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Simultaneous leaching of zinc sulphide concentrate and manganese ore in sulphuric acid

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Abstract: The kinetics of simultaneous leaching of zinc sulphide concentrate and manganese ore in sulphuric acid has been studied in the temperature range of343 to 373 K. The rate of reaction increases with the increase in temperature. The leaching reaction of zinc and manganese was observed to be topochemical in nature. An activation energy of 6.33 kJ/mole was calculated for zinc extraction whereas for manganese extraction it was found to be 1.85 kJ/mole. The disparity in the activation energy value was also found in leaching efficiency. A recovery of 81% zinc and 95% manganese was observed with 1.8 M H_2SO_4 in 120 minutes duration at 373 K. The kinetic data examination indicates that the reaction takes place on surface of the mineral via chemically control mode. The zinc concentrate and leach residue were characterized by X-ray diffractometric (XRD) studies.

Keywords: *Zinc sulphide, Manganese ore, Sulphuric acid leaching, Sulphur, Simultaneous leaching*

1. INTRODUCTION

Zinc is produced by sulphide-roasting, leaching and electrowinning method[1]. The process consists of zinc sulphide roasting and then leaching in sulphuric acid or spent electrolyte. After the removal of impurities, zinc metal from solution is deposited. In the same way electrolytic grade manganese dioxide is recovered by oxidative roasting of high grade manganese ore to MnO and thereafter leaching in mild sulphuric acid. The leached solution is then purified to produce anodic deposition of manganese dioxide.

To eliminate the roasting steps in zinc and manganese extraction, various attempts have been made by several workers[2,3,4,5] on pressure leaching of concentrate in sulphuric acid. In this case it was necessary to employ pressure in an oxygen atmosphere at about 383K. For the simultaneous electro deposition of zinc and manganese dioxide, several workers[6,7,8] have shown interest to establish a process for simultaneous recovery of zinc and manganese from their ores. A commercial process has not been established to utilize manganese simultaneously in leaching and electrowinning cell. It has been recognized by Stander et al.[9],1960 that the beneficial effects of the presence of manganese during zinc leaching from sulphide ore. The research work done by Pande et al[10], (1997) confirms that the simultaneous leaching of zinc and manganese is possible in sulphuric acid. From the leach liquor the electro deposition of zinc metal and electrolytic manganese dioxide is also possible. The process is energy efficient as the power required for deposition of zinc from its electrolyte additionally produces battery grade manganese dioxide. The elemental sulphur can also be recovered from the leach residue as saleable product. The overall reaction of simultaneous extraction of zinc and manganese is as follows,

$$ZnS + MnO_2 + 2H_2SO_4 = ZnSO_4 + MnSO_4 + S^o + 2H_2O \quad (1)$$

The process is under developmental stage and also there is no kinetics data available for the simultaneous leaching of zinc and manganese in sulphuric acid. Therefore, the present investigation was undertaken to understand the process and kinetics of reaction of zinc and manganese extraction during leaching in sulphuric acid.

2. RAW MATERIALS

Zinc suphide concentrate and manganese ore was used as the raw materials for the experiments. The zinc sulphide concentrate used was obtained from M/s Nepal Metal company Limited of Ganesh Himal Region of Nepal. The manganese ore (pyrolusite) available in our laboratory was used for the study. The chemical analyses of the concentrate and ore are shown in Table 1. Sulphuric acid and inorganic additive used in this study was of Analytical grade (AR).

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Table1. Chemical analysis of zinc concentrate and manganese ore.

