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NON-REDUCTIVE ACIDIC LEACHING AS A METHOD FOR RECOVERY OF ZINC AND MANGANESE FROM Zn-C AND Zn-MnO$_2$ BATTERY WASTE

The dynamic growth of mobile technologies is a driving need for portable power sources. The most popular division of electrochemical cells relies on the type of chemical reaction within the cell. Current data coming from the Polish market show that despite the growth in the sale of secondary power sources, zinc-carbon and alkaline batteries are still the most popular. The results of non-reductive acidic leaching of zinc and manganese from the waste batteries stream have been presented. Manganese was leached with almost 100% yield in an experiment with a solid to liquid ratio equal to 4/1, pH of 1.04, and H$_2$SO$_4$ concentration of 72.5 wt. %. High yields were also obtained for zinc recovery from the waste stream (100% for two series with solid to liquid ratio 4/5, pH of 0.80; H$_2$SO$_4$ concentration of 37.2 wt. %, and solid to liquid ratio 1/2; pH of 1.01; H$_2$SO$_4$ concentration of 27.3 wt. %). Besides, the quantitative and qualitative analysis of Zn-C and Zn-Mn batteries introduced to the Polish market and waste generated in the years 2010–2018 has been presented.

1. INTRODUCTION

The dynamic growth of mobile technologies, both in industry and private life, is a driving need for portable power sources. The most popular division of electrochemical cells relies on the type of chemical reaction within the cell. Therefore, it is possible to distinguish: single-use batteries (primary cells) and rechargeable batteries (secondary

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cells/accumulators). In the first group most popular are zinc-carbon (Zn-C) and zinc--manganese batteries (alkaline, Zn-Mn) [1], whereas lithium-ion (Li-ion) accumulators are the most popular among rechargeable solutions [2].

Chemical power sources may be also divided basing on the use as (i) industrial batteries and accumulators (batteries and accumulators designed exclusively for industrial, professional purposes, or the use in electric vehicles); (ii) car batteries or accumulators used in starter, lighting or ignition in vehicles; (iii) portable batteries and accumulators (all-sealed batteries and accumulators, including button cells, that an average person can carry in hand without any difficulty) which may be found in most of the portable electrical devices [3, 4].
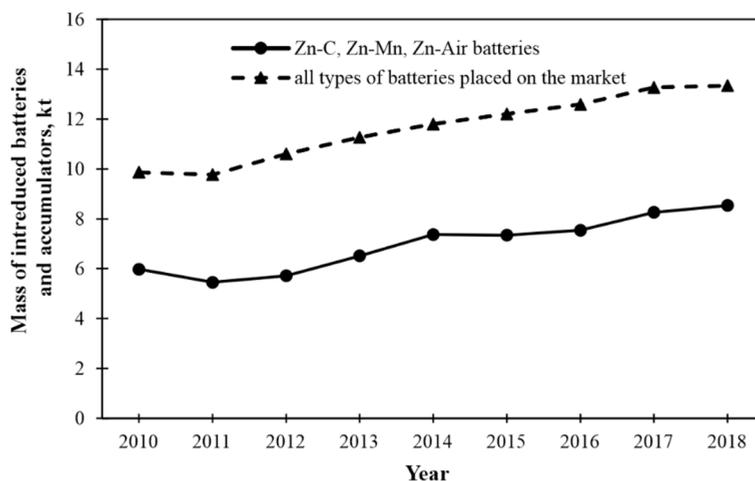
Fig. 1. A type and amount of portable batteries and accumulators
launched onto the Polish market (based on [1])

Current data from the Polish market show that despite the growth in the sale of secondary power sources (Fig. 1), zinc-carbon and alkaline batteries are still the most popular, which is related to their favorable prices. Due to the presence of zinc, manganese, cadmium, mercury, and other heavy metals as well as other compounds present in an electrolyte (NH_4Cl, $ZnCl_2$, KOH) [5, 6] spent Zn-C and Zn-Mn batteries are considered sources of high risk for human health and environment and should be disposed of in a proper manner [2].

