CHAPTER 3
RESULTS

3. RESULTS

3.1 THE CHEMICAL COMPOSITION AND THE COMPONENTS OF ZINC-MANGANESE DRY BATTERY CELL

Table (11) shows the chemical composition and the components of the fresh zinc–manganese battery cell as well as the spent sample. For simplicity, 100Kg of spent batteries and 5Kg of fresh one were examined. It is seen that:

1. There is no correlation between the battery size and its chemical composition. However, variable weight percentages of the chemical constituents are specifically determined for certain battery mark sizes; a matter seems to be dependent or related to the patent of the manufacturing technology of the dry battery cell.

2. The weight loss during mechanical cutting of the dry battery cell, results from the toothed cutting disc of the machine. The loss weight percent value is more or less constant for a given battery size. It is also inversely proportional to the cell size and weight. In another words, weight loss percentage decreases with increasing the size of the dry battery cell.

3. The external envelope of the cells is made of printed hard paper in some types or thin steel sheets in other types. This causes a marked

difference in the global weight of the battery cells. However, most of the dry cell batteries in Egypt are usually produced having a paper envelopes.

4. The steel discs sealing the dry battery cells are made of galvanized steel having a 150um in thickness. The weight percentage of these sealing discs is nearly constant for all sizes or the different types.

5. There is a considerable difference in the weight of the zinc cans of the different types and sizes of the fresh dry battery cells. With small battery size "AA", the weight percentage of the zinc cans amounts to 28%. The corresponding value for the "D" size is 14.3%. Determination of the weight percent of zinc cans of the spent dry battery samples reveals that it varies according to the life time of the cell, the extent of discharging and the storage periods. In other words, a wide range of the weight of metal zinc in the spent battery cells is seen.

6. Some water-soluble salts amounts to 5.7% of the total weight of the fresh battery cell of size "AA" and "D". This value decreased to 4.5 % for the battery size "C".

7. The weight percent of the black paste of the fresh types ranges from 47.3% to 34.1% according to the patent technology of the producer.

8. Determination of moisture content reveals that this property amounts to 17 - 18%. Spent batteries contain only 11.7%.

Table (11), The chemical composition and components of the fresh and spent zinc-manganese battery cell having different types and sizes.

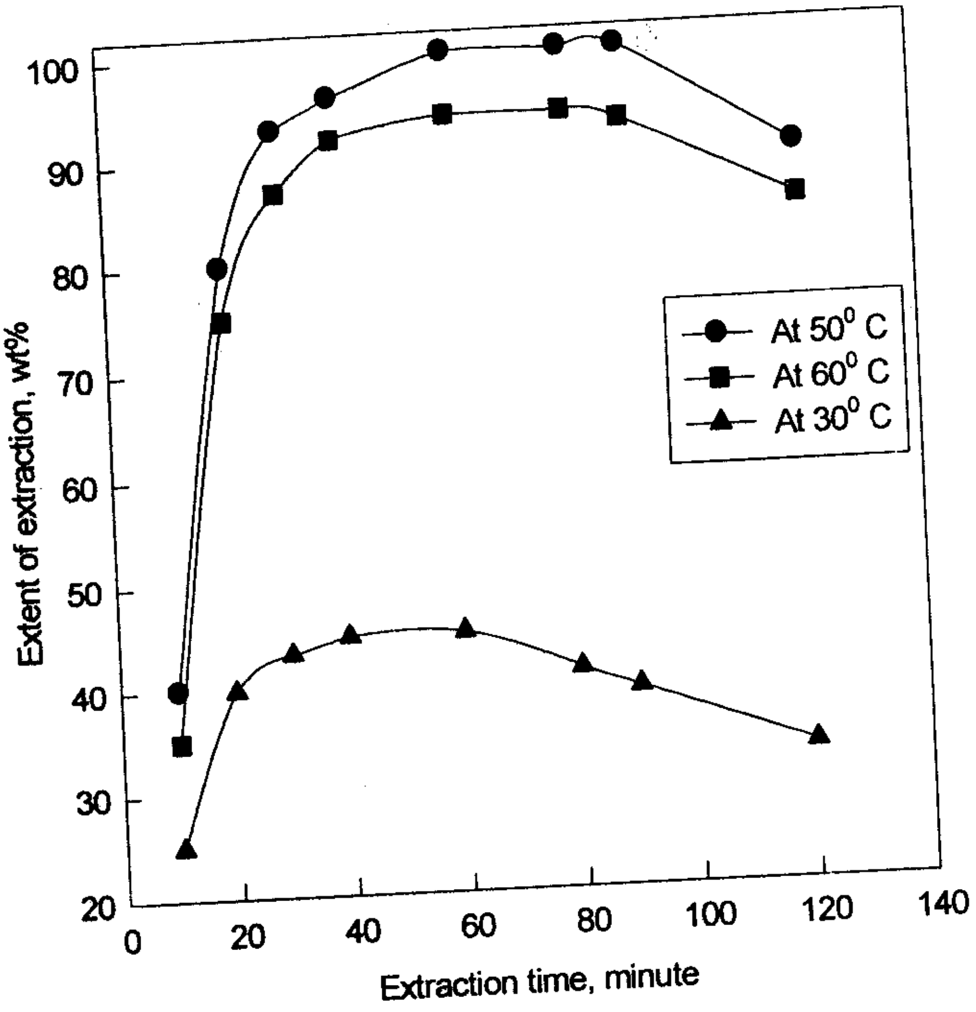
Component	Fresh (unused) battery sample				Spent battery all sizes and ages wt %
	Type A		Type B		
	Size D wt %	SizeAA wt %	Size D wt %	Size C wt %	
Loss on cutting	0.09	0.18	0.06	0.11	0.06-0.18
Paper	4.72	4.2	13.1	17.2	9.0
Steel	4.75	3.7	3.6	3.9	4.2
Zinc (can)	14.3	28.0	16.7	16.6	8.0
C.rod	5.6	6.4	4.9	4.7	6.5
Water soluble salts	5.7	5.7	5.68	4.5	6.0
- Zn^{2+}	–	–	–	–	0.144
Black paste	47.3	34.3	39.0	34.1	54.5
- carbon black	–	–	–	–	6.85
- Zn^{2+}	0	0	0	0	6.9
Moisture	17.6	18.0	17.0	18.0	11.7
Total	100	100	100	100	100

3.2 SEPARATION OF THE WATER- SOLUBLE COMPONENTS OF THE SPENT DRY BATTERY CELLS

3.2.1 Separation the Whole Mass of Soluble Salts from the Spent Dry Battery Cells

The sample of the spent battery cells was placed in a suitable plastic or glass container containing a suitable quantity of water. The charge was then agitated with the help of a mechanical propeller. This water leaching process was repeated three successive times for a suitable period. Different leaching conditions are applied. These include the quantity of the water used, temperature and time. Different sets of experiments are carried out under specific leaching conditions, provided that only one factor of the above mentioned factors is subject to change. After each experiment, the charge was left for complete settlement of the solids. Process water was removed by decanting. The residual slurry was then filtered. The filtrate was added to the process water and the whole quantity was re-filtered using a narrower sieving medium.

After filtration, the water-soluble salts in the process water are qualitatively and quantitatively determined. Fig. (7), shows the efficiency of leaching the water- soluble salts as affected by the leaching time up to 120 minutes using cold (30^0 C) and hot ($50\&60^0$ C) water. In this set of the experiments, the used solid: liquid (S: L) mass ratio is kept constant at 1: 5. It is seen that the extent of extraction increases drastically with increasing in the time during the early periods of leaching. However, with hot water, a plateau of the maximum value is achieved after 60 and 50 minutes using hot water at 50 and 60^0 C respectively. Extraction using



Fig(7) The effect of leaching time on the extent of extraction of the water- soluble salts, at pH 7.8 and S: L mass ratio 1: 5

cold water, 30 ° C, yields a lower leaching extent (45%). The complete leaching amounting to (100%) is acquired with hot water (50°C).

Fig. (8), shows the extent of extraction of these water-soluble salts as a function of the liquid: solid (L: S) mass ratio at 50° C . It can be seen that the extent of extraction proceeds with increasing the (L: S) mass ratio. A maximum extent of leaching is attained with L: S value of 5: 1. It is also seen a gradual decrease in the extent of extraction with further increasing the used water weight ratio or decreasing the solid weight.

Fig. (9), shows the effect of leaching temperature on the extent of leaching of the water- soluble salts from the spent batteries. In these experiments, the S: L mass ratio is kept constant at 1: 5. It can be seen that an inverted parabola-shaped curves are obtained, the maximum value of which (100% extent) is achieved at 50 ° C and after 60 minutes. It is clear that the maximum extent of leaching amounts to 100%, 90% and 80% after leaching for periods of 60, 120 and 20 minutes respectively.

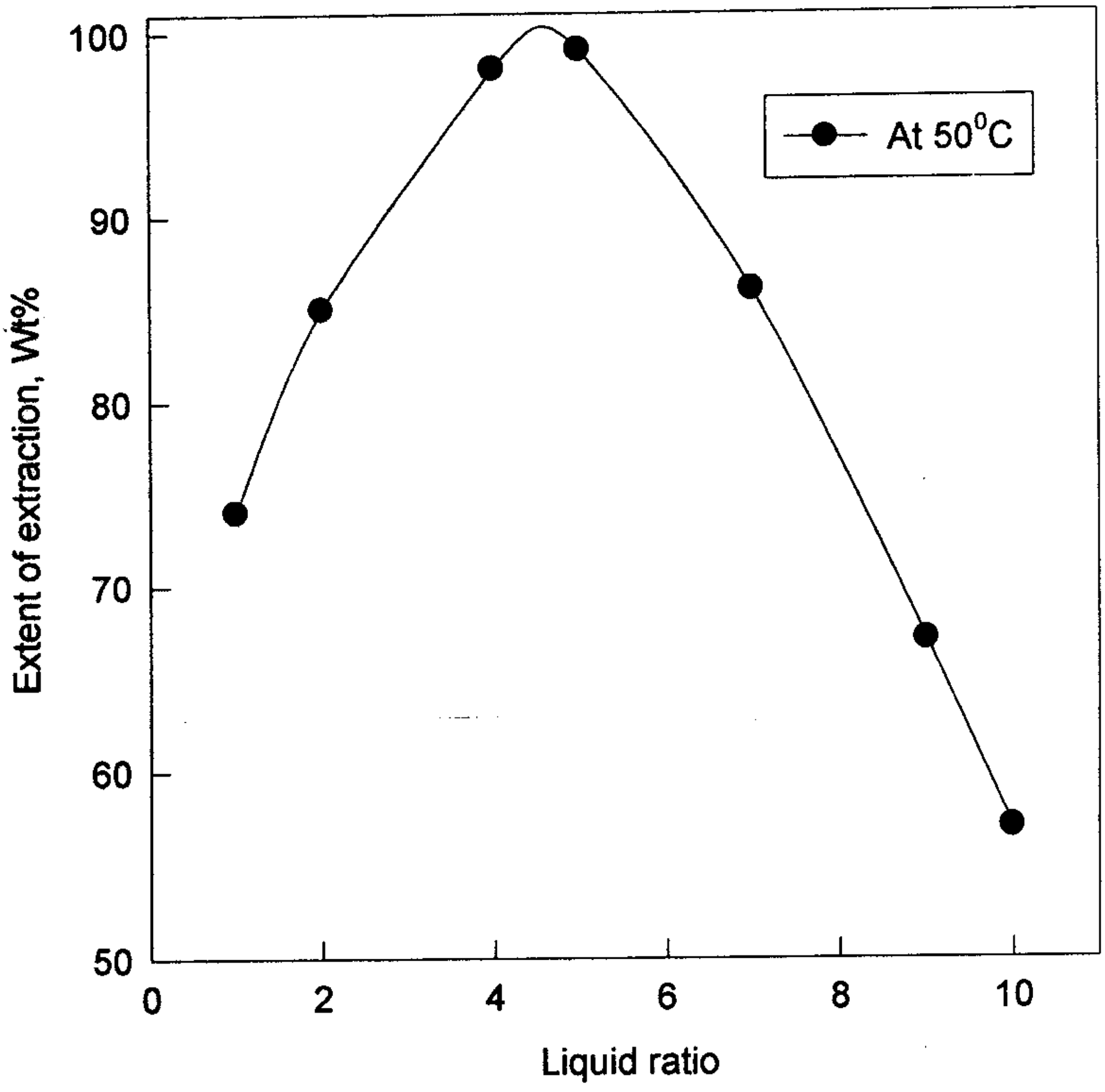


Fig. (8), Effect of liquid ratio on the extent of extraction of water soluble salts at t = 60 min.

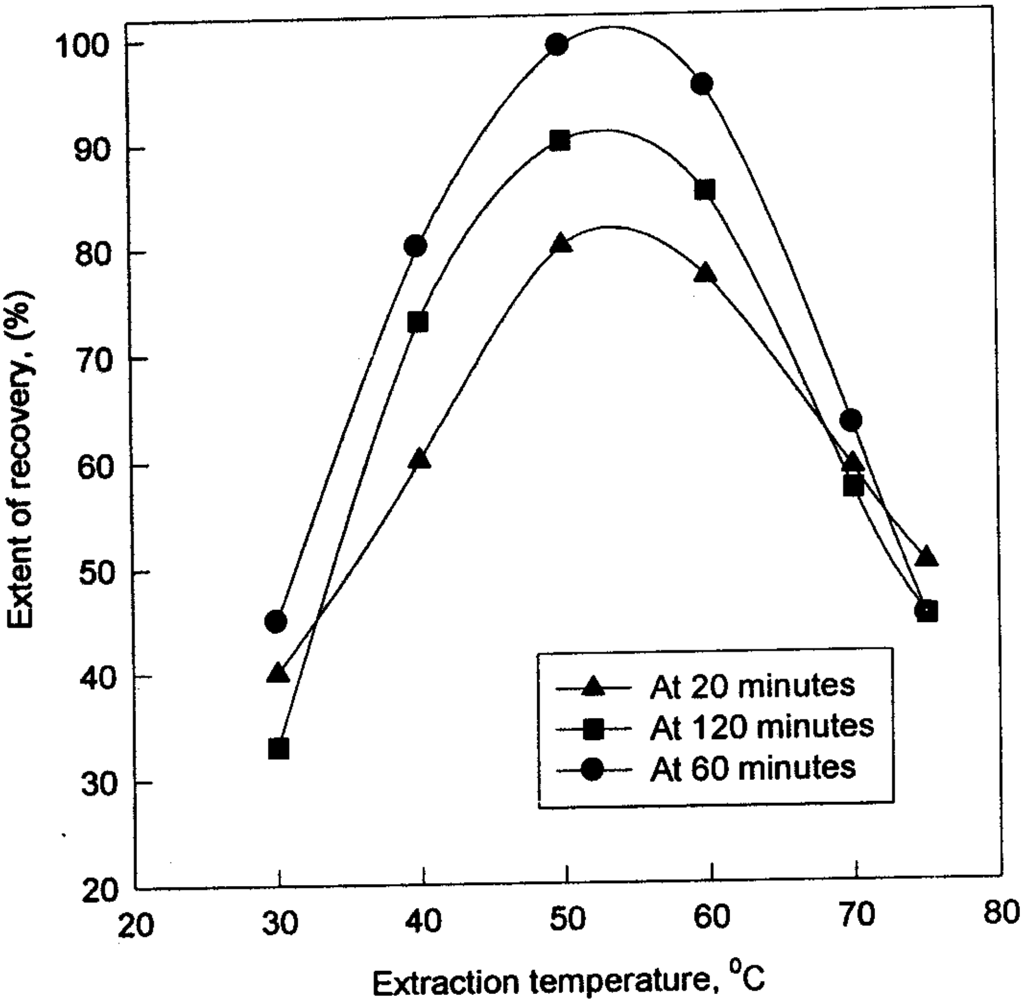


Fig.(9) The effect of extraction temperature on efficiency of recovery of white paste % at pH 7.8 and S: L ratio 1: 5

3.2.2 Recovery of the Chemical Compounds Constituting the Water-Soluble Salts (White Paste)

The leached water-soluble salts are identified. These are white crystalline salts, liberate ammonia gas after reacting with sodium hydroxide. The salts are also analyzed with an atomic absorption photometry and X- ray diffractometry.

