

## AN OVERVIEW ON POTENTIAL HYDROMETALLURGICAL PROCESSES FOR SEPARATION AND RECOVERY OF MANGANESE

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### Abstract

With rapid economic progress worldwide, the search for new resources for materials has become a priority due to mineral resource depletion. Enhanced requirements for manganese alloys and compounds for several commercial applications created a desperate demand for manganese recovery technologies from primary as well as secondary resources. The future demand for manganese alloys and compounds is expected to increase. The growing need of electrolytic manganese dioxide (EMD) for different battery usage in automobile and energy sectors could create a gap in the supply and demand of manganese. There is an urgent necessity for eco-friendly and efficient technologies to boost the production of manganese from low-grade ores as well as post-consumer products. The framework of effective leaching processes and proper solvent extraction techniques for the recovery of manganese could be a novel pathway to get a clean, green and healthy environment for a sustainable future in the automotive and energy segment where this metal has a significant contribution.

**Keywords:** manganese; ores; leaching; solvent extraction; post-consumer products.

### Introduction

Manganese (Mn) is one of the 3d transition metals, which plays a vital role in human life and industries. The need for manganese ore has increased significantly due to an upsurge in the fabrication of steel [1]. It is an effective metal used in metal alloys, such as in stainless steel. Manganese has no satisfactory substitute in its major applications in metallurgy and is the fourth most-traded metal worldwide. Due to its diverse applications, the extraction of manganese is vital from ores and secondary resources with the aid of an

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economically viable process. The 3d series of metals have an extensive range of commercial demands in various sectors [2]. They can behave both as thermal and electrical conductors due to their malleable and ductile nature. The unique property of transition metals to form coordination complexes has initiated the development of metal-based drugs with an encouraging pharmacological application. From the point of view of human health, manganese serves as an important element to carry out metabolic and vital antioxidant activities [3]. The extensive use of manganese in different sectors, such as steel production, dyes, and batteries, makes it a strategic element. It is reported that nineteen million metric tons of manganese were consumed in 2017, with a global production of twenty million metric tons. The demand for manganese has been anticipated to reach 28.2 million metric tons by 2022, with a decline in manganese production to 19.1 million metric tons [4]. The growing exploitation of these metals and their consequent expulsion is piling on in the environment with worrying concentrations. In the present scenario, the industries are in search of implementing novel, effective, and environment-friendly methods for recycling of resources due to the massive depletion of natural mineral sources [5]. A comprehensive outlook on various methods used for the increasing manganese concentration in ores has been summarized by *Singh et al.* [6]. Manganese occurs in nature and hardly exists in a pure and elemental state. It is generally distributed in the terrestrial crust and is often found allied with iron ores in a comparatively smaller amount. The polymetallic sea nodules are also being considered as an important source of manganese alloy [7]. The ores of Mn are generally categorized as chemical, non-metallurgical, and metallurgical [8]. Higher than 80% of the high-grade manganese ore i.e. >35% manganese, is mined in India, Australia, Brazil, South Africa, Gabon, China and in Commonwealth of Independent States (CIS). Manganese is distributed in the earth's crust as approximately 0.1% and is found in more than 100 minerals. Carbonates, oxides, and silicates are the most vital among the manganese-containing minerals. Manganese occurs at the bottom of the ocean and also present as a natural trace element in crude oil. Pyrolusite ( $MnO_2$ ), manganite ( $MnO(OH)$ ), braunite ( $3Mn_2O_3 \cdot MnSiO_3$ ), and hausmannite ( $Mn_3O_4$ ) are prominent manganese ores which are mostly found in India and African countries. The percentage of manganese content in the manganese minerals are presented in Table 1 [9].

Table 1. Principal manganese ores with the percentage of manganese content.

Manganese ores	Mn, wt.%
Manganite	62.5
Pyrolusite	63.2
Braunite	66.6
Hausmannite	72

The less important manganese ores are rhodochrosite ( $MnCO_3$ ) and rhodonite ( $MnSiO_3$ ). The data released by United states geological survey in 2014 for distribution of manganese ores all over the world has been represented in Fig.1 [10].

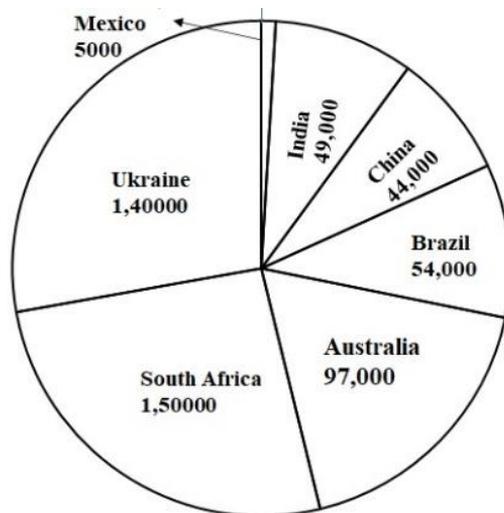


Fig. 1. Reserves of Manganese ores in metric tons in different countries.

