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Selective leaching of zinc

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Selective leaching of zinc from spent zinc portable batteries

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This paper concerns the recovery of zinc from alkaline and zinc-carbon spent batteries. After the dismantling of batteries, the black powder was analyzed and found to contain 19,68 wt.% Zn. Therefore, it was considered that recovery of this metal would be interesting due to its relatively large amount in this kind of waste. Hydrometallurgical route was used for zinc extraction. Two leaching media were used for zinc leaching: $(\text{NH}_4)_2\text{CO}_3$ and NaOH. Using leaching medium $(\text{NH}_4)_2\text{CO}_3$ the influence of addition of NH_4OH as reductant was observed. The results have shown that 100 % zinc extraction has been obtained in 2 M $(\text{NH}_4)_2\text{CO}_3$, with addition of 20 ml of NH_4OH as reductant at ambient temperature, liquid/solid ratio of 40/1 within 10 min. Used leaching medium NaOH has shown as not effective medium for zinc extraction. The presence of hydro/hetaerolite (ZnMn_2O_4) phase was found by XRD analysis in the solid residue after leaching. Then annealing of solid residue was performed. It has been proved that the stable phase of hydro/hetaerolite can be decomposed under these conditions: 1 hour of annealing under the temperature at 850 °C.

It is well known production of municipal and industrial waste has increased in the last few decades. As a result of the concurrent increase in demand for zinc and the gradual depletion of this nonrenewable source, an attention had to be directed at the recovery of zinc from the secondary sources. These alter-

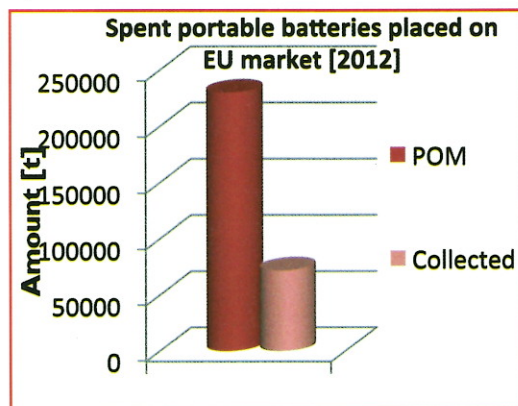


Fig. 1: The overview of batteries placed on the EU market in 2012 [t].

native sources include automobile shredder scrap, dust from steelmaking, zinc ash, zinc dross, waste from brass smelting, spent zinc-carbon and the alkaline batteries.

There is approximately 230.000 tons of portable batteries placed on market every year and almost 90 % of the quantity of this batteries are zinc based. The average content of zinc in such batteries is approximately 20 %, whereas the content

of zinc in primary ore is less than 10 %. The European Union Directive 2006/66/EC published on September 26, 2006, which prohibits the ultimate disposal of portable, industrial and automotive batteries and accumulators by incineration or landfill, is applied to all batteries and accumulators regardless of their shape, volume, weight, material composition, or use. Member States shall achieve the following minimum collection rates: 25 % by September 26th 2012, and 45 % by September 26th 2016. The European Union (EU) Battery Directive Extended Impact Assessment (2012) reports that each year, approximately 230.000 tones of portable batteries are placed on the community market. The collection of spent portable batteries is approximately 70.000 tones in the same year. It represents 32 % collection rate as it is shown in Fig. 1. By this amount EU has met the quota collection [1-3].

Among primary cells, the most used are the zinc-carbon and the alkaline-manganese batteries. Typically these batteries come in sizes AAA, AA, C, D and 9V [5]. In general zinc-carbon (Zn-C) batteries also known as "Leclanché batteries" and they belongs to one of the first commercially used batteries. Zn-C batteries have a carbon rod in contact with carbon and MnO_2 as cathode and a zinc case as anode. A paste of NH_4Cl and ZnCl_2 is the acid electrolyte. On the cylindrical cell the zinc electrode is usually recovered with a stain-

less steel jacket. A plastic or paperboard separator and an asphalt seal are usually present [5-8].

Alkaline batteries were developed after the zinc-carbon and work on the similar principles. These are usually composed of a brass rod in contact with powdered zinc as anode and a steel case in contact with carbon and MnO_2 as cathode. A paste of KOH is used as alkaline electrolyte (pH ~ 14). These batteries have a stable voltage, higher energy density and higher resistance than Zn - C batteries [5-9].

A mixture of anode, cathode and electrolyte material is called a black powder or active mass. The composition of black powder is dependent on type of spent batteries.

There are basically three methods for battery-recycling: pyrometallurgy, hydrometallurgy and its combination [10,11].

Pyrometallurgical treatment essentially consists of recovering materials by using high temperatures. The Process itself is based on evaporation and condensation of recovering metal followed by concentrating of additional agent in the rest of the solution. Although pyrometallurgy does not require mechanical removal of batteries and the process is relatively simple, it is characterized by few disadvantages as high investment and operating costs, high energy consumption to ensure the melting process, dust generation and gas emission, etc.[11].

In contrast, hydrometallurgical routes are commonly found more economical and efficient than pyrometallurgical ones. Hydrometallurgy requires a pretreatment to ensure leaching process of active mass followed by metal recovery from the solution in the most effective way. Recycling through hydrometallurgy basically consists of the acid or base leaching of scrap to put the metals in a solution. Once in a solution, metals can be recovered by various methods [12].

Mechanical pretreatment is a certain disadvantage of hydrometallurgy. It increases the total costs of treatment. Also a big amount of chemicals is consumed during the process which is connected to residual solution followed by secondary environmental pollution. Compared with pyrometallurgy, this process has a several benefits as lower energy consumption of the operation, lower initial investment costs, zero air pollution, flexibility of process, possibility of adapting for a small batch, etc [11, 13, 14].