Fig. (10), and table (12) show the XRD chart and its physical data. Results reveal the presence of ammonium chloride and water- soluble zinc and manganese compounds. The presence of soluble zinc and manganese compounds is emphasized with atomic absorption photometry according to table (13).Table (14) represents the composition of the white paste.

Table (12), XRD chart physical data

2θ	d	I	Intensity value, %	compound
26.4	3.92	2.0	17.7	NH_4Cl
29.0	3.5751	0.5	4.4	-
32.8	3.1704	1.2	10.6	-
34.8	2.99335	0.8	7.1	-
37.8	2.76347	11.3	100.0	NH_4Cl
46.8	2.25391	0.6	5.3	NH_4Cl
54.8	1.9451	0.9	7.9	NH_4Cl
62.0	1.738	0.8	7.1	NH_4Cl
68.6	1.58845	1.5	13.3	NH_4Cl
81.4	1.3727	1.1	9.7	NH_4Cl
87.4	1.29564	0.4	3.5	NH_4Cl

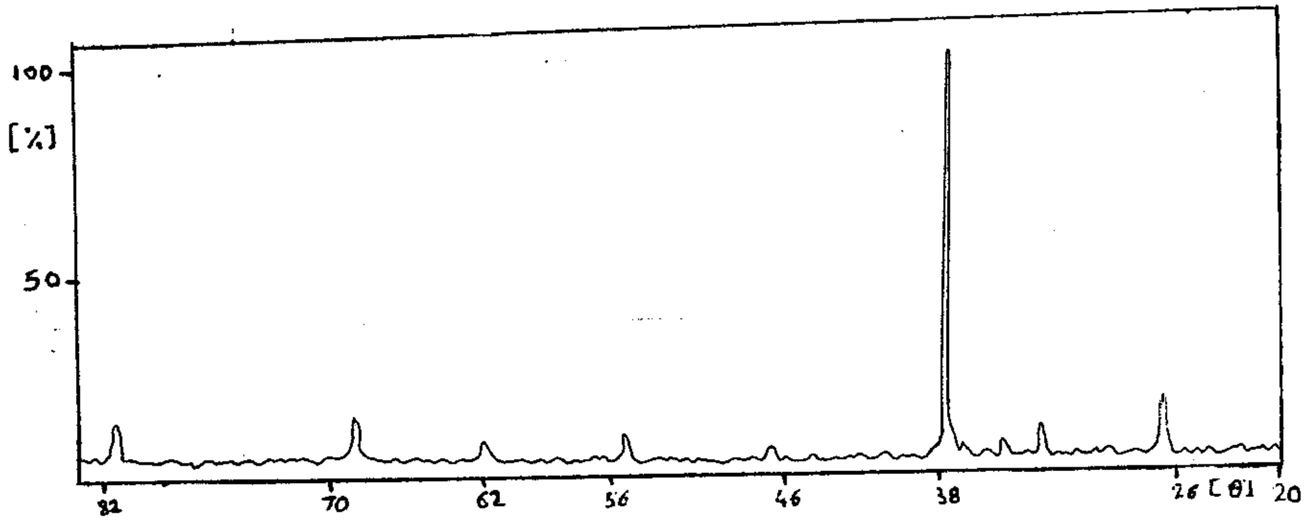


Fig.(10): XRD chart of white paste

Table (13), Atomic absorption analysis for Zn^{2+} and Mn^{2+} of the white paste

Cation	Concentration, %
Zn^{2+}	2.4
Mn^{2+}	0.13

Table (14), Composition of the extracted water-soluble salts

Compound	Weight, %
Ammonium chloride	94.93
Zinc chloride	4.80
Manganese chloride	0.27

In the light of these facts, it is necessary to study the extraction of these chemical compounds separately.

3.2.2.1 Recovery of manganese compounds

Experiments were carried out to recover manganese compounds and then zinc salts. Manganese compounds are successfully recovered by oxidizing the Mn^{2+} compounds to MnO_2 in alkaline media (pH = 9.7) using hydrogen peroxide as oxidizing agent. Fig. (11), shows the effect of temperature on the extent of oxidation in terms of the recovery percentage of manganese. It can be seen that $Mn^{2+}$is completely oxidized at temperature $\leqslant 70\ ^0C$ in alkaline media. With further rasing in temperature up to 80^0C, the extent of manganese recovery drops suddenly to a non-significant value.

Fig.(12), shows the effect of pH value on Mn^{2+} extraction. It is seen that in acidic, neutral or even slightly alkaline media (pH 0-9.5), the Mn^{2+} ions is very little oxidized to MnO_2. However in alkaline solution, at pH value$\geqslant$9.7, Mn^{2+} completely oxidizes to insoluble MnO_2.

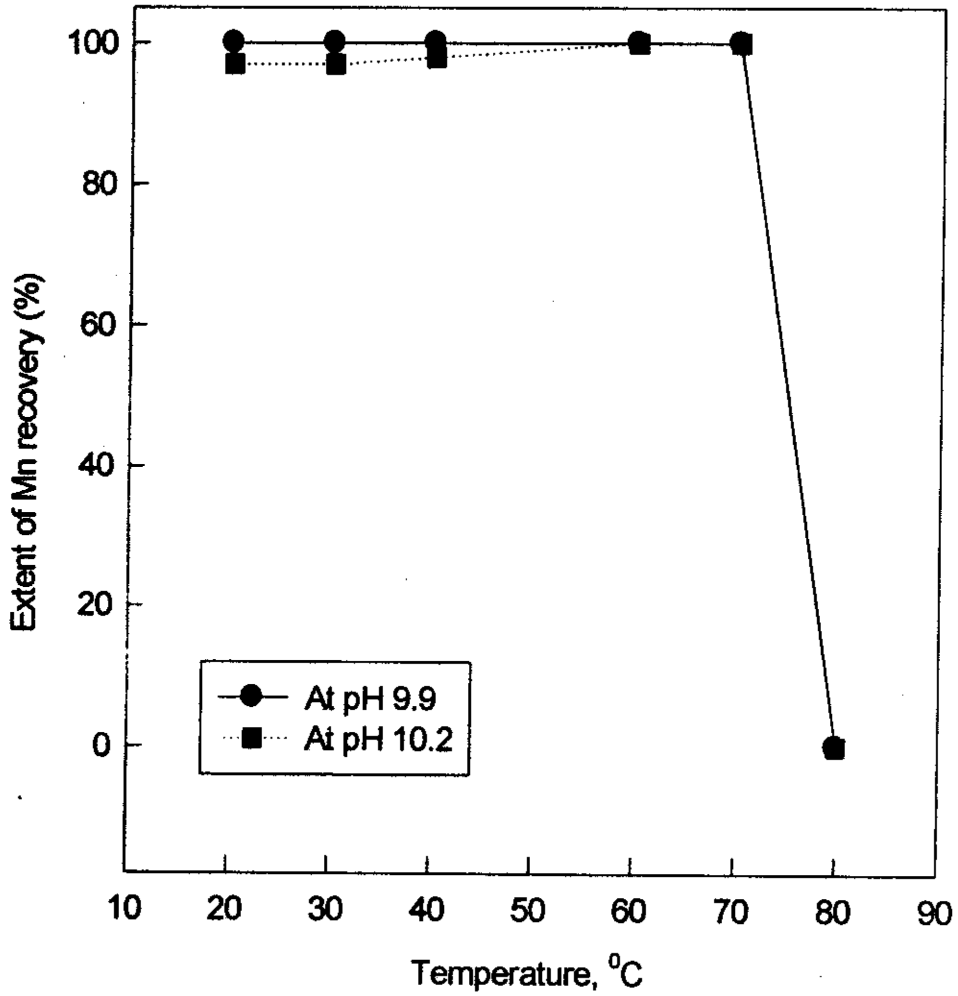


Fig.(11) The effect of temperature on the efficiency of Mn recovery (%) at pH 9.9 & 10.2

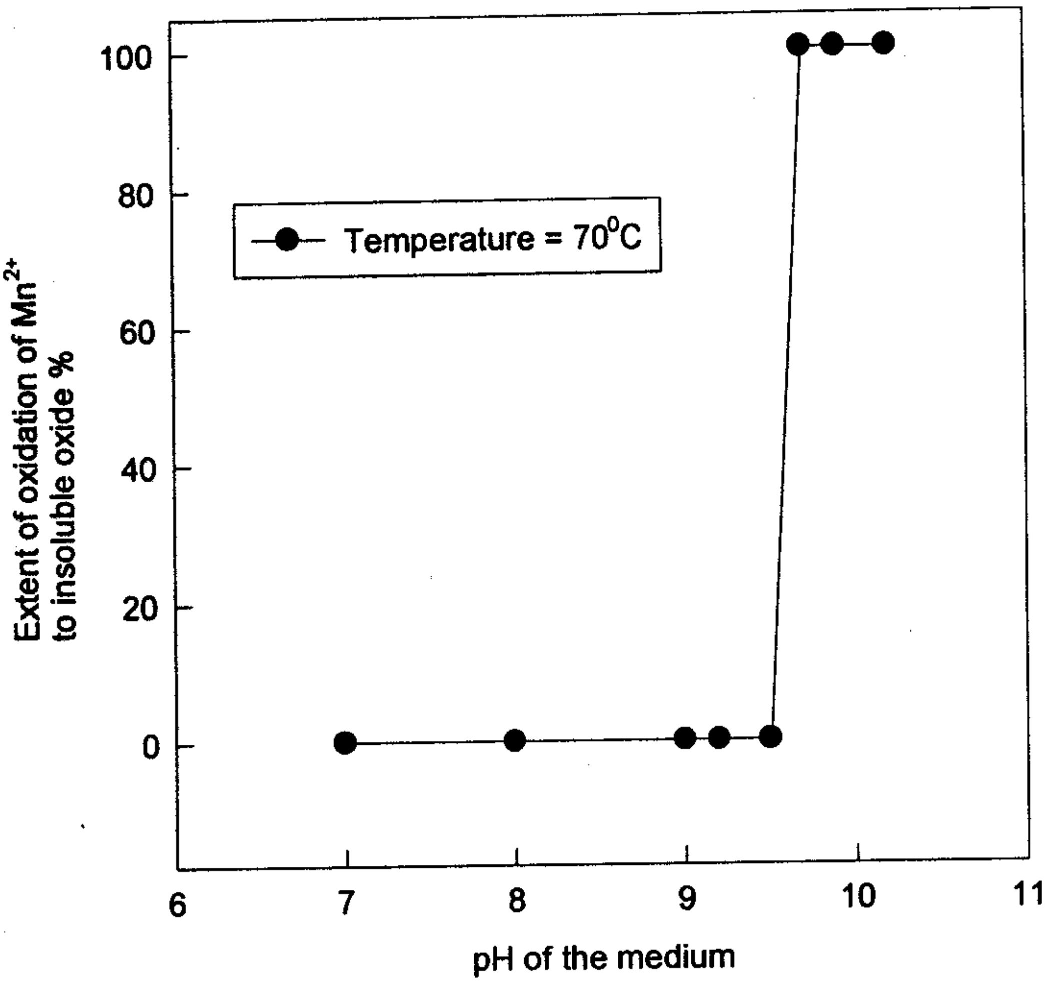


Fig.(12) Effect of pH of the medium on the extent of oxidation of Mn^{2+}

3.2.2.2 Recovery of zinc compounds from the residual ammonium chloride

Analysis reveals that, zinc is present in the extracted salts as zinc chloride, together with ammonium chloride. Separation of zinc is carried out from this mixture by precipitation as zinc sulphide in alkaline medium. To achieve this goal, the soluble salt was reacted with ammonium sulphide containing variable amounts of hydrogen sulphide. Equi-molecular weight of the reagent was added to the zinc-containing solution. After equilibrating at the required temperature, the pH value was adjusted to the required level by ammonium hydroxide. Fig. (13), shows that formation of zinc sulphide takes place in alkaline medium at a pH value more than 9.9. However, the zinc sulphide formation is accomplished independent to temperature.

After removal of zinc, the filtrate was tested for the presence of sulphide ion. If present, drops of hydrochloric acid were added and the solution was boiled to expel hydrogen sulphide gas. The crystallized salt of ammonium chloride was obtained by drying the above solution till dryness. Recrystallization of ammonium chloride was obtained by successive re-dissolving and crystallization. The purity of the obtained salt was tested with the help of an atomic absorption measurements.

