Manganese recovery from secondary resources: A green process for carbothermal reduction and leaching of manganese bearing hazardous waste

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ABSTRACT

During the hydrometallurgical extraction of zinc by electrowinning process, a hazardous solid waste called anode mud is generated. It contains large quantity of manganese oxides (55–80%) and lead dioxide (6–16%). Due to the presence of a large quantity of lead, the anode mud waste is considered hazardous and has to be disposed of in secure landfills, which is costly, wastes available manganese and valuable land resources. For recovery of manganese content of anode mud, a process comprising of carbothermal treatment using low density oil (LDO) followed by sulphuric acid leaching is developed.

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1. Introduction

Zinc is an important non-ferrous metal next only to copper and aluminum. It is brittle at room temperature, but becomes ductile in the temperature range 100–150 °C and can be rolled into sheets or drawn into wires [1]. The hexagonal close-packed crystal structure governs the behavior of zinc during fabrication [2]. It finds applications in batteries, galvanizing, automobile and die-casting industries. Zinc compounds are used in cosmetics and pharmaceutical compositions, as micro-nutrient in agriculture and in textile industries, etc.

The world production of zinc in 2008 was reported to be 11.683 million tons [3]. In India, its production for the 12-month period between April 2006 and March 2007 was about 0.237 mT against a demand of 0.333 mT. The corresponding values for 2005–2006 were 0.331 mT and 0.430 mT, respectively [4]. The gap in production and demand was primarily met by imports. In primary production, zinc sulphide (Sphalerite) ore is widely employed while in secondary sector zinc and brass ash, dross, skimmings, etc. are used as raw material. Zinc can be produced either by pyrometallurgical or hydrometallurgical process [5]. However, the latter process, which involves grinding, roasting, leaching in acid and removal of impurities followed by metal electrowinning using aluminum cathode and lead (with 0.5–1% silver addition) anode, is more com-

monly employed [6]. During electrolysis, zinc metal deposits on the cathode and is removed in the form of sheets by peeling. To protect anodes from excessive corrosion, manganese compounds are added (2.5–7 gpl). On the surface of lead anodes, lead dioxide is formed by electro-oxidation and manganese (present in the bath) deposits as manganese oxide. The deposited oxides are powdery in nature and fall off to the bottom of the bath. At the end of the electrowinning cycle the powder (anode mud) is removed from the bottom of the electrowinning cell. The quantity of anode mud generated depends on the composition of the bath and conditions of electrolysis and generally varies between 25 and 35 kg for every ton of zinc produced [7]. Due to the presence of significant content of lead (as dioxide) in the anode mud (about 6–16% depending on the electro-winning process parameters, purity of electrolyte and anode composition, etc.), it is categorized as hazardous waste and has to be disposed of in secure landfills. The increasing transportation and land costs make its disposal very costly. Further, the high manganese oxide content (55–80%) makes it attractive and imperative to recover and recycle manganese content of anode mud.

As manganese is a multi-valent ion, anode mud contains a mixture of different oxides of manganese, some of which are insoluble in sulphuric acid. To achieve maximum recovery of manganese, the insoluble oxides need to be converted to soluble forms. It has been reported [8–10] that carbo-thermal treatment of pyrolusite ore using coal as reducing agent helps in improving leachability of manganese content in H_2SO_4. However, Indian coals have high ash content (30–45%) and their usage will cause generation of large quantity of solid waste, the disposal of which may again pose problems due to the presence of lead. Other reducing agents

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Table 1
Chemical composition of raw anode mud, washed and carbothermally reduced anode mud. Compositions are in weight percentage (%).

% Constituent (As element) →	Mn	Pb	Zn	Fe	Ca	Ag	Moisture
Raw anode mud (% w/w)	43.9	3.87	2.10	0.087	9.01	0.028	2
Water washed anode mud sample (% w/w)	46.65	6.54	0.13	0.11	9.25	Not estimated	0.45
Carbothermally reduced anode mud (% w/w)	50.50	7.18	0.14	0.12	9.94	Not estimated	–

reported in literature for partial reduction of the ore include iron sulphide (pyrite) [11,12], graphite [13], sulphur slag [14], oxalic acid [15], carbohydrate (as glucose [16,17], as sucrose [18,19]), coal pellets containing coal, bituminous lacquer, shale oil [20], non-coking coal [21], and hydrogen [22]. Kholmogorov et al. [11] as well as Parida et al. [12] leached manganese values from manganese ores using sulphuric acid in the presence of pyrite in the temperature range of 80–100 and 70–95 °C respectively. Welham [13] achieved the reduction of manganese bearing ores in the range of 500–700 °C by extended milling of the ore with graphite for 10 h prior to thermal treatment. Abou-EI-Sherbini [14] used sulphur slag for reducing low grade pyrolusite ore at a temperature in the range of 300–400 °C in air or in a closed stainless steel tube. Akdogan and Eric [23] reduced manganese ore using carbon and carbon monoxide in the temperature range of 1100–1350 °C. Literature survey also reveals that partially reduced manganese dioxide is highly reactive in acid/alkaline medium. Manganese dioxide can be leached in ammonical solution (containing ammonia and ammonium salt) [24,25], SO_2 [26,27], $FeSO_4$ solution [28] and dilute nitric acid [29,30] as well as in dilute hydrochloric [31–33]. Abbruzzese et al. [34] achieved maximum leaching of manganese values from low grade manganese ores with aqueous SO_2 or through bio-leaching using heterotrophic micro-organisms in 15–20 days operation. Das et al. [25] studied the reaction kinetics of reduction of manganese dioxide with ammonium sulfite solution by heating in the temperature range of 80–110 °C in an autoclave. To obviate the disadvantages encountered in above processes such as high cost of reducing agents, e.g., glucose/sucrose/oxalic acid, high processing time/fuel cost, need of autoclave and use of environmentally hazardous chemistry, a carbothermal treatment process for anode mud utilizing low density oil (LDO) – a liquid phase reducing agent has been developed in our laboratory to render its manganese content leachable in H_2SO_4 [35] as leaching of partially reduced manganese ore in dilute sulphuric acid is by far the most commonly employed method in the industry for making

