

Article

Recycling of Alkaline Batteries via a Carbothermal Reduction Process

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Abstract: Primary battery recycling has important environmental and economic benefits. According to battery sales worldwide, the most used battery type is alkaline batteries with 75% of market share due to having a higher performance than other primary batteries such as Zn–MnO₂. In this study, carbothermal reduction for zinc oxide from battery waste was completed for both vacuum and Ar atmospheres. Thermodynamic data are evaluated for vacuum and Ar atmosphere reduction reactions and results for Zn reduction/evaporation are compared via the FactSage program. Zn vapor and manganese oxide were obtained as products. Zn vapor was re-oxidized in end products; manganese monoxide and steel container of batteries are evaluated as ferromanganese raw material. Effects of carbon source, vacuum, temperature and time were studied. The results show a recovery of 95.1% Zn by implementing a product at 1150 °C for 1 h without using the vacuum. The residues were characterized by Atomic Absorption Spectrometer (AAS) and X-ray Diffraction (XRD) methods.

Keywords: alkaline battery; battery recycling; Carbothermal process

1. Introduction

In many countries, the recycling of batteries is an important issue because of environmental sanctions that regulate the disposal of these products. Research has been conducted in various laboratories to develop new recycling processes for used batteries or to develop new solutions to ensure safe final disposal in certain situations [1]. This situation requires a new approach in the management of these devices when they exhaust. In this case, the use of recycled metals instead of primary sources in battery production will have a positive environmental impact by reducing energy consumption and minimizing pollution [2]. Using recycled materials for new battery production will conserve exhausting primary resources.

Alkaline batteries include many components which can be recycled using various methods. Veloso et al. investigated this kind of battery and analyzed its components. Table 1 presents alkaline battery ingredients [3].

Primary batteries work according to irreversible chemical reactions (Equation (1)).



This process has some valuable ingredients such as are ZnO, Mn₃O₄ and KOH. There are some investigations about Zn recovery from ZnO in literature. Xiong et al., published a paper about the carbothermal reduction of ZnO and achieved 95% Zn yield at 900 °C under vacuum in 50 min with C/Zn_{Total} 2.5 ratio [4].

Table 1. Alkaline batteries paste analysis [3].

Element	Weight, %
Zn	12–21
Mn	26–33
K	5.5–7.3
Fe	0.17
Pb	0.005
Cd	-
Hg	-

As Xiong's study states, ZnO recycling is an important process. With the expansion of the scope of Zn-based applications, the consumption of Zn is rapidly increasing, resulting in a gradual decrease of the amount of zinc sulphide. Zn has the highest amount of consumption, just after steel, aluminum, and copper [5]. Zn has good corrosion resistance and thus has wide use in the protective coating of metallic structures. [6]. Almost 35–50% of total Zn consumption is used in galvanizing, 20% is used in brass production, 15% in casting, 8% in zinc oxide production and 7% in semi-fabricated products [7]. In particular, Zn's particulate form is a useful anti-corrosion pigment in paints, cathode materials for battery technologies, and has been receiving increasing interest as a catalyst for chemical reactions [8–12]. The recycling of Zn is a difficult process not only because of the difficulty of finding suitable waste sources, but also because of technological constraints. Alternatively, the black mass of alkali and zinc-carbon (Zn-C) batteries can be an important secondary source for the recovery of 20,000 t/year for Zn, as well as a similar quantity of manganese [13].

Therefore, how to develop and use zinc oxide effectively from waste has become an increasingly important issue [14]. There are two basic processes to evaluate the zinc oxide as a zinc raw material. The first one is the hydrometallurgical method. In this method, acid leaching, alkaline leaching and ammonia leaching are applied [15]. Hydrometallurgical processes have many advantages, but also have many disadvantages, such as impurities in the leach liquor due to difficulties in the treatment process, and the difficulties in solid-liquid separation [4]. However, alkaline battery wastes are melted at 1500 °C to produce iron based alloys (steel and FeMn) via pyrometallurgical processes. During this process, the Zn can be recovered by evaporation and condensation in the form of oxide powder. However, it is usually found as waste in steel production powder [16–18]. Although various hydrometallurgical and pyrometallurgical methods have been developed for the recycling of batteries, the existing processes are not economically suitable for the widespread recycling of these batteries [19].

The main purification methods for Zn are electrolytic purification, vacuum distillation, zone melting and so on. The vacuum technology used in metallurgy is an environmentally friendly and resource-saving method that shortens metal recovery processes. The low melting point and vaporization temperature of Zn permits technologically applicable vacuum processes [20–22].

In this study, the possibility of Zn recycling from alkaline and Zn-carbon battery waste were investigated via carbothermal and vacuum aided carbothermal reduction. Results are evaluated with thermodynamic data and a suitable way of recycling waste alkaline batteries is suggested.