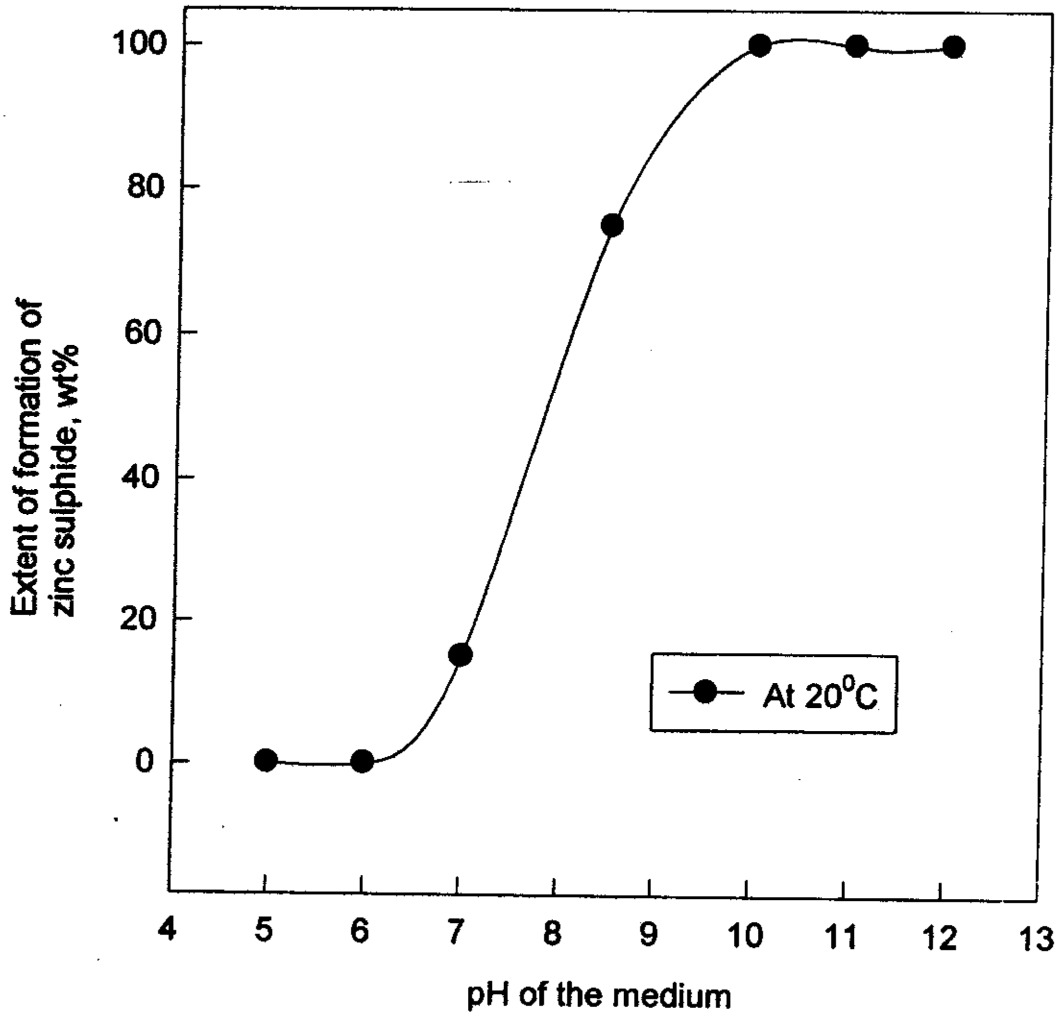


Fig.(13) The effect of pH of the leachant on extent of formation of zinc sulphide, wt%, at 20°C

3.3 RECOVERY OF ZINC METAL AND ZINC SALTS FROM THE CORRODED (SPENT) ZINC CANS

Metal zinc as well as zinc salts were recovered from the spent zinc cans. Two methods were applied involving pyrometallurgical and hydrometallurgical treatments.

3.3.1 Pyrometallurgical Treatment

The pyrometallurgical recovery of metal zinc from corroded cans of the dry battery cells involves re-melting under different conditions. In some cases, inorganic salts are used as fluxes to achieve high extent of recovery and grade of the obtained zinc metal, (see experimental p55). The corroded zinc cans were first freed from foreign inorganic manganese-carbon black paste or other adhered foreign materials. The cleaned cans were then pressed into compacted bodies. These were melted in a silicon carbide crucible. After the temperature of the furnace was brought to the required level, the crucible containing the compacted cans blocks was introduced into the furnace hearth.

Fig.(14), shows the effect of smelting temperature on the extent of recovery of zinc metal from these spent cans. Experiments were conducted for different periods up to 25 minutes. Ammonium chloride (10% by weight) was used as a fluxing material. It is seen that the extent of recovery proceeds with temperature within the range of 450-600^{0}C. At higher temperatures up to 700^{0}C, the extent of recovery decreases again. It is also seen that the extent of recovery increases in the order 10, 15 and 25 minutes. The maximum extent of recovery values obtained for these periods amounts to 70%, 82% and 90% respectively.

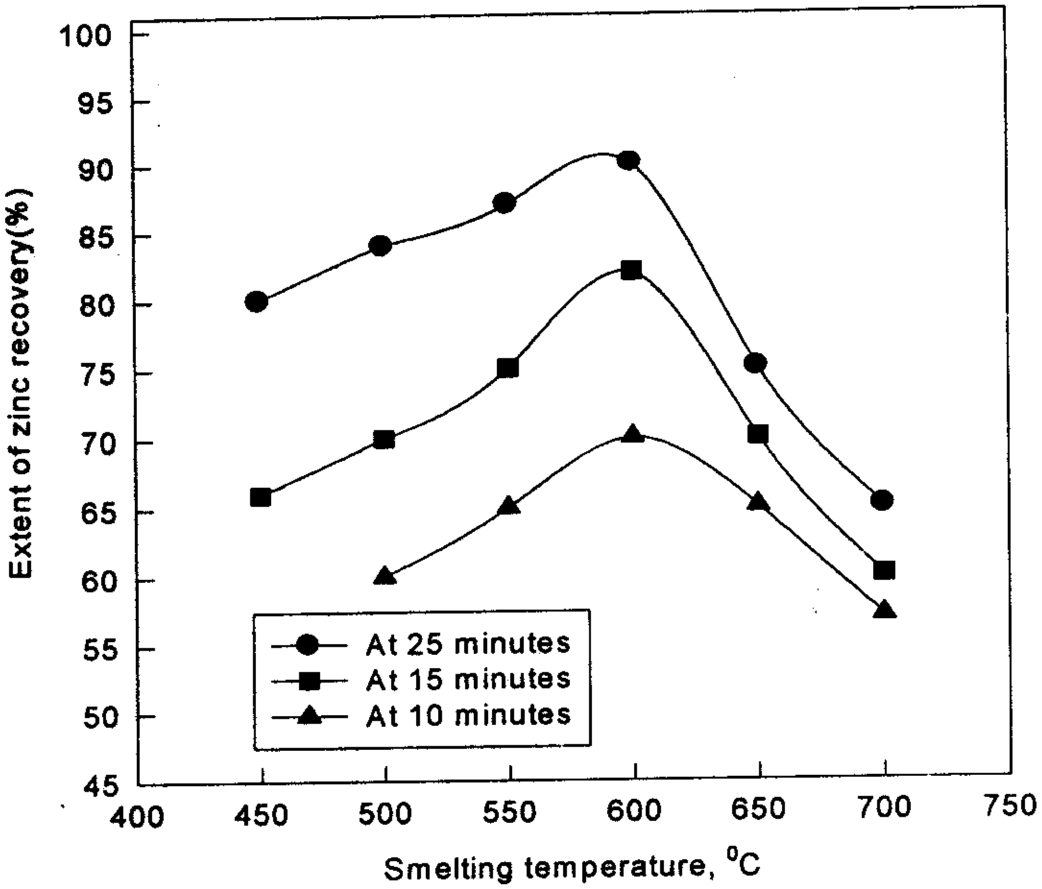


Fig.(14) **The extent of recovery of metal zinc as affected by the recovery temperature [450 - 700^{0}C] for different periods up to 25 minutes**

Fig.(15), shows the effect of smelting time up to 55 minutes on the extent of recovery of metal zinc from the spent zinc cans. Experiments are performed at 600^0C using 10% ammonium chloride as a fluxing agent. It is seen that the extent of recovery value amounts to 25% after 5 minutes. The extent of recovery then increases drastically with increasing in time approaching a maximum value of 90% after 25 minutes. When recovery experiments are carried out for longer periods up to 55 minutes, a gradual decrease in extent of recovery of metal zinc takes place.

Fig.(16), shows the effect of addition of ammonium chloride as a fluxing material on the extent of recovery of zinc metal at 600^0C and for 25 minutes. It is seen that the extent of recovery gradually increases with increasing the amount of the added ammonium chloride. With 10% by weight of the salt, the maximum extent of recovery amounting to 90% is achieved. However, with further increase in the added amount of the fluxing salt to 15%, the extent of recovery value decreases drastically to 70%. This value is the minimum extent of recovery and is constant with higher weight percentages of the fluxing salt up to 20%.

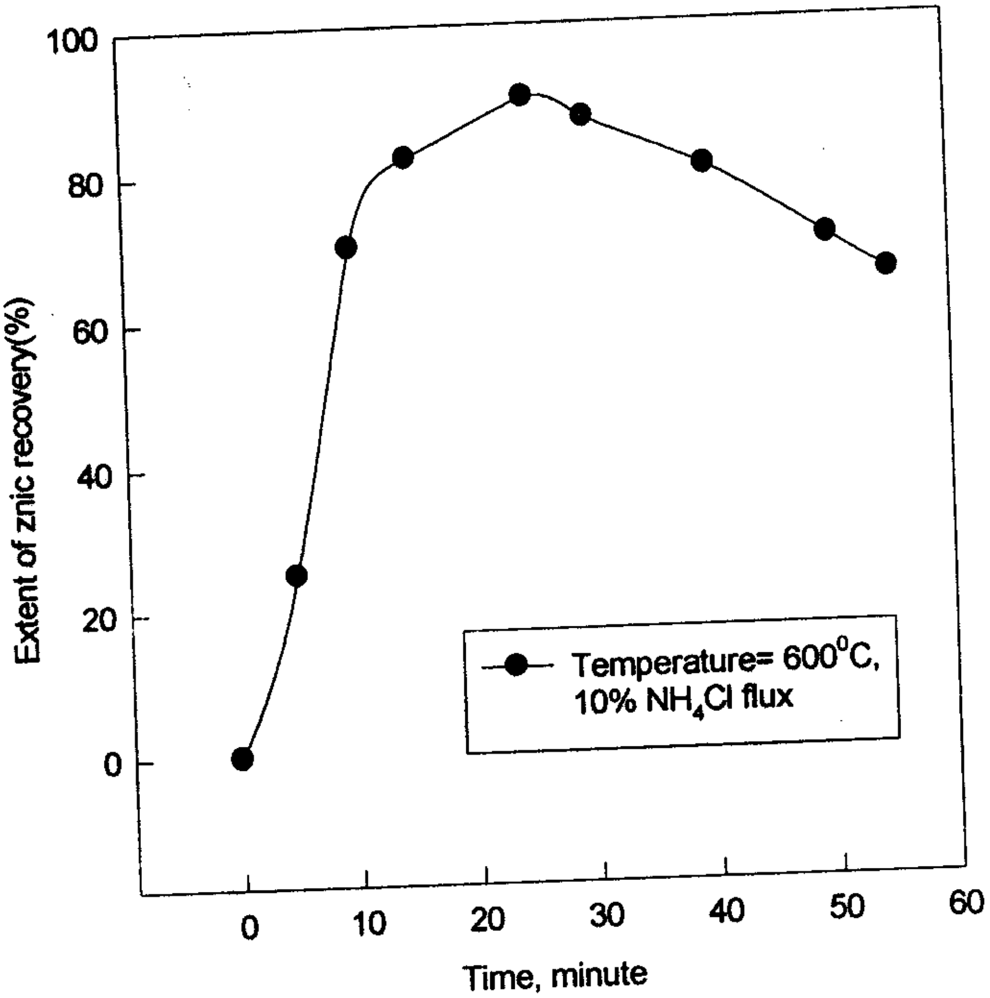


Fig.(15) The effect of time on zinc recovery (%) at 600^{0}C with 10% NH_4Cl flux

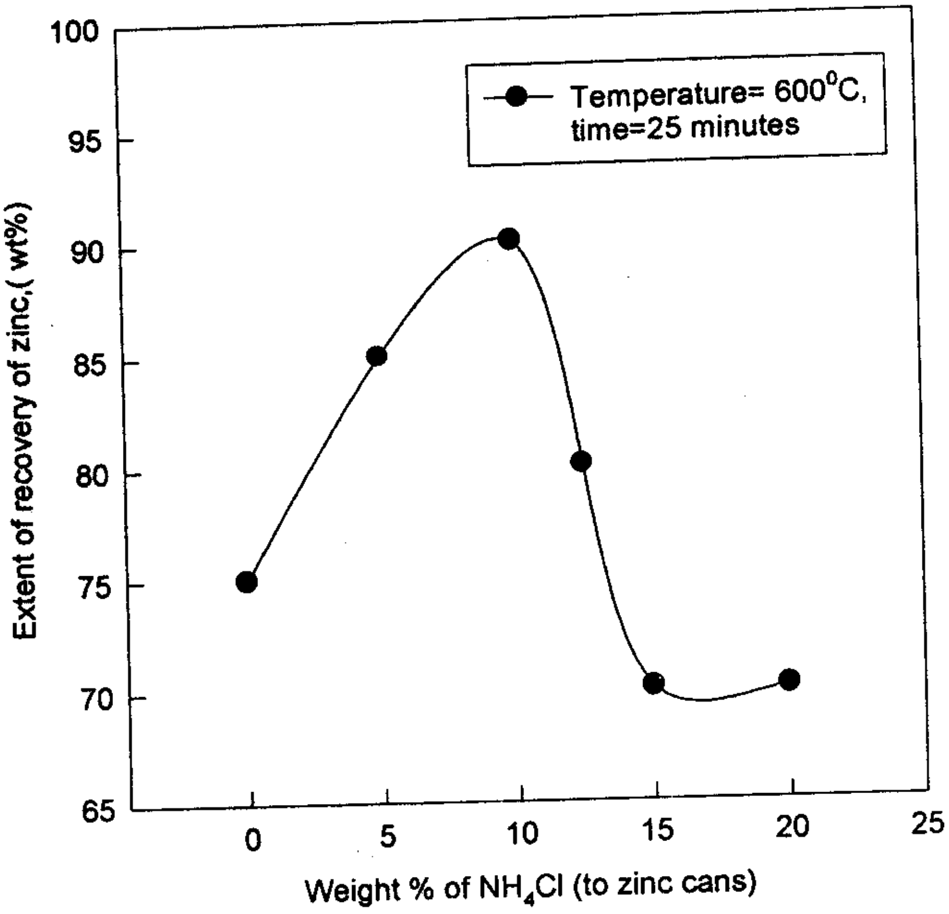


Fig.(16) The effect of flux amount on extent of recovery of zinc,wt%, at 600 °C for 25 minutes

Fig(17), illustrates the effect of addition of 10% by weight of different fluxing materials on the extent of zinc recovery. Experiments were carried out within the temperature range 500-900^{0}C. The used salts are sodium, potassium and ammonium chlorides. Experiments were carried out for 25 minutes. It is seen that; the extent of recovery is in the order, ammonium chloride > potassium chloride > sodium chloride which have maximum of 90%, 55%, and 45%, respectively. However, potassium and sodium chlorides acquire their maximum values of the extent of the recovery at higher temperature (800^{0}C) as compared to ammonium chloride (600^{0}C).

