Hydrochloric Acid Leaching of Sea Nodules with Methanol and Ethanol Addition

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A study has been made to investigate the effects of methanol and ethanol additions in dilute hydrochloric acid leaching of polymetallic sea nodules. In the absence of additives, the hydrochloric acid solution in an aqueous medium (2.75 kmol/m^3) leaches out only copper and iron in considerable amounts and more than 90% recovery of all the metals are achieved only when a very strong concentration of acid (11 kmol/m^3) is used. It has been found that metal recoveries can be considerably improved even in 2.75 kmol/m^3 hydrochloric acid solution if an appropriate amount of methanol or ethanol is incorporated with it. The addition of 75 vol% of methanol in the 2.75 kmol/m^3 hydrochloric acid system has been found to recover more than 90% of each metal. The requirement of ethanol has been found to be 18.5 vol% to achieve the same degree of recovery of metals in dilute hydrochloric acid solution. The effects of other parameters such as period of leaching and acid concentration on the recovery of metals in the alcoholic hydrochloric acid leaching system have also been studied.

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I. Introduction

The polymetallic sea nodules obtained from the Ocean floor contain valuable metals like copper, nickel, cobalt, iron and manganese. These metals are present in the sea nodules as CuO , Ni_3O_4 , Co_2O_3 , Fe_2O_3 and MnO_2 ⁽¹⁾. Cobalt oxide and to some extent nickel oxide are reported to be embeded in the manganese dioxide lattice⁽²⁾. In order to get high recoveries of these metals, they should be released from the manganese dioxide lattice by a suitable treatment of the ore body. A number of processes following hydrometallurgical and pyro-hydrometallurgical routes have been suggested in the literature to recover metals from sea nodules⁽³⁾⁻⁽⁶⁾. Owing to a very high moisture content of the sea nodules, purely hydrometallurgical routes are, however, considered to be more economical. Amongst various hydrometallurgical processes developed, the leaching of sea nodules in mineral acids is considered to be more economical and simpler. Amongst mineral acids, the use of hydrochloric acid in leaching process has drawn special attention as this acid is comparatively cheaper and also the energy requirements in the recovery of metals from the chloride salts by electrometallurgy route is lesser. The processing of sea nodules by this route, however, requires a very high concentration of acid to achieve good recovery of metals⁽⁶⁾. The use of higher concentration of acid not only makes the process uneconomical but also creates other problems such as pollution and necessity of construction of plant machineries using special materials. Attempts were, therefore, made to minimise the acid consumption by the addition of suitable reducing agents like

sodium sulphite, pyrite etc in the leaching system⁽⁷⁾. These processes again suffer from the drawback of high consumption of reducing agents without any possibility of their recycling and thereby increase the impurity level of the final leach solution.

The above-mentioned problems associated with the existing processes led us to explore the possibilities of using such additives which could be helpful in dilute acid leaching at a lower dosing and also could be recycled. It has been reported in the literature that manganese dioxide reacts with hydrochloric acid and ethanol to form manganese chloride⁽⁸⁾. Further, many investigators have also established that the presence of methanol and ethanol in dilute hydrochloric acid solution enhances the dissolution of pure metals⁽⁹⁾⁽¹⁰⁾. It was, therefore, considered interesting to test the leaching of sea nodules in the alcoholic hydrochloric acid solution. The present paper describes the leaching of sea nodules in different concentrations of acid with/without addition of alcohols for the various leaching periods.

II. Experimental

Indian Ocean nodules received from the National Institute of Oceanography, Goa, India was air dried and ground to -152 to $+100 \mu\text{m}$ size. The composition of ground sea nodules is shown in Table 1. All the chemicals used in this study were of analytical grade. Leaching experiments were carried out in conical flasks which were fitted in wrist action shaking machine providing to and fro motion. The speed of the shaking machine (90 oscillations per minute) and the temperature of the experimentation (303 K) were kept constant through out the study. In

Table 1 Composition of ground sea nodules.

