Self sustained autogenous dissolution of medium grade manganese ore of Gujarat in NH₃OHCl-H₂SO₄-H₂O medium

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Leaching studies have been carried for dissolution of manganese from medium grade manganese ore in hydroxyl ammine hydrochloride-sulphuric acid medium. Due to exothermic nature of reaction no external heat is required for quantitative extraction of manganese confirming the self sustained autogenous nature of leaching process. Initially, the effects of individual parameters including time, sulphuric acid concentration, amount of reductant, pulp density, and particle size have been studied. One parameter has been changed at a time while keeping the other parameters constant. Per cent manganese extraction is found to be dependent on acid concentration and amount of reductant. Within 20 min, manganese could be quantitatively dissolved. A comparison of FTIR spectra of synthetic solution with actual leach solution indicates the formation of ClO₄⁻ ions during leaching. The XRD pattern of the residue shows only quartz as the crystalline phase. Response surface methodology is adopted applying a central composite design for 2⁴ factorial set of experiments. A statistical analysis is done to evaluate interactive effects. Using the model, optimised parameters in the range of pulp density 25 - 35 % wt/v, acid concentration 6.5-7.5% v/v, amount of reductant 15-16 g and time 10 - 30 min have been considered for maximum desirability. The experimental data is found to be fitted well with the predicted ones.

Keywords: Hydroxyl ammonium chloride, Leaching, Manganese ore, NH₃OHCl-H₂SO₄-H₂O medium, Response surface methodology, Sulphuric acid

The principle ores of manganese are pyrolusite (MnO₂) and rhodochrosite (MnCO₃). Depending on the grade of ore, manganese can be extracted economically for commercial purpose. High grade ores (>45%) are usually processed through conventional pyro-metallurgical route¹. Due to depletion of high grade manganese ores, the low and medium grade manganese ores have gained importance for their commercial exploitation². Pyrolusite and other manganese oxide ores have manganese in Mn⁴⁺ state, which needs a reductant to solubilise during the leaching process³. Leaching of manganese from its ores with sulphuric acid in the presence of reducing agents is a well-known approach⁴. So far, numerous studies have been carried out for dissolution of manganese using different kinds of reducing agents such as coal⁵, methanol–sulphuric acid⁶, oxalic acid-sulphuric acid⁷-⁸, ferrous sulphate⁹,¹⁰ aqueous sulphur dioxide¹¹-¹⁴, sulphuric acid and hydrogen peroxide¹⁵-¹⁸, ferrous sulphide¹⁹,²⁰ metallic iron¹¹, hydroxyl amine²¹, organic reductants and carbohydrates²²-⁴⁰. However, reductant like sulphur dioxide is toxic in nature and strict environmental regulations will not allow their use for commercial processes. So far as the carbohydrates are concerned, though may prove to be cost effective as well as eco-friendly but their oxidised products are not well defined. The leach liquors may contain numerous hydrolyzed/degradable products of carbohydrates. In the present study hydroxyl ammonium chloride (NH₂OHCl) in combination with sulphuric acid has been used as the leachant. The leaching is carried out under non-isothermal conditions as the heat generated during mixing of reagents and spontaneous reactions is sufficient to complete the dissolution process within 20 min. Initially the experiments have been conducted to study the effect of individual variable on the dissolution of manganese. With a view to study the interaction of experimental parameters and for achieving optimised conditions, response surface methodology (RSM) is adopted. RSM is one of the best empirical statistical techniques employed for multiple regression analysis of quantitative data obtained from statistically designed experiments by solving the multivariate equations simultaneously⁴¹.

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Experimental Procedure

Materials
In the present work, medium grade manganese ore supplied by M/s Gujarat Mineral Development Corporation (GMDC) Gujarat, India was used. The ore was crushed, ground and sieved to prepare various size fractions. Hydroxyl ammonium chloride (HAC), disodium salt of EDTA and triethanolamine of Merck, India were used. Thymolphthalexone was procured from sd-Fine Chemicals, India. Distilled water was used to carry out the experimental work.