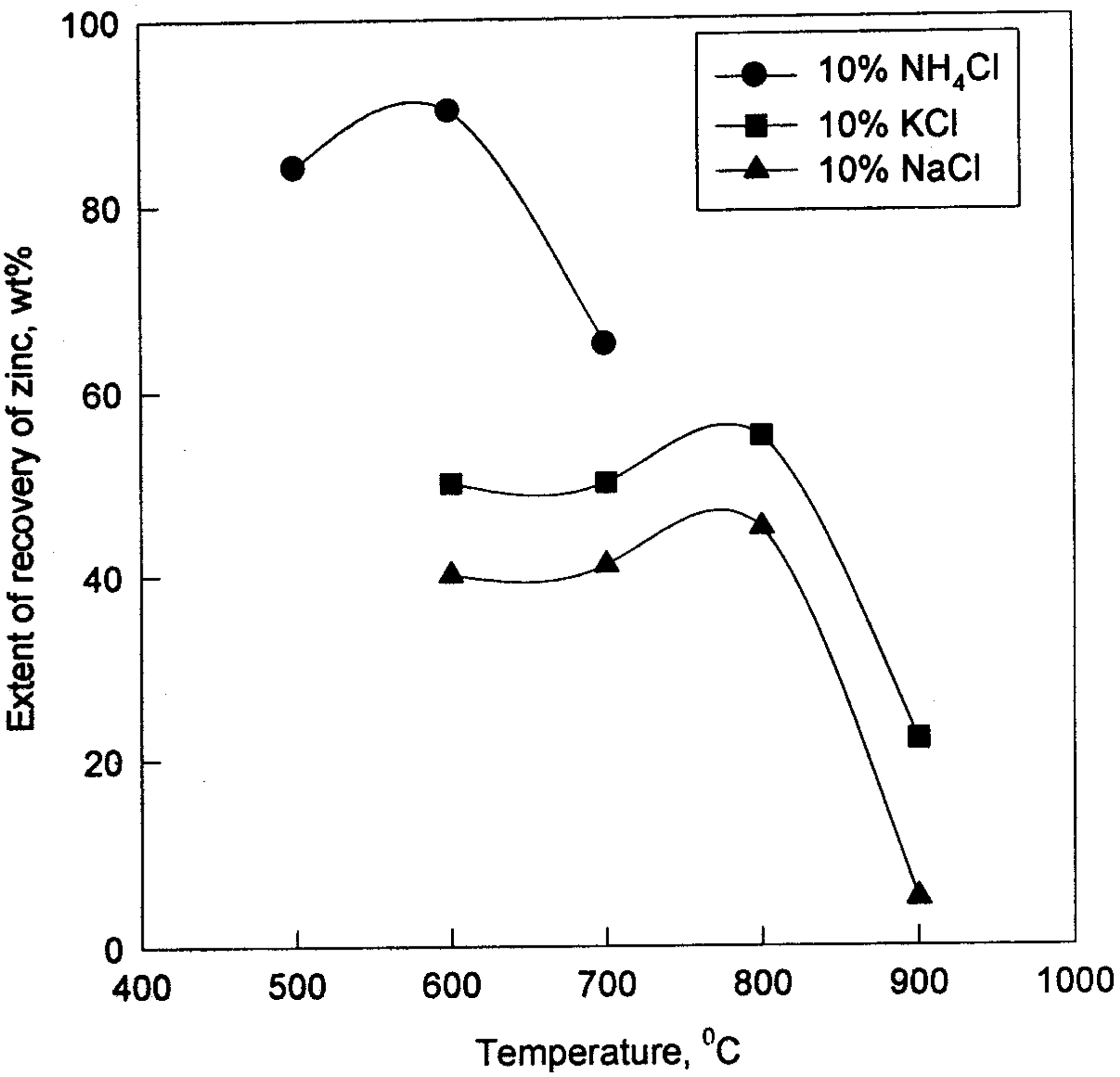


Fig.(17) Effect of temperature on the extent of recovery of zinc metal using 10% by weight of NaCl, KCl and NH_4Cl. Time=25 minutes

3.3.2 Preparation of Valuable Zinc Salts from the Formed Slag (Hydrometallurgical Treatment)

Valuable zinc salts are prepared by hydrometallurgical treatment of the slag obtained from the thermal recovery process of zinc metal. Fig.(18), shows the XRD analysis of zinc slag [see pp. 89, 90]. The main components are zincite (ZnO) and simonkolleite [$Zn_5(OH)_8Cl_2.H_2O$]. The slag is first ground to pass a mesh size 190 um. The slag is then leached by 50% hydrochloric acid after fusion to obtain zinc chloride concentrate. Other zinc salts and compounds are prepared by carbonation using stoichiometric sodium carbonate at room temperature to obtain the complete transformation to carbonate salt according to:

$$ZnCl_2 + Na_2CO_3 \rightarrow ZnCO_3 + 2NaCl \qquad (10)$$

The formed zinc carbonate is taken as a base material to prepare zinc organo-compounds. Previous work in the laboratory enabled the preparation of different zinc compounds such as zinc oxide and stearate. In this work, more zinc salts are also prepared such as zinc sulphide, acetate, tartarate and phosphate. Table (15) shows some of the physical properties of these compounds after their crystallization.

Table (15), Physical properties of the prepared zinc compounds

Compound	Physical properties	
	Melting temperature	Color
Zinc sulphide	1700	White
Zinc acetate	d 200	Colorless
Zinc tartarate	–	White
Zinc phosphate	900	Colorless

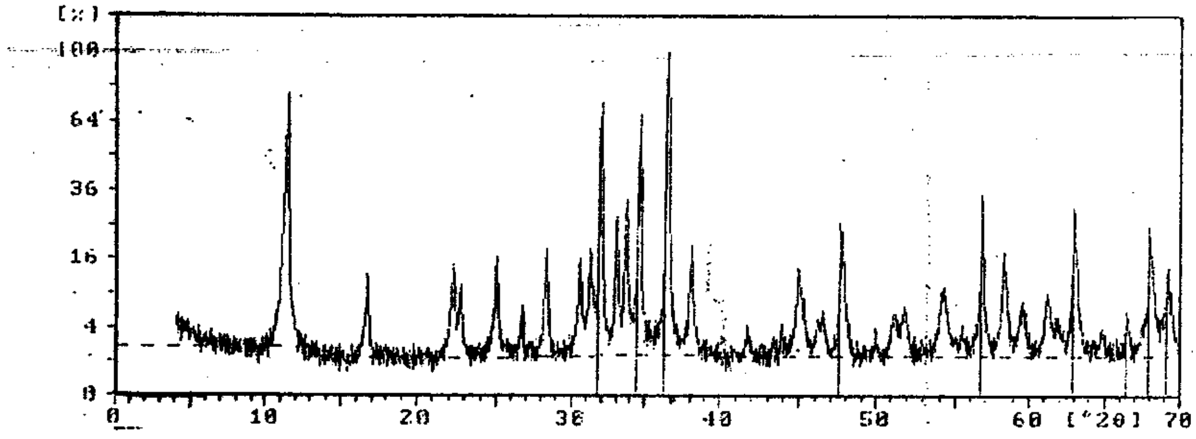


Fig.(18): XRD chart of zinc slag

Angle	d-value	Intensity
11.415	7.74541	74.5
16.725	5.29637	11.0
22.240	3.99390	13.0
22.730	3.90890	7.3
24.995	3.55957	13.2
26.730	3.33233	5.4
28.305	3.15039	14.6
30.495	2.92895	13.4
30.585	2.92053	14.4
31.220	2.86256	17.1
31.930	2.80051	70.3
32.965	2.71491	25.6
33.650	2.66119	30.6
34.555	2.59354	58.8
36.390	2.46686	100.0
36.480	2.46098	72.9
38.045	2.36326	17.1
44.850	2.01922	10.2
46.505	1.95115	4.3
47.870	1.90614	20.0
51.140	1.78465	3.6
51.810	1.76314	5.1
54.040	1.69553	6.8
54.275	1.68874	7.1
56.705	1.62200	30.6
56.885	1.61730	15.1
58.265	1.58224	16.3
59.580	1.55041	5.1
61.150	1.51432	6.5
62.950	1.47528	28.9
68.015	1.37722	20.3
69.170	1.35702	12.5

Table 16: XRD physical data of zinc slag

3.4 SEPARATION OF Zn-MnO_2 COMPOUNDS

Mass balance calculation of zinc in fresh battery cell as compared to that recovered from the corroded cans given in table(11) p(67), reveals a significant difference of the metal. A study to explore where the escaping zinc exists is carried out. Precise analysis of the black paste shows the presence of zinc in the black paste combined with manganese dioxide to form a zinc-manganese compound. The composition as well as identification of such compound show that, it is a crystalline salt having the chemical formulae ($Zn_2Mn_4O_8.H_2O$). Fig.(19) and table(17)show the XRD chart of the conventional black paste and its physical data. Part of zinc was in the form of zincite (ZnO) together with γ-manganese dioxide.

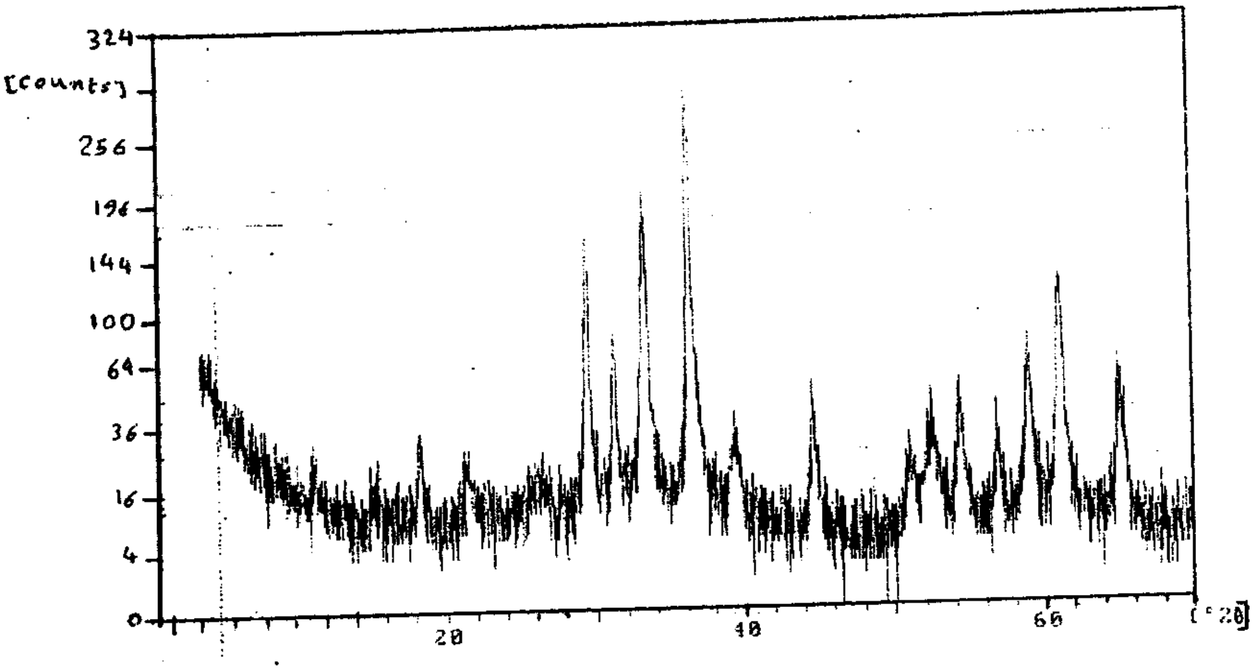


Fig.(19): XRD chart of original black paste

Angle	d-value	Intensity
4.360	20.24977	9.2
11.310	7.81708	2.8
15.390	5.75267	2.2
18.285	4.84787	7.0
21.450	4.13917	4.5
26.295	3.38647	2.4
27.690	3.21894	2.0
29.535	3.02193	47.7
31.285	2.85676	23.4
33.355	2.68405	58.9
36.420	2.46489	100.0
39.465	2.28144	6.7
44.730	2.02436	14.0
51.160	1.78400	6.3
52.570	1.73943	10.8
54.385	1.68558	14.0
56.790	1.61978	9.6
58.955	1.56535	21.0
60.940	1.51903	30.1
64.945	1.43470	13.1

Table (17): XRD physical data of original black paste

Separation of the present form of zinc-manganese compound by leaching using distilled water under different leaching conditions failed to recover this compound. This confirms that zinc-manganese compounds are fairly water- insoluble.

A set of experiments has been carried out to extract zinc-manganese compound from the black paste. Different leachants are used; alkali solutions (such as sodium hydroxide and ammonium hydroxide) or acidic leachants of mineral acid solutions. Optimum conditions of water leached experiments are applied here. Experiments are conducted for 60 minutes. The solid: liquid ratio is 1:5 and the leaching temperature is up to 100^{0}C. The leached products are analyzed for zinc content to satisfy the weight that lost.