The theoretical value of materials, i.e., paper, polymers, steel, found in spent batteries and accumulators also should be taken into consideration. Currently, the recycling of spent portable batteries in the world, apart from mechanical treatment, is conducted mainly based on pyrometallurgical and hydrometallurgical technologies although vacuum distillation at reduced pressure may also be used. The main aim of the pyrometallurgical process is to divert metals present in waste batteries into usable solid-state or

vapor state with further condensation [7]. Regarding the examples coming from industry, 1 ton of portable batteries recycled with Sumitomo process (pyrometallurgical process dedicated for all batteries' type excluding Ni-Cd type) yields ca. 360 kg of ferromanganese alloy, 200 kg of zinc, 1.5 kg of mercury, and 20.0 kg of slag [6].

The hydrometallurgical process is based on acidic or alkali leaching of mechanically treated waste batteries. Hydrometallurgical methods allow efficient recovery of the individual components of metallic and non-metallic fractions, however, they are more expensive due to a larger number of indirect technological operations. As a result, after leaching with sulfuric acid from 1 ton of zinc-carbon and zinc-manganese batteries, 200 kg of zinc and 130 kg of manganese can be obtained [8]. Due to the abundance of Zn-C and Zn-Mn waste batteries, they could serve as a suitable source of metals for making Mn-Zn ferrites, $LiCo_xMn_{2-x}O_{4-y}F_y$ spinels, Al-Zn-Mg alloys, and $Zn_xMn_{1-x}O$ nanoparticles [9–11].

Regarding the Directive 2006/66/EC, the main objective of the Act on batteries and accumulators is to minimize the negative impact of batteries and accumulators as well as spent batteries and accumulators on the environment and, at the same time, to contribute to the protection, preservation, and improvement of the environment. The Act distinguishes between three categories of batteries and accumulators, namely: industrial, portable, and automotive ones. The Act also sets out the permissible content of toxic metals in marketed portable cells. The content of mercury should not exceed 0.0005% (in button-cell batteries – 2%), the content of cadmium – 0.002%, and lead – 0.004% [3]. In Poland, the management of spent batteries and accumulators is regulated by the act on batteries and accumulators of 24 April 2009 (OJ No. 79, item 666, as amended) [4]. Additionally, basing on the Act of 2009 [12] yearly targets for waste batteries and accumulators were set up.
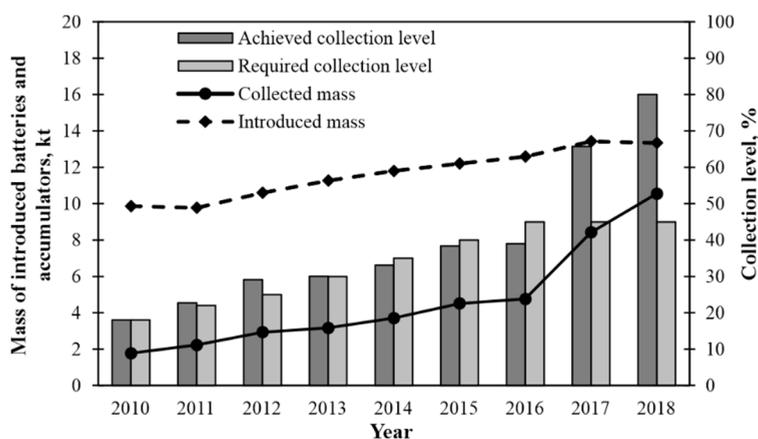
Fig. 2. Collection levels of used portable batteries and accumulators in Poland (based on [1])