Experiment methodology
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 were carried out under different experimental conditions using <100 μm (100% passing through 150 Mesh BSS) particle size except for the set of experiments wherein effect of particle size variation was studied. First the required amount of HAC was added to sulphuric acid solution of desired concentration. To this mixed solution weighed amount (10-20 g) of ore was added. Due to exothermic nature of the reaction on addition of ore the temperature of slurry increased and effervescence with evolution of gas was observed. The slurry was agitated for desired period of time, immediately filtered, and analysed. No external heat was applied during the reaction period. The experiments were carried out by varying one parameter at a time while keeping the rest constant. The FTIR spectra were obtained using Thermo Scientific Nicolet 6700 Research FTIR Spectrometer. A smart Orbit ATR module accessory with a diamond crystal as an internal reflection element was used. For background and sample, 256 scans at 8 cm\(^{-1}\) resolution were collected. The X-ray diffraction (XRD) measurements for the as prepared samples were done over a range of 10-90° using a Phillips Powder Diffractometer Model PW1830 with Cu Kα radiation at a scan speed of 1.2°/min.

Analysis procedure
The ore sample was analysed by wet chemical procedure. A weighed amount of sample was subjected to tri acid digestion. The acid insolubles were separated by filtration followed by making up the volume to 250 mL. Manganese was analysed volumetrically by EDTA method using thymolphthalexone as an indicator\(^{41}\). The other minor metal ions, i.e. Fe, Co, Ni, and Cu were analysed using Perkin Elmer (Model AAnalyst 200) atomic absorption spectrophotometer after desired dilutions.

<table>
<thead>
<tr>
<th>Independent variable</th>
<th>Range and level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulp density (X₁), %</td>
<td>20 - 40</td>
</tr>
<tr>
<td>Acid (X₂), %</td>
<td>6.0 - 8.0</td>
</tr>
<tr>
<td>Reductant amount (X₃), wt/v</td>
<td>14.5 - 16.5</td>
</tr>
<tr>
<td>Time (X₄), min</td>
<td>0 - 40</td>
</tr>
</tbody>
</table>

Table 1 — Experimental ranges and levels of the independent variables

Response surface methodology
Response surface methodology (RSM) was used for optimization of multivariate parameters for dissolution of manganese\(^{43}\). The modelling of the system facilitates the interpretation of multivariate phenomena and is a valuable tool for scaling up\(^{44}\). The four variables namely pulp density, amount of acid, amount of reductant, and time were chosen. The parameters chosen and levels used for the design of experiments are given in Table 1.

Results and Discussion

Analysis and chemical reactions
The wet chemical analysis shows that medium grade Mn ore contains 39.5% Mn, 6.25% Fe, 0.01% Cu, 0.01% Zn, 0.02% Ni, 0.01% Co and acid insoluble 23.0%. The XRD pattern shows crystalline phases of pyrolusite (MnO\(_2\)) and quartz (SiO\(_2\))\(^{29}\). During reductive dissolution of Mn(IV) in presence of HAC, the following overall chemical reaction will take place:

\[
\text{MnO}_2 + 2\text{NH}_3\text{OHCl} \rightarrow \text{MnCl}_2 + \text{N}_2 + 4\text{H}_2\text{O} \quad \text{(1)}
\]

There is also a likely hood of formation of ammonium perchlorate and manganese chloride as given by the following equation:

\[
\text{MnO}_2 + 3\text{NH}_3\text{OHCl} + \text{H}_2\text{O} \rightarrow \text{NH}_4\text{ClO}_4 + \text{MnCl}_2 + 2\text{NH}_3\text{OH} \quad \text{(2)}
\]

In the presence of sulphuric acid, requirement of hydroxyl ammonium chloride can be reduced as given below:

\[
2\text{MnO}_2 + 2\text{NH}_3\text{OHCl} + \text{H}_2\text{SO}_4 \rightarrow \text{MnSO}_4 + \text{N}_2 + \text{MnCl}_2 + 6\text{H}_2\text{O} \quad \text{(3)}
\]

\[
2\text{MnO}_2 + 3\text{NH}_3\text{OHCl} + \text{H}_2\text{SO}_4 \rightarrow \text{MnSO}_4 + \text{MnCl}_2 + \text{NH}_4\text{ClO}_4 + 2\text{NH}_3\text{OH} + 1/2\text{O}_2 \quad \text{(4)}
\]