2. Experimental Studies

In the experimental step, raw materials were collected from battery collection locations. Collected raw materials were classified manually for alkaline and Zn-C batteries. Alkaline batteries were dismantled by hand. The steel covering and battery paste that contains anode and cathode with electrolyte, were separated via sieving. 1.5 kg of alkaline battery paste was washed in water with 1/10 solid/liquid ratio for 72 h. The obtained solution is analyzed with AAS (Perkin Elmer Analyst 800) for chemical analysis. Washed and filtered battery paste was used for Zn recovery experiments. Washed and filtered battery paste was analyzed by using chemical analysis and AAS (Perkin Elmer Analyst 800) techniques. Aqua regia leaching method was employed for preparing AAS samples. 0.30 g of the

sample was dissolved in a borosilicate beaker on a hotplate at 110 °C for 30 min. Afterward, the cooled sample was diluted in 100 ml of 5% HNO₃. The samples were analyzed for zinc and other elements by AAS (Perkin Elmer AAnalyst 800, USA) using a standard protocol. XRD pattern of the reduced residue obtained by PANalytical PW 3040/60 (Panalytical B.V., Almelo, The Netherland) (Cu K α , $\lambda = 0.154$ nm). Xpert highscore software was used in order to collect data. During the experiment, two different retorts were used. The argon aided experiments were carried out in a 9 L 304 stainless steel retort with a cylindrical shape of 20 cm height and a 12 cm radius. This retort has high temperature resistance, gas tightness, a sufficient reaction chamber and a gas cleaning unit. In the second type of experimental set, another retort were used which was coherent with vacuum. This retort was produced by centrifugal casting method because of its vacuum tightness properties. It is also 304 stainless steel, and has the same properties as the first retort. On the other hand, this retort also has a cooling zone in order to obtain crystallized metallic particles.

In the experiments two types of production techniques were used: the vacuum aided method and the Ar flowing carbothermal reduction method. Experiments without vacuum were conducted in a stainless steel retort with a volume of 9 L, under Ar flowing conditions. Ar gas was supplied to retort with a flowing rate of 1 L/min. We produced reaction gases and purged Ar to keep the retort atmosphere in reducing conditions while also carrying gas for Zn vapor. Zn evaporated after the oxide reduction occurred and was carried out of the retort via Ar gas. CO₂ gas re-oxidizes Zn at lower temperatures, thus Zn was obtained as ZnO in fume dust. Coke used as a carbon source in order to reduce the ZnO. Experiments were done on a stainless steel plate with 150% excess carbon without considering the initial carbon of battery paste. The flowchart of the experimental studies is given in Figure 1.

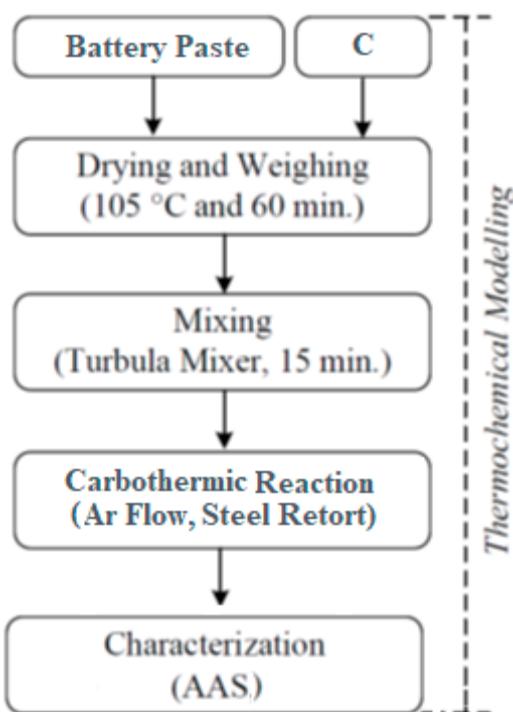


Figure 1. Flowchart of the Ar aided experimental studies.

During vacuum aided experiments, a 1 L cylindrical retort which was made of stainless steel was used. The retort was placed in an oven with a DC1010 temperature control unit, which can reach up to 1400 °C. The Zn metal was vaporized and the residue was placed in the retort inside an aluminate crucible (Height: 15 mm, Width: 25 mm, Length: 153 mm with 1700 °C stabilization capacity). In order to obtain the vacuum atmosphere inside the retort, a dual-stage Edwards 8 E2M8

rotary vane mechanical vacuum pump was used, which can hold a final pressure of 10 Pa (0.1 mbar) (Edwards High Vacuum, Crawley, UK). The retort was externally heated by using a SiC resistance furnace. Figure 2 presents a detailed vacuum reduction system.

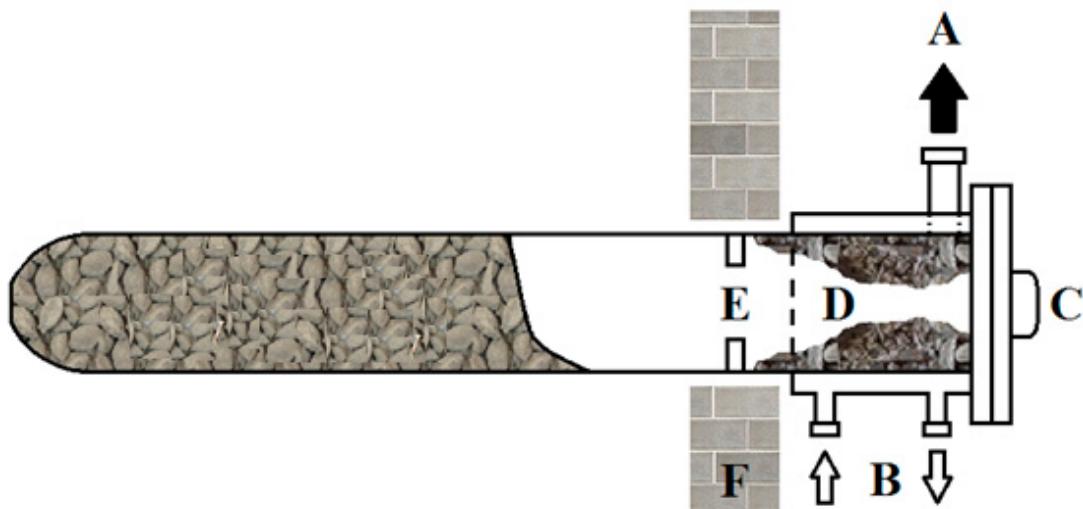


Figure 2. Schematic sketch of experimental setup: (A) vacuum pump; (B) water inlet-outlet; (C) retort cap; (D) crown Zn; (E) radiation shield; (F) furnace wall.