According to the law of batteries [4], since 2016 Poland has been obliged to achieve the 45% collection rate of portable batteries and accumulators. The data published by

the Chief Inspectorate of Environmental Protection shows that Poland achieved a collection rate of over 65% in 2017 [1] (Fig. 2). Over 42% of reclaimed waste batteries and accumulators were collected from households (group 20 according to the waste catalogue [13] (Fig. 3).
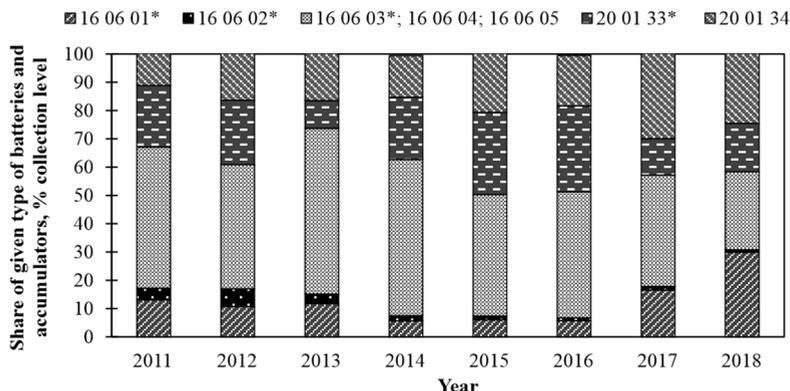
Fig. 3. Share of various types of portable batteries and accumulators in the collected waste stream (according to waste catalogue [1]); 16 06 01* – Pb-acid batteries and accumulators; 16 06 02* – Ni-Cd batteries and accumulators; 16 06 03* – batteries containing Hg, 16 06 04 – alkaline batteries (excluding 16 06 03); 16 06 05 – other batteries and accumulators; 20 01 33* – household batteries and accumulators including batteries specified in 16 06 01, 16 06 02 or 16 06 03 and unsorted batteries containing these batteries; 20 01 34 – other household batteries and accumulators

The collection rate was estimated based on data from reports submitted by collectors of waste batteries. It should be noted that until 2017 the level of the collection was calculated based on data provided by entities placing portable batteries and accumulators on the market. These data did not include the whole mass of collected waste batteries. Moreover, the Chief Inspectorate of Environmental Protection corrected the reports on the management of waste batteries and accumulators for 2015 and 2016. As a result, the collection rates increased from 38.35% to 54.92% in 2015 and from 39.00% to 78.14% in 2016. Achieving such high collection rates is very improbable under the fact that in 2017 the average collection rate in the 28 EU Member States was 45.7%. Moreover, the social research shows that Polish society is still missing ecological awareness. As a result, many batteries still end up in landfills.

In 2014 in Leszno (city with a population above 64k) as well as in 2016 in Bełchatów (city with a population above 59k) there was social research on people's behavior connected with waste batteries and accumulators treatment. The results showed a significant lack of knowledge in this field s [14, 15]. Exactly 20% and 28% of respondents, from Leszno and Bełchatów respectively, confessed that they were not segregating waste chemical power sources from their waste, the reasons for that were lack of time and lack of dedicated collection boxes in their neighborhood. One of the

solutions for that situation is the possibility of free-of-charge disposition of waste chemical power sources in household waste recycling centers (HWRC) which should be established under the Act on waste treatment[16]. Although 59% and 30% of respondents, from Leszno and Bełchatów respectively, were aware of the existence of HWRC in Leszno, only 32% and 28%, respectively, could locate it correctly. Most of the respondents pointed that there is no proper communication concerning the need for selective collection of waste chemical energy sources. Only some of them (25%) were aware of how important it is to recycle waste batteries and accumulators correctly.

It is also very important that none of the Polish companies recycling waste power sources possesses a full technology for that purpose. As most of the processes used to treat waste chemical energy sources are based on pyrometallurgical technologies (Table 1), their cost and complexity are stopping potential investors from starting them. Due to those facts, there are several activities performed in industrial and academic centers leading to the development of complete technology for waste batteries and accumulators treatment.