Effect of leaching parameters on Mn dissolution
The various parameters chosen for studying the leaching efficiency of manganese ore are: time, amount of reductant, sulphuric acid concentration, pulp density, and particle size.
Effect of leaching time
Effect of leaching time is studied in the range of 5–20 min. The rest of the parameters were kept constant e.g. pulp density 10% (wt/v), reductant amount 0.55 g/g ore and sulphuric acid 2.5% (v/v). The results given in the Fig. 1(a) show that more than 96% Mn is extracted within 15 min and further increase in time to 20 min has no effect, confirming fast kinetics of Mn dissolution.

Effect of amount of reductant
Figure 1(b) shows the variation in reductant from 0 g/g to 0.6 g/g of ore, keeping the rest of the conditions constant as pulp density 10%, sulphuric acid 2.5% (v/v) and temperature ambient. The results show that in the absence of reductant, only 0.98% Mn is extracted, thereby confirming the need of reductant for dissolution of manganese. With further increase in HAC from 0 g/g to 0.6 g/g ore, Mn extraction is increased from 0.98% to 97% within 20 min.

Effect of sulphuric acid concentration
The effect of H₂SO₄ concentration was studied in the range of 0–3% (v/v) per 10 g of ore. Rest of the conditions were pulp density 10%, amount of reductant 0.55 g/g ore, and temperature ambient. The results (Fig. 1(c)) show that with the increase in acid concentration from 0% to 3% (v/v), manganese extraction is increased from 47.3% to 97%.

Effect of particle size
In order to study the effect of particle size, the average particle size was varied from 82 µm to 252 µm (from -90+75 µm to -300+212 µm). The results [Fig. 1(d)] show that manganese dissolution is practically independent of particle size in the studied

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Fig. 1 — Effect of different parameters on % Mn extraction
range. Manganese extraction in 20 min time under these conditions is varied between 96% and 98%.

**Effect of pulp density**

To study the effect of pulp density, acid concentration and amount of reductant were increased proportionally. The results given in Fig.1(e) show that the leaching efficiency of manganese remains more or less same (~97%) up to 30% pulp density.

**Temperature profile**

As mentioned above, the leaching was carried out under non-isothermal conditions. The temperature profile under various conditions is presented in Fig. 2. The heat of solution of H$_2$SO$_4$, HAC and heat generated on addition of ore to the leachant (instantaneous dissolution of ~60% of Mn) are sufficient to complete the leaching process without need of any external heat. As shown in Fig. 2, temperature of 42°C is obtained on addition of 2.5% (v/v) H$_2$SO$_4$ and 5.5g HAC in 100 mL of water. On addition of Mn ore the temperature of reaction mixture is raised in the range of 59-65°C. As the reaction proceeded gradually the temperature decreases to 30-32°C. Within this temperature range metal values present in the manganese ore could be leached out.

**FTIR and XRD studies**

The FTIR spectra of a synthetic solution (containing hydroxyl ammine hydrochloride, sulphuric acid, manganese sulphate and water) and actual leach solution immediately after the completion of reaction are taken to examine the formation of new bands after leaching. The spectra are compared in Fig. 3. For the synthetic solution a broad band and a sharp band are observed in the region of 3000-3500 cm$^{-1}$ and at 1635 cm$^{-1}$ respectively which can be attributed both to N-H in ammines$^{45}$, and O-H stretching vibrations while the sharp band at 1635 cm$^{-1}$ can be due to N-H in ammines$^{45}$, and O-H bending vibrations. In case of leach solution a very sharp peak appears at 3154 cm$^{-1}$ corresponding to only O-H stretching vibration. The peak at 1635 cm$^{-1}$ becomes smaller which may be attributed to only bending mode of O-H. These observations indicate that the leach solution was perhaps free of hydroxyl ammine hydrochloride due to its oxidation during leaching thereby affecting the bands at 3000-3500 cm$^{-1}$ and 1635 cm$^{-1}$ positions. One more very sharp band is also appeared at 1093 cm$^{-1}$ which is a very typical band for ClO$_4$.$^{46,47}$ From FTIR spectra it is envisaged that perhaps reactions given by Eq. (4) do participate in the dissolution process of manganese under the studied conditions. The XRD pattern of leach residue is shown in (Fig. 4). It shows sharp peaks corresponding
to SiO₂ (JCPDS file No 78-1254). There is no peak corresponding to pyrolusite, confirming quantitative dissolution of manganese.