In all experiments, 20 g samples were weighted, mixed via Turbula mixer and charged in to the retorts. The retorts were externally heated with 10 °C/min heating rate from room temperature to the desired temperature under Ar or vacuum conditions. At the end of the reduction, the retort was left in the furnace at the same vacuum values and it was cooled to room temperature. Then, the cover was opened, and the residue left in the boat was weighted and analyzed. The degree of Zn metal recovery was calculated from the residue by using the formula given below.

$$\text{Zn recovery\% (from residue)} = \{[(\text{Zn}_0\% \times W_0) - (\text{Zn}_1\% \times W_1)] / (\text{Zn}_0\% \times W_0)\} \times 100 \quad (2)$$

where W_0 is the weight of battery waste, $\text{Zn}_0\%$ is the weight percentage of Zn in battery waste, W_1 is the weight of residue, and $\text{Zn}_1\%$ is the weight percentage of Zn in residue. The residues were characterized via the AAS and XRD techniques.

3. Results and Discussion

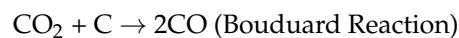
3.1. Thermodynamic Background

FactSage is a powerful self-teaching aid. With regular program usage, one can rapidly acquire a practical understanding of the principles of thermochemistry, especially those relating to complex phase equilibria. The program has a built-in database of chemical compounds and calculates the equilibrium conditions of given reactions. Starting or final conditions of reaction can be determined at the start and results could be obtained as a table or a figure [23]. This study's thermodynamic calculation was realized via FactSage 7.1. database.

The change of reaction products with increasing reaction temperature is given in Figure 3 with a vacuum of 10 Pa for the reduction of ZnO from battery residues by using carbon as a reductant in the vacuum and an Ar purged scenario in Figure 4 without a vacuum.

Figure 3 clearly shows that after reaching 500 °C, ZnO amount reduced dramatically and 1 mole Zn is the stable phase beyond 700 °C. According to these calculations, ZnO reduction starts at 500 °C and it reaches to maximum recovery values after 700 °C. On the other hand, C and CO₂ are the

dominant carbon-based phases until 500 °C is reached. Boudouard reaction occurs at approximately 580 °C, CO₂ and C converts to CO [24].



CO oxygen affinity is higher than CO₂ and C, so ZnO reduction exponentially increased after the Boudouard reaction was realized. Decreasing the vapor pressure of the chamber enhances Zn reduction and Zn vaporization. Mn₂O₃ dissociates to MnO through the vacuum effect.

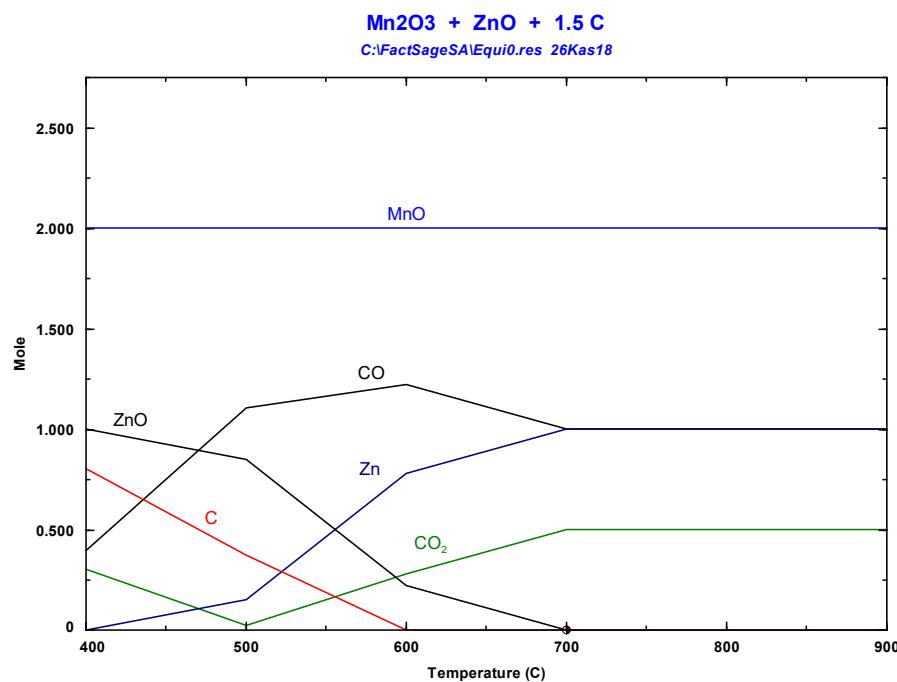


Figure 3. The change of reaction products with increasing process temperature for 10 Pa vacuum conditions.

