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Simultaneous recovery of manganese and zinc from electrolyte paste of spent zinc-carbon dry cell battereis

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ABSTRACT

Electrolyte paste of spent zinc-carbon dry cell batteries were leached in sulfuric acid with hydrogen peroxide as a reducing agent. Effects of operating variables such as, concentration of sulfuric acid and hydrogen peroxide in the leaching solution, temperature, stirring speed and solid/liquid ratio were investigated to determine the optimum leaching conditions. Optimum leaching conditions were identified as: concentration of sulfuric acid: 2.5M, concentration of hydrogen peroxide: 10 %, Temperature: 60^0C, stirring speed: 600 rpm; and solid-liquid ratio 1:12. Under these conditions a maximum of 88% manganese could be dissolved from the electrolyte paste within only 27 minutes of leaching. Dissolution of zinc under the same conditions was 97%. A maximum of 83.29% of zinc could be precipitated from the leach liquor in the form of oxalate while the precipitation of manganese in the form carbonate was 69.89%.

KEYWORDS

Dry cell battery;
Leaching;
Hydrometallurgy;
Manganese recovery;
Zinc recovery.

INTRODUCTION

Zinc-carbon dry cell batteries have a limited life and are discarded at the end of useful life. In recent years the generation of dry cell battery wastes and its subsequent disposal with the municipal solid waste has increased significantly. The disposal of waste dry cell batteries with municipal solid waste is being viewed as a serious environmental problem. At the same time the quantum of metal values contained in these batteries is also significant. Due to continuous depletion of natural ore bodies, these batteries are now being considered as secondary source of such metals as manganese and zinc. Thus recovery of metal values from spent Zn-C dry cell batteries can reduce the amount of solid waste to be disposed and at the same time be a secondary source of metals. Increased attention is, therefore, being given to the recovery of metal values from such wastes.

Both hydro-, and pyro-metallurgical processes have been developed for the recovery of metal values from spent dry cell batteries[1, 2]. Early attempts for the recovery of metal values from the spent dry cells concentrated on the pyrometallurgical processes. Environmental concern and high energy consumption in pyrometallurgical processes have shifted the emphasis towards the hydrometallurgical processes[3, 4]. Effects of pre-treatment of the electrolyte paste on the extent of recovery of metal values have also been examined[4, 5]. The electrolyte paste was washed with water to reduce the chlorine content of the zinc-carbon type batteries; and to remove KOH from alkaline batteries[4]. Washing with water lowers the weight of electrolyte paste for subsequent leaching and also increases the metallic portions on it.

Leaching in both acids and bases has been tried for dissolution and subsequent recovery of zinc and manganese. The basic leaching generally involves a two step process; in the first step, zinc is removed by leaching in basic media like in NaOH, Na_2CO_3 etc[5]. In this condition, less than 0.1% manganese is dissolved in the leach liquor. In the second step, the remaining solid residue is again leached in acids to recover manganese.

In the acidic leaching process, H_2SO_4 was found to be the most efficient leaching agent to dissolve the metallic values from the electrolyte paste[6]. However, manganese dissolution was very low when only sulfuric acid was used as a leaching reagent. Introduction of a reducing agent with the acid enhances the dissolution of manganese. A variety of reducing agents like oxalic acid, ascorbic acid, citric acid, ozone, sulfur dioxide, sulfur dioxide/oxygen mixture etc. have been tried to increase the extent of dissolution of manganese[7-9]. The addition of H_2O_2 as a reducing agent to recover manganese has also been tried[5]. However, a complete documentation on the use of H_2O_2 as a reducing agent in the leach liquor is still unavailable. H_2O_2 is an oxidizing agent, in presence of strong oxidizers like MnO_2, it acts as a strong reducing agent[5].