Constituents	Percentage by mass
Cu	0.70
Ni	0.90
Co	0.13
Fe	7.40
Mn	18.30
Zn	0.08
Mo	0.04
SiO ₂	16.00
Na ₂ O	0.95
Free moisture	13.67
Loss on ignition	28.20

all the experiments, 20 g sea nodules were taken and the nodule:liquid ratio was kept 1:10 (w/v). In order to optimize the different parameters, the time of leaching was initially fixed at 4 h. This time of leaching was chosen for studies as it was observed that a satisfactory recovery of metals was found to be achieved after this period. The different parameters such as the requirement of acid concentration with/without alcohol addition, amount of alcohol addition and the time of leaching were optimized. Mainly two kinds of solutions were prepared for leaching. These were hydrochloric acid solutions and alcoholic hydrochloric acid solutions. In some of the alcoholic hydrochloric acid leaching systems, the solutions were prepared in such a way that the concentration of acid always remained 2.75 kmol/m³ as below this concentration of acid, poor recovery of metals were observed. Some examples of leaching solution preparation methods are given in Table 2 and other leaching solutions were prepared in similar fashion. All the metal analysis was carried out by Atomic Absorption Spectrophotometer.

To interpret some leaching results, zeta potential of sea nodules in different electrolytes were determined (Table 3). The zeta potential of sea nodules in different electrolytes were measured with the help of a Lazer Zee Meter-Model 501 (PEN KEM INC, USA). The zeta potential measurements were carried out only in dilute acid solutions to avoid the damage of the electrodes of the cell due to the action of strong acid.

Table 2 Leaching solution preparation. Concentration of HCl used for preparation of solution = 11 kmol/m³. Total volume of each of the leaching solution = 2 × 10⁻⁴ m³.

Sl. No.	Leaching solution	Components		
		Acid (m ³)	Alcohol (m ³)	Water (m ³)
1	2.75 kmol/m ³ HCl	5 × 10 ⁻⁵	—	15 × 10 ⁻⁵
2	75 vol% methanolic 2.75 kmol/m ³ HCl	5 × 10 ⁻⁵	15 × 10 ⁻⁵	—
3	18.5 vol% ethanolic 2.75 kmol/m ³ HCl	5 × 10 ⁻⁵	3.7 × 10 ⁻⁵	11.3 × 10 ⁻⁵
4	18.5 vol% ethanolic 2.20 kmol/m ³ HCl	4 × 10 ⁻⁵	3.7 × 10 ⁻⁵	12.3 × 10 ⁻⁵

Table 3

Electrolyte condition	Zeta potential (mV)
Sea nodule in distilled water (pH=7.0)	-50.4
Sea nodule in hydrochloric acid solution (pH=5.2)	-30.2
Sea nodule in hydrochloric acid solution (pH=2.84)	-16.5
Sea nodule in hydrochloric acid solution (pH=1.5)	-12.0
Sea nodule in hydrochloric acid solution (pH=1.5)+5 vol% methanol addition	+15.5
Sea nodule in hydrochloric acid solution (pH=1.5)+5 vol% ethanol addition	+19.2

III. Results and Discussion

1. Hydrochloric Acid Leaching

Figure 1 shows that the percentage recovery of metals increases with the increase in molar concentration of hydrochloric acid solution. More than 90% of Cu, Ni, Co, Fe and Mn are extracted in 11 kmol/m³ HCl leaching of sea nodules. At lower acid strengths, Cu and Fe exhibit better leaching tendency followed by Ni, Co and Mn.

It is reported that highly concentrated hydrochloric

Fig. 1 Effect of the concentration of HCl on extraction of different metals from sea nodules.

acid reduces the manganese dioxide mineral present in the sea nodules and the valuable metals embedded in its lattice are released in the electrolyte to form soluble metal salts⁽²⁾⁻⁽⁴⁾. The reductive dissolution of manganese dioxide may be presented by the following reaction.

The marked decrease in recoveries of metals particularly manganese, nickel and cobalt on lowering the acid concentration may be ascribed to the decrease in activity of chloride ion which is mainly responsible for the reduction of higher valence metal oxides. The leaching of CuO and Fe₂O₃ in dilute hydrochloric acid solution is possible even without any reductive treatment as they are not embedded in the MnO₂ lattice. Moreover, the formation of halogen compounds of copper and iron are quite probable in their oxidation state of (II) and (III), respectively⁽²⁾⁽¹¹⁾.