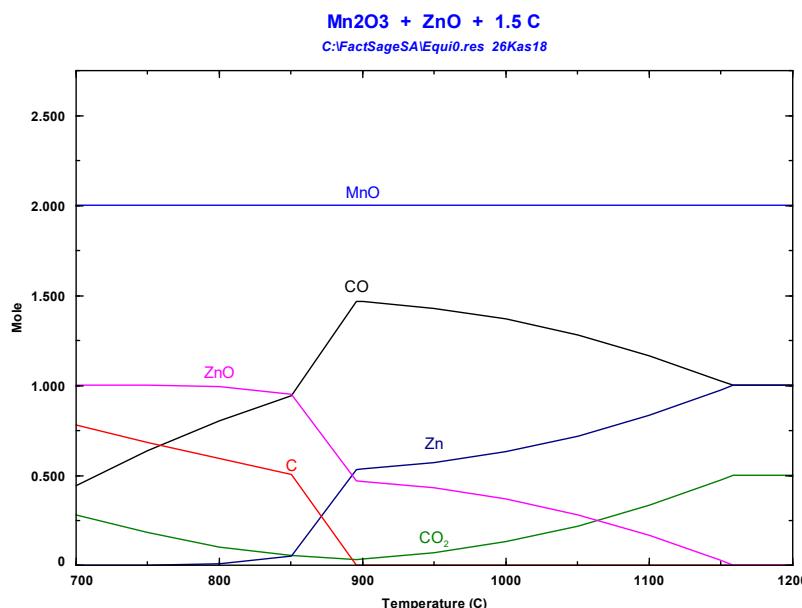


Figure 4. The change of reaction products with increasing process temperature for 1 atm condition.

Figure 4 shows reaction products in an Ar flowed situation. ZnO reduction starts at 850 °C and the reaction is completed at 1150 °C. MnO is produced by thermal dissociation of Mn₂O₃ at elevated temperatures and thus decreases the C content in the mixture. The reaction starts with direct reduction of ZnO by C then proceeds with indirect reduction by CO in the retort atmosphere and equilibrium observed at 1150 °C.

3.2. Carbothermal Reduction of Battery Wastes without Vacuum

In the first experimental set, carbothermal reduction conditions of zinc oxide are examined under Ar atmosphere. The produced reaction gases and purged Ar to keep the retort atmosphere in reducing conditions while also having the role of carrying gas for Zn vapor. Zn evaporated after the reduction from the oxide form and was carried out of the retort via Ar gas. CO₂ gas re-oxidizes Zn at lower temperatures and thus Zn was obtained as ZnO in fume dust. Battery paste is washed and dried before reduction experiments. 65% of KOH is washed out in the washing process and a solution of KOH is obtained. Chemical analysis of the battery paste that is used for reduction experiments is given in Table 2. The chemical composition of KOH solution obtained after washing is given in Table 3.

Table 2. Battery paste analysis.

Element	Weight, %
Zn	27.1
Mn	38.12
K	6.47
Fe	1.35
Pb	0.0018
Loss of Ignition	20.21
Moisture	6.75

Table 3. KOH solution analysis.

Element	mg/L
K	6400
Zn	0.0147
Mn	0.0007

The experiments were done at 950, 1000, 1050, 1100 and 1150 °C. Zn reductions results are given in Figure 5. It can be seen in Figure 5 that a significant change in Zn reduction occurred at 1050 °C. Above 1050 °C the Zn amount in the residue decreased to an acceptable level of reduction. The best result was seen at 1150 °C, with 1.32% weight Zn in the residue. This result means recovery of 95.1% of Zn in alkaline battery paste.