manganese sulphate [36–43], which may subsequently be used for making manganese compounds such as manganese oxide [44,45].

The results of the process developed in our laboratory on carbothermal treatment of anode mud using LDO followed by leaching in dilute H_2SO_4 are presented in this paper.

2. Materials and methods

2.1. Raw materials and chemicals

The anode mud sample was collected from a primary zinc producing industry. The low-density oil (LDO) was used as a liquid source of carbon. L.R. (Merck India) sulphuric acid was used in leaching experiments.

2.2. Carbothermal reduction process

The anode mud collected from primary zinc industry was found to be acidic in nature, having a pH of about 1. To avoid corrosion of the reactor, the raw anode mud was thoroughly washed with water and dried in air-oven and then mechanically homogenized with appropriate quantity of liquid reducing agent (LDO). The homogenized mixture was placed in a steel hood (15 cm × 15 cm × 30 cm) fitted with a steel nozzle to provide escape for evolving gases. The hood, with mix inside, was placed in an electric muffle furnace and the temperature of the furnace was raised at a rate of 10 °C/min to required temperature. After heating for desired duration, the hood was withdrawn from the furnace and the contents were allowed to cool to ambient. A reducing atmosphere was maintained in the reaction vessel during cooling. The carbothermally treated anode mud sample was leached with sulphuric acid. The process parameters were optimized with regard to concentration of LDO, temperature and duration of heat treatment for optimum recovery of manganese content available in the anode mud.
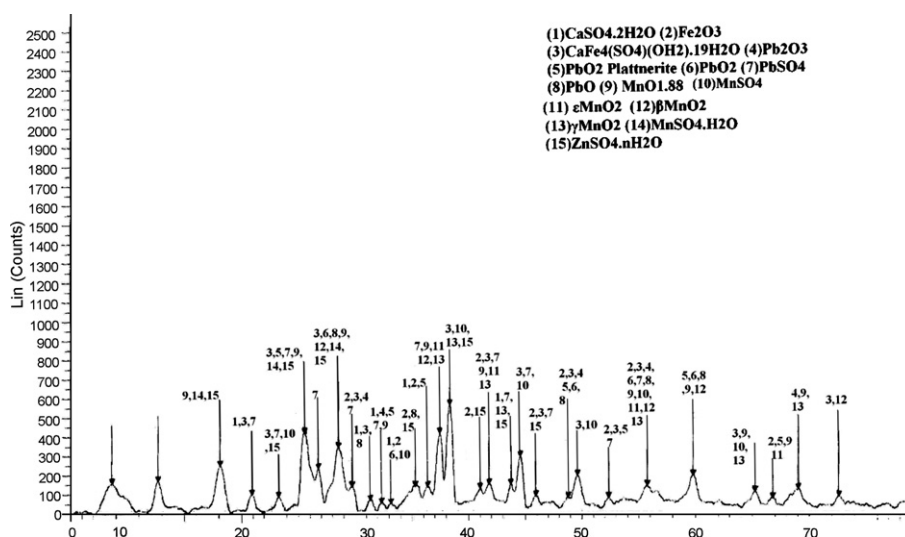

Fig. 1. X-ray diffractogram of raw anode mud.

2.3. Procedure for acid leaching of the carbothermally treated anode mud

For acid leaching process, 10 g of carbothermally treated anode mud was leached with 200 ml sulphuric acid of appropriate concentration in a double walled cell under continuous stirring with the help of a magnetic stirrer for desired duration. The temperature of the contents was maintained by circulation of the thermostated oil through the jacket of the cell. After leaching, the contents were diluted with distilled water and filtered to separate manganese-bearing leachate from the residue. The leaching parameters were optimized based on the percent of manganese recovered in the leachate.

3. Results and discussion

3.1. Physical and chemical characterization of raw, washed and carbo-thermally treated anode mud

The average particle size of the raw anode mud sample, as measured by Malvern Instruments particle sizer (Model MS 14), was 37 μm with 25% below 12 μm and 90% below 125 μm. The surface area of raw anode mud was observed to be 17.47 m^2/g.