In the present study, simultaneous dissolution of zinc and manganese in H_2SO_4 containing H_2O_2 as a reducing agent has been investigated. Effect of pre treatment, primarily washing, of the electrolyte paste on the extent of dissolution of zinc and manganese has also been explored. The optimum values of the variable parameters like concentration of H_2SO_4, concentration of H_2O_2, temperature, stirring speed and solid/liquid ratio were determined. The value metals, zinc and manganese, were precipitated from the leach liquor and the separated products were characterised.

EXPERIMENTAL

Spent zinc-carbon batteries of all types (AAA, AA, C, D and 9V) were collected from local sources. The batteries were dismantled manually and different component parts were separated. Electrolyte paste from all types of batteries was mixed together for subsequent processing. Electrolyte paste was put in water at 80°C and stirred at 1000 rpm for 3 hours. Later, the washed electrolyte paste was dried in an oven at 110°C to a constant weight and was used for the leaching experiments.

A 500 ml three necked round bottom flask with a mechanical stirrer, a thermometer and a refluxing con-

TABLE 1 : Leaching experimental designs (Particle size and time were kept fixed)

No. of Experiments	Parameters studied	Parameter Values	Constant Parameters
1	Concentration of leaching reagent (H_2SO_4)	0.5M	H_2O_2 concentration 6%, temperature 50°C, stirring speed 400 rpm, solid/liquid ratio 1:5
2		1 M	
3		1.5 M	
4		2 M	
5		2.5 M	
6		3.0 M	
7	Concentration of Hydrogen peroxide	0%	H_2SO_4 concentration 2.5M, temperature 50°C, stirring speed 400 rpm, solid/liquid ratio 1:5
8		3%	
9		6%	
10		10%	
11		12.5%	
12	Temperature	40°C	H_2SO_4 concentration 2.5M, H_2O_2 concentration 10%, stirring speed 400 rpm, solid/liquid ratio = 1:5
13		50°C	
14		60°C	
15		70°C	
16	Stirring Speed	200 rpm	H_2SO_4 concentration 2.5M, H_2O_2 concentration 10%, temperature 60°C, solid/liquid ratio = 1:5
17		400 rpm	
18		600 rpm	
19		800 rpm	
20	Solid/Liquid ratio	1:5	H_2SO_4 concentration 2.5M, H_2O_2 concentration 10%, temperature 60°C, stirring speed 600 rpm
21		1:8	
22		1:12	
23		1:15	

denser was used for leaching. Leaching was done in sulfuric acid solutions in presence of hydrogen peroxide as a reducing agent. Each time 20 gm of dried electrolyte paste was taken in the leaching solution under predetermined experimental conditions (TABLE 1). Manganese in solution was analyzed by a Shimadzu UV-Vis spectrophotometer using potassium periodate (KIO_4) as a complexing agent. Analysis of zinc was carried out in SensAA atomic absorption spectroscope. Average composition of the dried electrolyte paste was determined by analyzing three randomly taken samples by x-ray fluorescence (XRF) spectroscopy.

RESULTS AND DISCUSSION

Pretreatment of the electrolyte paste

Before leaching in sulfuric acid solution, spent battery paste was washed in warm water to reduce the weight of the paste by removal of nonmetals such as chlorine. Water washing of the electrolyte paste removed over 67% of chlorine, consequently increasing the value metal portions in the paste. X-ray fluorescence analysis of the dried and water washed spent electrolyte paste is shown in TABLE 2.

TABLE 2 : X-ray fluorescence analysis of the spent and water washed electrolyte paste*

Elements (%)	Cl	Mn	Zn	Other minor elements
Electrolyte paste (as-received)	14.44	60.1	22.07	3.72
Electrolyte paste (water washed)	4.77	61.4	31.1	2.73

*Excluding the amounts of C, H and N

TABLE 3 : Elemental analysis of the spent electrolyte paste for determination of C, H and N

Elements	Percentage in paste	Total C, H and N percentage
C	4.370	5.43
H	0.411	
N	0.653	

Although the proportion of zinc and manganese in the water washed sample increased, chlorine could not be removed completely (TABLE 2). Moreover, atomic absorption spectroscopic analysis showed the presence of around 3% zinc in the wash water. Therefore, water washing of the spent battery paste was not considered to be beneficial and was omitted. The amounts of carbon, hydrogen and nitrogen in the paste were detected by EuraEA Elemental Analyzer machine and the result is shown in TABLE 3.

