temperature leaching process is reported for treating low and medium grade manganese leaching, however in case of manganese nodules higher temperature was required due to optimum extractions of other valuable metals i.e., Cu, Ni and Co.

#### Acknowledgements

The authors are thankful to Prof. B.K. Mishra, Director, Institute of Minerals and Materials Technology, Bhubaneswar, for his kind permission to publish this paper. D. Hariprasad wish to thank CSIR Newdelhi for providing Senior Research Fellowship. The authors are also thankful to the Head of the Department, Hydro & Electro Metallurgy IMMT.

**References**

- [1] D. J. Fray, H. A. Hancock, U.S. Patent No. 4,645,650. (1987).
- [2] F. W. Y. Momade, Zs G. Momade, Hydrometallurgy, 51 (1999) 103.
- [3] F. W. Y. Momade, Zs G. Momade, Hydrometallurgy, 54 (1999) 25.
- [4] R. N. Sahoo, P. K. Naik, S. C. Das, Hydrometallurgy, 62 (2001) 157.
- [5] S. C. Das, P. K. Sahoo, P. K. Rao, Hydrometallurgy, 8 (1982) 35.
- [6] T. Tekin, M. Bayramoglu, Hydrometallurgy, 32 (1993) 9.
- [7] C. Abbruzzese, In: Separation Processes in Hydrometallurgy (Ed. Davis, G.A.), Ellis Horwood Ltd., Chichester, (1987) 77.
- [8] C. Abbruzzese, Hydrometallurgy, 25(1) (1990) 85.
- [9] C. Abbruzzese, M. Y. Duarte, B. Paponetti, L. Toro, Miner Eng 3(3-4) (1990) 307.
- [10] D. Grimanelis, P. Neou-Syngouna, H. Vazarlis, Hydrometallurgy, 31(1-2) (1992) 139.
- [11] J. D. Miller, R. Y. Wan, Hydrometallurgy, 10 (1983) 219.
- [12] P. K. Naik, L. B. Sukla, S. C. Das, Hydrometallurgy, 54 (2000) 217.
- [13] Z. Zhang, L. Q. Liu, S. F. Peng, Engineering Chemistry and Metallurgy (China), 21(1) 2000 103.
- [14] T. Jiang, Y. Yang, Z. Huang, G. Qiu, Hydrometallurgy, 72 (2004) 129.
- [15] P. R. Raison, S. G. Dixit, J Chem Technol Biotechnol, 42(3) (1988) 167.
- [16] M. Trifoni, F. Veglio, G. Taglieri, L. Toro, Miner Eng 13(2) (2000) 217.
- [17] M. Trifoni, L. Toro, F. Veglio, Hydrometallurgy, 59 (2001) 1.
- [18] F. Veglio, M. Trifoni, L. Toro, Ind Eng Chem Res 40(18) (2001) 3895.
- [19] F. Pagnanelli, G. Furlani, P. Valentini, F. Veglio, L. Toro, Hydrometallurgy, 75 (2004) 157.
- [20] F. Veglio, L. Toro, Hydrometallurgy, 36 (1994) 215.
- [21] F. Veglio, I. Volpe, M. Trifoni, L. Toro, Ind Eng Chem Res 39(8) (2000) 2947.
- [22] A. A. Ismail, E. A. Ali, I. A. Ibrahim, M. S. Ahmed, The Canadian J. Chem. Eng. 82 (2004) 1296.
- [23] D. Hariprasad, B. Dash, M. K. Ghosh, S. Anand, IJCT, 16 (2009) 322.
- [24] D. Hariprasad, B. Dash, M. K. Ghosh, S. Anand, Miner Eng, 20 (2007) 1293.
- [25] D. Hariprasad, M. K. Ghosh, S. Anand, Trans Ind Inst Met, 62(6) (2009) 551.
- [26] J. N. Brook, A. P. Prosser, Trans Instn Min Metall 78 (1969) C64.
- [27] S. C. Das, S. Anand, R. P. Das, P. K. Jena, Aus. IMM Bulletin and Proceedings, 294(1) (1989) 73.
- [28] S. Mohanty, S. Anand, R. P. Das, Metals, Materials and Processes, 13(1) (2001) 9.
- [29] K. N. Han, D. W. Fuerstenau, Mar Min, 2 (1986) 155.
- [30] S. B. Kanungo, R. P. Das, Hydrometallurgy, 20 (1988) 135.
- [31] J. E. Pahlman, S. E. Khalafalla, U.S. Patent 4,138,465 (1979).
- [32] S. E. Khalafalla, J. E. Pahlman, J Metals, Aug. (1981) 37-42.
- [33] J. H. Lee, J. Gilje, H. Zeitlin, Environ. Sci. & Tech., 12(13) (1978) 1428.
- [34] R. Acharya, M. K. Ghosh, S. Anand, R. P. Das, Hydrometallurgy, 53(2) (1999) 169.
- [35] M. K. Ghosh, S. P. Barik, S. Anand, Trans Ind Inst Met 61(6) (2008) 477.
- [36] A. I. Vogel, A Text Book of Quantitative Inorganic Analysis, English Language Book Society and Longmans Green Publishers, (2000).
- [37] K. Rout, M. Mohapatra, B. K. Mohapatra, S. Anand, International Journal of Engineering, Science and Technology, 1(1) (2009) 106-122.