Chemical analysis of raw and washed anode mud samples was carried out using standard procedures. The contents of iron, zinc, manganese and lead were analyzed using Atomic Absorption Spectrometer (GBC make model No. 902). As a countercheck, the content of manganese was analyzed by potentiometer titration method [46] also. The chemical compositions of raw, washed and carbothermally treated anode mud are given in Table 1. It is observed that due to water washing the adherent/adsorbed zinc sulphate is removed and hence the concentration of insoluble constituent's like manganese oxides and lead dioxide/lead sulphate increases. On carbothermal treatment of the washed anode mud, due to reduction of oxides to form CO_2, the net metal content in the treated anode mud is observed to increase (see Table 1).
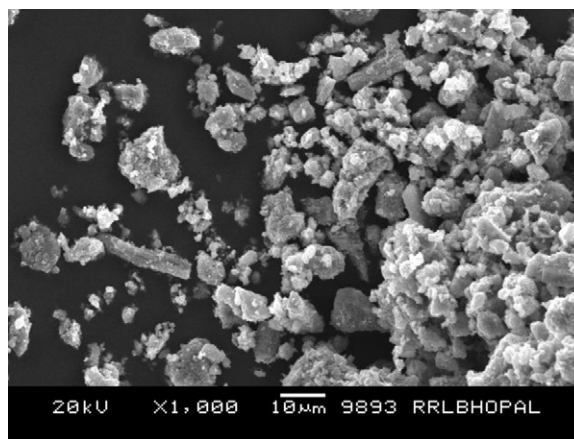

Fig. 2. SEM micrograph of raw anode mud.

3.2. Mineralogical and morphological characterization of raw, washed and carbothermally treated anode mud samples

For identification of the mineralogical phases, X-ray diffraction Spectrometer (Bruker make model D-8 Advance) with nickel-filtered Cu Kα radiation was used. The identification of the phases present in the sample was done by comparing the experimentally observed inter-planer spacing ('d' values) and the intensity of the peaks with the 'd' values of the respective likely substances/phases given in the JCPDS files [47] and search manual. The X-ray diffraction study of raw anode mud (Fig. 1) shows the presence of different phases of manganese oxide like $MnO_{1.88}$, εMnO_2, γMnO_2, βMnO_2, Mn_2O_3 as well as some phases of $MnSO_4 \cdot H_2O$, $PbSO_4$, PbO_2, $CaSO_4 \cdot 2H_2O$, $CaSO_4$, $CaFe_4(SO_4)(OH)_2 \cdot 19H_2O$, $ZnSO_4 \cdot nH_2O$, Fe_2O_3, etc. And the morphology of the waste materials was studied using Jeol make Scanning Electron Microscope (Model JSM 5600). The SEM (Fig. 2) micrograph of anode mud shows a mixed morphology of manganese oxide along with lead components.
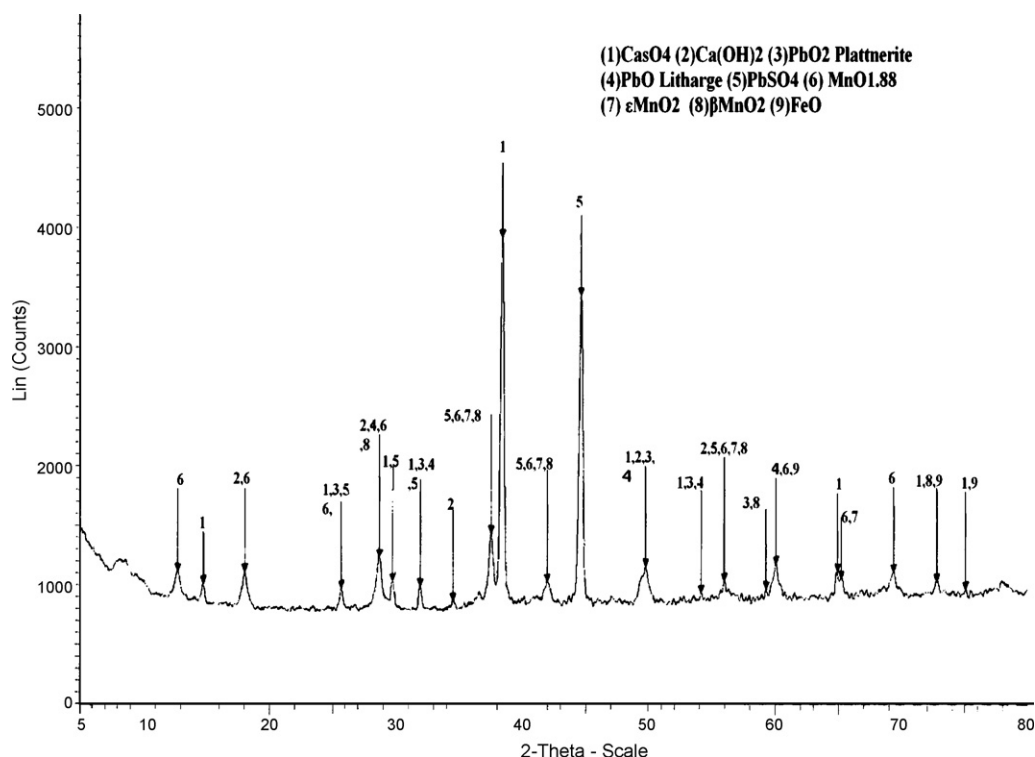