2. Hydrochloric acid leaching with methanol and ethanol addition

Effects of incorporation of different amounts of methanol and ethanol in 2.75 kmol/m³ HCl on the recovery of metals have been plotted in Figs. 2 and 3. These plots reveal that 2.75 kmol/m³ HCl solution without any alcohol addition affords very poor recovery of Ni, Co and Mn (28, 22 and 16%, respectively) while Cu and Fe recoveries are higher (81 and 58%, respectively). Incorporation of methanol in 2.75 kmol/m³ HCl effectively improves the metal recoveries specially for Mn, Ni and Co (Fig. 2). It can be seen that the leaching of sea nodules in 2.75 kmol/m³ HCl having 75 vol% methanol recovers about 95% Cu, 95% Ni, 90% Co, 97% Fe and 98% Mn. Similarly, it has also been ob-

served that in the ethanolic 2.75 kmol/m³ HCl system, the metal recoveries increase with increasing amount of ethanol additions (Fig. 3).

Better recoveries of metals in dilute HCl (2.75 kmol/m³) leaching system containing methanol and ethanol are probably due to the increase in anion activity (a_{Cl^-}). It has been reported that with the addition of some organic reagents in the aqueous chloride solution, the activity of chloride ion rises sharply⁽¹²⁾⁽¹³⁾. Ethanol is one such reagent. It has been shown that ethanol increases both the cation and Cl⁻ activity and can promote the chloro-complex formation of metal ions⁽¹³⁾.

Figures 2 and 3 show that for the optimum recovery of metals, the requirement of ethanol addition (18.5 vol%) is lesser compared to methanol (75 vol%). Addition of only 18.5 vol% of ethanol in the 2.75 kmol/m³ HCl leaching system recovers about 97% Cu, 98% Ni, 96% Co, 95% Fe and 97% Mn.

In our separate studies we have found that requirements of still higher chain length alcohols such as propanol and butanol are drastically reduced (9 and 4.5 vol%, respectively) to achieve more than 90% recovery of each metal from sea nodules⁽¹⁴⁾. It appears from these results that the requirement of alcohol for a satisfactory recovery of metals decreases as the chain length of alcohol increases. This observed phenomenon has somewhat resemblance with the fact of cationic collector adsorption on the negatively charged hydroxylated mineral oxide surfaces, where the charge reversal of the mineral surface (zeta potential) takes place more efficiently in the presence of lower amount of collectors of longer hydrocarbon chain compared to the shorter chain length. This is due to the fact that hydrophobic bonding energy,

Fig. 2 Effect of addition of methanol in hydrochloric acid leaching of sea nodules.

Fig. 3 Effect of addition of ethanol in hydrochloric acid leaching of sea nodules.

$\Delta G^\circ \text{CH}_2$ increases with the chain length of the organic compound⁽¹⁵⁾⁽¹⁶⁾. Methanol and ethanol are shown to react with hydrogen chloride as follows⁽⁹⁾⁽¹⁰⁾.

In the first few hours the equilibrium reactions (3) and (5) are reported to be very slow⁽⁹⁾⁽¹⁰⁾. As an inorganic group (OH) is attached in both CH_3OH_2^+ and $\text{C}_2\text{H}_5\text{OH}_2^+$, they can be considered as good cationic collectors⁽¹⁶⁾. These cationic collectors (act like proton) are readily adsorbed on the negatively charged sea nodules, which may cause the sign reversal of zeta potential from negative to positive value. To examine this, zeta potentials of sea nodules in different electrolytes were measured, which are shown in Table 3. The zeta potential of water slurried sea nodules is -50.4 mV . The zeta potential of sea nodules in hydrochloric acid solution ($\text{pH}=1.5$) is -12.0 mV which changes to $+15.5 \text{ mV}$ and $+19.2 \text{ mV}$ when 5 vol% methanol and 5 vol% ethanol, respectively are added in the same solution. The higher positive charges acquired by the interface as described above may attract more anions (chloride ions) at the interface which facilitates the reductive dissolution of various metal oxides present in the sea nodules. The primary leaching reaction in the mixed solvent system is, perhaps, as shown below:

This reaction clearly indicates that the alcohols incorporated with the acid during the leaching are regenerated. After leaching in optimised conditions, we had recovered about 30% of each of the alcohols from the filtered leach liquors by distillation method. The lower recoveries are perhaps, due to the evaporation losses of regenerated alcohols during leaching and filtration. Further investigations are being carried out to improve the recovery of alcohols.