Response surface methodology

Results of a total number of thirty experiments carried out based on central composite design (CCD) using 2^4 factorial design are presented in Table 2. The empirical relationship between % Mn dissolution (Y) and the four variables in coded values obtained by the application of RSM is given by the following equation:

\[ Y = 92.86 - 11.0x_1 + 0.88x_2 + 1.75x_3 + 2.72x_4 - 2.15x_1^2 - 0.78x_2^2 + 0.57x_3^2 - 3.46x_4^2 - 0.029x_1x_2 + 1.67x_1x_3 + 0.20x_1x_4 - 0.024x_2x_3 - 0.088x_3x_4 - 0.042x_1x_4 \]  

... (5)

where Y is the response variable (% Mn extraction); and \( x_1, x_2, x_3 \) and \( x_4 \), the coded values of the independent variables, i.e. pulp density, amount of acid, amount of reductant and time respectively.

The results of analysis of variance (ANOVA) for the model terms are given in Table 3. The significance of the model terms is evaluated by ‘t’ test and P-values. Values of ‘t’ more than 3.5 and smaller P-values indicate the more significant model term. In this case, the first order main effect of pulp density shows Prob > ‘t’ values of <0.0001 with the coefficient value of -11 indicating major influence of this parameter. Second order effect of time is also significant. The interactive effects are not found to be significant in the studied range of parameters.

Optimization using desirability function

A multiple response method, called desirability function (D), was applied for optimizing any combination of four goals, namely pulp density, amount of acid, amount of reductant and time. Desirability is an objective function that ranges from zero outside of the limits to one at the goal. Range of pulp density (25–35% wt/v), acid concentration (6.5–7.5% v/v), amount of reductant (15–16 g) and time (10–30 min) have been set for maximum desirability. A numerical optimization found ten points that maximizes the desirability function. The importance for all of the goals was set to three plusses. Figure 5 shows a graphical desirability generated from 10 optimum points via numerical
optimization. The value of desirability obtained for Mn extraction is found to be one for all the ten points showing that the estimated function may represent the experimental model and the desired conditions. To compare the experimental results, six experimental conditions have been chosen within the desirability of 1. The predicted as well as experimentally obtained values are given in Table 4. An excellent agreement is observed.

Conclusion

Medium grade manganese ore of Gujarat has been leached under self sustained autogenous non-isothermal conditions using hydroxyl ammonium chloride in sulphuric acid medium. The optimum conditions established for maximum recovery of manganese are found to be pulp density 20% (wt/v), $H_2SO_4$ 5% (v/v), reductant 0.55g/g ore and time 20 min. Under the optimum conditions > 97% Mn is dissolved. From the series of experiments it is observed that variation in acid concentration and reductant amount shows pronounced effects on leaching of metal values. In-situ generation of temperature is sufficient for manganese dissolution. Formation of per chlorate is observed from the FTIR spectrum of the leach solution. Response surface methodology is adopted for optimization of parameters based on central composite design (CCD). Four parameters chosen are pulp density, time, amount of reductant, and amount of acid. Maximum desirability is estimated for optimised parameters values within the ranges as pulp density 25–35% wt/v, acid concentration (6.5–7.5% v/v), amount of reductant 15–16 g and time (10–30 min). A numerical optimization has found ten points that maximized the desirability function. Predicted and actual extractions show good agreement.

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References