T a b l e 1

Technologies of processing used batteries and accumulators in Poland

Technology	Recycling method	Remanufactured battery	Recovered metals and compounds
BatEko	mechanical processing	Zn–C Zn–Mn Zn–air	ferromagnetic fraction diamagnetic fraction paramagnetic fraction
Recupyl Polska, sp. z o.o.	pyrometallurgical	Zn–Mn Zn–air	metallic Zn and zinc products steel and steel products
Baterpol S.A.		Pb–acid	alloys Pb solid Na_2SO+ polypropylene
Orzeł Biały S.A.		Pb–acid	Pb alloys polypropylene pellets
ZM Silesia S.A.		Ni–Cd	metallic Cd ferro-alloys containing Ni
MB Recycling, sp. z o.o.	mechanical processing	Zn–C Zn–Mn Zn–air	ferromagnetic fraction diamagnetic fraction paramagnetic fraction

The starting point for the literature review of hydrometallurgical parameters of metal recovery (mainly zinc and manganese) from Zn-C and Zn-Mn batteries can be the study by Abid Charef et al. [7]. The authors compiled research published from 2001 to 2016 presenting the results of acidic and alkaline leaching of spent cells of the first type. They showed that the most commonly used leaching agent was sulfuric(VI) acid, hydrochloric acid was less frequently used. In this case, reducers in the form of perhydrol or organic acids, including oxalic acid, citric acid, and ascorbic acid, were added. Alkaline leaching was carried out with the use of sodium hydroxide or an ammonia solution.

The metals from the solutions were recovered mainly by co-precipitation, electrodeposition, or solvent extraction. The main parameters of leaching processes were in the following range: concentration of the leaching agent 0.5–6.0 mol/dm^3, process duration 30–600 min, process temperature 25–90 °C, and the ratio of solid to liquid phases (s/l) ranging from 1/5 to 1/50 [5].

In the last three years (2017–2019), few works related to the recycling of used zinc-carbon and zinc-manganese batteries have been published. Published works were covering both acidic and alkaline leaching processes in which inorganic acids were used: H_2SO_4 and HCl with or without the addition of reducing agents and alkaline reagents: NaOH and $(NH_4)_2CO_3$. It should be noted, however, that in most of the presented works, the authors focused on the recovery of metals from the obtained leaching solutions and the optimization of the leaching process was not the most important part of their work.

The main research goal presented in the experimental work was to show that it is possible to use acidic leaching as a solution for the recovery of metals, mainly Mn and Zn from "black battery mass" at a low ratio of solid to liquid phase and without the addition of reducers. Given approach was chosen as it was noticed that the research material "black battery mass", after the mechanical treatment process, contains in its composition a lot of impurities, among others cellulose and various types of plastics, which may be reducers for the basic reaction: $MnO_2 + 4H^+ + 2e = Mn^{2+} + H_2O$ [5].

2. MATERIALS AND METHODS

Spent batteries. The material to be tested is the paramagnetic fraction derived from a Polish company dealing with: buying and recycling batteries and small accumulators, collection and waste electrical and electronic equipment processing, collection and disposal of hazardous waste, and comprehensive services in the field of industrial waste. The used batteries are delivered to companies mainly by large organizations through their recovery and collection system. The battery waste is sorted manually on the conveyor belt and subjected to generic segregation. Only zinc-carbon batteries and zinc-manganese batteries are sent for further mechanical treatment. In the mechanical process, waste batteries are consequently crushed, grounded, and subjected to magnetic separation. As a result of these operations, three fractions are obtained: ferromagnetic (consisting of metals such as Fe, Cr, Ni), diamagnetic (consisting of ground plastics: films, mesh, a spacer made of PE, PVC, paper, and tar) and paramagnetic (consisting of the non-ferrous waste and residue in the ferrous fraction).

Paramagnetic fraction samples. The paramagnetic fraction, which is the subject of research, is not homogeneous. Except for the battery black mass, it is possible to find large pieces of polymer battery housings, various polymer pads, pieces of paper and cardboard, cotton, different pieces of broken graphite electrodes, and metal parts of housings.