In the last few years, the advancements of power technologies employing batteries as a power source have increased the quantity of spent batteries that are reaching landfill sites. The alkaline batteries contain manganese dioxide as the cathodic material. The concentration of manganese in various types of battery wastes are enlisted below in Table 2 [11]. The disposition of exhausted zinc- $MnO_2$  batteries has been a major environmental concern [12]. The rise in demand for manganese and consequent increase in the gap between supply and demand has led to a price hike of both manganese ores and manganese alloys [13, 14].

Table 2. Manganese concentration in mg/kg in different types of battery wastes.

Alkaline	Ni-MH	Li-M	Li-ion	Ni-Cd	Zn-Cd
329,700	15,915	513	30.5	494	265,720

This review pronounces a detailed report on potential hydrometallurgical processes such as leaching and solvent extraction used to recover manganese from ores and secondary resources such as diverse types of battery wastes. A summary of various leaching processes and the use of different organic extractants have been presented. The recent developments in the hydrometallurgical recycling strategies and challenges associated with these have also been discussed.

### Recovery from ores

Hydrometallurgical processes include leaching and extraction of metals from ores and different secondary resources from aqueous solutions using a number of extracting agents. This option is highly commercialized because of the high purity of the resulted metal and the consumption of less energy [15]. The scheme for recovery of manganese from ores through leaching and solvent extraction is represented in Fig. 2.

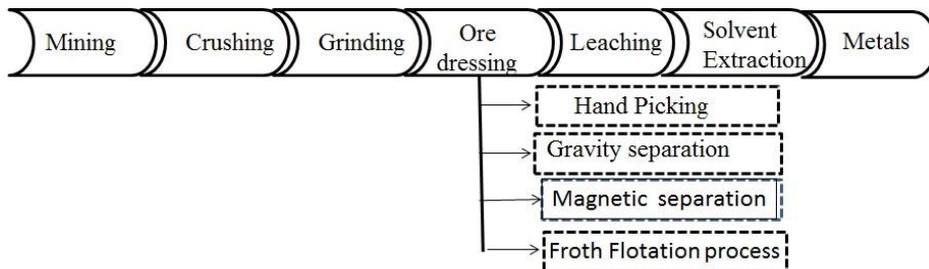


Fig. 2. Schematic representation of recovery of manganese from ores using a hydrometallurgical route.

#### a. Leaching

Leaching is a process extensively adopted in extractive studies where chemicals are used to treat the ores to obtain soluble salts of valuable metals. Chemicals, both organic and inorganic, are utilised as reducing agents in the leaching process. To make this process eco-friendlier and more cost effective, new low-cost reductants such as carbohydrates [16], molasses [17], sawdust [18], and waste paper [19] are being utilised as reducing agents. Following the traditional hydrometallurgical technique, the recovery of Mn (II) has been scrutinised from low-grade manganese ores by leaching in sulphuric acid medium without using reducing agents. Different parameters that affect the leaching, such as dissolution time, the concentration of sulphuric acid, have been examined. Under the optimal leaching condition, the leaching efficiency has been recorded to be 96.73% [20]. The use of low-grade manganese ores has been considered for the leaching and extraction of manganese due to the inadequacy of high - quality manganese ores.

Y. Zhang *et al.* [21], have performed roasting using sulphur as reductant prior to the leaching process; thus, the leaching was carried out in an acidic medium. Sulphur reduces manganese oxide ores to form different oxides of manganese and under the optimised conditions, 96% Mn has been leached effectively. Dundua and Agniashvili [22], recovered manganese from the residual slimes using  $\text{FeSO}_4$  as the leaching agent in the electrochemical production of manganese dioxide. Consequently, leaching of 98.3% for manganese from a manganese oxide ore was obtained by C. Zhang *et al.* with the use of EDTA to manganese molar ratio 1:1 at pH 5.5, 70 °C and liquid to solid ratio of 3:1. Finally,  $\text{Mn}_3\text{O}_4$  was synthesized as a result of the roasting of Mn- EDTA complex [23].

E.K. Addai *et al.* have carried out reductive leaching of a mixture of manganese carbonate and pyrolusite ores in sulphuric acid with ferrous carbonate as reductant. The influence of different parameters like leaching time, temperature, the concentration of  $\text{H}_2\text{SO}_4$  were studied. It has been observed that 96% of Mn has been extracted under the optimal condition when the ratio of manganese carbonate and pyrolusite was 5:1 by weight [24]. The reductive leaching of pyrolusite ore has also been performed by

*Ekmekyapar et al.* using sawdust as a reductant to produce manganese sulphate. It was observed that the leaching efficiency enhanced with an increase in the concentration of  $H_2SO_4$ , sawdust amount, leaching time, and temperature. And finally, manganese in the form of manganese sulphate was recovered through evaporative crystallization of leach liquor [25].