Leaching

The electrolyte paste was leached in sulfuric acid solutions to dissolve manganese and zinc. Hydrogen peroxide was added to the sulfuric acid solution to reduce manganese. The recovery of the value metals in solution was accomplished by precipitation of zinc as zinc oxalate and of manganese as manganese carbonate. Initial leaching experiments were continued for 120 minutes. It was, later, found that leaching for a period of 75 minutes for manganese and 50 minutes for zinc was sufficient to observe the effects of different variables on the leaching of manganese and zinc. The effects of process parameters on the extent of leaching were determined to identify the optimum leaching conditions.

Effect of sulfuric acid concentration

The effect of sulfuric acid concentration, in the range 0.5 to 3M, on the extent of dissolution of manganese from the electrolyte paste was investigated. Dissolution of manganese was found to increase up to sulfuric acid concentration of 2.5M. At higher concentrations, the extent of dissolution decreased to some extent. This may be attributed to the formation of Caro's acid at higher concentrations of sulfuric acid[9].

$$H_2SO_4 + H_2O_2 \rightarrow H_2SO_5 \text{ (Caro's acid)} + H_2O$$

$$Mn^{2+} + H_2SO_5 + H_2O \rightarrow MnO_2(s) + 2H^+ + H_2SO_4$$

The dissolution of zinc showed a trend similar to that of manganese up to sulfuric acid concentrations of 2.5M (Figure 2). However, above this concentration, the extent of dissolution of zinc continued to increase in contrast to that of manganese. As the amount of zinc in the electrolyte paste is only around one third to that of manganese, 2.5M sulfuric acid was taken to be the optimum for simultaneous leaching study of manganese and zinc.

Effect of hydrogen peroxide concentration

Leaching without any H_2O_2 addition to the acid solution was rather slow. The dissolution of manganese reached only 25% in 23 minutes of leaching, which further increased to 39% in 75 minutes. Zinc dissolution under this condition was only around 20%. The extent