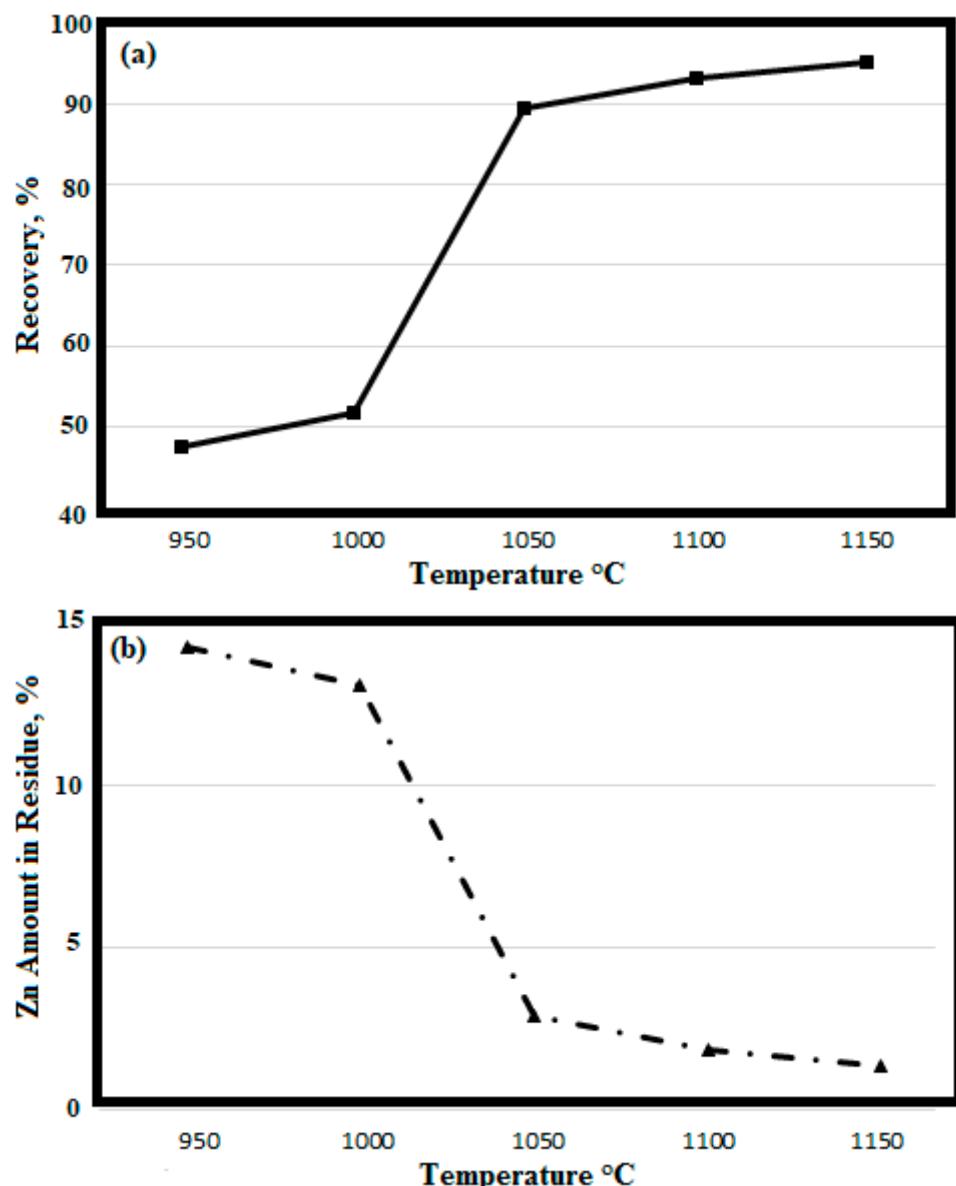


Figure 5. (a) Zinc recovery of ambient condition experiments, (b) Zn amount in the residue (1 h, various temperature, Ar flow).

In the second experiment, the set effect of time was investigated. The experiments were conducted 1100 °C for 30, 60 and 120 min of duration time. Figure 6 shows that best result has been detected for the 60 min experiment with 93.1% Zn recovery. In parallel with this result, the lowest amount of Zn in the residue was determined as being 1.86% in the same experiment.

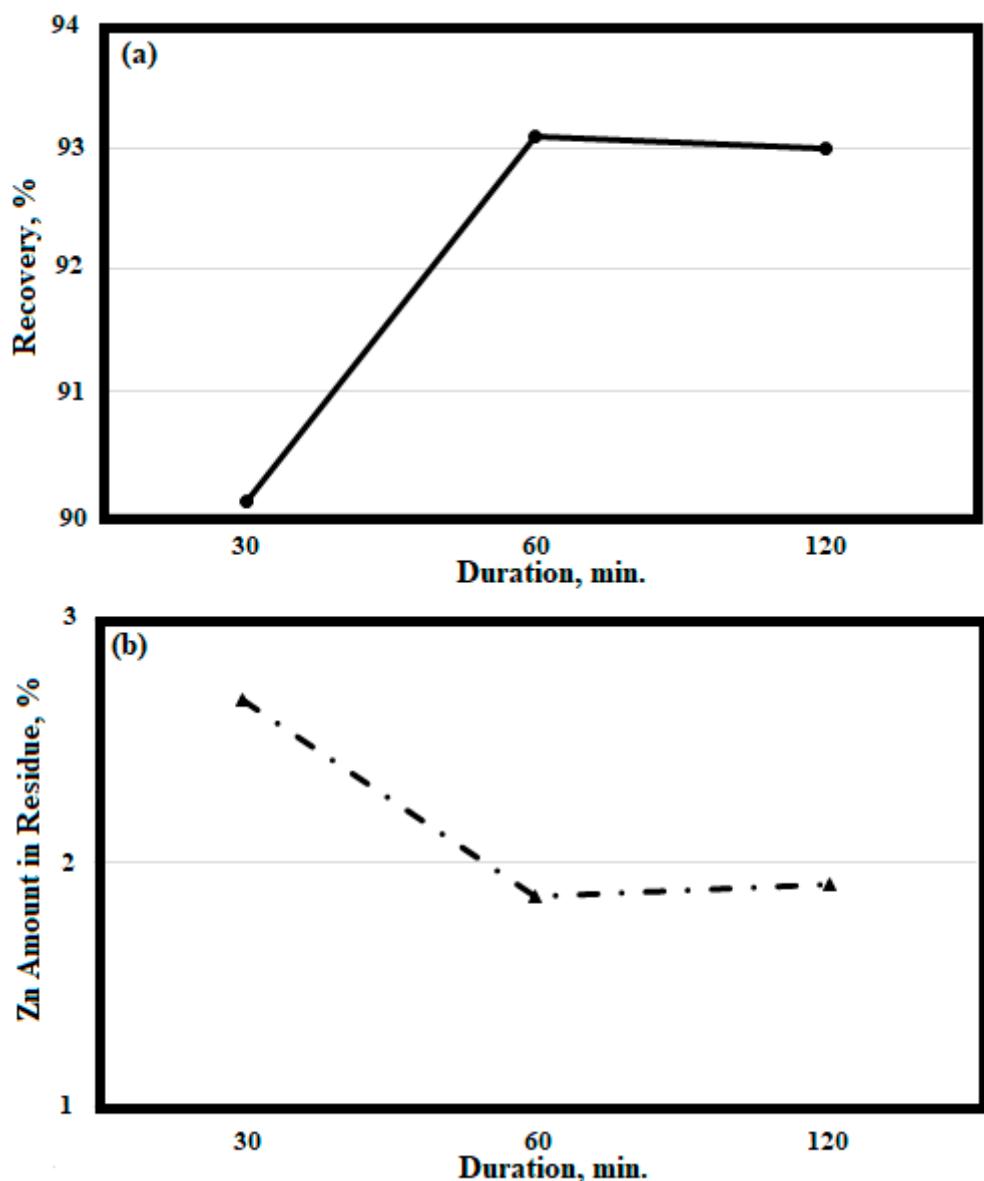


Figure 6. (a) Zn recovery of ambient condition experiments, (b) Zn amount in the residue ($1100\text{ }^{\circ}\text{C}$ various duration, Ar flow).