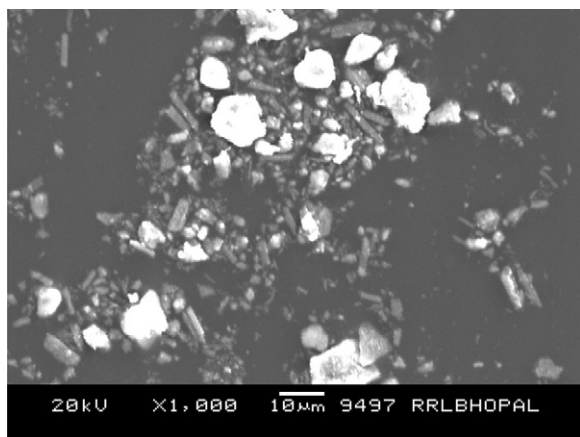**Fig. 3.** X-ray diffractogram of washed anode mud.

Fig. 4. SEM micrograph of washed anode mud.

The mineralogical phases present in the water washed anode mud sample, as identified by X-ray diffraction studies (see Fig. 3) are PbO_2, $PbSO_4$, γMn_2O_3, γMnO_2, $MnO_{1.88}$, βMnO_2, MnO_2 (Remsdellite) and $CaSO_4$ (arising due to neutralization of highly acidic anode mud by lime). $ZnSO_4$, $MnSO_4$, $MnSO_4 \cdot H_2O$, $CaSO_4 \cdot 2H_2O$, $CaFe_4(SO_4)(OH)_2 \cdot 19H_2O$ are observed to be absent. SEM (see Fig. 4) of washed anode mud shows a mixed morphology and all the particles are observed to be agglomerated.

The carbothermal treatment of anode mud at elevated temperatures is effective in reducing acid-insoluble higher oxides of manganese oxide phases into acid soluble phases. Thus peaks corresponding to formation of new phases MnO ('d' values 2.56, 1.57, 1.34, 1.28) and εMnO_2 appear while the intensity of the peaks corresponding to phases $MnO_{1.88}$ and γMn_2O_3, increases. The lead compounds are reduced to PbS ('d' values 2.97, 2.09, 1.79) lead metal and Pb_4SO_7 phases. Fig. 5 shows the X-ray diffractogram of carbothermally reduced anode mud. SEM (see Fig. 6) of CRT anode mud shows the presence of rod shaped and spherical shaped structures.

3.3. Effect of LDO concentration in carbothermal treatment process on recovery of manganese

To determine the content of oil required for carbothermal treatment, 100 g anode mud was thoroughly homogenized with 10, 15,

20 and 25% (v/w) low density oil (LDO) and treated at 650 °C for 120 min following the procedure described above. The carbothermally treated anode mud was then leached with sulphuric acid and the residue was separated by filtration with Whatman filter paper (No. 42; pore size 2.5 μm). The content of manganese in the leachate was evaluated using potentiometric titration method. The results are shown in Fig. 7. The percentage of leached manganese is observed to increase rapidly with increase in LDO content up to 20% (v/w) where after it becomes practically constant. Hence the use of 20% (v/w) LDO in the anode mud–LDO mix was considered to be sufficient and further experiments were carried out using this composition.

3.4. Effect of temperature of carbothermal treatment on the recovery of manganese from anode mud

To optimize the temperature of carbothermal treatment, thoroughly homogenized mix of 100 g anode mud with 20% (v/w) LDO was treated for 120 min at different temperatures ranging from 450 to 750 °C. The results are shown in Fig. 8. The percent manganese content recovered in the leach is observed to increase with increase in treatment temperature up to 650 °C where after it becomes constant. Hence it is concluded that 650 °C is the optimal temperature for carbothermal treatment of anode mud.

3.5. Effect of treatment time on the recovery of manganese from anode mud

To optimize the time required for carbothermal treatment, thoroughly homogenized mix of 100 g anode mud with 20% (v/w) LDO was treated at 650 °C for different time periods varying in the range of 30–120 min. The percentage manganese content recovered is observed to increase with duration of treatment up to 120 min beyond that there is no appreciable gain in manganese recovery (see Fig. 9). Hence a treatment time of 120 min is considered to be optimum for maximum recovery of manganese.