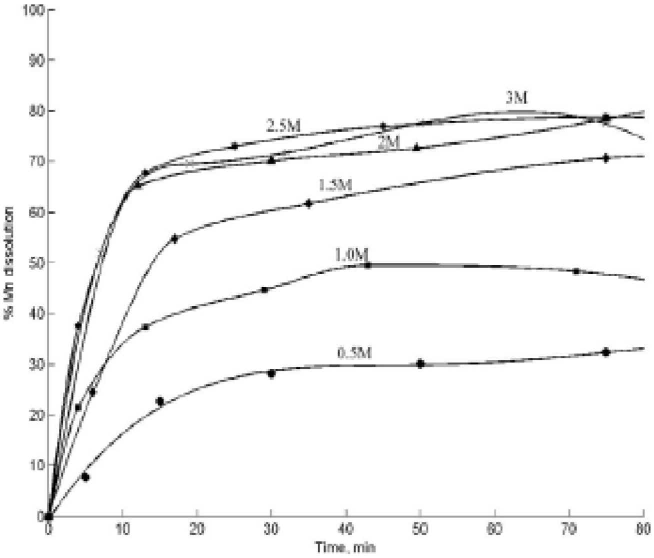

Figure 1 : Effect of H_2SO_4 concentration on manganese dissolution percentage

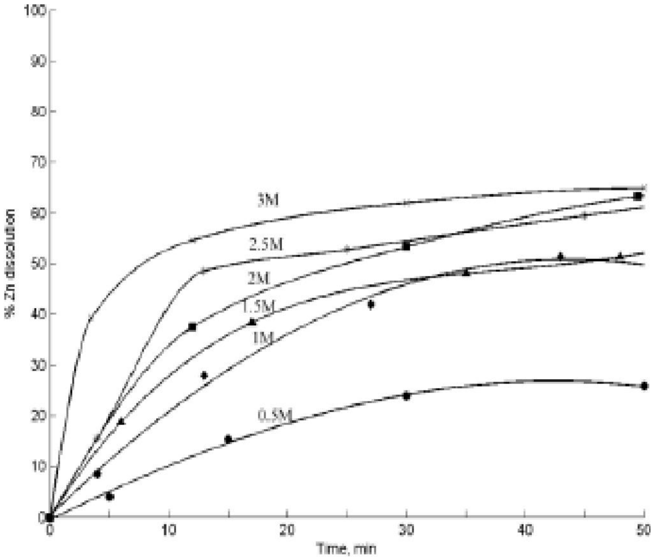

Figure 2 : Effect of H_2SO_4 concentration on zinc dissolution percentage

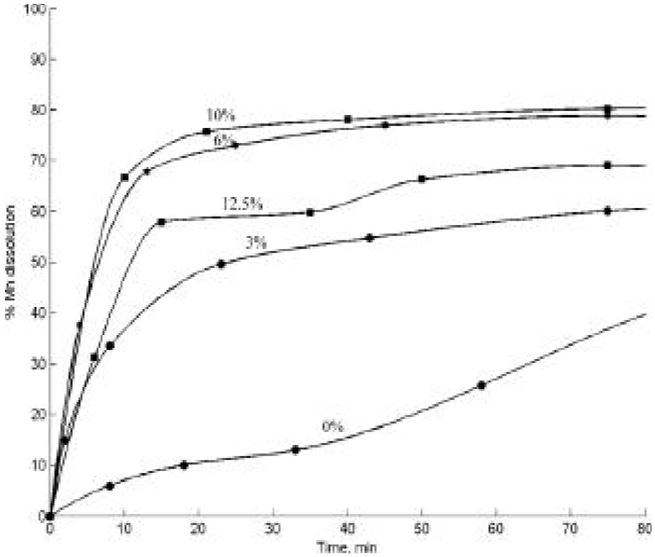

Figure 3 : Effect of H_2O_2 concentrations on dissolution efficiency of manganese

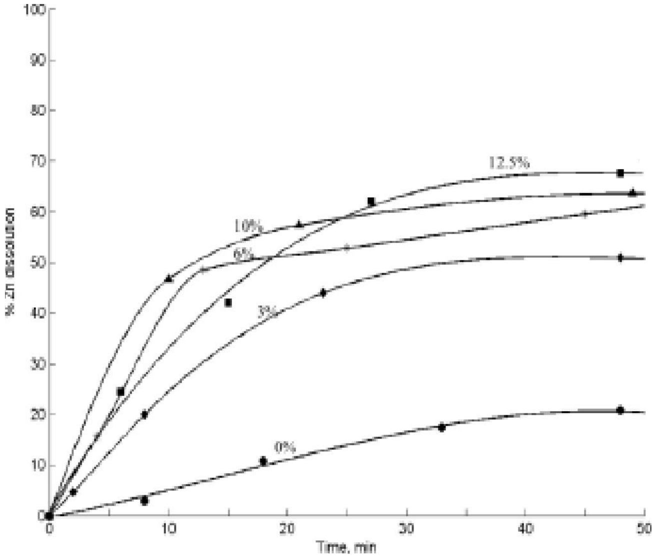

Figure 4 : Effect of H_2O_2 concentrations on the dissolution efficiency of zinc

of dissolution of manganese and zinc with varying hydrogen peroxide concentration in the leaching solution are shown in Figure 3 and Figure 4.