3.4.1 Leaching with Alkali Solutions

Fig.(20), shows the extent of extraction of zinc-manganese compounds using sodium hydroxide having 0.6M, 1.2M, 1.8M and 2.4M solutions, as affected by the leaching temperature. The leaching process is maintained for 60 minutes and the solid : liquid ratio is 1:5. It can be seen that the extent of leaching at 30^{0}C amounts to 8.5% using 0.6M sodium hydroxide solution. This extent of leaching increases gradually with increase in temperature up to 70^{0}C. However, complete leaching is not readily attained at the higher molarity of the leachant. For example, at 30^{0}C, the extent of extraction amounts to 8.5%, 17%, 25.5% and 34.2% with 0.6M, 1.2M, 1.8M and 2.4M respectively. It is also important to note that complete leaching of zinc-manganese compounds can not be

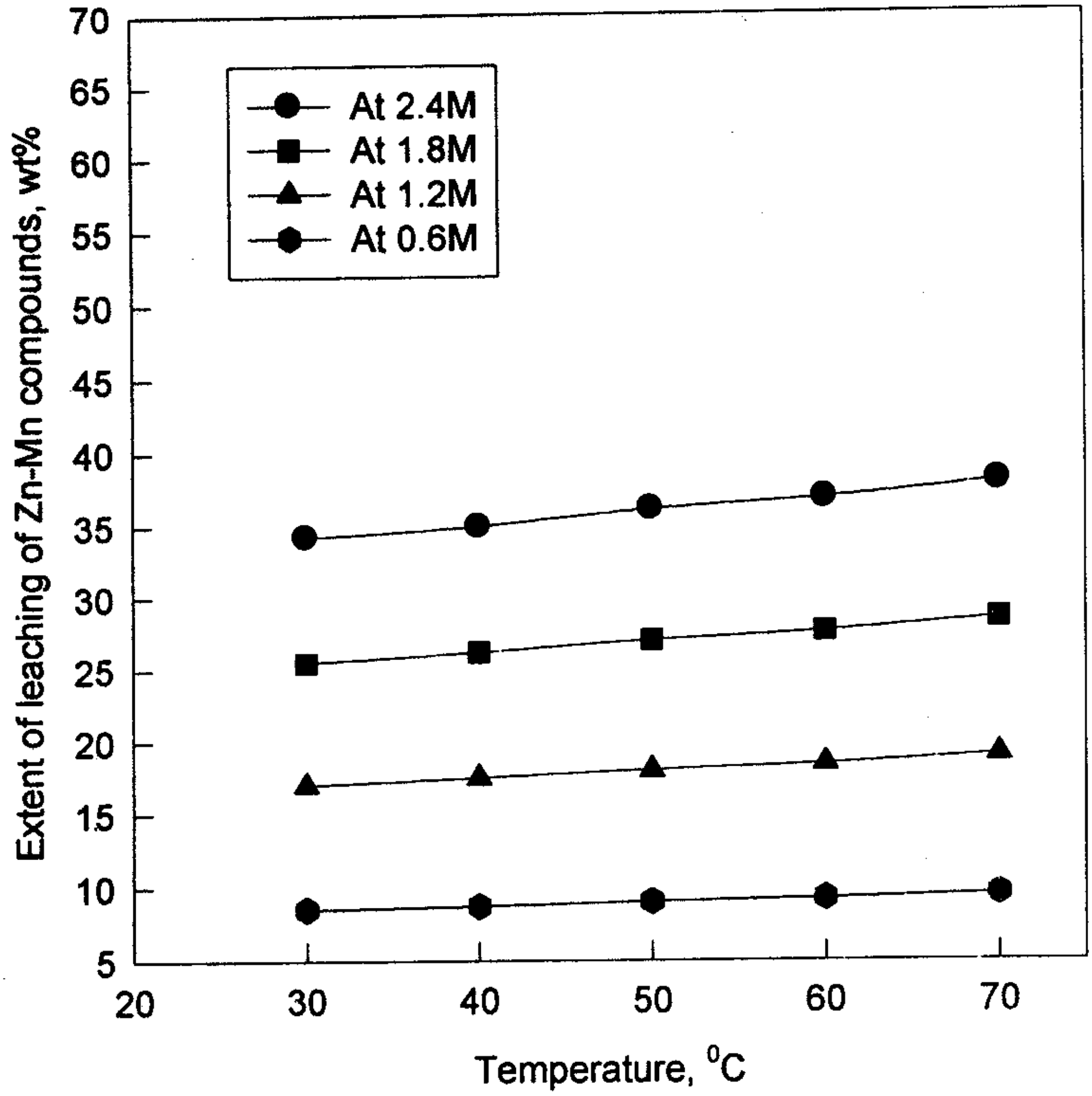


Fig.(20), Effect of leaching temperature onZn-Mn compounds from battery black paste using NaOH solution. t = 60 min. and S / L = 1: 5

achieved using leachants at 70^0C, even using alkali solutions with high molarities(2.4M).

Results given in fig.(21) confirm these findings. It is also seen that for one and the same temperature, the extent of extraction increases with increase in molarity of the sodium hydroxide solution approaching a maximum value with 2.4M.

Fig.(22), shows the extent of leaching of the zinc-manganese compounds using ammonium hydroxide and sodium hydroxide solutions. The conditions of leaching are the same as those given previously in fig.(21) with respect to the leaching temperature. Experiments are carried out for 60 minutes and the solid: liquid ratio is 1:5.The molarity of leachants are 0.03 to 2.4M. It is seen that, the extent of leaching using sodium hydroxide is higher than that acquired with ammonium hydroxide solution. When using sodium hydroxide, the extent of extraction increases gradually with increase in solution molarity. With ammonia solution, the leaching curve acquires nearly a mirror image as that displayed with sodium hydroxide. It is also seen that the maximum leaching extent amounts to 8.5%, 17% and 34.2% with 0.6M, 1.2M and 2.4M sodium hydroxide. With ammonium hydroxide, the corresponding values obtained with the same molarities are 6%, 8% and 20% respectively.

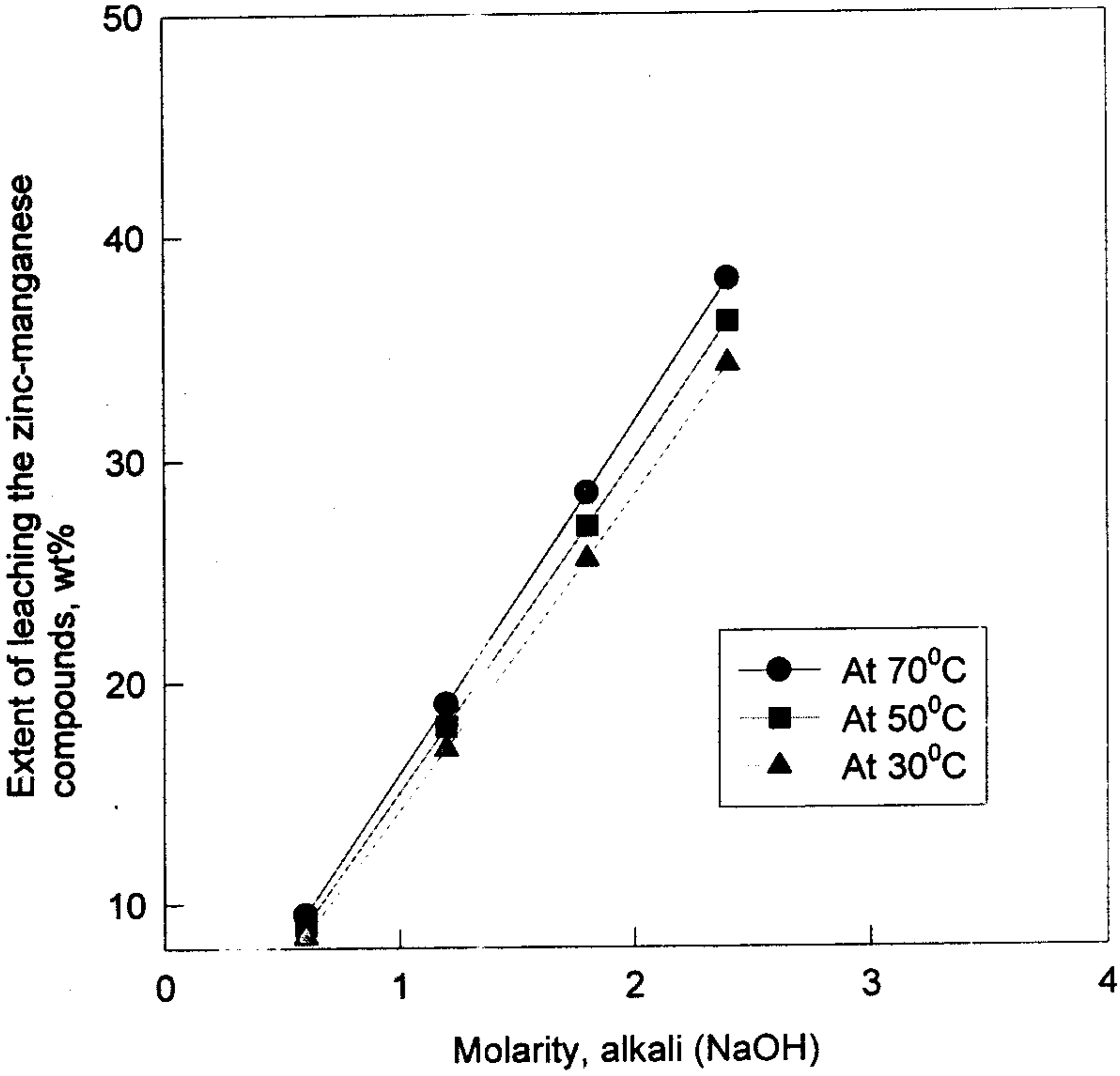


Fig.(21) Effect of molarity on the extent of leaching the zinc- manganese compounds. Time = 60 minutes and S: L ratio 1: 5

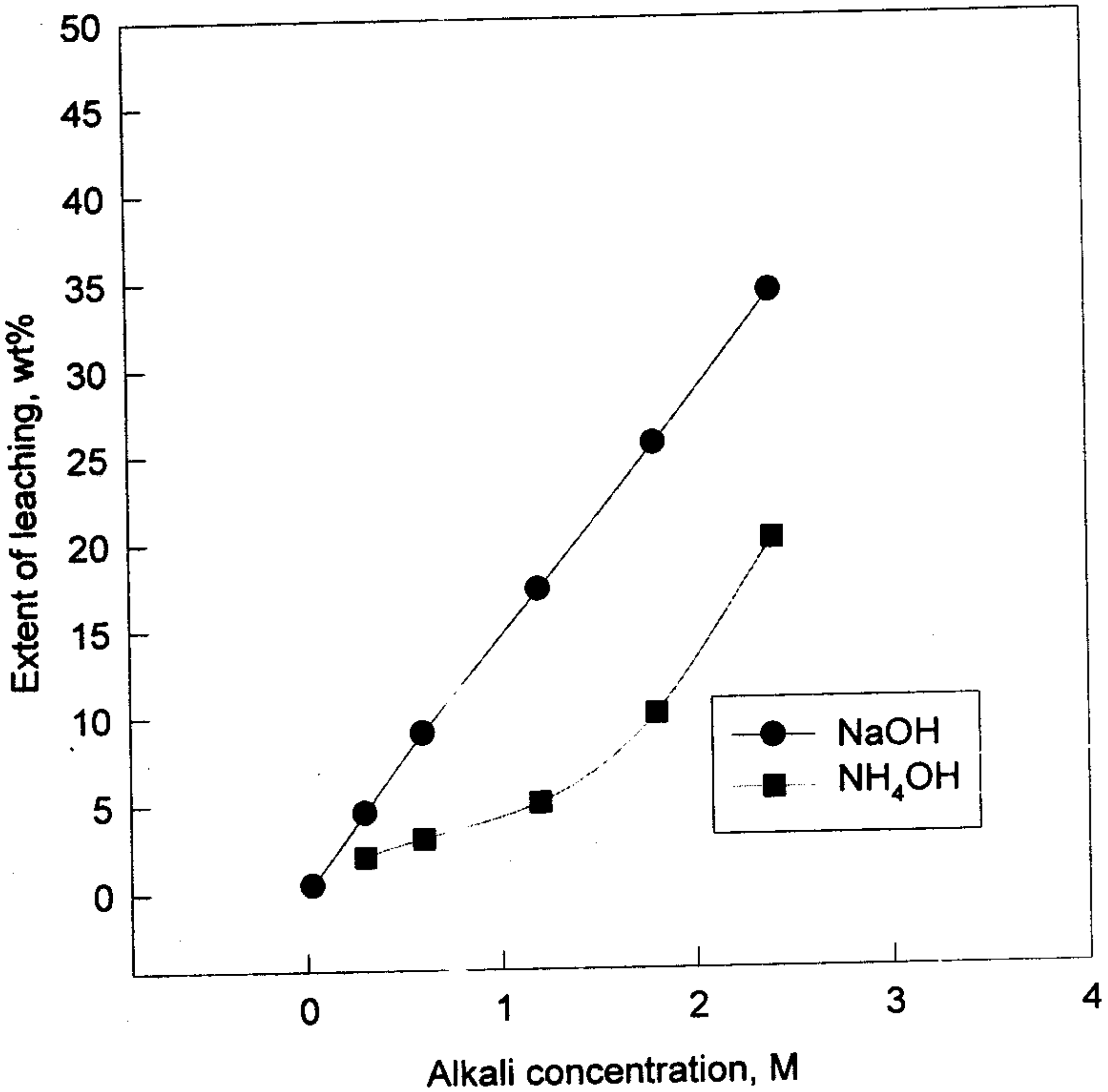


Fig.(22) The effect of the molarity of sodium hydroxide and ammonium hydroxide solutions on the extent of leaching the Zn - Mn compounds.

T = 30^{0}C, t=60min.and S: L ratio1:5

3.4.2 Leaching with Acid Solutions

Leaching of zinc-manganese compound from the black battery paste has also been studied using mineral acid solutions. The leaching conditions are kept the same as those implemented with the experiments using alkali solutions.

Fig.(23), shows the extent of leaching of the zinc-manganese compound using nitric acid solution as affected by the leaching temperature up to 90^0C. Leaching experiments are carried out for 60 minutes using a solid: liquid ratio of 1: 5. It is seen that the extent of leaching increases with increase in temperature. The maximum extent of leaching is attained at 90^0C. It is also seen that the response of the extent of leaching becomes more pronounced at higher the molarity of the acid and temperature >60^0C.

Fig.(24), shows that, the extent of leaching proceeds with increase in the acid molarity. Complete extraction amounting to 100% is achieved using 2.4M nitric acid at 90^0C. The maximum extent of leaching using 0.6M at the same temperature amounts to 51%. However, with the same acid solutions having lower temperature, the extent of leaching acquires the corresponding lower values.