3.6. Effect of acid concentration on leachability of manganese

For optimizing the acid concentration required during leaching, 10 g of carbo-thermally treated anode mud was leached with 200 ml of sulphuric acid of different concentrations ranging between 5 and 50% (V/V) at 100 °C for 7 h. After this period, the solution containing manganese was separated from the residue by
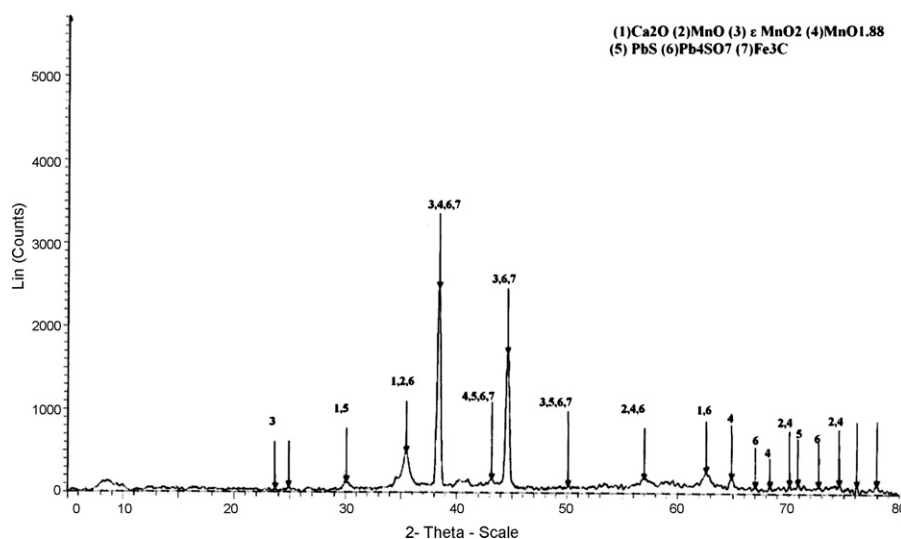

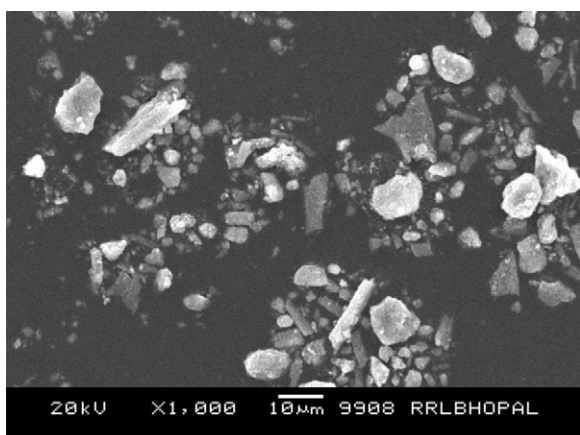**Fig. 5.** X-ray diffractogram of carbothermal treated anode mud.

Fig. 6. SEM of carbothermal treated anode mud.

filtration and analyzed. The results are shown in Fig. 10. The content of leached manganese with 15–30% H_2SO_4 is observed to be almost constant. Since the concentration of acid decreases during leaching and hence 20% acid concentration was considered to be suitable for the leaching of the treated anode mud in sulphuric acid. The manganese leachability in the experiments using 5, 10, 40 and 50% is observed to be lower. While the low leachability of manganese in dilute acid is easily understandable, its decrease in concentrated acid solutions may be attributed to a decrease in the solubility of manganese sulphate.

3.7. Effect of temperature on leachability of manganese

To optimize the temperature of leaching, 10 g carbo-thermally treated anode mud was leached with 200 ml of 20% sulphuric acid solution at different temperatures ranging between 25 °C and 100 °C for 7 h and the results are shown in Fig. 11. It is observed that with increase in temperature of leaching, the manganese recovery increases. However, at temperatures above 100 °C, the acid vapors generated cause severe corrosion and also pose health hazard. Hence a temperature of 100 °C for leaching was considered to be sufficient.

3.8. Effect of time on the leaching of manganese

To optimize the time of leaching process, 10 g of carbothermally treated anode mud was leached with 20% (V/V) H_2SO_4 at 100 °C for different durations ranging between 3 and 8 h. The results are shown in Fig. 12. It is observed that with the increase in
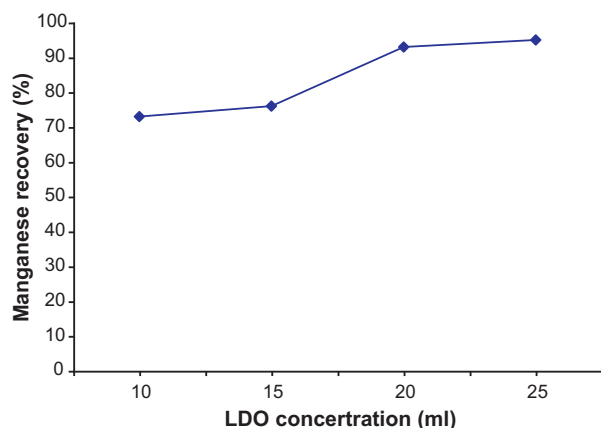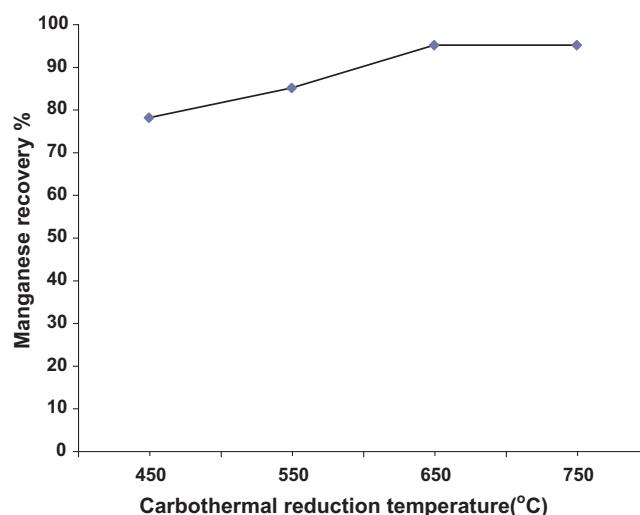