Employing oxalic acid as reductant in sulphuric acid leachant, leaching of low-grade manganese ore (Mn: 24.7%) has been carried out by *Sahoo et al.* [26]. They reported that the concentration of oxalic acid had a strong influence on the extraction of manganese, whereas temperature and leaching time showed a positive effect on the extraction of iron and aluminium. Recovery of Mn (II) from pyrolusite ore was followed by leaching using  $H_2SO_4$  as leachant and  $H_2O_2$  as reductant [27]. Leaching of manganese oxide ore obtained from *Gabon and Xiangxi* has been carried out using sulphuric acid and waste tea as reductant. The influence of strength of sulphuric acid, temperature, the concentration of reductant on the leaching process has been investigated [28].

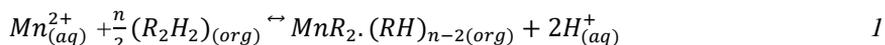
The extraction of manganese from low-grade manganese oxide ores by means of calcium sulphide was analysed by *Li et al.* [29]. The influence of CaS to ore mass ratio, operating leaching variables, the concentration of  $H_2SO_4$  on the rates of leaching of Mn and Fe were examined. The leaching percentage was 96.47% for manganese and 19.24% in the case of iron under the optimized conditions at a reduction temperature of  $95^\circ C$  with 1.5 M  $H_2SO_4$ . The reductive leaching has also been performed by *Hai Feng et al.* using cane molasses as the reductant in the sulphuric acid medium [30]. Using 1.9 M  $H_2SO_4$ , leaching percent of 97.0% for Mn, 21.5% for Al, and 32.4% for Fe were obtained from low-grade manganese ore. Leaching of manganese from low-grade  $Mn_2O_3$  ores by concentrated  $H_2SO_4$  (0.9:1 ratio with ore) and subsequent reduction using biomass, sawdust, and straw as reducing agents has been carried out by *Sun et al.* at  $95^\circ C$ . The leaching efficiency of 91.8% was achieved [31].

Leaching of Mn (II) from Sinai ore (Mn: 8.52%) in HCl has been carried out using  $H_2O_2$  as reductant. About 97% Mn leaching has been leached using the 0.4M reductant along with 2M HCl maintaining a temperature of  $60-95^\circ C$  [32]. Manganese has been extracted from siliceous manganese ores using sulphuric acid and corncob as a reducing agent. In order to reduce the manganese dioxide at low temperature, hydrolysis of corncob has been performed to release glucose in acidic condition. Using this economical and eco-friendly reductant, 90% manganese has been successfully extracted [33]. On the other hand, *Cheng et al.* have effectively utilised cornstalk as a reducing agent along with sulphuric acid as a leaching solvent for reduction and roasting of low-grade manganese dioxide ore. Approximately 90.2% of manganese has been recovered, maintaining the weight ratio of the ore: reductant as 10:3. Polymetallic manganese nodules contain 18 % Mn along with Cu, Ni, Co, and Fe [34]. Several researchers have investigated the leaching of polymetallic nodules to get Mn in a substantial amount using reductive acid leaching procedure as reported by *Allen et al.* [35].

### b. Solvent extraction

Chemical separation methods are usually designed to adopt simple procedures in order to consume less amount of solvents with an aim to marginally cut down the waste [36]. The liquid-liquid extraction schemes using modern equipment such as homogenous liquid-liquid extraction (HLLE) have been designed for this purpose [37]. In the hydrometallurgical process, after leaching the ores and scraps, either by precipitation or solvent extraction recovers the metal values. In case of precipitation, due to nearly equal values of solubility products, there are chances of simultaneous precipitation of other metals along with the desired metal. Solvent extraction is a prominent technique for the separation and purification of metals that are not possible using conventional hydrometallurgical processes. In the solvent extraction, the organic phase containing the extracting agent drags the desired metal ion species from the aqueous feed attributable to the formation of a strong hydrophobic complex with higher solubility in the organic phase. For efficient extraction, choice of extractant is a vital factor, and numerous organic extractants are used by different researchers to perform the extraction and separation studies of manganese efficiently as described by *Ali et al.* and *Ahn et al.* [38, 39]. The extraction percentage enhanced with the increase in equilibrium pH of the solution, and the highest separation for both the metals has been achieved with 0.05M sodium salt of DEHPA. The extraction order of manganese with the three extractants is Na DEHPA > Na PC 88A > Na Cyanex 272, but a reverse trend was observed for cobalt.