Addition of up to 10% H_2O_2 to the leaching solution increased the extent of dissolution of both manganese and zinc (Figure 3 and Figure 4). At higher percentages of H_2O_2, excessive swelling occurred in the electrolyte paste due to the formation of CO_2. This swelling caused mechanical loss of electrolyte paste at 12.5% H_2O_2 and the extent of dissolution of both the elements decreased significantly. However, up to 10% H_2O_2 in the leach liquor, the dissolution of manganese and zinc was quite satisfactory, reaching 70% and 60% respectively within 30 minutes of leaching. Thus addition of 10% H_2O_2 was considered to be the optimum quantity.

Effect of temperature

Temperature was varied from 40°C to 70°C, keeping the other variables in the leaching experiment constant. Up to 60°C, the dissolution of manganese and zinc was fast at the initial stages of leaching. The rate of leaching did not increase significantly after about 10 minutes of leaching (Figure 5 and Figure 6). At 70°C,

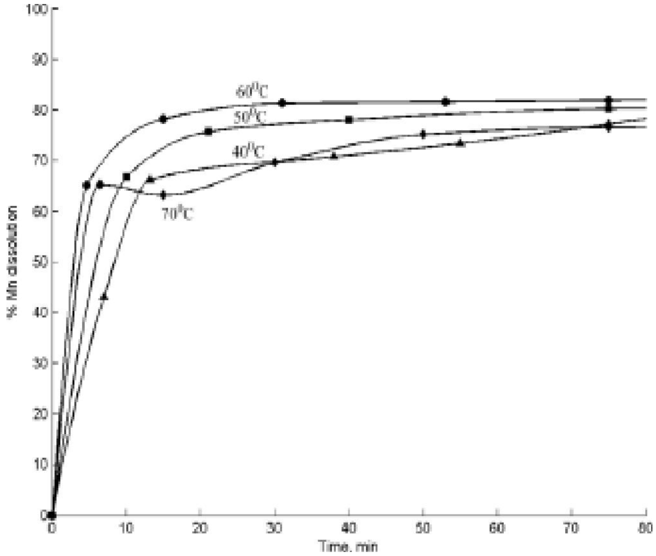

Figure 5 : Effect of temperatures on dissolution percentage of manganese

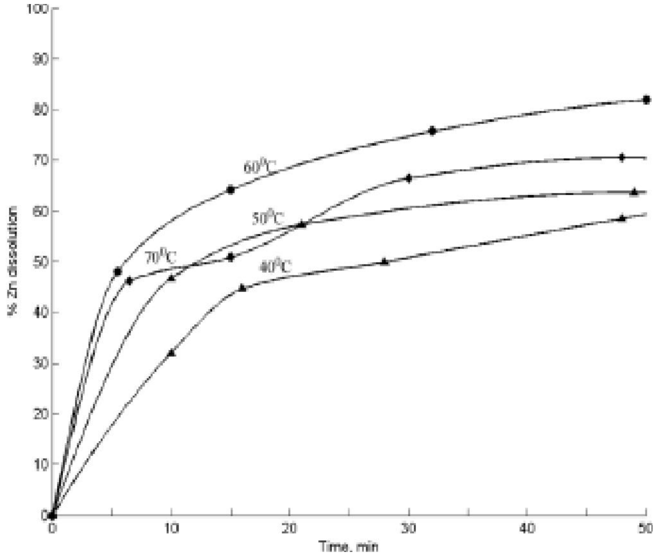

Figure 6 : Effect of temperatures on dissolution percentage of zinc

the extent of dissolution of both the elements dropped drastically. This has been attributed to the decomposition of H_2O_2 at this high temperature[10].

The extent of dissolution of manganese and zinc increased with time at all temperatures under investigation. The increase was significant during the first 10 minutes of leaching. For manganese, recovery was up to 80% within only 21 minutes, and zinc dissolution reached to 75% within 32 minutes of leaching at 60⁰C.

Effect of stirring speed

Stirring speed was varied from 200 to 800 rpm to determine the effect of stirring on the extent of dissolution of manganese and zinc. These effects are shown in Figure 7 and Figure 8.