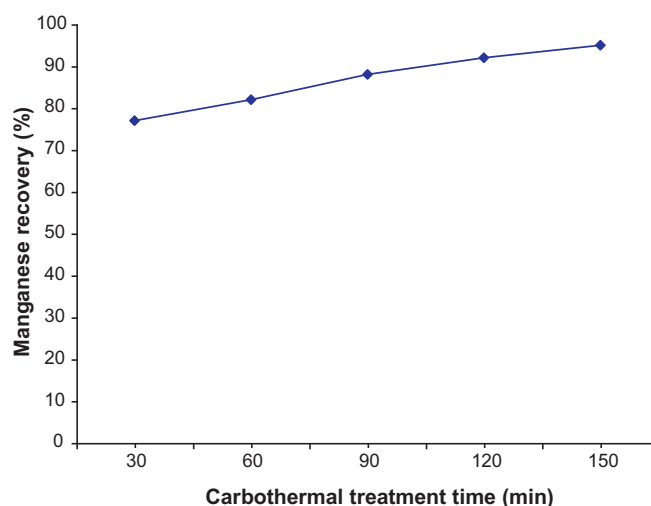**Fig. 8.** Effect of temperature on the carbothermal treatment of anode mud.

Fig. 9. Effect of time on the carbothermal treatment of anode mud.

leaching time, the recovery of manganese increases, but becomes constant beyond 7 h. Thus, it can be concluded that 7 h is sufficient time for the maximum recovery of manganese during acid leaching.
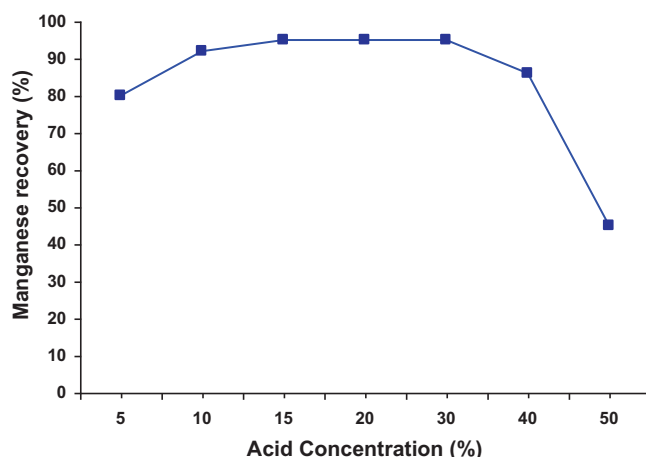

Fig. 7. Effect of oil concentration on the carbothermal treatment of anode mud.

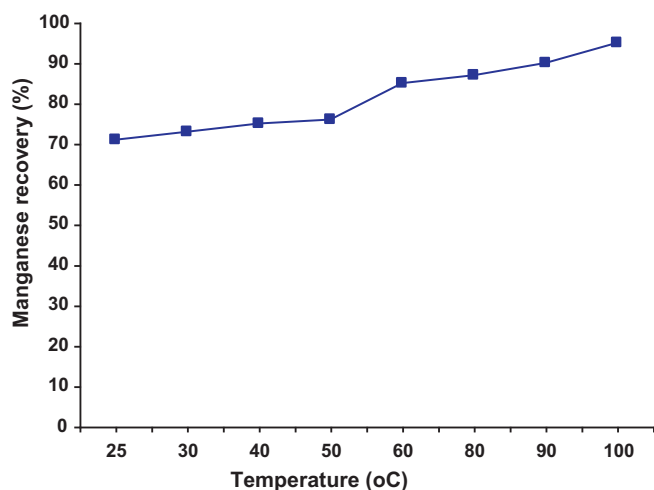**Fig. 10.** Effect of acid concentration on the recovery of manganese.

Fig. 11. Effect of leaching temperature on the recovery of manganese.
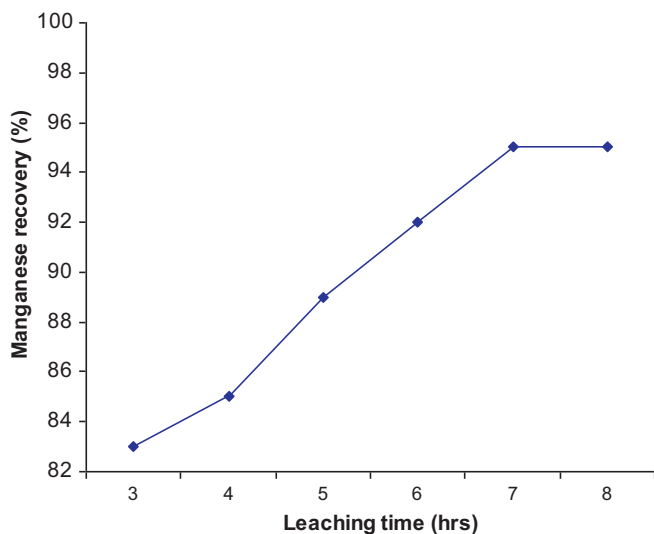

Fig. 12. Effect of leaching time on the recovery of manganese.

