



Electrochemical evaluation of manganese reducers – Recovery of Mn from Zn–Mn and Zn–C battery waste



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HIGHLIGHTS

- The reduction reaction of MnO₂ to Mn²⁺ was studied.
- The analysis of oxidation-reduction potentials for specific reducers was carried out.
- It was found that the best results of leaching were obtained by the use of oxalic acid as the reducer.

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ABSTRACT

Extraction of manganese from ores or battery waste involves the use of reductive reagents for transformation of MnO₂ to Mn²⁺ ions. There are many reducers, both organic and inorganic, described in the literature. A series of 18 reducers has been discussed in the paper and they were classified according to standard redox potential ($pE = -\log a_{e^-}$ where pE is used to express formal electron activity and a_{e^-} is formal electron activity). The experiments of manganese extraction from paramagnetic fraction of Zn–C and Zn–Mn battery waste in the laboratory scale have been described for 3 reducers of different origin. The best result was achieved with oxalic acid (75%, with the lowest redox potential) and urea (with typical redox potential) appeared inactive. Extraction supported by hydrogen peroxide resulted in moderate yield (50%). It shows that formal thermodynamic scale is only preliminary information useful for selection of possible reducers for manganese extraction resources.

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1. Introduction

Both in the case of natural manganese resources (ore) and waste sources (batteries), the basic condition of activation of this element and extraction it to the solution is the change of the oxidation level to 2+ (which is specific to MnSO₄) and the most problematic is the change from the 4+ oxidation level (which is specific for MnO₂). This requires the application of a reducer which is efficient in a highly acidic environment of the leaching solution.

Batteries waste, depending on the type, contain various heavy and toxic metals being dangerous for soil and groundwater. Most types of batteries can be recycled based on pyro- and hydrometallurgical processes [1]. According to a review of literature, non-

ferrous metal ions (including Zn(II)) can be effectively separated and removed from aqueous solution in ions flotation, liquid–liquid extraction, or transport across liquid membrane processes [2–6].

2. Manganese ores

2.1. Non-organic reducers

According to the literature one of the most studied non-organic reducer for manganese ores is hydrogen peroxide (30% solution of H₂O₂). The work of Jiang et al. [7] presents the test results of the continuous manganese and silver leaching with the application of sulphuric acid and the addition of hydrogen peroxide. The obtained results corresponded to 98% output of manganese and 85% output of silver.

Literature provides a great number of studies on the simultaneous leaching of oxide manganese ores and sulphide minerals (which at the same time functioned as reducing factors). Sulphuric

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(H₂SO₄) or hydrochloric (HCl) acid were used in this process, the following minerals were tested: galena (PbS) [8], sphalerite (ZnS) [8–10], pyrite (FeS₂) [8], [11–14], nickel ores [15] and pyrite lignite [16]. In the majority of works, authors obtained a level of over 90% for manganese leaching from ores and sludge containing manganese in the amount both under and over 40% of the weights. Another non-organic reducer which could be applied in order to increase the level of recovery of Mn from manganese ores is hydrazine [17]. The application of acid solutions of iron(II) ions for leaching of poor ores and industry wastes was described in the works of Brantley et al. [18], Das et al. [19] and Vu et al. [20].

2.2. Organic reducers

The review of literature allows for the assumption that some organic substances can function as efficient reducers for manganese(IV) oxide contained in ores [21]. These substances include: glucose and sucrose [22,23], cellulose [24], lactose [25,26], glycerol [27], alcohols (MeOH, EtOH, n-BuOH, i-PrOH) [28], thiourea [29] and organic weak acids such as oxalic acid [30].

The literature also provides examples of studies on bio-reducing leaching of manganese oxides. The authors of several works [31,32] indicate the potential application of autotrophic microorganisms for reduction of leaching from ores containing manganese oxides. Chemolithotrophic microbes use non-organic compounds as an energy source, and simultaneously a large amount of organic acids (citric, oxalic acid) is created during their metabolism [33,34]. The acids can contain the MnO₂ reducer.

3. Zn–C and Zn–Mn (alkali) battery wastes

3.1. Characteristics of zinc–carbon (Zn–C) and zinc–manganese (Zn–Mn) batteries

Electrochemical energy sources – that are currently applied – can be divided into three basic groups: (1) the first type cells (so called primary, irreversibly utilising the electrochemical process), (2) the second type (often referred to as reversible due to application of reversible electrochemical processes, otherwise known as accumulators), and (3) fuel cells (burning fuels in electrochemical reactions).