Chemical analyses

Constituents	Percent
Zinc concentrate	
Zinc	55.97
Sulphur(total)	32.55
Iron	6.5
Lead	0.51
Cobalt	0.10
SiO_2	0.20
Al_2O_3	trace
Silver	trace
Loss of ignition	4.17
Manganese ore	
Manganese dioxide (MnO_2)	70.74
Iron	10.62
SiO_2	11.62
Al_2O_3	1.50
Loss of ignition	5.52

3. EXPERIMENTAL

The experiment was done in 2 dm^3 capacity of steel reactor lined with polypropylene. It was connected with a steam coil to heat the liquid to about 373K. The leaching was done with a non-corrodible stirrer. A stoichiometric amount of zinc sulphide concentrate and manganese ore was mixed. The calculated amount of sulphuric acid solution was taken in the reactor and heated up to defined temperature. With continuous stirring the mixed mass was added slowly into the reactor along with inorganic additive like 1% copper sulphate[11]. The addition of additive assists in accelerating the speed of reaction rate by making a catalytic film on zinc and manganese metal during leaching and it was confirmed in the patent. During the course of all leaching experiments this additive was maintained. Finally, the leaching was done and leach liquor sample was taken, cooled and filtered. The metal content extracted was analyzed with the help of atomic absorption spectrophotometer (Thermo Scientific ICE 3000 series). The X-ray diffraction of few samples were also carried out with the help of Bruker D8 advance X-ray diffractometer and d-values were calculated.

4. RESULTS AND DISCUSSIONS

In the initial stage of leaching reaction, it was necessary to observed the rate of leaching in different operating conditions. The variables such as particle size of solid feed, temperature and concentration of sulphuric acid were studied. The optimum particle size of zincsulphide concentrate and manganese ore were found to be -75µm and -425µm respectively. The best result at a constant stirring speed of 100 rpm was optimum. The solid to liquid ratio throughout the experiment was maintained to 1:10. These were mixed in stoichiometric proportion according as per the reaction(1).

Effect of Temperature on Metal Recovery

The temperature of reaction was varied from 208 K to 373 K and the corresponding metal recovery was calculated. The results are depicted in Fig. 1.

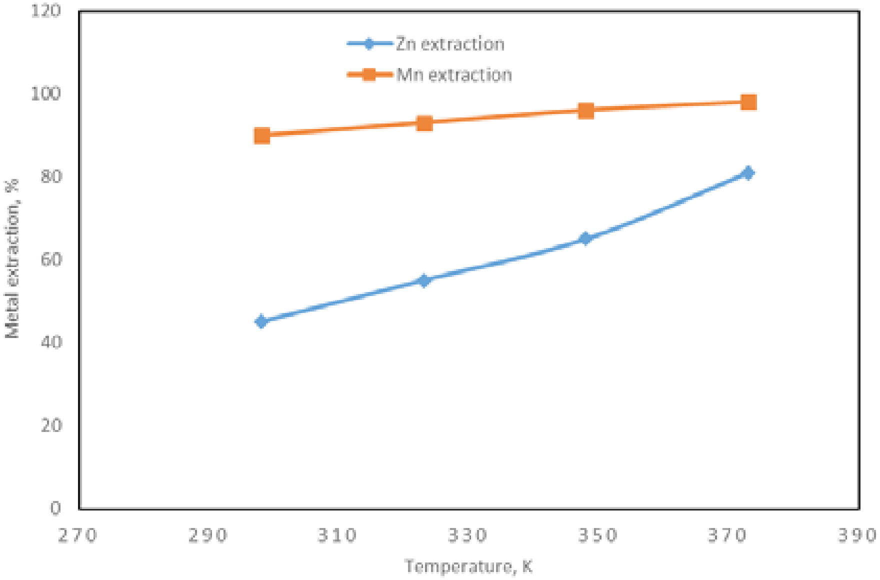

Fig.1. ***Effect of temperature on metal extraction***

From the plot it can be seen that at lower temperature in 1.8 M H_2SO_4 and 120 minutes the zinc recovery is low (45%) whereas manganese recovered well (90%). As soon as temperature increases the recovery of zinc also increases and at 373 K it is 81 % whereas manganese recovery rose to 95%. It can be seen that both zinc and manganese recovered at this temperature under the similar conditions.

Effect of Leaching Time on Metal Recovery

Under the optimum condition (1.8 MH_2SO_4, 373 K temperature) the time of reaction was varied and the results are shown in Fig. 2.