4. Conclusions

1. A lab scale process comprising of carbothermal reduction using low density oil followed by dilute sulphuric acid leaching has been developed whereby about 95% of the manganese available in anode mud is recovered.
2. For carbothermal treatment, use of 20% (v/w) LDO and heating at 650 °C is found to be optimum.
3. For the leaching process, use of 20% (v/v) sulphuric acid at 100 °C for 7 h has been observed to be optimum.

Acknowledgements

References

[1] Snell-Ettre, Encyclopedia of Industrial Chemical Analysis, vol. 19, Interscience Publisher, 1974, pp. 545–547.
[2] Krik-Othmer, Encyclopedia of Chemical Technology, vol. 24, John Wiley & Sons (A Wiley Interscience Publication), 1982, pp. 807–808.
[3] Asian Metal Ltd., Annual Report on Zinc Market, 2008, downloaded on 05/10/2007 from http://www.asianmetal.com/report/en/2008xin_en.pdf.
[4] Indian output of lead, Zinc decline; consumption expected to increase downloaded on 23/09/2007 from the website http://findarticles.com/p/articles/mi_m3MKT/is_44-_113/ai_n15866741.
[5] Zinc Metallurgy – Introduction, sited on 19/04/2007 from the website http://prchandna.tripod.com/zincprocess.htm.
[6] Morgan, Zinc and its Alloys and Compounds, Ellis Harwood Limited, 1985, p. 111.
[7] R. Raghavan, R.N. Upadhyay, Innovative hydrometallurgical processing technique for industrial zinc and manganese process residues, Hydrometallurgy 51 (1999) 207–226.
[8] C.A. Hampel, The Encyclopedia of Electrochemistry, Robert E. Krieger Publishing Company, 1972, pp. 789–790.
[9] Krik-Othmer, Encyclopedia of Chemical Technology, vol. 14, A Willy Interscience Publication, 1982, pp. 824–843.
[10] V.A. Peretyagin, A.V. Povlov, Aspects of high-temperature reduction of manganese ore with coal, Metallurgist 47 (2003) 419–423.
[11] A.G. Kholmogorov, A.M. Zhyzhaev, U.S. Kononov, G.A. Moiseeva, G.L. Pashkov, The production of manganese dioxide from manganese ores of some deposits of the Siberian region of Russia, Hydrometallurgy 56 (2000) 1–11.
[12] K. Parida, B.B. Nayak, S.B. Rao, An improved process for recovery of manganese from manganese ores, Indian Patent No. 186399.
[13] N.J. Welham, Activation of the carbothermic reduction of manganese ore, International Journal of Mineral Processing 67 (2002) 187–198.
[14] K. Abou-El-Sherbini, Simultaneous extraction of manganese from low grade manganese dioxide ore and beneficiation of sulphur slag, Separation and Purification Technology 27 (2002) 67–75.
[15] R.N. Sahoo, P.K. Naik, S.C. Das, Leaching of manganese from low-grade manganese ore using oxalic acid as reductant in sulphuric acid solution, Hydrometallurgy 62 (2001) 157–163.
[16] M. Trifoni, L. Toro, F. Vegliò, Reductive leaching of manganiferous ores by glucose and H_2SO_4: effect of alcohols, Hydrometallurgy 59 (2001) 1–14.
[17] F. Paganelli, M. Garavini, F. Veglio, L. Toro, Preliminary screening of purification process of liquor leach solutions obtained from reductive leaching of low-grade manganese ores, Hydrometallurgy 71 (2004) 319–327.
[18] F. Beolchini, M. Petrangelipapini, L. Toro, M. Trifoni, F. Veglio, Acid leaching of manganiferous ores by sucrose: kinetic modeling and related statistical analysis, Mineral Engineering 14 (2001) 175–184.
[19] f. Veglio, L. Toro, Reductive leaching of a concentrate manganese dioxide ore in acid solution: stoichiometry and preliminary kinetic analysis, International Journal of Mineral processing 40 (1994) 257–272.
[20] V.A. Peretyagin, A.V. Povlov, Mechanism of reduction in an oxygen reactor for ore-coal pellets prepared with low-grade manganese ore, Metallurgist 47 (2003) 447–452.
[21] A.K. Saha, Z.H. Khan, D.D. Akerkar, An improved process for the extraction of nickel, copper and cobalt from manganese sea nodules using high volatile non-coking coal as reductant, Indian Patent No. 178480.
[22] H.E. Barner, C.L. Mantell, Kinetics of hydrogen reduction of manganese dioxide, Industrial & Engineering Chemistry Process Design and Development 7 (1968) 285–294.
[23] G. Akdogan, R.H. Eric, Carbothermic reduction of vessel manganese ores, Mineral Engineering 7 (1994) 633–645.
[24] R.P. Das, S. Anand, S.C. Das, P.K. Jena, Leaching of manganese nodules in ammonical medium using glucose as reductant, Hydrometallurgy 16 (1986) 335–344.
[25] P.K. Das, A.S. Anand, R.P. Das, Studies on reduction of manganese dioxide by $(NH_4)_2SO_3$ in ammonical medium, Hydrometallurgy 50 (1998) 39–49.
[26] P.K. Naik, L.B. Sukla, S.C. Das, Aqueous SO_2 leaching studies on Nishikhal manganese ore through factorial experiment, Hydrometallurgy 15 (2000) 217–228.
[27] G. Senanayake, A mixed surface reaction kinetic model for the reductive leaching of manganese dioxide with acidic sulphur dioxide, Hydrometallurgy 73 (2004) 215–224.
[28] S.C. Das, P.K. Sahoo, P.K. Rao, Extraction of manganese from low-grade manganese ore by $FeSO_4$ leaching, Hydrometallurgy 8 (1982) 35–47.
[29] F. Pagnanelli, G. Furlani, P. Valentini, F. Vegliò, L. Toro, Leaching of low-grade manganese ores by using nitric acid and glucose: optimization of the operating condition, Hydrometallurgy 75 (2004) 157–167.
[30] T.A. Lasheen, M.N. El-Hazek, A.S. Helal, W. El-Nagar, Recovery of manganese using molasses as reductant in nitric acid solution, International Journal of Mineral Processing 92 (2009) 109–114.
[31] M.N. El Hazek, T.A. Lasheen, A.S. Helal, Reductive leaching of manganese from low grade Sinai ore in HCl using H_2O_2 as reductant, Hydrometallurgy 84 (2006) 187–191.
[32] D.A. Johannes Swinkels, Peter H. Scaife, John B. Lean, Processing of Manganese Ores, US Patent No. 3770868.
[33] S.B. Kanungo, Rate process of the reduction leaching of manganese nodules in dilute HCl in presence of pyrite: Part II: leaching behavior of manganese, Hydrometallurgy 52 (1999) 331–347.
[34] C. Abbruzzese, M.Y. Duarte, B. Paponetti, L. Toro, Biological and chemical processing of low-grade manganese ores, Minerals Engineering 3 (1990) 307–318.