Organo-phosphorus acidic extractants have been broadly in use for the separation and recovery of metal values because of their chemical stability, high solubility in an organic solvent, and high selectivity. *Devi et al.* [40] reported the extraction of manganese from sulfate solutions employing DEHPA (HR) diluted in kerosene.  $MnR_2(HR)_2$  and  $MnR_2(HR)_3$  complexes were proposed to be there in the extracted organic phase with the use of DEHPA and Cyanex 272. *Devi and Mishra* [41] have studied the extraction of Mn (II) sulphate using Cyanex 302 in kerosene. It has been observed that the rate of extraction enhances at higher pH and higher Cyanex 302 concentration. Cyanex 302 containing oxygen and sulphur proves to be an efficient extractant for Mn (II). The reaction mechanism of the extraction process is expressed as



*Biswas & Rahman* [42] have studied the removal of Mn (II) from sulphate-acetate medium with the help of acidic extractant, Cyanex 272 diluted in kerosene. *Devi* [43] has studied the extraction Mn (II) from acetic acid-acetate buffer medium using two extractants, DEHPA and Cyanex 272, in kerosene. Variation in metal and extractant concentration, influence of pH and temperature has been investigated on the extraction efficiency of Mn (II). During the extraction, the author has also reported the possibility of separation in the presence of other transition metals like copper and cobalt. It has been observed that by enhancing the extractant concentration and equilibrium pH, the extraction percentage of Mn (II) increases. DEHPA exhibited better extraction proficiency in comparison to Cyanex 272, and 100% extraction of Mn (II) has been achieved.

*Jouni et al.* [44] investigated the recovery of manganese from mixed metal solutions containing cobalt, magnesium, calcium, and sodium by solvent extraction process in sulphuric acid medium taking DEHPA and Cyanex 272 as the extractants. It has been reported that the efficiency of Cyanex 272 has been marginally more than DEHPA, and increased temperature decreased the extraction rate of Mn (II). *Filiz* [45] reported the extraction of Mn(II) from the aqueous solution of HCl media by means of Alamine 336 in m-xylene.

*Aoki et al.* [46] performed investigation on solvent extraction of manganese in ethylene glycol containing HCl as an aqueous medium using TOPO as an extractant and cyclohexane or toluene as the diluent. The efficiencies of DEHPA, PC 88A and Cyanex 272 in kerosene have been compared for the separation process of two transition metals such as manganese and cobalt from sulphate solutions. It has been reported that DEHPA is the most appropriate extractant for the separation of manganese from cobalt. The separation of manganese from cobalt and nickel has also been examined with only DEHPA. Separation of manganese from nickel has been possible at high temperatures (40-60 °C), whereas 23 °C was found to be the optimum temperature for effective separation of manganese from cobalt [47]. *Niroomanesh et al.* [48] observed that 97.5% manganese had been extracted by taking 0.4 M DEHPA at pH 3.5 and O/A ratio of 1. The stoichiometry of the complex formed after extraction was ascertained from slope analysis as MA<sub>2</sub>.

Ionic liquids have gained importance as green extractants used in liquid-liquid extraction techniques due to their unique physicochemical properties such as high thermal stability and higher flashpoint. The extraction and stripping of transition metals like Fe and Mn have been performed using Cyphos IL 101 and Aliquat 336 by *Ola et al.* [49]. From the investigation, it has been found that the extraction ability of Cyphos IL 101 has been higher than Aliquat 336 for Fe (III) in comparison to Mn (II). The extraction mechanism has been explained on the basis of anion exchange taking place between the anions of ionic liquid and FeCl<sub>4</sub><sup>-</sup> and MnCl<sub>3</sub><sup>-</sup> chloro-complexes.

The extraction of Mn (II) along Co (II) and Ni (II) from acidic chloride solution has been examined with variations in the structure of alkyl groups present in the organophosphorous acidic extractants. The pKa values of extractants have a significant influence on the extraction process. Extraction of Mn (II) is adversely affected by increasing the hydrophobicity of the cationic exchanger [50].

*Ahmadipour et al.* [51] performed the synergistic investigation on the separation of Mn (II) and Zn (II) using a mixture of DEHPA and Cyanex 272 as the extractants by solvent extraction method. It has been recommended that DEHPA/Cyanex 272 ratio of 1:3 in a mixture is suitable for separation of zinc and manganese. *Batchu et al.* [52] performed the investigation on extraction of Mn (II) from chloride medium where Cyanex 301 and Cyanex 272 in kerosene. On the basis of the slope analysis method, the mechanism for synergistic extraction has been proposed as