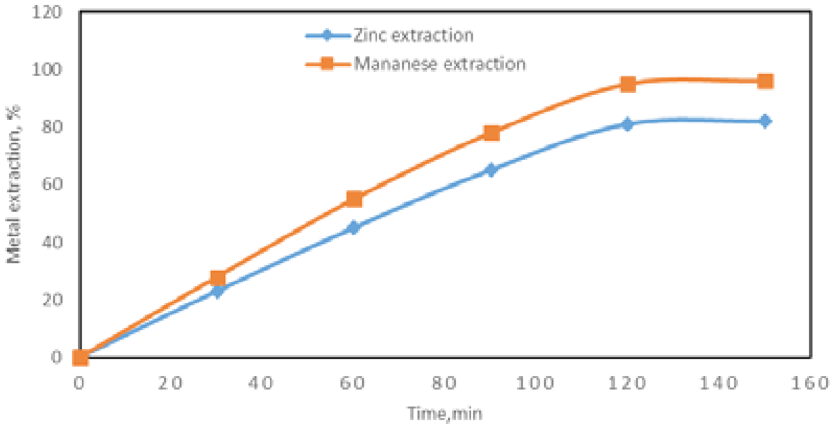

Fig.2. ***Effect of leaching time on metal extraction***

It is evident from the figure 2 that at 120 minutes the recovery of zinc and manganese were 81% and 95% respectively. Beyond this time of reaction there was no increase in leaching. Thereafter, the increase in time does not show appreciable change in the recovery.

Effect of Acid Concentration on Metal Recovery

The leaching was done at varying acid concentration at 373 K and for 120 minutes leaching duration. As indicated by figure 3 the maximum extraction of metal in 120 minutes duration was found to be 81% zinc and 95% manganese at 373 K in 1.8 M sulphuric acid concentration.

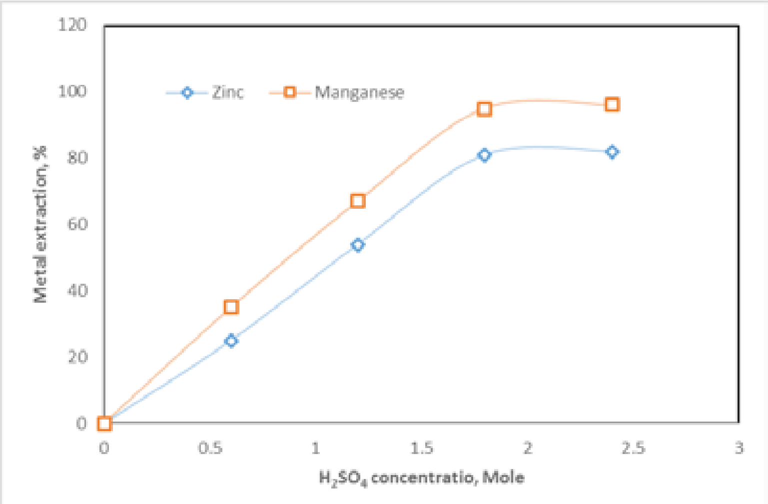

Fig.3. ***Effect of acid concentration on metal extraction***

The optimum concentration of sulphuric acid from the figure 3 was found to be 1.8 M concentration. Beyond 1.8 M of sulphuric acid concentration there was no appreciable change in recovery. Therefore, the optimum condition for these two ores for metal recovery was, temperature 373 K, time 120 minutes and H_2SO_4 concentration 1.8 M. The elemental sulphur formed during the leaching reaction settled in the leach residue. It was recovered by dissolving in carbon disulphide and thereafter distillation to remove sulphur. After distillation of carbon disulphide, the sulphur remained in the flask. The total mass balance was done at the end of experiment and it was found that all metal and elemental sulphur were balanced.

Kinetics Study of Metal Recovery

At the optimum acid concentration, particle size and stirring speed the kinetics study was undertaken. The extraction of manganese at 1.8 M H_2SO_4concentration was carried out in the range of temperature 298 to 373 K and the results obtained with varying time is as shown in figure 4. As temperature increases the fraction extracted (α)increased and the maximum conversion was observed at 373 K in 120 minutes. With further increase in time (beyond 120 minutes) there was no appreciable change in manganese recovery.