Due to the inhomogeneity of paramagnetic fraction, it was sieved through a 5 mm sieve and 2 mm sieve. The obtained powder (black mass; a fraction of <2 mm grain sizes) was selected for further work. The content of fraction below 2 mm was approximately 78% of the tested material weight. The metal composition of black mass was determined in the solutions that resulted from: a) conventional acid digestion with concentrated H_2SO_4 and HNO_3, and b) microwave digestion. After digestion, the solutions with a solid phase were diluted with deionized water, filtered and placed into the volumetric flask. Metals were determined by atomic absorption spectrometry (AAS) using a GBC AVANTA. The presented results are the average values of two black mass digestions: 22.8 Mn, 21.0 Zn, 0.85 Fe, 0.007 Cr, 1.49 K, 0.17 Na, 0.11 Hg, 0.26 Ni, 0.64 Cd, 0.032, Co and 0.017 Cu presented as g/kg.

To determine the forms of zinc and manganese occurrence in the tested battery powder, XRD analyzes were performed. The powder X-ray diffraction patterns were recorded using an X'PERT Phillips X-ray powder diffractometer (PXRD) with a PW 1830 generator with CuK_α radiation. The XRD analysis showed that zinc in the tested powder was in the form of ZnO. At the same time manganese in studied black mass occurs in form of $ZnMnO_4$, $MnOOH$, Mn_2O_3, Mn_3O_4, and MnO_2, which makes it necessary to use inorganic or organic reducers to successfully leach manganese into the solution (MnO_2/Mn^{2+}) [17].

It should also be considered whether impurities contained in the analyzed material cannot be potential reducers for manganese dioxide. The metallic iron and plastic from the housings of used batteries as well as paper and cardboard (cellulose) are potential reducers for the basic reaction of $MnO_2 + 4H^+ + 2e = Mn^{2+} + 2H_2O$. Therefore, it was decided to carry out the experiments on the sieved battery mass which was not subjected to the additional chemical and/or thermal treatments to remove the small residues of these components.

Acidic leaching of paramagnetic fractions. The tested battery black mass was leached with the use of sulfuric(VI) acid as a leaching agent (95% analytical grade, STANLAB). Acid was added in an amount that guaranteed maximum recovery of zinc and manganese (various percentage concentrations between 5.97 and 72.5 wt. %). Experiments were carried for different ratios (mass/volume: g/cm^3) between solid and liquid phases which were varying from 4/1 to 1/12. The process parameters for each experiment are presented in Table 2.

20 g of the paramagnetic fraction was mixed with the appropriate amounts of water and sulfuric(VI) acid in 250 cm^3 beakers (Table 2). Experiments were carried out for 7 days each, during which the leaching solution was mixed (500 rpm) for 10 min every day. The temperature was recorded. After that period phases were separated by filtration. In the obtained solution (solution 1, S1), the content of metals was determined by the AAS method. The material remaining after filtration was washed with 200 cm^3 of boiling water,

mixed for 30 minutes, and filtered. In the obtained solution (solution 2, S2) the metal content was also determined by the AAS method. Then the leaching yields of Zn and Mn were determined as the ratio of metal concentrations in the solutions after leaching to the original content of these metals in the tested battery powder. The resulting Zn and Mn leaching yields were expressed in %. The total leaching yield was determined as the sum of the yields reported for the first and second leaching steps (S1 + S2). pH measurements were also made in both solutions.

Table 2

Leaching parameters for experiments carried out with sulfuric acid (VI)
on a paramagnetic fraction (20 g)

Solid/liquid ratio (s/l) [g/cm^3]	Volume of H_2O [cm^3]	Concentration of H_2SO_4 (0.156 M)	
		Percentage [wt. %]	Molar [mol/dm^3]
4/1	5	72.5	11.3
2/1	10	58.6	8.32
4/3	15	49.2	6.57
1/1	20	42.4	5.42
4/5	25	37.2	4.62
2/3	30	33.2	4.02
1/2	40	27.3	3.20
2/5	50	23.1	2.65
4/11	55	21.5	2.45
1/3	60	20.1	2.27
4/13	65	18.9	2.11
1/4	80	15.9	1.76
1/5	100	13.2	1.43
1/6	120	11.2	1.21
1/7	140	9.80	1.05
1/8	160	8.69	0.924
1/9	180	7.80	0.826
1/10	200	7.08	0.747
1/12	240	5.97	0.627