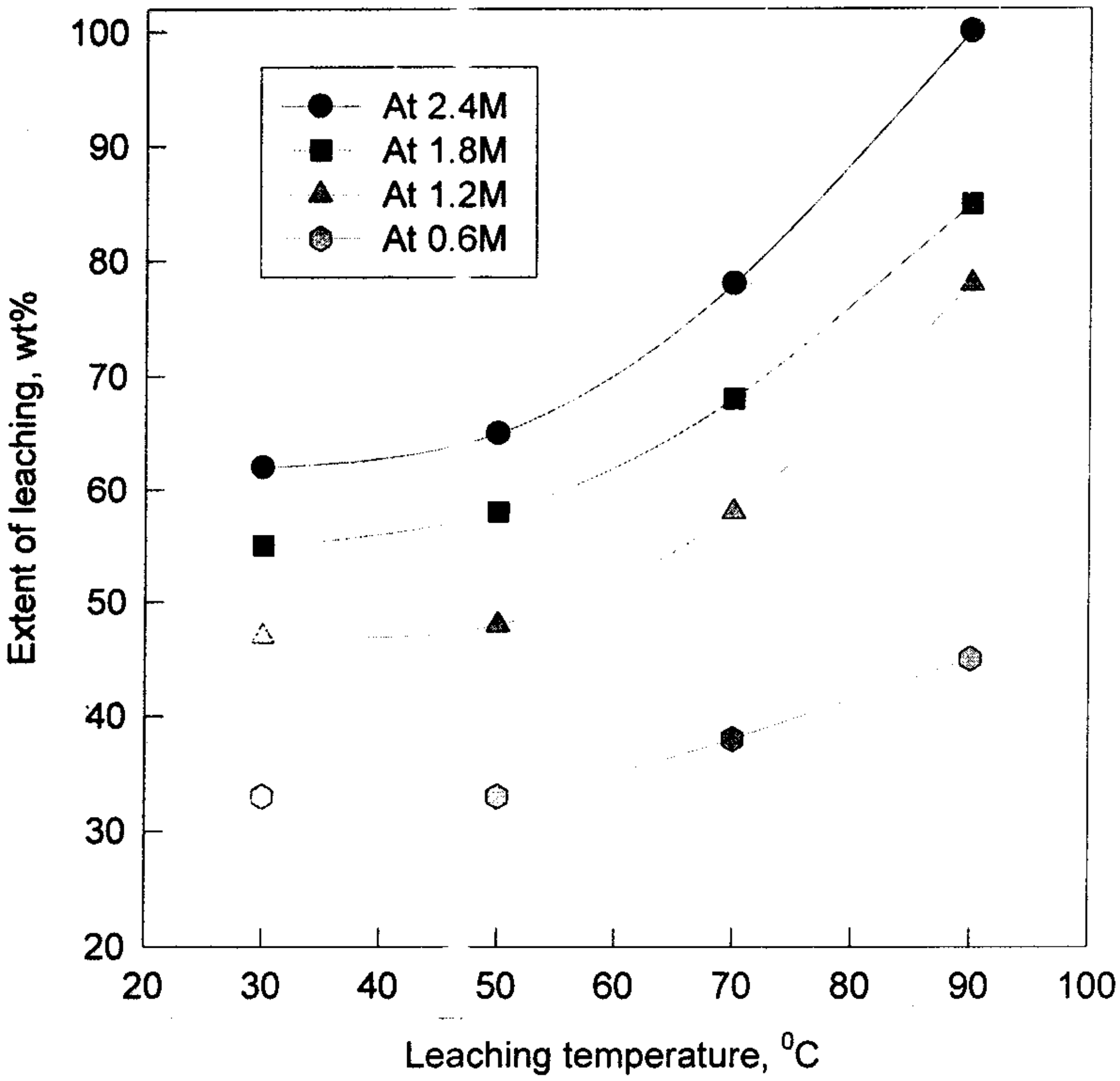


Fig.(23) Effect of leaching temperature on the extent of leaching of Zn - Mn compounds from black paste with nitric acid at t = 60 minutes and S: L ratio 20%

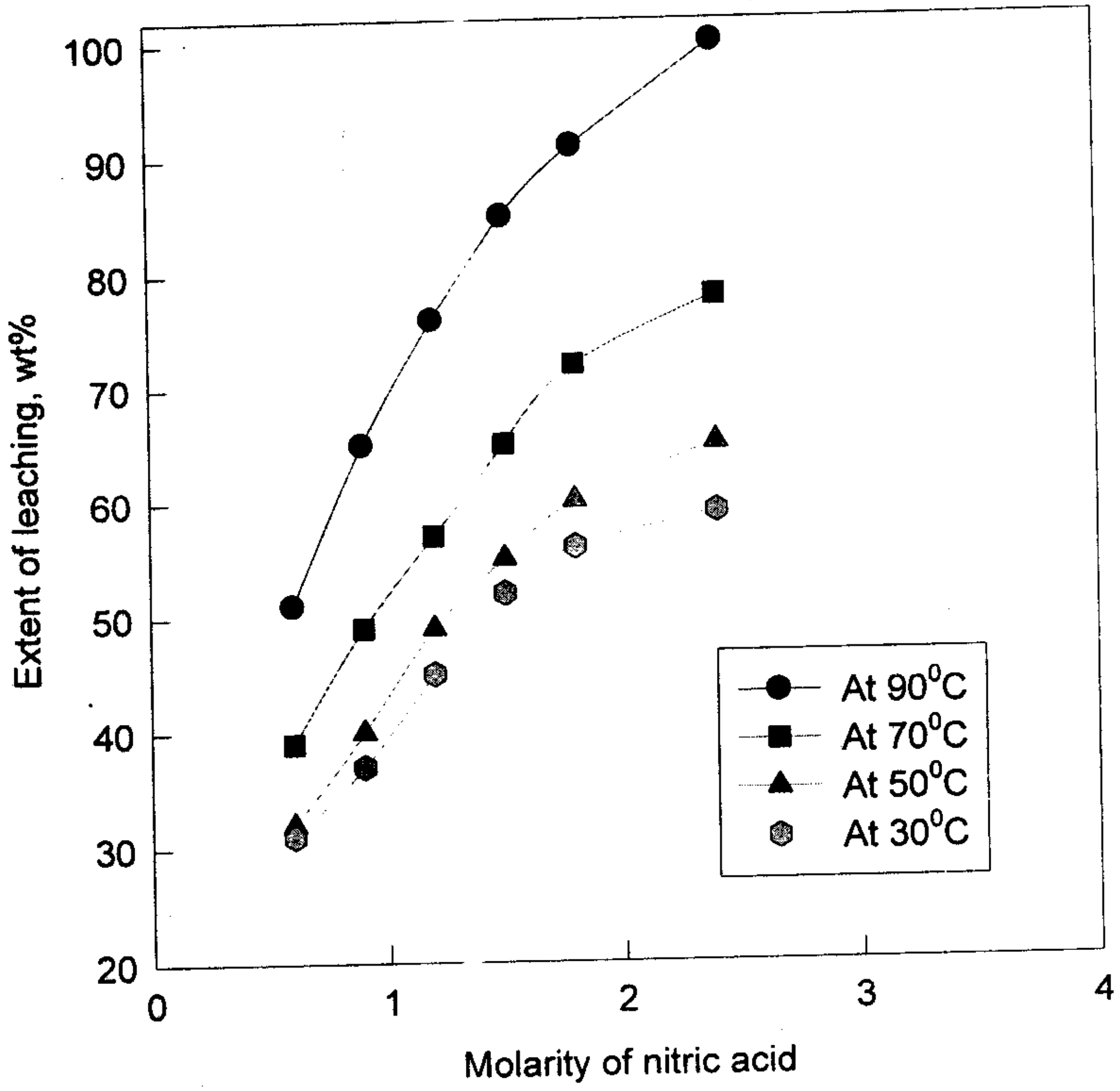


Fig.(24) Effect of nitric acid molarity on the extent of leaching the zinc-manganese compound form black paste at t = 60 minutes and S: L ratio 1: 5

A similar set of experiments is conducted using sulphuric acid leachant under the same leaching conditions. Fig.(25), shows the results for leaching of the zinc-manganese compounds as affected by the sulphuric acid molarity. It is seen that the extent of leaching increases linearly with increase in the sulphuric acid molarity. However, the slop of the curves also increases with the increase in the temperature of the leaching process. Complete extent of leaching (100%) has been achieved using 2.4M sulphuric acid at 70^0C for 60 minutes.

Fig.(26), shows the results obtained using hydrochloric acid leachant. The extent of extraction increases with increase in the acid molarity. The maximum extent of leaching amounts to 85% is achieved after 60 minutes using 2.4M hot hydrochloric acid at 70^0C. When the experiment is carried out at 50^0C, the extent of leaching amounts to 70%.

Comparing the results given in figs.(25) and (26), it can be seen that hydrochloric acid gives low extent of extraction the zinc-manganese compound with respect to sulphuric acid.

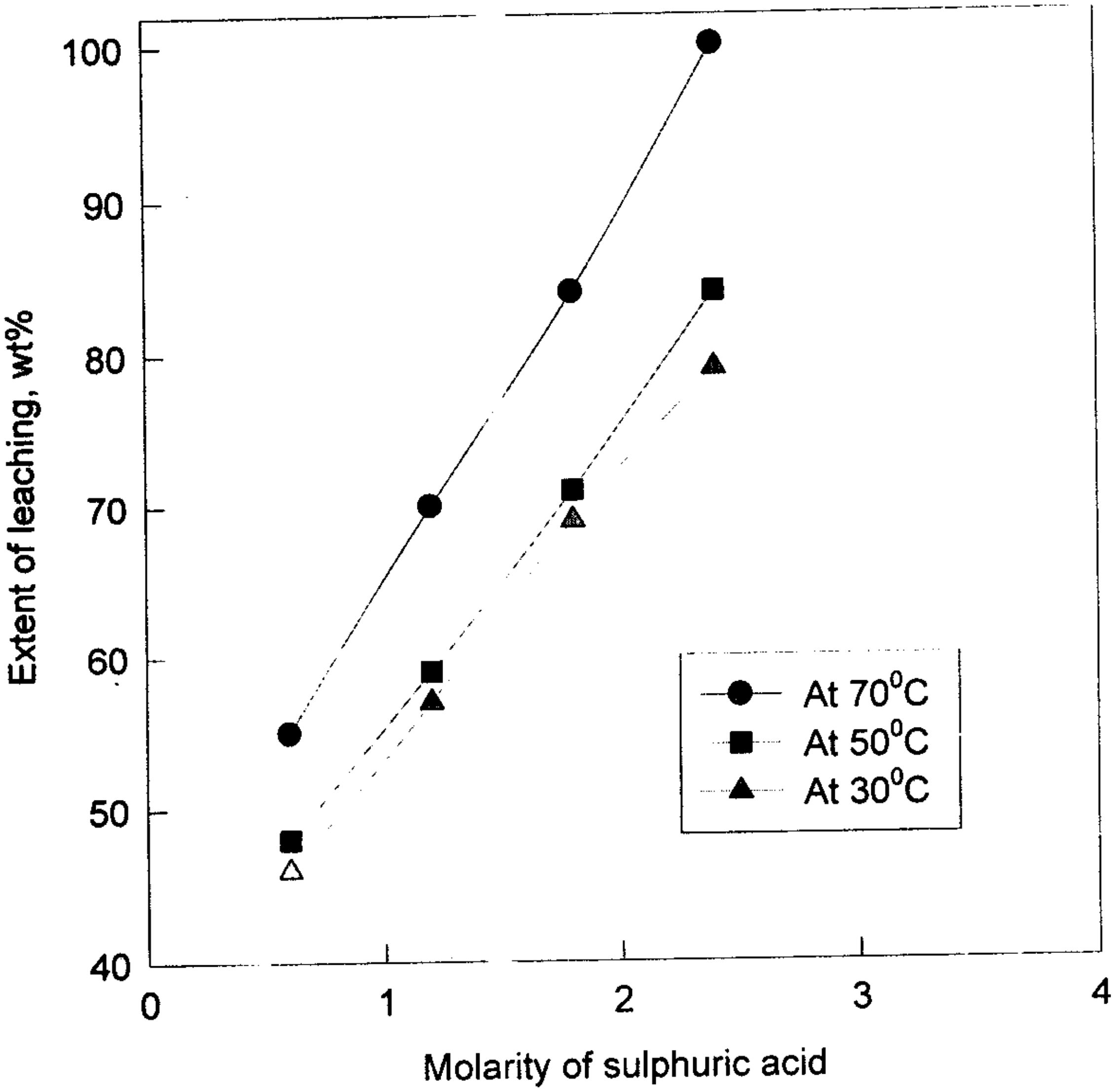


Fig.(25) Effect of sulphuric acid molarity on the extent of leaching the zinc-manganese compound from the black paste of the spent dry cell at t=60minutes and S:L ratio 1: 5

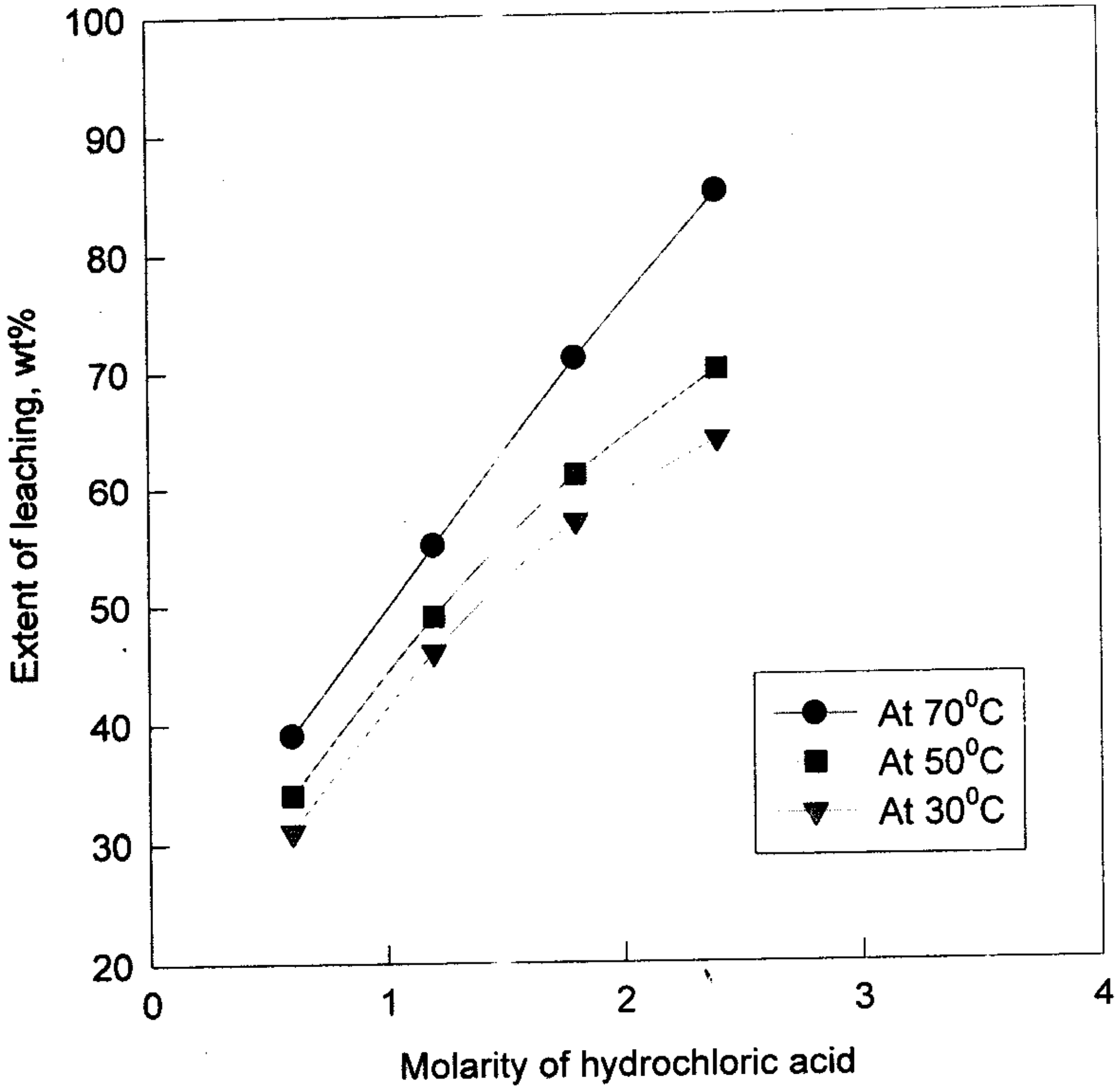


Fig (26) Effect of molarity of hydrochloric acid on extent of leaching the Zn- Mn compounds at t = 60 min. and S: L ratio 1: 5

Fig.(27), shows the effect of pH value of strong leachants; hydrochloric acid and sodium hydroxide, at 50^{0}C on the extent of leaching of zinc-manganese compound from the black paste of the spent cells. It is seen that a V-shaped parabolic curve is obtained, the minimum value (5%) of which is obtained at pH value of 7.8. Maximum value obtained with 2.4M hydrochloric acid (pH = 0), is 70%. The maximum value obtained with 2.4M sodium hydroxide (pH = 14) amounts to 36.1%. In other words, leaching with strong acids such as hydrochloric acid is more effective to leach zinc-manganese compound than the strong alkali solutions. However; neutral solutions, pH=7, water is seen immaterial to bring about significant extent of leaching whereby only 5% of the sample is leached. Figs. (28) and (29), and tables (18) and (19) show the XRD analysis of acid leached samples. It is seen that zinc-manganese compound is removed while non-crystalline γ-manganese dioxide and carbon are only present.