The first type of cells primarily includes the most popular today zinc–carbon and zinc–manganese (alkali) batteries [36]. The structure of these cells and their overall material and elemental composition were developed long ago. The first prototype was the Leclanché's cell. It was composed of a zinc anode and cathode from manganese dioxide, formed with the addition of graphite, immersed in ammonium chloride solution. At the beginning of the nineteenth century it was modified by replacing the liquid electrolyte with a paste from partially dehydrated gypsum and ammonium chloride, with the addition of zinc chloride. In a so called “dry” carbon–zinc cell, the positive electrode (cathode) is a graphite rod surrounded with a mixture of manganese oxide (MnO₂) and powdered graphite whereas the negative electrode (anode) is a zinc cup, acting simultaneously as a container. The electrolyte is a water solution of starch saturated with ammonium chloride (NH₄Cl) and zinc chloride (ZnCl₂), separated from the cathode with a paper spacer. Due to corrosion of the zinc container and possibility of “spilling” of the aggressive electrolyte, the cells can be very dangerous for the electronic equipment. The anode material in an alkali zinc–manganese cell is zinc powder in a gel matrix (e.g. starch or poly-acrylic acid gel). The cathode material is manganese dioxide (MnO₂), mixed with carbon (graphite or carbon black), obtained by electrochemical processes. The cell is enclosed in a steel container, acting simultaneously as the cathode power collector. The electrolyte is a

concentrated solution of potassium hydroxide (KOH). To prevent from corrosion of metallic zinc (which is the anode material) zinc oxide was added. In some cases, electrolyte in the form of a gel is used. Solution of potassium hydroxide guarantees a high ion movement in a wide range of temperature in which the cells may be used. For zinc–manganese cells, the following electrode reactions can be proposed: (anode) $\text{Zn} = \text{Zn}^{2+} + 2\text{e}^-$ and (cathode) $2\text{MnO}_2 + 2\text{H}_2\text{O} + 2\text{e}^- = 2\text{MnO}(\text{OH}) + 2\text{OH}^-$.

3.2. Battery waste processing

Currently, there are three methods of spent battery processing, i.e.: separative (mechanical), pyrometallurgical and hydrometallurgical (both chemical in the origin). The separative (mechanical) methods are frequently used for large batteries (industrial type) and as preliminary operations in other processing technologies. They consist in mechanical loosening of the structure (body) of the battery and separation of components of characteristic physical properties (i.e. density, size, magnetic properties). These operations are easier and cheaper than other processes, and thus, are used for the preparation of the material stream for further chemical processing.

Pyrometallurgical methods are based on material recovery (metals in particular) by their alteration in adequately high temperatures into specific condensed phases (including metallic alloys) or into gas phase with latter condensation. Generally, these methods are suitable for phases rich with recovered components or concentrated in higher temperatures in the gas phase (this relates to e.g. removal of mercury, acquisition of cadmium or zinc). In terms of batteries, these processes can also be performed in a traditional way, i.e. by oxidising–reducing equilibrium of the HCO (hydrogen, carbon, oxygen) system, as well as in a broad manner, which is appropriate for advanced chemical metallurgy, e.g. when chlorination processes are used. However, it is important to remember that this classification is conventional and is not appropriate for precise chemical or technological considerations. The advantage of pyrometallurgical methods is the possibility to recycle various types of cells (batteries), including also cells containing various organic materials.

Hydrometallurgical methods are frequently based on acidic or alkaline leaching of appropriately prepared battery wastes (after phases of mechanical processing). It is followed by a series of physical and chemical operations that leads to the separation and concentration of valuable or troublesome components between appropriate phases and gives commercial products or intermediates for separate technological processes (pyrometallurgical or hydrometallurgical) or wastes. Generally, hydrometallurgical processes are less energy-consuming than pyrometallurgical ones, however the waste generated in these processes are more troublesome. The advantage of hydrometallurgical processes is that they allow simultaneous processing of mixtures of various types of batteries Table 1.

Table 1
Typical composition of zinc–carbon and zinc–manganese batteries, in wt. % [35].

Component	Input, wt. %		
	Zn–C, type D	Zn–C, type A	Zn–Mn, type D
Paper	0.96–2.24	3.21–5.80	1.15
Steel	18.30–24.06	30.48–35.79	11.66
Plastic	2.11–3.08	2.66–2.87	1.27
Graphite rod	4.54–6.12	5.85–6.86	–
Powder	52.47–64.46	46.33–49.19	40.76
Water (moisture)	5.80–13.91	1.50–4.93	2.71
Black paste	–	–	41.81
Other	0.34–1.28	1.24–3.31	0.64

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