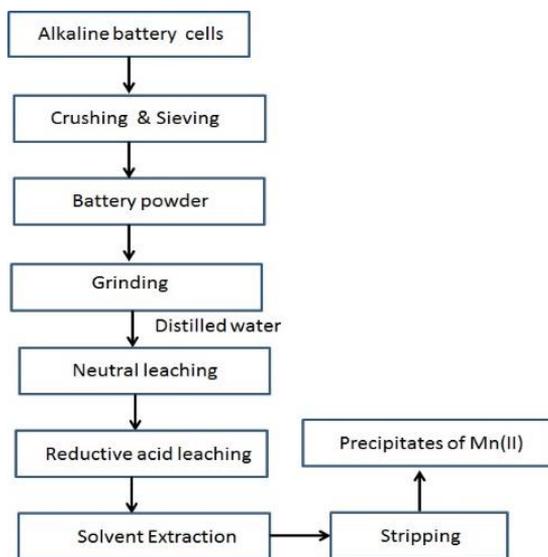


*Hosseini et al.* [13] conducted the synergistic separation of Mn (II) and Zn (II) using a mixture of DEHPA and Cyanex 302 in sulphate medium. Cyanex 302 behaved as a synergist when added to DEHPA in the extraction process, and with this, the separation of zinc over manganese increased. *Batchu et al.* [53] studied the modeling of the

extraction equilibrium of Mn from aqueous solutions of sulphate with the help of TBP and Cyanex 301(HA). It has been reported that substantial synergism has been exhibited in the case of extraction of Mn (II) by the combination of two extractants. From the slope analysis method, the stoichiometry of the extracted complex has been formulated as  $MnA_2 \cdot TBP$ . The use of extractants like Cyanex 302, Cyanex 302, along with Aliquat 336 in toluene, were successful in extracting 50% manganese at pH 4. The efficiency of Cyanex 301 for extraction Mn (II) was more in comparison to the binary mixture of Cyanex 301 and Aliquat 336 [54]. The synergistic extraction of manganese carried out in chloride and sulphate solutions have also been reported [55, 56].

#### *Recovery from secondary resources*

There are several secondary resources such as spent batteries, effluents from steel plants, spent catalysts etc., from which manganese extraction can be exploited. The progress of modern electronic technologies by deriving energy from the battery has given rise to an enhancement in the manufacture of batteries over the last few decades. Manganese recycling is essential to iron and steel production. The metallurgical applications of manganese accounts for the fact that most of it gets consumed along with iron in steel making [57]. In the past few years, numerous hydrometallurgical processes have been operating for the minerals of Mn. From the waste batteries, sludges, industrial wastes, spent catalysts, manganese can be recovered by adopting an economically feasible process like leaching followed by different purification steps. The recycling of manganese from various secondary sources with efficient and economically viable hydrometallurgical processes such as leaching and solvent extraction have been investigated by several researchers. The general procedure for recycling of manganese from spent batteries by a hydrometallurgical process is illustrated in *Fig. 3*.



*Fig. 3. Flow sheet for recycling of manganese from spent batteries using the hydrometallurgical technique.*

*a. Leaching*

Acid leaching process has been adopted for the recovery of zinc and manganese from the spent alkaline Zn–MnO<sub>2</sub> batteries [53]. It has been observed that by increasing the leaching time and reducing agent concentration the leaching efficiency gets enhanced from the spent batteries. Upon mixing 30% H<sub>2</sub>O<sub>2</sub> in the H<sub>2</sub>SO<sub>4</sub>, reductive leaching enhanced the extraction efficiency of Mn (II) from 43.5% to 97.5% without influencing the extraction behaviour.

*Chen et al.* [58] performed reductive leaching using sulphuric acid from spent Zn-MnO<sub>2</sub> battery electrode powder containing 30.1% Mn and 25.6% Zn. The selective precipitation using NaOH at pH 13 has been carried out, and further, the hydroxides get converted to oxides by calcination. The leaching rate of manganese has been reported as 60%. The leaching efficiency of both the metals increased up to 98% with the use of ascorbic, citric, and oxalic acids as reducing agents.

The extraction and purification of transition metals such as Mn, Ni, and Co from spent battery material have been performed with HCl to carry out a faster and easier leaching process. *Sayilgan et al.* [59] performed the investigation on Zn and Mn by reductive leaching of alkaline spent batteries and zinc-carbon batteries in sulphuric acid or in HCl medium. The role of oxalic acid as a reductant has been checked. The negative influence of oxalic acid on Zn leaching in both sulphuric and hydrochloric acid media has been observed. On the other hand, the concentration of both the acids showed a positive influence on Mn and Zn extraction.

*De Michelis et al.* [60] have examined the recovery of Zn and Mn from alkaline and Zn-C spent batteries using a similar medium as *Sayilgan et al.*; they have reported that 70% Mn and 100% Zn extractions have been obtained by reductive leaching taking 20% pulp density along 1.8M sulphuric acid, 59.4 g/L oxalic acid. The process has been carried for five hours at 80 °C.

A method for leaching spent Zn-C battery scraps have been anticipated by [61]. It has been observed that almost 90% Zn and Mn have been leached within 30 minutes using sulphuric acid in the presence of sulphur dioxide at 30°C. *Ferella et al.* [62] recovered Zn and Mn from spent batteries using sulphuric acid/oxalic acid and sulphuric acid/hydrogen peroxide leaching systems. Finally, the oxides of the metals are obtained in purified form and recovered by electrolysis.