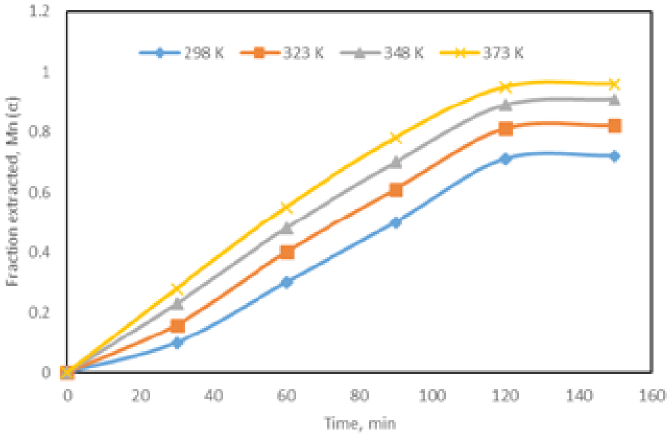

Fig.4. ***Effect of leaching time on manganese extraction***

The extraction of zinc and manganese is dependent on temperature approximately and at 373 K, the sulphate formation may be considered to occur through *in situ* chemical reaction of zinc-manganese-sulphuric acid. The proceeding of reaction in the process, used the topochemical model of kinetics expression may be expressed as below[12].

$$1-(1-\alpha)^{1/3} = kt$$

Where k and t are a specific rate constant and time of reaction respectively. The data obtained in the case of manganese extraction were found to follow this expression when $1-(1-\alpha)^{1/3}$ was plotted against t at different temperature. The figure 5 represents the straight lines confirming the topochemical kinetic model.

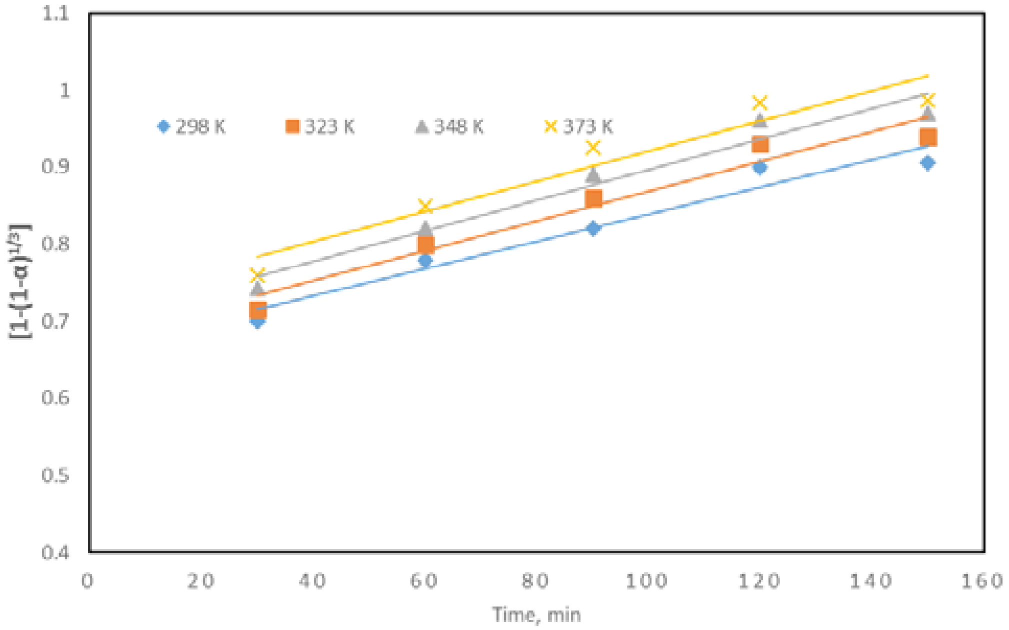

Fig.5. ***Effect of kinetic data with time***

The equations governing diffusion control and mixed control were also used, but the kinetic data did not fit well as the plots were nonlinear. Based on the best fit of kinetic data, it was concluded that the leaching of zinc and manganese occurs on the surface of the ore following the topochemical control mode [10]. The corresponding k values at different temperatures were calculated with the slope of plot. Based on Arrhenius plot, the activation energy of reaction was determined to be 1.85KJ/mole for manganese extraction as demonstrated in figure 6.