3.3. Vacuum Carbothermal Reduction of Battery Wastes

In the third stage, vacuum applied experiments were done with two different carbon source types: coke and lignite. Coke was used for its high carbon content, yet lignite is the more reactive carbon source. In the light of thermodynamic calculations, experiments were done at lower temperatures. In the first two experimental set reactions the temperature was above $1050\text{ }^{\circ}\text{C}$, in the third stage it changed from 500 to $800\text{ }^{\circ}\text{C}$ with $100\text{ }^{\circ}\text{C}$ intervals. During experiments, samples were placed in alumina crucible then charged in the stainless steel retort. The retort was vacuumed and heated to desired values at the same time. After the experiments were finished, the samples cooled to room temperature under vacuum atmosphere. Then Zn recoveries were calculated from residue according to Equation (2) for both coke and lignite used experiments. Results are given in Figures 7 and 8 respectively.

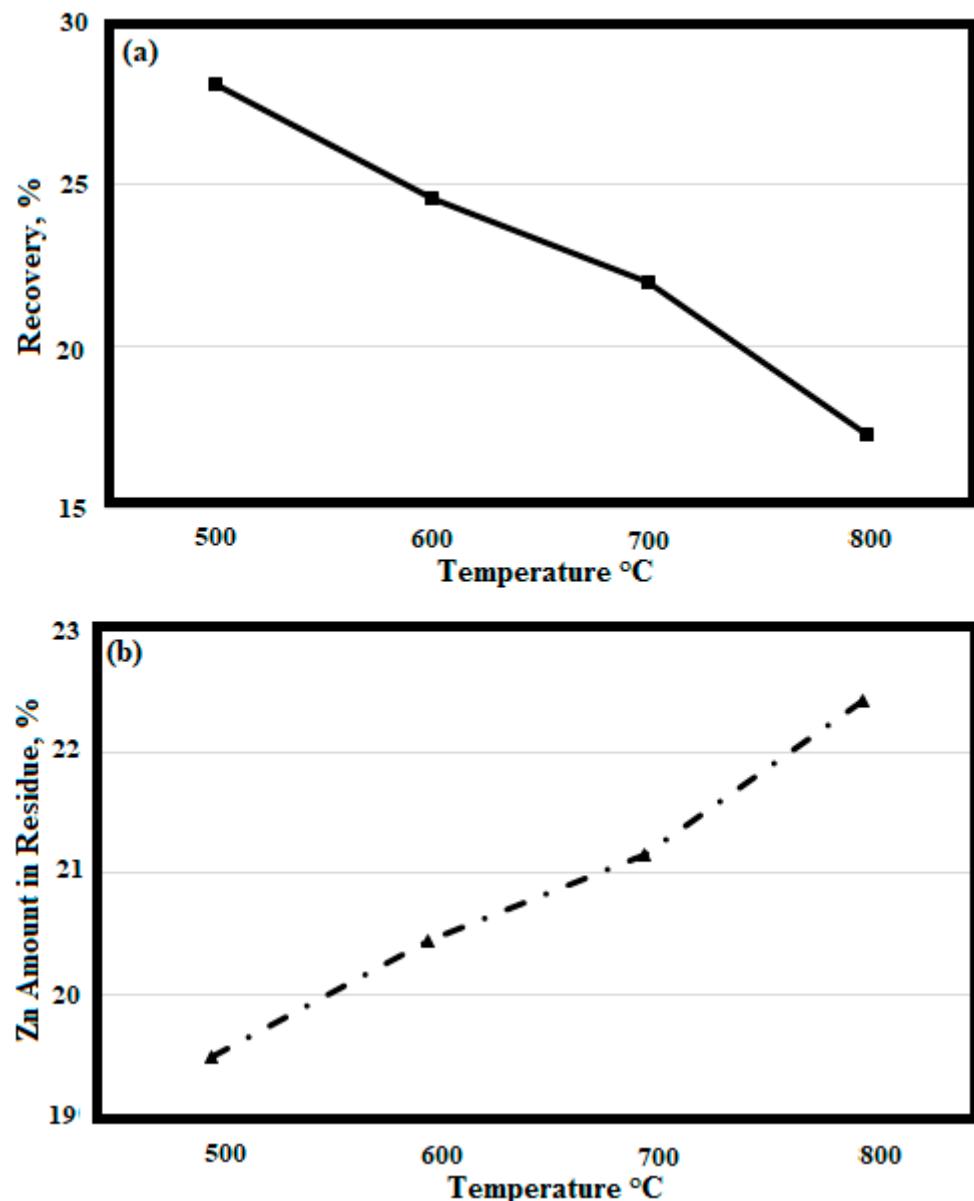


Figure 7. (a) Zn recovery, (b) Zn amount in residue (1 h, 0.1 mbar vacuum, various temperature).

Zn residue is analyzed for both carbon sources, with lignite showing a higher Zn recovery rate under vacuum. Coke coal is known for high stability at high temperatures, therefore with the increasing temperature recovery rate of coke, the used vacuum reaction is decreased.