Recovery of Zn and Mn from zinc-manganese dioxide batteries has been carried out by the leaching process using aqueous sulphuric acid. The effect of leaching time, sulphuric acid concentration, and temperature have been investigated. With the increase in concentration of sulphuric acid, the recovery of Mn increases [63]. Ascorbic acid, citric acid, and oxalic acid have been used for the reductive acidic leaching of spent alkaline and Zn-carbon alloy battery powders. Leaching has been reported to be high at a temperature of 90 °C. Precipitation of Mn has been done at pH 9-1 [64]. The leaching of spent Zn-C- batteries containing 20% Mn has been tested using H<sub>2</sub>SO<sub>4</sub> and NaOH. The addition of H<sub>2</sub>O<sub>2</sub> to 2M H<sub>2</sub>SO<sub>4</sub> enhanced the dissolution rate of Mn to 82.2% at 60 °C, whereas, with 4M NaOH at 80 °C, the dissolution rate has been negligible [65, 66]. Table 3 enlists the summary of recovery of manganese from primary and secondary resources using leaching.

Table 3. Summary of recovery of manganese from primary and secondary resources using leaching.

Source	Leachant	Reductant	Leaching Mechanism	Reference
Manganiferous ore	H <sub>2</sub> SO <sub>4</sub>	Glucose	$C_6H_{12}O_6 + 12MnO_2 + 24H^+ \rightarrow 6CO_2 + 12Mn^{2+} + 18H_2O$	[16]
Low-grade Sinai manganese ore	HNO <sub>3</sub>	Molasses	$Mn^{4+} + CH_2(COOH)_2 + 2H^+ \rightarrow Mn^{2+} + CH_2(COO)^{2-} + H_2O$	[17]
Low-grade manganese oxide ores	H <sub>2</sub> SO <sub>4</sub>	Sulphur	$MnO + H_2SO_4 \rightarrow MnSO_4 + H_2O$ $4Mn_3O_4 + H_2SO_4 \rightarrow 13MnSO_4 + 12H_2O$ $MnS + H_2SO_4 \rightarrow MnSO_4 + H_2S$	[21]
Pyrolusite ore	H <sub>2</sub> SO <sub>4</sub>	Manganese carbonate, which contained ferrous carbonate	$MnCO_3 + H_2SO_4 \rightarrow MnSO_4 + H_2O + CO_2$ $FeCO_3 + H_2SO_4 \rightarrow FeSO_4 + H_2O + CO_2$ $FeSO_4 + MnO_2 + 2H_2SO_4 \rightarrow MnSO_4 + Fe_2(SO_4)_3 + 2H_2O$	[24]
Pyrolusite ore	H <sub>2</sub> SO <sub>4</sub>	Sawdust	$12nMnO_2 + (C_6H_{10}O_5)_n + 12nH_2SO_4$ $\rightarrow 12nMnSO_4 + 6nCO_2 + 17nH_2O$	[25]
Low-grade Sinai ore	HCl	Hydrogen peroxide	$MnO_2 + HCl + H_2O_2 \rightarrow MnCl_2 + 2H_2O + O_2$	[32]
Pyrolusite ore	H <sub>2</sub> SO <sub>4</sub>	Hydrogen peroxide	$MnO_2 + H_2SO_4 + H_2O_2 \rightarrow MnSO_4 + 2H_2O + O_2$	[27]
Spent alkaline Zn – MnO <sub>2</sub> batteries & spent Zn-C batteries	2M H <sub>2</sub> SO <sub>4</sub>	Hydrogen peroxide	$MnO_2 + 4H^+ + 2e^- = Mn^{2+} + 2H_2O$ $2MnO_2 + 2H_2O + 2H^+ = Mn^{2+} + 2H_2O$ $MnO_2 + H_2O_2 + H_2SO_4 = MnSO_4 + 2H_2O + O_2$	[53]
Spent Zn–MnO <sub>2</sub> battery	0.5 M H <sub>2</sub> SO <sub>4</sub>	Ascorbic acid, Citric acid and Oxalic acid	$10MnO_2 + 10H_2SO_4 + C_6H_8O_6 \rightarrow 10MnSO_4 + 14H_2O + 6CO_2$ $9MnO_2 + 9H_2SO_4 + C_6H_8O_7 \rightarrow 9MnSO_4 + 13H_2O + 6CO_2$	[58]
Spent alkaline Zn – MnO <sub>2</sub> batteries & spent Zn-C batteries	30% H <sub>2</sub> SO <sub>4</sub> / HCl	Oxalic acid	$MnO_2 + H_2SO_4 + H_2C_2O_4 \rightarrow MnSO_4 + 2H_2O + 2CO_2$ $MnO_2 + HCl + H_2C_2O_4 \rightarrow MnCl_2 + 2H_2O + 2CO_2$	[59]
Spent alkaline Zn – MnO <sub>2</sub> batteries & spent Zn-C batteries	1.8 M H <sub>2</sub> SO <sub>4</sub>	Oxalic acid	$Mn_2O_3 + H_2SO_4 \rightarrow MnO_2 + MnSO_4 + H_2O$ $Mn_3O_4 + 2H_2SO_4 \rightarrow MnO_2 + 2MnSO_4 + 2H_2O$ $MnO_2 + H_2SO_4 + C_2H_2O_4 \rightarrow MnSO_4 + 2H_2O + 2CO_2$	[60]
Zn-C batteries	2M H <sub>2</sub> SO <sub>4</sub> in the presence of sulphur dioxide		$MnO_2(s).H_2O + SO_2 \rightarrow MnOOH(s) + HSO_3MnOOH(s) + HSO_3 \rightarrow MnSO_4 + H_2O$ $MnOOH(s) + HSO_3 \rightarrow Mn(II)(OH)HSO_4(s)$ $Mn(II)(OH)HSO_4(s) + SO_2 \rightarrow MnSO_3 + H_2SO_4$ $Mn(II)(OH)HSO_4(s) \rightarrow MnSO_4 + H_2O$	[61]
Spent batteries	H <sub>2</sub> SO <sub>4</sub>	Oxalic acid/Hydrogen peroxide	$MnO_2 + H_2SO_4 + H_2C_2O_4 \rightarrow MnSO_4 + 2H_2O + 2CO_2$ $MnO_2 + H_2SO_4 + H_2O_2 \rightarrow MnSO_4 + 2H_2O + O_2$	[62]