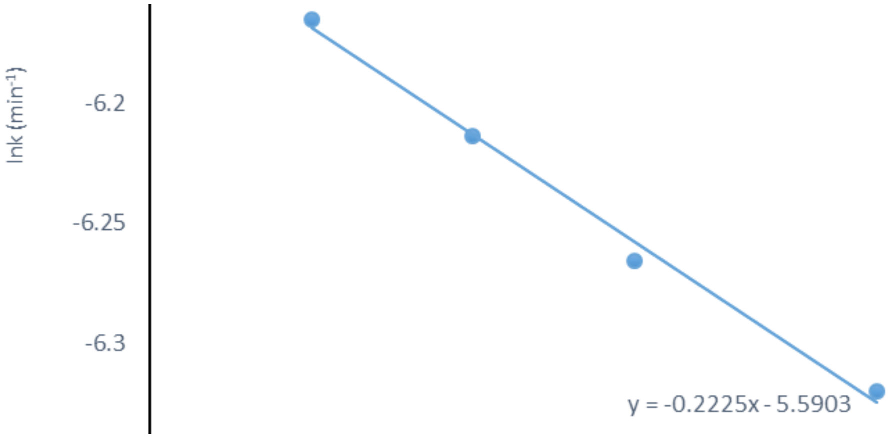

Fig.6. ***Arrhenius plot for manganese extraction***

The low activation energy of the manganese extraction reaction defined as the reaction is exothermic in nature and only 373 K temperature is required to obtain 95% recovery. Because of exothermicity the additional heat was not required which could further lower the value of activation.

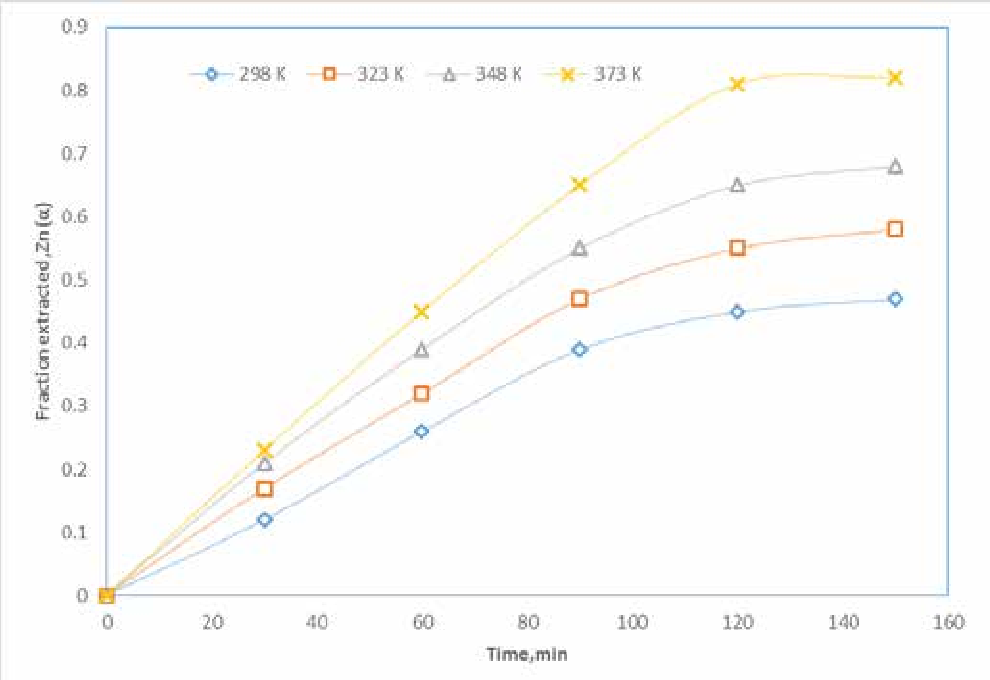

Fig.7. ***Effect of leaching time on zinc extraction***

Extraction of zinc in the same leaching experiment was studied at 1.8M H_2SO_4 and in the temperature range of 298 to 373 K. The fraction extracted (α) with respect to time (t) at different temperature is shown in figure 7.