3. RESULTS AND DISCUSSION

3.1. ZINC LEACHING YIELD AS A FUNCTION OF ACID CONCENTRATION

The reactions taking place during the acidic leaching process of tested battery powder may be as follows [5]:

$$ZnMn_2O_4 + 2H_2SO_4 = ZnSO_4 + MnSO_4 + MnO_2 + 2H_2O \tag{1}$$

$$MnOOH + H_2SO_4 = MnSO_4 + MnO_2 + 2H_2O \tag{2}$$

$$Mn_2O_3 + H_2SO_4 = MnSO_4 + MnO_2 + H_2O \tag{3}$$

$$Mn_3O_4 + 2H_2SO_4 = 2MnSO_4 + MnO_2 + H_2O \tag{4}$$

In the solutions obtained after the leaching, pH was measured and the contents of individual metals, i.e., zinc, and manganese, were determined as leaching yields – all results are summarized in Table 3.

<div align="right">T a b l e 3</div>

Zinc and manganese leaching yields (*Y*) in non-washed paramagnetic fraction

s/l	H_2SO_4 conc. [wt. %]	S1		S2		S1 + S2	S1		S2		S1 + S2
		Zn					Mn				
		Y	pH	*Y*	pH	*Y*	*Y*	pH	*Y*	pH	*Y*
4/1	72.5	0[a]	–	76.5	1.04	76.5	0[b]	–	100	1.04	100
2/1	58.6	0[a]	–	93.9	1.02	93.9	0[b]	–	73.9	1.02	73.9
4/3	49.2	0[a]	–	91.5	0.55	91.5	0[b]	–	75.6	0.55	75.6
1/1	42.4	8.35	0.00	82.2	1.07	90.6	4.67	0.00	54.6	1.07	59.2
4/5	37.2	8.30	0.00	91.7	0.80	100	7.30	0.00	58.5	0.80	65.8
2/3	33.2	17.5	0.00	43.6	0.74	61.1	20.8	0.00	22.3	0.74	43.1
1/2	27.3	44.0	0.00	56.0	1.01	100	25.4	0.00	23.3	1.01	48.7
2/5	23.1	19.0	0.00	19.7	1.00	38.7	38.8	0.00	11.2	1.00	50.0
4/11	21.5	79.2	0.00	14.3	1.03	93.5	45.4	0.00	7.84	1.03	53.2
1/3	20.1	61.7	0.00	15.8	0.99	77.5	42.9	0.00	8.34	0.99	51.2
4/13	18.9	72.4	0.00	12.7	1.03	85.1	42.6	0.00	6.88	1.03	49.5
1/4	15.9	65.8	0.00	14.9	1.19	80.7	33.1	0.00	7.62	1.19	40.7
1/5	13.2	72.7	0.00	8.58	1.43	81.3	34.8	0.00	3.73	1.43	38.6
1/6	11.2	73.5	0.00	8.53	1.40	82.0	34.7	0.00	3.65	1.40	38.3
1/7	9.80	80.3	0.06	5.13	1.65	85.4	36.5	0.06	2.38	1.65	38.8
1/8	8.69	76.4	0.25	5.71	1.73	82.1	36.0	0.25	2.84	1.73	38.8
1/9	7.80	77.9	0.16	2.47	1.55	80.4	35.5	0.16	1.51	1.55	37.0
1/10	7.08	80.6	0.28	2.66	1.69	83.3	36.5	0.28	1.44	1.69	38.0
1/12	5.97	74.6	0.38	4.68	1.61	79.3	31.5	0.38	2.32	1.61	33.9

[a]After 7 days products were solid.

The obtained results showed that leaching with sulfuric acid brings positive results. For experiments with the acid concentration in the range of 21.5–58.6 wt. %, the observed cumulative yields for most of the experiments were higher than 90%, as shown in Table 3. For experiments with an *s/l* ratio equal to 2/3 and 2/5, which corresponds to the acid concentration of 33.2 and 23.1 wt. %, the obtained yields were much lower and

equaled 61.1 and 38.7 wt. %, respectively. That fact was linked with the possible inho-mogeneous nature of sampled material. Lower yields were observed also for the highest acid concentration (76.5 wt. %). It might be connected with high evaporation losses of water caused by self-heating of leached material during the experiment. Obtained results are in line with Gilchrist's results [18] who reports zinc leaching yield increase together with temperature increase as well as with acid concentration.