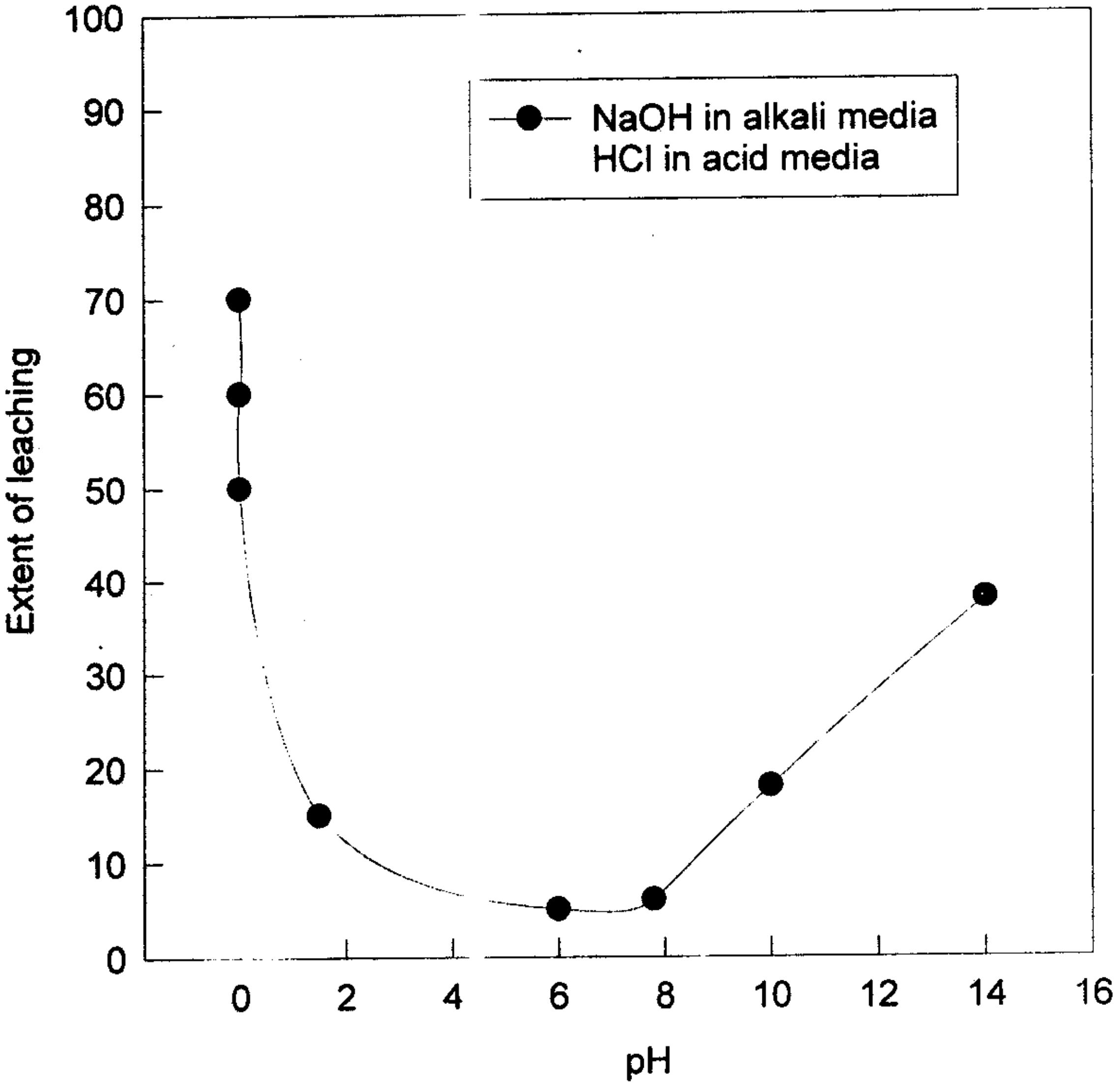


Fig.(27) The effect of the leachant pH on the extent of leaching of Zn - Mn compounds from the black paste of spent cells. T=50^{0}C, t=60minutes

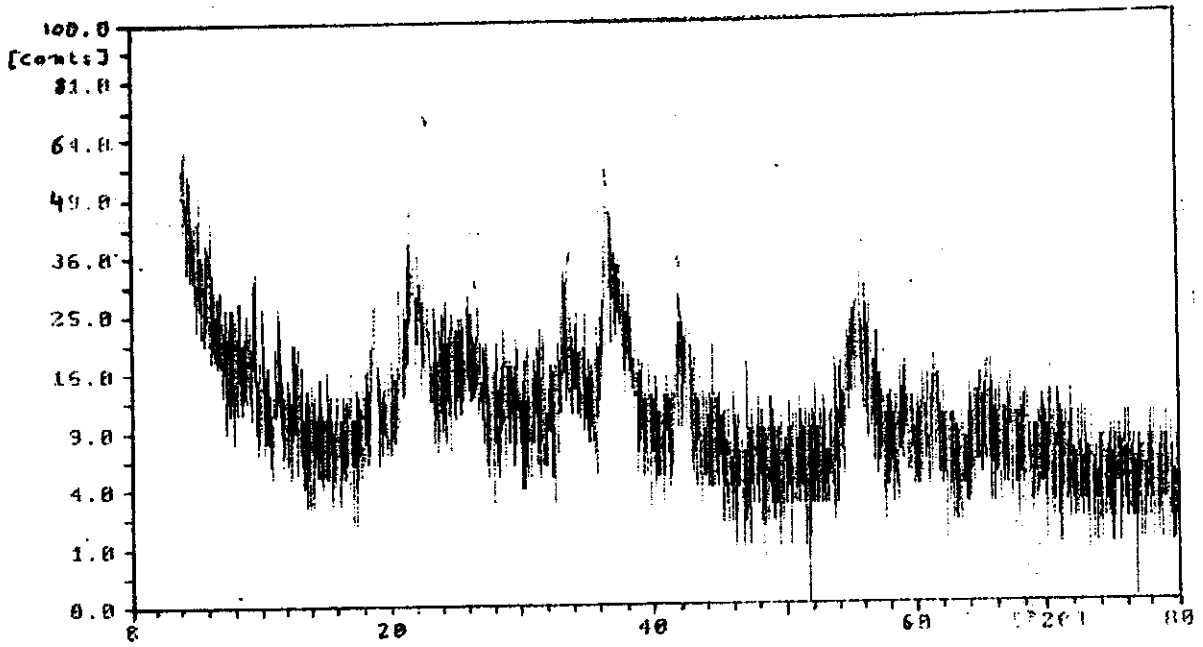


Fig.(28): XRD chart of HCl leached black paste

Angle	d-value	Intensity
9.520	9.28249	58.7
11.500	7.68835	49.3
12.790	6.91566	16.3
18.955	4.67800	76.1
21.910	4.05330	100.0
29.215	3.05429	10.2
33.495	2.67315	52.3
36.580	2.45448	87.6
42.125	2.14090	52.3
44.825	2.02029	16.3
55.380	1.65763	49.3
59.080	1.56234	18.1
61.280	1.51142	30.6
65.325	1.42727	21.9

Table (18): XRD physical data of HCl leached black paste

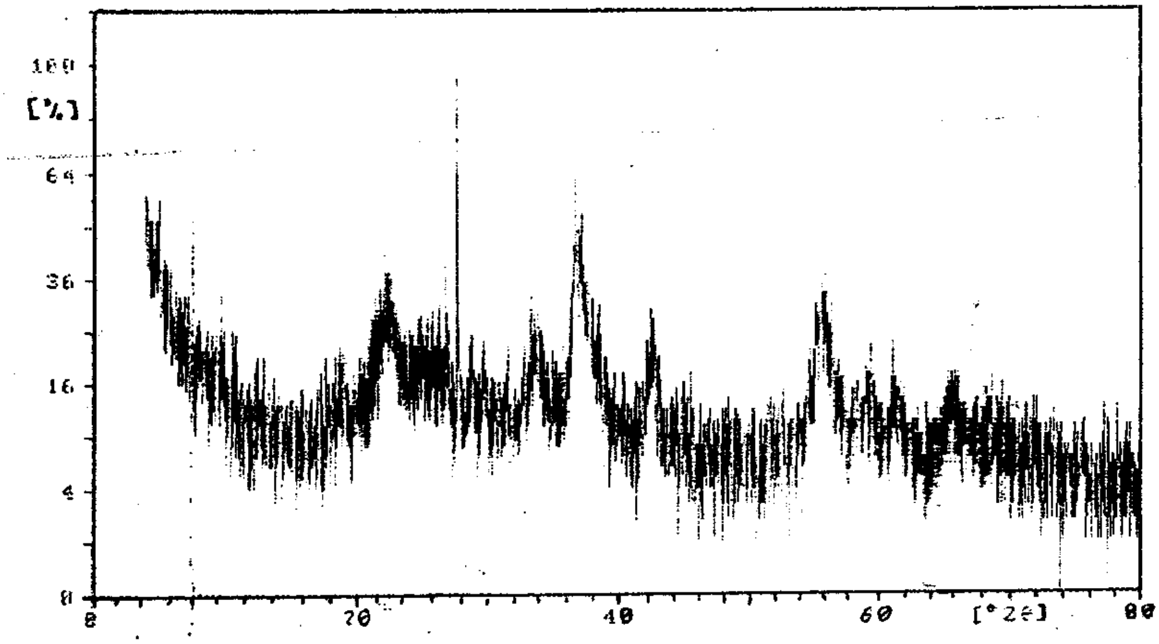


Fig.(29): XRD chart of nitric acid leached black paste

Angle	d-value	intensity
18.965	4.67556	18.4
26.825	3.32075	8.8
27.655	3.22294	100.0
28.750	3.10263	5.5
29.735	3.00205	6.5
33.500	2.67277	10.0
36.580	2.45448	30.4
59.185	1.55982	6.0
61.005	1.51757	6.0
65.325	1.42727	6.5

Table (19): XRD physical data of nitric acid leached black paste

3.5 ELECTROCHEMICAL STUDY ON THE BLACK BATTERY PASTE

3.5.1 Reaction of γ-Manganese Dioxide with Zinc Chloride under Normal Conditions

One gram of zinc free powdered black paste was soaked with 50ml 0.2 M zinc chloride solution for 7 days then filtered. The filtrate was analyzed by an atomic absorption and chemical analysis. The zinc concentration in the solution was determined. It is found that zinc concentration in the mother liquor does not change (0.2M). This indicates that no chemical reaction taking place between zinc chloride and manganese dioxide under ordinary conditions.

3.5.2 Reaction of γ-Manganese Dioxide with Zinc Chloride under Polarization Conditions

Formation of the zinc –manganese compound by electrochemical process was performed. The cell, shown in fig. (30), is used. The cathode is a mixture of γ-manganese dioxide and carbon black free from zinc ions. The anode is a zinc sheet with 3cm (in length), 2cm (in width) and thickness of 0.9mm. Both cathode and anode are immersed in an electrolyte made of 1M ammonium chloride solution. Fig.(31) illustrates the cyclic –voltametry curve for the discharge of the cathode of this cell. It seems that γ-manganese dioxide starting transformation to MnOOH and Mn^{2+} (part A) with the proceed of the cathodic reaction. Increasing the cathodic potential, causes the deposition of zinc on manganese dioxide and / or hydrogen evolution (part B). When the electrode potential of the cell is reversed (γ-manganese dioxide behaves as anode), the previously deposited zinc metal is oxidized to zinc ions which goes