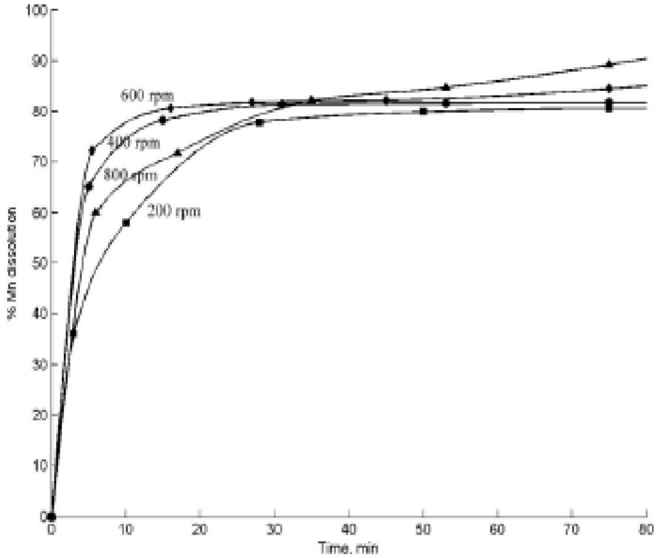

Figure 7 : Effect of stirring speed variations on the extent of dissolution of manganese

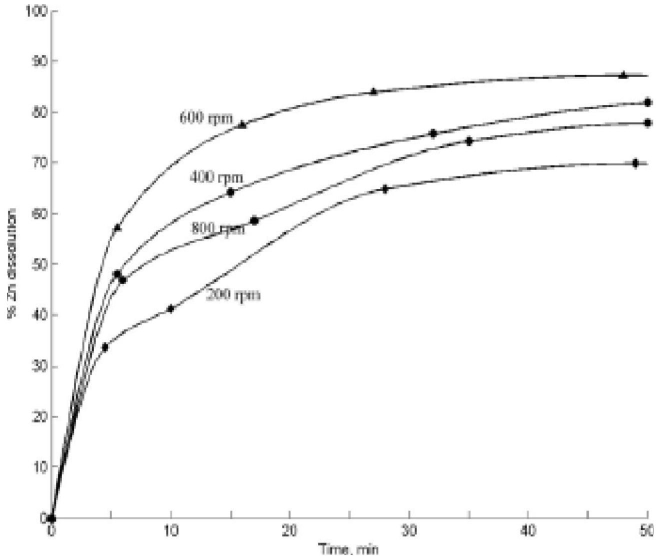

Figure 8 : Effect of stirring speed variations on the extent of dissolution of zinc

The extent of dissolution increased with increasing stirring speed, up to 600 rpm. At a stirring speed of 800 rpm a spilling out tendency was observed and it was difficult to contain the leach liquor within the reaction vessel. Hence, for the first 5-6 minutes, the solution was needed to be kept in without stirring condition. At 800 rpm, the extent of dissolution surpassed that of 600 rpm only at higher time periods. Therefore, 600 rpm stirring speed was taken to be the optimum for maximum recovery of manganese, keeping the other

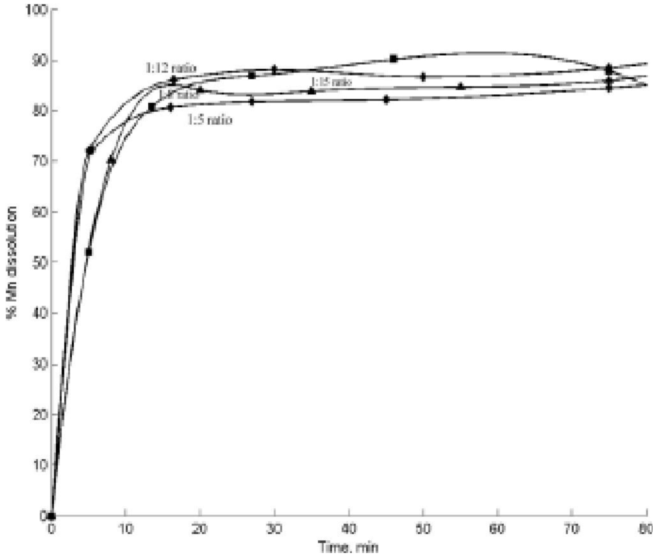

Figure 9 : Effect of solid/liquid ratio on the dissolution percentage of manganese