In most of the sources cited [7, 19, 20], the s/l ratio 1/10 or higher, adequate to sulfuric acid concentration from 0.543 to 1.9 mol/dm^3 (2.91–10.18 wt. %) was pointed out as the most proper for zinc acidic leaching and guaranteed yield values between 80% and 100%. The only papers showing different approach were those by El-Nadi et al. [21] and Bartolozzi et al. [22], in which zinc was leached from mixes with s/l value as low as 1/5. Both papers show high yields, 86.6 and 100%, respectively, for final sulfuric acid concentration equal to 2 and 6 mol/dm^3 (10.72–32.16 wt. %).

3.2. MANGANESE LEACHING YIELD AS A FUNCTION OF ACID CONCENTRATION

Manganese leaching is much stronger affected by sulfuric acid concentration. The highest yield (100%) was obtained for s/l ratio equal to 4/1, for the next two experiments representing the s/l equal to 2/1 and 4/3, the yield of 75% was obtained (Table 3). Upon further addition of sulfuric acid, the yield decreases to the value as 31.5% obtained for s/l equal to 1/12.

The analysis of all obtained results confirms that high concentrations of sulfuric acid together with low s/l values are helpful in manganese extraction. It is also worth noticing that high yields were obtained without the addition of a manganese reducer. It might be proved that the paramagnetic phase, due to its complex composition, contains some kind of organic manganese reducer. It is also possible that leaching processes, taking place in semi-liquid conditions and high temperatures (ca. 100 °C), lead to more efficient leaching. As there is no available data in the literature, this topic might be worth further investigation.

The obtained results were also confirmed by the Pourbaix diagrams created with HSC Chemistry R for Windows, ver. 5.11. The diagram calculated for the Zn–S–H$_2$O system in natural conditions at equilibrium (T = 25 °C, p = 0.1 MPa, C_{Zn} = 0.2641 g/kg H$_2$O, C_S = 0.2894 g/kg H$_2$O) is presented in Fig. 4a.

In the case of Mn–S–H$_2$O system (T = 25 °C, p = 0,1 MPa, C_{Mn} = 0.1581 g/kg H$_2$O, C_S = 0.3894 g/kg H$_2$O) equilibrium state chart (Fig. 4) is much more complicated, it may be found that in experimental conditions (pH = 8 and lower), manganese in water solu-tion may exist in a form of Mn^{2+}, MnO$_2$, MnOOH or Mn$_3$O$_4$. Due to that reason, a re-ducer capable to stop manganese oxidation in given conditions might be necessary for effective manganese leaching operation. Nevertheless, in the conducted experiments, the leaching of the tested battery powder was not supported by any reducing agents, and a high (even complete) Mn separation was obtained with optimal process parameters.