It can be observed from the figure that at lower temperature the extraction of zinc is low whereas with the increase in time and temperature the fraction extracted (α) increased. The data obtained on different fraction extracted (α) at different temperature and time were fitted on different kinetic model. It was observed that the kinetic data were found to be best fitted in the topochemical model. The expression $1-(1-\alpha)^{1/3}$ was plotted against time t at different temperature as shown in figure 8.

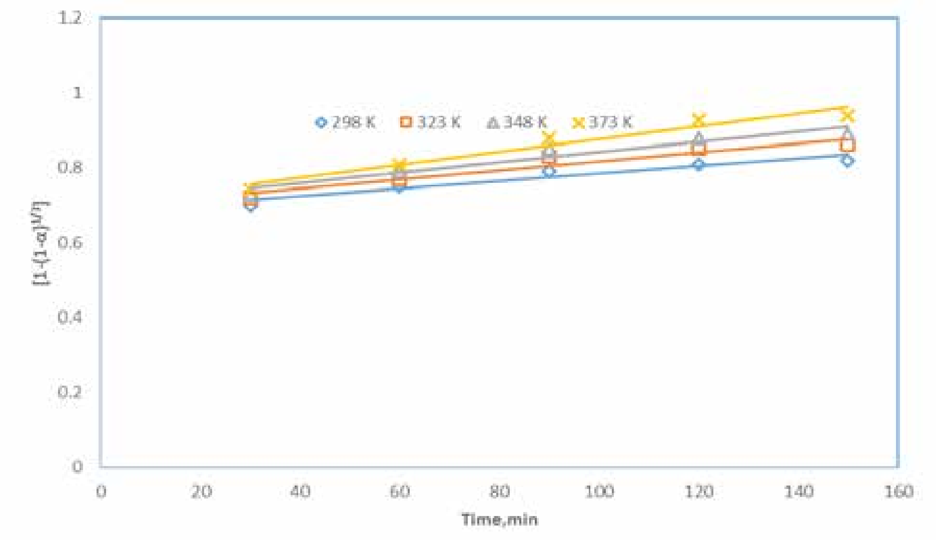

Fig.8. ***Effect of kinetic data with time***

The plot 1-$(1-\alpha)^{1/3}$ against time showed the straight lines which confirmed that the reaction of zinc extraction followed the topochemical kinetic model. The corresponding k values at different temperatures were calculated with the slope of the straight lines. Based on Arrhenius plot slope of the activation energy value was determined (figure 9). It was found that an activation energy of 6.33 kJ/mole was required for the extraction of zinc. This value is close to a reaction of topochemical kinetic model.