*b. Solvent extraction*

The solvent extraction of Mn (II) using DMNPA in heptane was investigated by [67, 68]. They proposed the stoichiometry of the extracted Mn complex as  $MnA_2(HA)_4$ . The extraction of metal ions such as  $Zn^{2+}$ ,  $Mn^{2+}$ ,  $Co^{2+}$ ,  $Cd^{2+}$ ,  $Ni^{2+}$  and  $Li^+$  were carried out using sulphuric acid and Cyanex 272 as organic phase extractant and the extraction follows the order,  $Zn^{2+} > (Mn^{2+} = Co^{2+} = Cd^{2+}) > Ni^{2+} > Li^+$  depending on aqueous phase pH.

*Li et al.* [69] proposed a process for extraction and purification of Ni, Co, and Mn from spent battery material in hydrochloric acid. They achieved the best results using hydrochloric acid with a concentration of 6 mol/L, a reaction temperature of 60°C, a liquid/solid ratio of 8:1, and a leaching time of 2 h. *Salgado et al.* [57], studied the recycling of zinc and manganese from spent alkaline batteries with the help of liquid-liquid extraction using Cyanex 272(RH) as extractant at 50°C.

*Zhao et al.* [70] studied the synergistic extraction and separation of cobalt (II), manganese (II), and lithium (I) from waste cathodic material of lithium ion batteries using mixture of Cyanex272 and PC-88A. *Hong et al.* [71], adopted solvent extraction techniques to separate Co, Ni, and Mn using different extractants like PC88A, Cyanex 272, and DEHPA from leaching solution of Li (NCM)O<sub>2</sub> secondary battery scraps.

Manganese has been separated from zinc in spent Zinc-MnO<sub>2</sub> dry cells by solvent extraction using organophosphorous extractants. In this study, Mn and Zn from spent dry cells were recovered through leaching by H<sub>2</sub>SO<sub>4</sub> or HCl. Spent zinc-MnO<sub>2</sub> dry cells have been leached in the presence of HCl and H<sub>2</sub>O<sub>2</sub> as reductant. Co-extraction of Mn (II) with Zn (II) was increased as free acidity increased using Cyanex 923 as extractant. Loaded organic phase with Mn (II) was scrubbed with 2M HCl. Zn (II) stripping needs 5M HCl. By adjusting the pH of the raffinate with the help of sodium oxalate, *Ibiapina et al.* [72], obtained pure manganese (II) oxalate in the form of crystals have been obtained by evaporation of the final solution. The flowsheet of the investigation has been given in Fig.4.

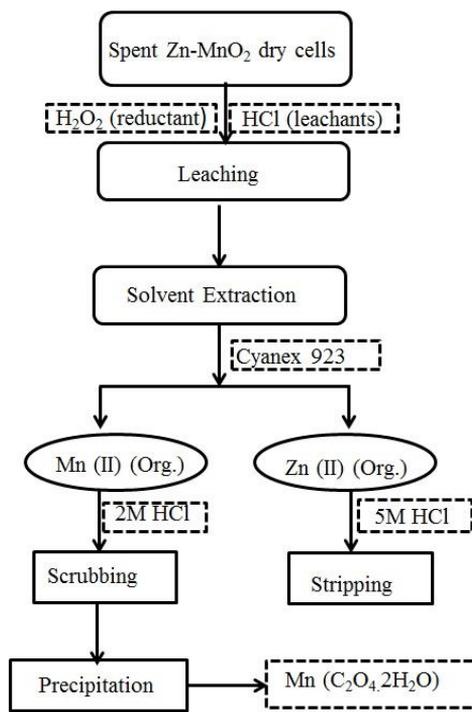


Fig. 4. Hydrometallurgical flow sheet for manganese recovery from spent Zinc- $MnO_2$  dry cells [72].