Therefore, it can be concluded that the impurities contained in the paramagnetic fraction may be acting as reducing agents concerning manganese, and thus the assumed research hypotheses were confirmed.
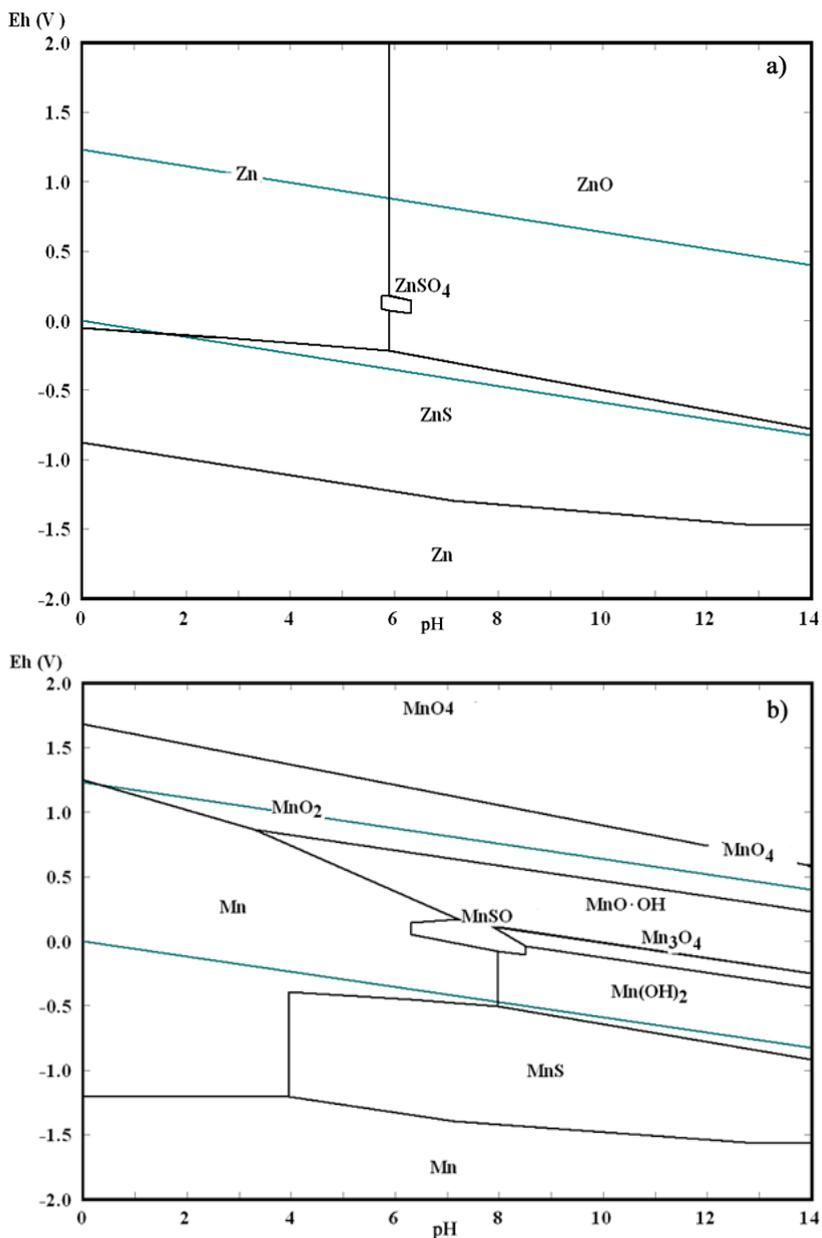
Fig. 4. Pourbaix diagrams of Zn–S–H$_2$O (a) and Mn–S–H$_2$O (b) systems at 25 °C

4. CONCLUSIONS

Zn-C and Zn-MnO$_2$ batteries are the most popular type of cells used to power various devices. Their popularity is primarily due to their easy availability and low price, but also the users' habituation to this type of battery. Although they are constantly replaced by various other cells, it can be expected that the amount of the produced Zn-C and Zn-MnO$_2$ batteries will continue to increase, which will determine the rapid increase in their waste.

The results of the analyzes showed that spent Zn-C and Zn-MnO$_2$ batteries are polymetallic waste containing many valuable metals, including zinc and manganese, which can be recovered in the acid leaching process. It was also confirmed that it is possible to completely separate both Zn and Mn from the tested battery powder under optimal conditions of the leaching process with sulfuric acid (VI). Moreover, the manganese can be successfully recovered from waste Zn-C and Zn-MnO$_2$ batteries stream without the need for additional reducer introduction for given reaction: $MnO_2 + 4H^+ + 2e = Mn^{2+} + 2H_2O$. On this basis, it might be stated that there are enough reducing compounds in battery black mass for successful manganese recovery in the described process conditions. Additionally, the obtained results give a good base for future studies on possible minimization of water usage in leaching processes of waste batteries. The conducted research can be also continued to develop a method of selective recovery of single metals, e.g., in an extraction process.

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