[35] Dr. Navin Chandra, Dr. S.S. Amritphale, Deepti Sarkar, Srabanti Ghosh, A process for preparation of leachable non-stoichiometric manganese oxide from manganese containing wastes and natural pyrolusite ore, Application No. 018/NF/2006.

[36] J.M.M. Paixao, J.C. Amaral, L.E. Memoria, L.R. Freitas, Sulphonation of Carajas manganese ore, Hydrometallurgy 39 (1995) 215–222.

[37] G.N. Srinivasan, S. Mookherjee, Studies on the leaching of reduced manganese ore sinters, Transactions of the Indian Institute of Metals 41 (1988) 553–558.

[38] P.P. Bhatnagar, T. Banerjee, An improved method for the production of manganes sulphate from manganese ores and its application for the regeneration of spent electrolytic manganese sulphate bath, Indian Patent No. 53390.

[39] D. Hariprasad, B. Dash, M.K. Gosh, S. Anand, Leaching of manganese ore using sawdust as a reductant, Minerals Engineering 20 (2007) 1293–1295.

[40] H. Su, Y. Wen, F. Wang, Y. Sun, Z. Tong, Reductive leaching of manganese from low-grade manganese ore in H_2SO_4 using cane molasses as reductant, Hydrometallurgy 93 (2008) 136–139.

[41] Z. Cheng, G. Zhu, Y. Zhao, Study in reduction-roast leaching manganese from low grade manganese dioxide using cornstalk as reductant, Hydrometallurgy 96 (2009) 176–179.

[42] H. Su, Y. Wen, F. Wang, X. Li, Z. Tong, Leaching of pyrolusite using molasses alcohol wastewater as a reductant, Minerals Engineering 22 (2009) 207–209.

[43] X. Tian, X. Wen, C. Yang, Y. Liang, Z. Pi, Y. Wang, Reductive leaching of manganese from low grade manganese dioxide ores using corncob as reductant in sulphuric acid solution, Hydrometallurgy 100 (2010) 157–160.

[44] A.M. Pande, Sanjay Prasad, Premchand, Simultaneous extraction of zinc and manganese dioxide from sulphide concentrate and manganese ore, in: Proceedings of Golden Jubilee International Conference, 1997, pp. 389–393.

[45] V.A. Altekar, A.M. Pande, K.N. Gupta, An improved process for the simultaneous electrolytic production of zinc metal and manganese dioxide from zinc sulphide concentrates and manganese ores, Patent No. 147948.

[46] A.I. Vogel, Text book of quantitative Inorganic analysis including elementary instrumental analysis, in: The English Language Book Society and Longman, 4th edition, 1978, 606.

[47] JCPDS, Mineral powder diffraction file search manual JCPDS-International Center for diffraction data, Swarthmare, USA, 1980.