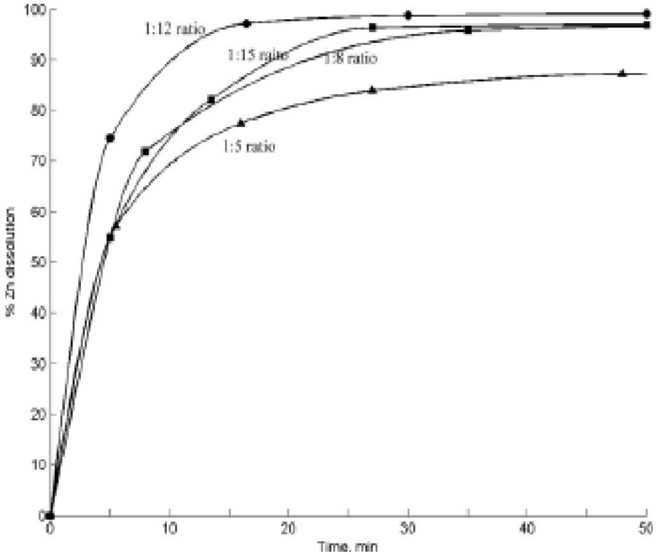

Figure 10 : Effect of solid/liquid ratio on the dissolution percentage of zinc

variables constant.

Effect of solid/liquid ratio

The ratio of solid to liquid was varied from 1:5 to 1:15. The effect of solid/liquid ratio on the extent of dissolution of manganese was not very significant. Dissolution of manganese increased from 80 to 88 percent within 20 minutes with an increase in the solid/liquid ratio from 1:5 to 1:12. However, under the same situation, zinc dissolution increased from 80 to 97 percent. The leaching curves of manganese and zinc for different solid/liquid ratios are shown in Figure 9 and Figure 10.

Dissolution of both manganese and zinc increased with an increase in the solid/liquid ratio up to 1:12. Above this, manganese dissolution did not increase and percentage zinc dissolution was found much lower. The reason for this decrease in the extent of dissolution of both manganese and zinc at a solid liquid ratio of 1:15 is not clearly understood and needs further investigations.

Precipitation study

A stock solution containing zinc and manganese was prepared by dissolving around 300gm of battery paste. 100 ml solution was taken from the stock solution and was diluted to 300 ml. 1M oxalic acid was slowly added to the solution at 60^0C which was stirred constantly by a magnetic stirrer. The pH was adjusted to 0 to precipitate zinc as zinc oxalate[12]. Small amounts of manganese and iron co-precipitated with zinc oxalate which can be observed from the AAS analysis of the solution (TABLE 4).

TABLE 4 : AAS analysis of zinc and manganese in solution after precipitation

Solution	Zn (ppm)	Fe	Mn (ppm)
Stock solution	14394	701	23782
After Zn separation	335.41	658.61	21910.23
After Fe separation	325.44	96.48	16622
After Mn separation	162.17	51.74	0.272

For the precipitation of iron pH was adjusted to 4.5 by adding concentrated sodium hydroxide to the solution. A small amount of manganese also co-precipitated with iron at this pH. After removal of iron concentrated Na_2CO_3 was added to the solution to precipitate manganese as manganese carbonate. The AAS analysis of the remaining solution showed that only 0.272 ppm manganese remained in the solution. Co-precipitation of zinc and iron with manganese carbonate was not significant (TABLE 4).