The leached solution of spent lithium-ion batteries containing 12,200 mg/L manganese along with elements like Co, Ni, and Li have been used for the separation of manganese. The separation studies have been executed using mixture of alkyl monocarboxylic acid and DEHPA. The extraction mechanism of the process has been sketched using the slope analysis method. It has been noticed that with the rise in strength of alkyl monocarboxylic acid in the extractant mixture, the distribution coefficient of the two transition metals, cobalt and manganese, declines. This is because alkyl monocarboxylic acid disturbs the extraction mechanism between DEHPA and cobalt. However, the separation factor of the two metals has been noted to be 4.5. But using continuous counter-current extraction in a mini-plant, manganese recovery from cobalt, nickel, and lithium was feasible. Solvent extraction has been successfully employed for the recovery of Mn along with Zn from spent Zn-Mn- C battery leachate. It has been observed that DEHPA has been better in extracting Zn at pH 3. Manganese has been completely separated from zinc since a longer extraction time is required for its extraction [73].

Separation of divalent and Zn from acid-bioleached spent Zn-Mn-C battery has been achieved using DEHPA and Cyanex 272. In this case, extraction of manganese showed dependence on equilibrium pH and concentration of extractants, DEHPA, and Cyanex 272 [74]. About 95% of Mn and 92% of Zn have been recovered from leached spent Zn-Mn batteries, using solvent extraction technique as reported by *Chen et al.* [58].

A separation scheme for recycling of NiMH batteries using Cyphos IL 101 or Aliquat 336 has been used. In the first stage Co, Mn, Fe, and Zn have been extracted from 8M chloride solution. Co and Mn were separated using Aliquat 336 thiocyanate [75]. Solvent extraction to recover Fe and Mn from chloride-rich solution using Aliquat 336 and Cyphos IL101 was done by *Ola et al.* [49].  $\text{MnCl}_3^-$  was extracted, and water was the stripping agent to back extract Mn from loaded Aliquat 336. The selectivity of [P44414] [Cl] was examined for the separation of Co (II) and Mn (II) and was found quite useful in the recycling of NiMH batteries [76]. The separation factors of 400 and 376 were obtained with the 17.8% IL, 25.9% HCl, 56.3%  $\text{H}_2\text{O}$  and 18.1% IL, 20.8% HCl and 61.1%  $\text{H}_2\text{O}$  at 50 °C, respectively. Cyanex 272 and PC 88A have been used for synergistic extraction of Mn (II) from waste cathodic materials of Li ion batteries at equilibrium pH of 4.95 [70].

## **Conclusions**

This present review demonstrates that the extraction and separation of manganese from its ores, solutions, and post-consumer products involve treatment of the source, leaching, solvent extraction, and separation under variable experimental conditions. From the above discussions, it can be concluded that the use of hydrometallurgical methods in the handling of manganese ores and secondary resources is generally preferred due to low cost and less environmental pollution. Among all the extractants, DEHPA is considered the cheapest, and it is quite selective for the solvent extraction of manganese. Various leaching agents like organic acids, mineral acids, alkalis, complexing agents have been used to solubilize manganese present in battery wastes. For leaching, sulphuric acid was found to be most suitable for manganese dissolution. Organophosphorus extractants like DEHPA, Cyanex 272, and PC88A have been used to recover Mn (II) from spent batteries with the help of solvent extraction techniques. The recent developments in the solvent extraction of Mn (II) can be witnessed through the clarification of reaction mechanism obtained from leaching and extraction kinetics studies.

The intricate techniques are generally in place for the up-gradation of low-grade ores of manganese available in nature. Due to the simplicity in operation and less energy consumption, the hydrometallurgical processes are getting priority in manganese separation and purification segments. There are few reports available in literature in the last decade on the use of green ionic liquids for the separation of manganese, mostly on a laboratory scale. The search for novel technologies using ionic liquids and recovery of metal values from the secondary resources like the end of life products as well as sea nodules on a commercial scale is a future challenge for the metallurgists in the field of manganese research.

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### *Abbreviations*

EDTA: Ethylenediaminetetraacetic acid

DMNPA: di-2-methyl-nonyl-phosphoric acid

DEHPA: di-2-ethylhexyl phosphoric acid

Cyanex 272:2,4,4-trimethylpentyl phosphinic acid

Cyanex 302: 2, 4, 4-trimethylpentyl thiophosphinic acid  
Cyanex 301: 2,4,4-trimethylpentyl dithiophosphinic acid  
PC 88A: 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester  
Versatic 10: Neodecanoic acid  
Alamine 336: Tri-n-octylamine

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