The XRD result of residue is given in Figure 9. The XRD pattern shows that residue contains ZnO, MnO and unreacted C. Therefore the vacuum dissociated Mn_3O_4 residue only had the MnO phase. Unreacted carbon could be the result of a lack of mixing.

Results showed that the reduction and evaporation of Zn from alkaline battery paste is possible for all three reaction schemes: Ar purged carbothermal reduction, lignite and coke used vacuum reactions. However, ZnO reduction is found to be easier for the Ar purged condition. Reactions conducted under vacuum were ineffective for Zn reduction and evaporation. High temperature with Ar purged reaction for 1150 °C experiment was found to be the optimum and most effective reaction. Boudouard reaction is known for being essential to carbothermal reduction processes. Thermodynamic calculations showed that Zn reduction is easier for vacuum applied situations, yet vacuum pumped out reaction gases out of the retort. Thus from the kinetical point of view, the reaction could not be continued. The time needed for the reaction between ZnO and CO could not be provided due to high vacuum conditions. Ebin et al.

investigated the recovery of Zn with pyrolysis and hydrogen reduction from battery waste [19]. Also Shuqing et al. studied pyrolysis of Zn battery waste and they obtained a 94% recovery rate at 950 °C [25]. Belardi et al. studied the carbothermal reduction of spent batteries under N₂, air and CO₂ media. They obtained 99% Zn recovery at 1200 °C-30 min. in N₂ atmosphere [26]. As a result of the experiments carried out in the N₂ atmosphere, they achieved 80% and 99.8% Zn recovery respectively at 950 °C [19,27]. Therefore, it's clearly seen that hydrogen reduction is the most effective way recover Zn from battery waste. A vacuumed retort for ZnO reduction was studied by Xiong et al. and the results showed that under an effective vacuum, ZnO reduction needs at least 250% more carbon due to this carbothermal reduction of ZnO under vacuum [4]. In this study, alternative reduction techniques were studied for hydrogen reduction and pyrolysis. Ar gas purge for carbothermal ZnO reduction needs less carbon and offers more effective reduction. Ar gas decreases the partial pressure of CO developed by reduction reaction, while vacuum completely takes away reaction gases. Thus vacuum needs lower temperatures but higher carbon content for effective reduction. In order to reduce carbon foot prints, it is logical to use the high temperature Ar purged way to recycle alkaline batteries.

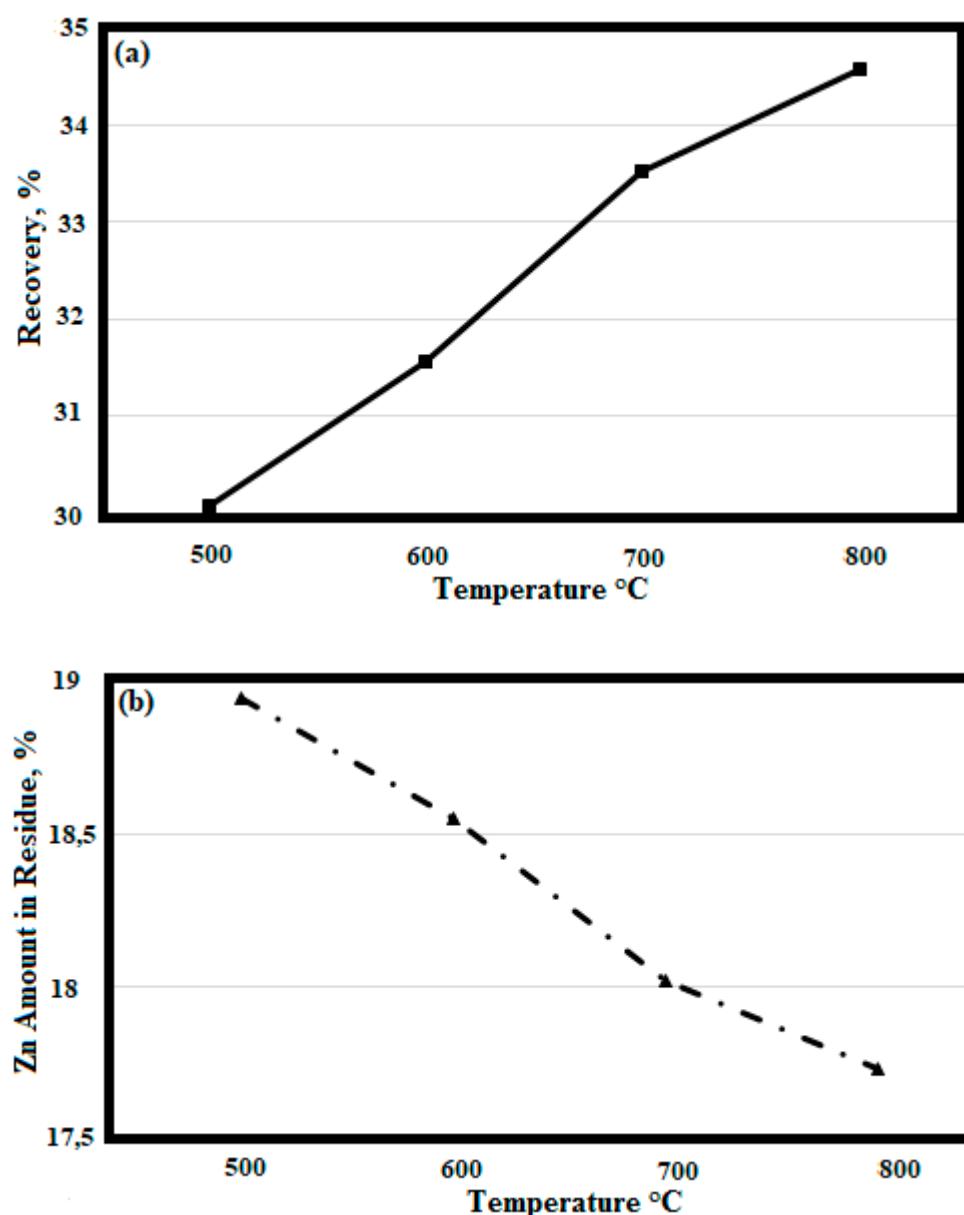


Figure 8. (a) Zn recovery, (b) Zn amount in residue (1 h, 10 Pa vacuum, various temperature).