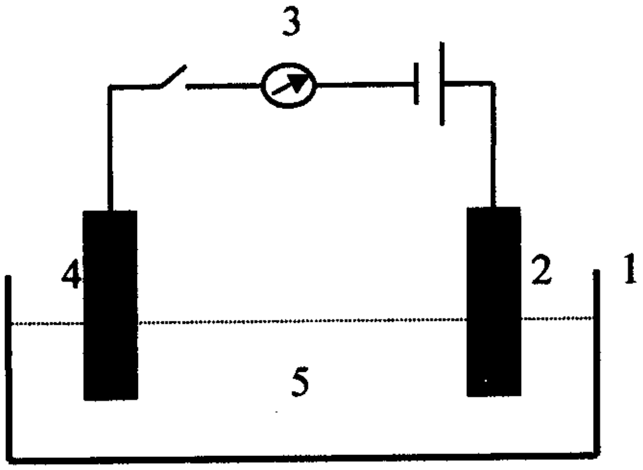


Fig.(30): The used electrochemical cell

1. Container
2. Anode
3. Detector
4. Cathode
5. Electrolyte

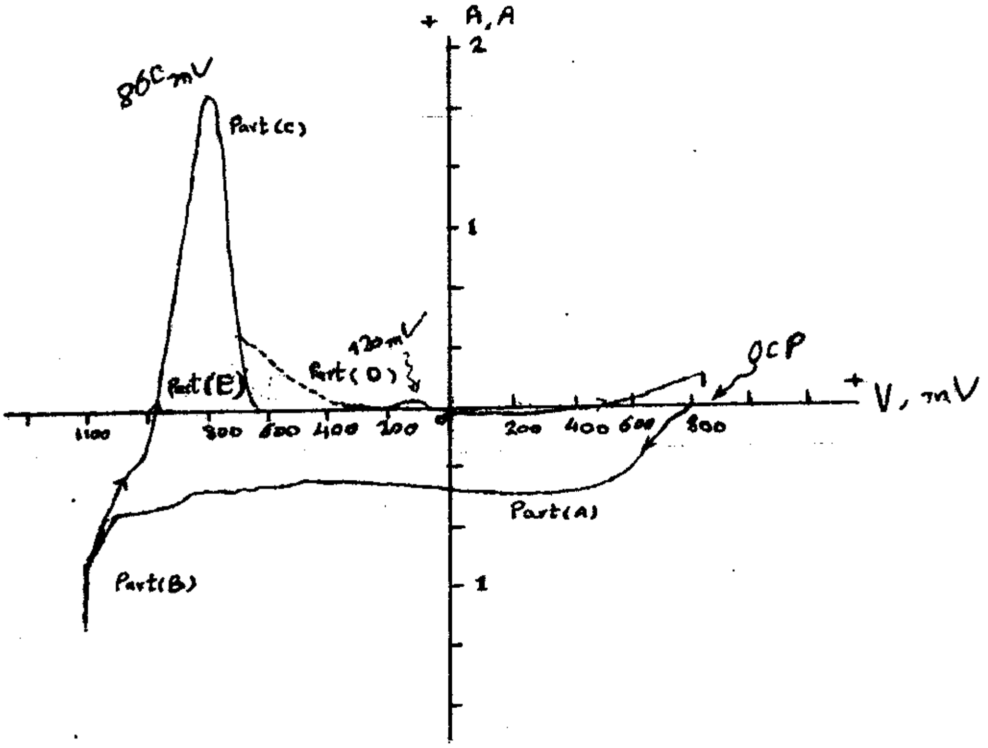


Fig.(31): The cyclic-voltametry of MnO_2 cathode discharge into the solution (part C). It seems that, under these electrolytic conditions no zinc is deposited on the manganese dioxide electrode. However, a zinc-manganese compound is formed as an insoluble compound and remains cohered to the γ-manganese dioxide. This process is detected from the gradual decrease in the all potential (part D), in contrivers to the sharp decrease if no zinc-manganese compound would take place (part E). The formed compound is further confirmed by XRD analysis of the cathodic powder. Fig.(32) and table(20) show the XRD chart and its physical data.

The galvanostatic study for the γ-manganese dioxide is illustrated in fig. (33). The electrode material is prepared from pure synthetic γ-manganese dioxide. The applied current is 40 mA. The curve involves different sections, each of which is chacterized by specific potential represented by a plateau. Each of these sections indicates the formation of certain compound only formed under a given potential.

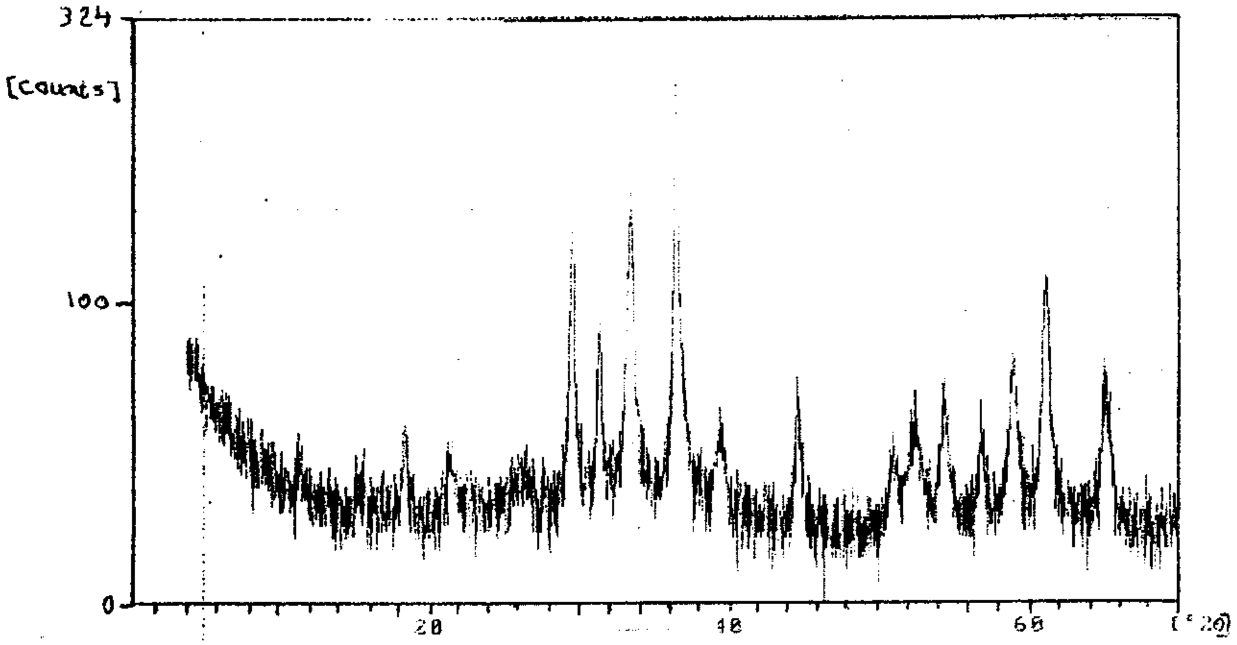


Fig.(32): XRD chart of the MnO_2 cathodic powder

Angle	d-value	Intensity
4.360	20.24977	9.2
11.310	7.81708	2.8
15.390	5.75267	2.2
18.285	4.84787	7.0
21.450	4.13917	4.5
26.295	3.38647	2.4
27.690	3.21894	2.0
29.535	3.02193	47.7
31.285	2.85676	23.4
33.355	2.68405	58.9
36.420	2.46489	100.0
39.465	2.28144	6.7
44.730	2.02436	14.0
51.160	1.78400	6.3
52.570	1.73943	10.8
54.385	1.68558	14.0
56.790	1.61978	9.6
58.955	1.56535	21.0
60.940	1.51903	30.1
64.945	1.43470	13.1

Table (20): XRD physical data of MnO_2 cathodic powder

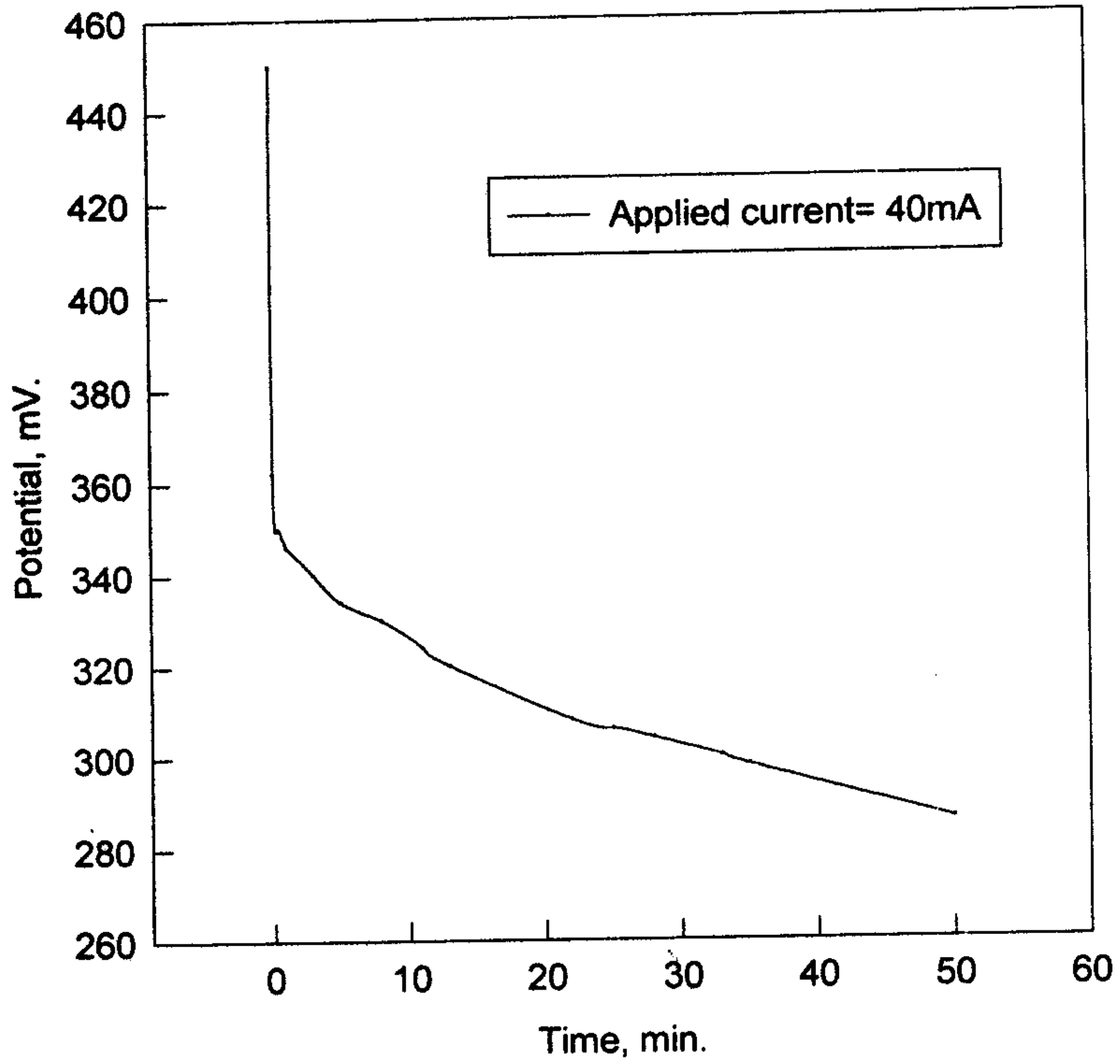


Fig.(33), Glvanostatic study of γ-MnO_2 cathode.

3.6 SEPARATION OF THE CARBON AND γ-MANGANESE DIOXIDE FROM THE BLACK PASTE BY FLOTATION AND MAGNETIC SEPARATION PROCESSES

A set of experiments has been carried out to study the efficiency of some materials to help separation of carbon, γ-manganese dioxide and other manganese compounds. The target was to make use of these minerals in the manufacture of the dry battery cells. Different frothers, collectors and depressing agents were used during the floatation process. In addition, magnetic separation experiments were tested using wet or dry technique. Results obtained from all these experiments revealed that the different forms of manganese are identical from the mineralogical aspects and these behave identically. Further more, carbon black is only removed by burning out at high temperature [900^0C]. This pyrometallurgical treatment spoils the γ-manganese dioxide form, transforming it to inactive form. So, the product becomes immaterial for the dry cell manufacture. For all these reasons, mineral processing methods have failed to achieve successful separation of the black paste ingredients.

Removal of zinc and manganese compounds by hydrometallurgical treatment seems more significant as the obtained products meet the standard specifications for use in different areas.

3.7 RECOVERY OF THE REMAINING BATTERY INCLUSIONS

3.7.1 Recovery of Carbon Rods

After cutting the spent battery cells, carbon rods were separated carefully to avoid their degradation. The adherent foreign materials were washed by flushing water. The weight percentage of these carbon rods amounts to 6.5%. These carbon rods are directed to battery industry.

3.7.2 Recovery of the Covering Paper

The quantity of the separated paper amounts to 9%. This quantity is directed to paper industry.

3.7.3 Steel Discs Treatment

Estimation of the weight percentage of steel discs revealed that for each cell, two steel discs are inserted with an average weight percentage of 4.2%. Chemical analysis using chemical methods to determine its chemical composition are carried out. Results show that, the tin % is 0.0173%. The reminder is iron. These discs are directed to the iron making industry.

3.8 SEPARATION OF METAL VALUES FROM THE SPENT DRY BATTERIES

3.8.1 From the White Paste

The white paste contains mainly ammonium chloride, [94.93%], and zinc chloride, [4.8%], and manganese impurity. In this work, ammonium chloride was leached with distilled water. The salt was freed from zinc and manganese by the addition of equimolecular weight of hydrogen peroxide to precipitate α-manganese dioxide. After filtration, the filtrate was treated with mixture of hydrogen and ammonium sulphides to precipitate zinc sulphide. After filtration, the filtrate was evaporated to obtain pure ammonium chloride. The latter zinc sulphide is heated at 600^0C to obtain zinc oxide.

Therefore the following metal values are prepared from the white paste:

1. Ammonium chloride ....5.6% by weight of battery cell.
2. Zinc chloride, sulphate, hydroxide, oxide or alkali zincate ......0.14% as zinc by weight of battery cell.
3. α-Manganese dioxide .... 0.03% by weight of battery cell.

3.8.2 From the Slag of the Pyrometallurgical Recovery of Metal Zinc from the Spent Cans

1. Zinc chloride ....1.7% by weight of the battery cell.
2. Zinc oxide ....1% by weight of the battery cell.

3.8.3 From the Black Paste

The black paste weighs 54.5% of the spent battery. It contains 6.9% zinc, 6.5% carbon and 41.1% of different manganese compounds especially γ-manganese dioxide. Zinc is coupled with manganese dioxide to form $ZnO.Mn_2O_3$ which is formed during the discharge process of the battery. This compound weighs 25.37% of the spent battery [8.59% as ZnO, and 16.77 as Mn_2O_3]. Therefore, the black paste composition is as follows:

$ZnO.Mn_2O_3$	25.59
Carbon	6.50
γ -MnO_2	22.61
Total	54.5%

It is found that, the total is 54.5% by weight of the spent battery.

The zinc-manganese compound was leached using acid or alkali leachants. The metal values prepared from the black paste depend on the type of the leachant as given in table (21)

Table (21), Metal values obtained from black paste using certain leachant

Leachent	Leaching product (% wt to spent cell)						
	zinc		Manganese		Un-leached		
	Formed compound	wt, %	Formed compound	wt, %	C wt,%	MnO_2 wt,%	$Mn(OH)_2$ wt,%
HCl	$ZnCl_2$	14.3	$MnCl_2$	26.6	6.5	22.6	–
H_2SO_4	$ZnSO_4$	16.0	$MnSO_4$	32.0	6.5	22.6	–
NH_4OH	$Zn(OH)_2$	10.5	–	–	6.5	22.6	18.9
	ZnO	8.6	–	–			
NaOH	$Zn(OH)_2$	10.5	–	–	6.5	22.6	18.9
	ZnO	8.6	–	–			