X-ray diffraction analysis of the precipitated salts confirmed that zinc was precipitated as zinc oxalate (Figure 11) and manganese was precipitated as manganese carbonate (Figure 12). The presence of any other phase could not be detected possibly due to very small quantity.

83.29% of zinc contained in the solution could be precipitated as zinc oxalate while 69.89% of manganese could be precipitated as manganese carbonate.

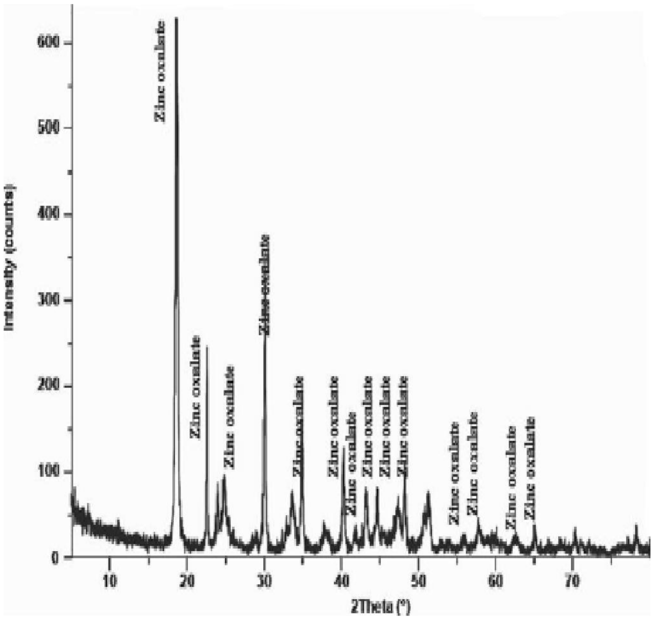

Figure 11 : X-ray diffraction pattern of the precipitate zinc oxalate

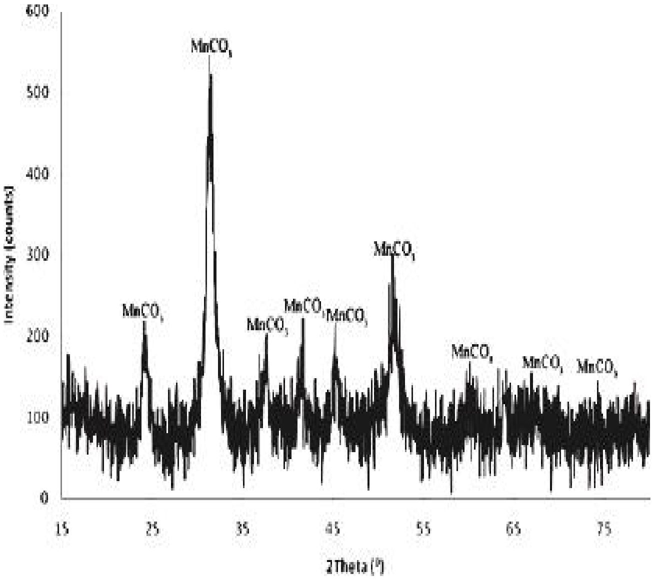

Figure 12 : X-ray diffraction pattern of the precipitate manganese carbonate

CONCLUSION

The optimum conditions for simultaneous leaching of zinc and manganese in the electrolyte paste contained by spent zinc-carbon dry cell batteries in sulfuric acid solutions containing hydrogen peroxide can be summarized as:

Sulfuric acid concentration = 2.5M, Hydrogen per oxide concentration = 10%, Temperature = 60^0C, Solid/ Liquid ratio = 1:12 and Stirring Speed = 600 rpm.

Under such conditions a maximum of 88 % manganese and 97% zinc could be dissolved in 27 minutes.

By controlling pH of the leach liquor, a maximum of 69.89% manganese could be precipitated as manganese carbonate while a maximum of 83.29 % zinc could be precipitated as zinc oxalate.

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