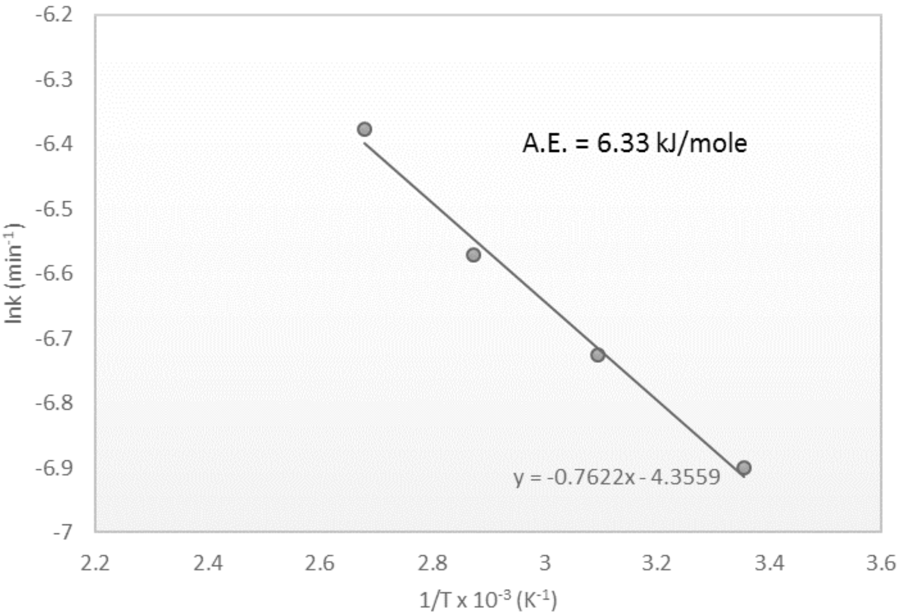

Fig.9. ***Arrhenius plot for zinc extraction***

The difference in the activation energy value of manganese extraction (1.85 kJ/mole) and zinc extraction (6.33 kJ/mole) affects the overall metal extraction. A recovery of 95% manganese and 81% zinc was observed in 1.8M H_2SO_4 in 120 minutes duration. The solution obtained after leaching was purified by normal purification method. The chemical composition of obtained purified leach solution is shown in Table 2. The solution obtained is suitable for the simultaneous electro deposition of zinc metal and manganese dioxide in a single cell.

Table2 Chemical composition of the purified leach solution.

Constituents	g/L
Zinc	49.3
Manganese	34.2
Iron (ppm)	0.33
Nickel (ppm)	0.14
Arsenic (ppm)	0.14
Cadmium (ppm)	0.30
Silver (ppm)	0.11
Lead (ppm)	n.f.
Cobalt (ppm)	n.f.

The correlated d-values obtained from the X-ray studies of the zinc concentrate and leach residue were tabulated in Table 3. The comparison of d-values of sphalerite and wurtzite phases present in zinc concentrate and leach residue with the JCPDS values were also made.

Table3 ***Comparison of d-values of sphalerite and wurtzite in zinc concentrate and leach residue.***

Zinc concentrate

Observed		**As per JCPDS.**		**Phase**
d A^{o}	**I/I_1**	**d A^{o}**	**I/I_1**	
3.129	100	3.123	100	Sphalerite
2.712	10	2.705	10	Sphalerite
1.915	51	1.912	51	Sphalerite
1.633	33	1.633	30	Sphalerite
1.243	14	1.239	4	Wurtzite
1.106	15	1.103	6	Wurtzite
1.041	5	1.039	4	Wurtzite

Leach residue

Observed		**As per JCPDS.**		**Phase**
d A^{o}	**I/I_1**	**d A^{o}**	**I/I_1**	
1.915	100	1.904	50	Wurtzite
1.243	13	1.239	4	Wurtzite
1.106	9	1.103	6	Wurtzite
1.041	4	1.039	4	Wurtzite

It was seen from the JCPDS data that the zinc concentrate was mainly associated with sphalerite and wurtzite phase. The X- ray studies indicated that leach residue was mainly comprising of wurtzite phase which remained unreacted during the course of reaction. It may be concluded that due to the presence of unreacted wurtzite phase in leach residue the recovery of zinc was low (81%).

5. CONCLUSIONS

The simultaneous leaching of zinc and manganese was studied in the absence of external mass transfer effect in sulphuric acid. Based on data obtained the following conclusions may be drawn.

1. The extraction of manganese and zinc insulphuric acid medium is 95% and 81% respectively at 373K at 1.8 M sulphuric acid in 120 minutes of leaching reaction.
2. The reaction of leaching kinetics followed the topochemical model in the temperature range of 298 to 373 K.
3. The activation energy value for manganese extraction was calculated to be 1.85 kJ/mole, whereas for zinc extraction it was 6.33 kJ/mole.
4. The XRD studies confirmed the presence of sphalerite and wurtzite phase in the zinc concentrate whereas unreacted wurtzite phase was found in the leach residue.

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