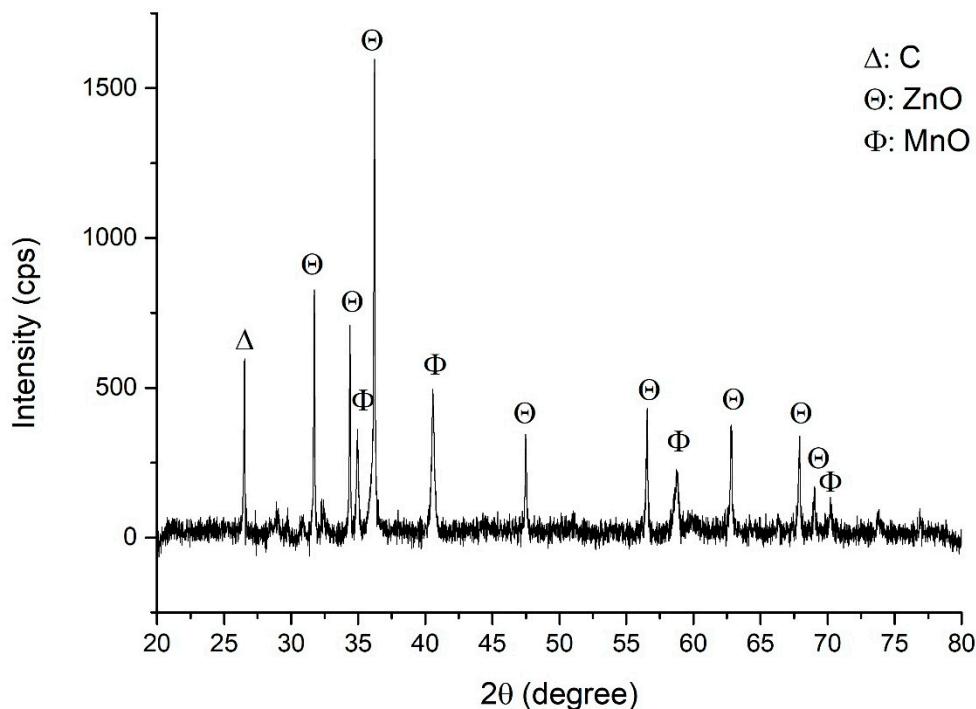


Figure 9. XRD pattern of residue after vacuum applied process with $800\text{ }^{\circ}\text{C}$ and 10 Pa vacuum conditions (lignite as carbon source).

In metallurgical processes, process efficiency can be increased as furnace sizes increase. This is because heat losses occur from the furnace surface and the increasing furnace size decreases the unit surface area where heat losses can occur. For this reason, it is expected that the process efficiency will be increased at a larger scale.

4. Conclusions

In conclusion the production of Zn from battery paste is possible via a carbothermal reduction under Ar atmosphere. During vacuum aided experiments, lignite coal is found to be a better reductant than coke. Lignite is known for having a higher reaction capability at lower temperatures than coke coal. On the other hand, coke coal has better chemical stability at higher temperatures, although it is found to be an ineffective reductant for ZnO under vacuum conditions. Both coal types are ineffective in vacuum environments against atmospheric conditions. Reaction gases pumped out of the system via vacuum show that an indirect reduction of ZnO by CO did not take place in the vacuum chamber. Thermodynamic results are based on stable reaction systems, however experimental conditions are dynamic and the produced reaction gases are pumped out of the system by vacuum. Boudouard reactions could not be formed in vacuum conditions, thus vacuum applied systems are found to be ineffective for recycling the Zn of alkaline batteries.

The Ar supplied non-vacuum system had the best results for reduction with 95.1% Zn recovery. CO formation was found to be essential for the reduction and evaporation of ZnO. Consequently, the vacuumed system only provided direct reduction because the produced CO was being pumped out of the system, resulting in lower Zn recovery rates. Boudouard reactions can take place under Ar purged situation, therefore, both direct and indirect reduction of ZnO by carbothermal technique is found to be effective way of recycling ZnO in alkaline batteries. Thermal dissociation of Mn_3O_4 may have caused the use of carbon by oxygen dissociated from Mn_3O_4 .

Thermodynamic calculations deviate from experimental results by higher reaction temperatures. This can be explained by the activation energy of reactions. Thermodynamic calculations show that the reaction influences the temperature, yet time is not taken into consideration. Experiments showed that

reactions need longer time or higher temperatures in practice. Vacuum is found to be an ineffective technique to recycle ZnO from alkaline batteries because of its limited indirect or gas–solid reaction. The direct reduction effect is seen with higher reactivity lignite coal. The need for direct reduction causes the use of more carbon in the reduction process and therefore increases the carbon foot print of the recycling process.

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