The above mentioned interpretation of the results is based on the general mechanism of leaching proposed by Warren and Devuyt⁽¹⁷⁾. However, further study is necessary to collect the kinetic data to confirm the actual mechanism of leaching in the aqueous-acid-organic system.

3. Effect of leaching time on the alcoholic hydrochloric acid leaching

Figures 4 and 5 show the effect of leaching period on the percentage recovery of metals in the methanolic and ethanolic solution of 2.75 kmol/m^3 HCl, respectively. The metal level in the solution is found to decrease after reaching an optimum value at 4 h of leaching in the case of methanolic system. In the case of ethanolic system, the decrease in metal recoveries starts after 5 h. These observed fact may be explained if it is taken into account

Fig. 4 Effect of time in methanol-hydrochloric acid leaching of sea nodules on the recoveries of metal values.

Fig. 5 Effect of time on ethanol-hydrochloric acid leaching of sea nodules.

that formation of equilibrium reaction product CH_3Cl [eq. (3)] is faster than the formation of $\text{C}_2\text{H}_5\text{Cl}$ [eq. (5)] as reported in the literature⁽⁹⁾⁽¹⁰⁾. The formations of CH_3Cl and $\text{C}_2\text{H}_5\text{Cl}$ compounds deplete the free chloride ions concentration in the solution and metal cations perhaps, precipitate as hydroxide.

4. Effect of acid concentration in the alcoholic hydrochloric acid leaching

The possibility of using lesser concentration of hydrochloric acid ($<2.75 \text{ kmol/m}^3 \text{ HCl}$) by the addition of optimum amount of methanol or ethanol in the leaching of sea nodules for the satisfactory recovery of

Fig. 6 Effect of hydrochloric acid concentration in the leaching of sea nodules with methanol addition.

Fig. 7 Effect of hydrochloric acid concentration in the leaching of sea nodules with ethanol addition.

metals was examined and the results are shown in Figs. 6 and 7. It is evident from these figures that the recovery of Ni, Co and Mn is less than 90% in the alcoholic $2.20 \text{ kmol/m}^3 \text{ HCl}$ system. The recovery of metals is found to further decrease with the lowering in acid concentration. This indicates that the availability of lesser chloride ions in the electrolyte due to lower amount of acid used is responsible for the poorer reductive dissolution of these metal oxides. A set of another experiments was therefore, performed in the methanolic $2.20 \text{ kmol/m}^3 \text{ HCl}$ system with the addition of 25 g sodium chloride in the electrolyte. The results showed that the extra chloride ions in the form of NaCl did not improve the metals recovery. This indicates that the decrease in $\text{H}_3\text{O}^+/\text{CH}_3\text{OH}_2^+/\text{C}_2\text{H}_5\text{OH}_2^+$ concentration as a result of using a lesser amount of acid was also responsible for the poorer recovery of metals. Therefore, a minimum $2.75 \text{ kmol/m}^3 \text{ HCl}$ is required to achieve satisfactory recovery ($>90\%$) of metals for the leaching of sea nodule in the alcoholic acid systems.

IV. Conclusion

(1) Leaching of sea nodules with hydrochloric acid in an aqueous medium ($2.75 \text{ kmol/m}^3 \text{ HCl}$) yields good recoveries of copper and iron but very poor recoveries of nickel, cobalt and manganese.

(2) In the concentrated hydrochloric acid (11 kmol/m^3) leaching, the recovery of all the metals are found to be more than 90%.

(3) Addition of alcohol in dilute hydrochloric acid (2.75 kmol/m^3) leaching of sea nodules improves the recoveries of all metals.

(4) The requirement of ethanol for the satisfactory recovery of metals ($>90\%$) is lesser compared to methanol.

(5) The optimum recovery of metals can be achieved in the HCl-methanol and HCl-ethanol systems in 4 to 5 h time beyond which the precipitation of metals takes place.

(6) The minimum acid concentration for the good recovery of metals from the sea nodules has been found to be $2.75 \text{ kmol/m}^3 \text{ HCl}$ in the presence of methanol or ethanol.

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