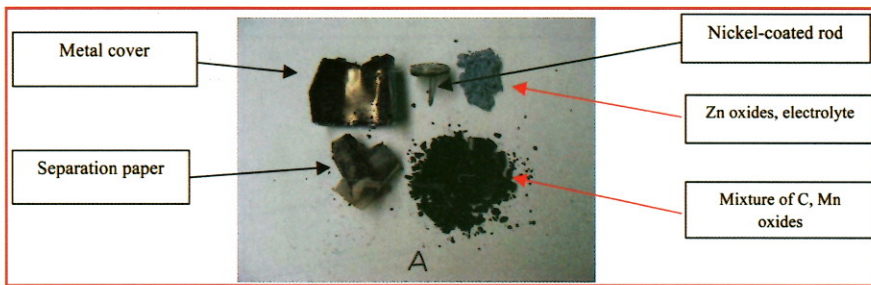


Fig. 2: Alkaline battery

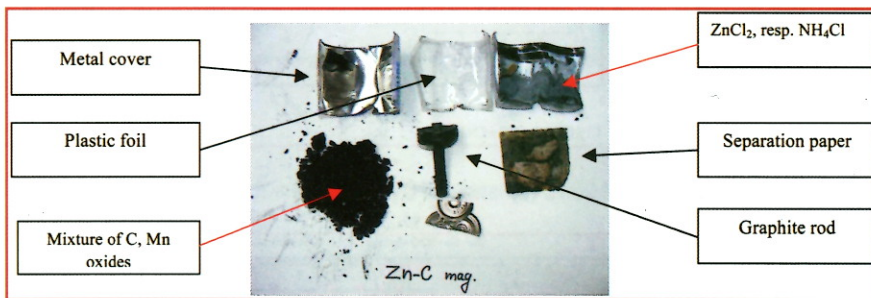


Fig. 3: Zn - C battery

Experimental material and procedures

For the purpose of this research, a sample of spent portable batteries was obtained. From spent alkaline and zinc-carbon batteries 3 kg of black powder was prepared.

Element	Amount [%]
Zn	19,68
Mn	23,05
Fe	0,88
K	0,93
Cl	17,71

Tab. 1: Chemical analysis of black powder

Fig. 2 and Fig. 3 show individual parts of alkaline and zinc-carbon batteries after manual dismantling. Leaching experiments were realized using various condi-

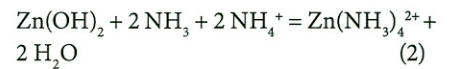
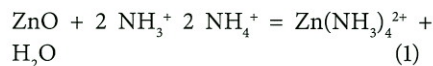
tions: type of leaching medium, concentration of leaching medium, temperature, and time of leaching. Based on results the optimal conditions for selective zinc leaching were determined.

Black powder sample was analyzed by AAS (atomic absorption spectrometry) and by XRD analyzer (X-ray diffractometer PANalytical X'pert PRO MPD), as shown in Tab. 1 and Tab. 2.

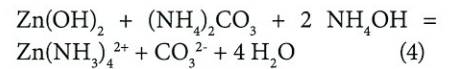
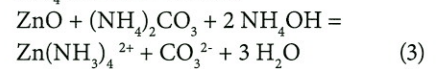
According to the Tab. 1, black powder contains almost 20 % Zn, 23 % Mn and approximately 18 % Cl.

As shown in Tab. 2, XRD phase analysis confirms presence of zinc in phase as Zn(OH)₂, ZnO, ZnMn₂O₄ and Zn₅(OH)₈Cl₂·H₂O.

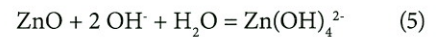
Reactions occurring in the leaching process in medium (NH₄)₂CO₃ are as follows:



Reactions occurring in the leaching process in medium (NH₄)₂CO₃ with addition of NH₄OH are as follows:



Reaction occurring in the leaching process in medium NaOH is as follows:



In order to find out the best leaching conditions of Zn the E-pH diagrams have been built.

The potential - pH diagrams in Zn - C - N - H₂O system in the temperature range 20 - 60 °C are shown in Fig. 4, and Fig. 5.

As it is shown zinc occurs in several forms under different conditions. During the leaching of black powder in the medium of (NH₄)₂CO₃ there is occurrence of formation of Zn (NH₃)₄²⁺ in very tight pH interval, specifically 8 - 10,5. The widest pH interval seems to be under the leaching temperature of 20 °C.

Fig. 6 shows potential - pH diagram in the system Zn - Na - H₂O at temperature of 20 °C, 40 °C, 60 °C and 80 °C.

Fig. 6 shows the potential-pH diagrams for zinc-water system to highlight the effect of temperature. At 20 °C the ZnO/ZnO₂²⁻ line shifts to the right indicating the need for a higher pH or concentrated alkali to dissolve a high concentration of zinc (II) in the form of ZnO₂²⁻ ions. However, the increase in temperature from 20 °C to 80 °C shifts the ZnO/ZnO₂²⁻ line to the left indicating the need for relatively low alkaline pH values at higher temperatures.

Experimental results

In Fig. 7 and Fig. 8, there are shown kinetics curves of zinc extraction in the temperature range 20 - 60 °C in ammonium carbonate with concentrations 1, 2 and 3 M. It can be seen from the kinetics curves in Fig. 7 and Fig. 8 that the amount of leached zinc in ammonium carbonate medium depends on both concentration and leaching time. Effect of temperature was negligible. The use of concentrated ammonium carbonate (3 M) at temperature of 20 °C

Ref. Code	Score	Compound Name	Chemical Formula
00-048-1066	37	Zinc Hydroxide	Zn(OH) ₂
00-036-1451	32	Zinc Oxide	ZnO
00-036-0791	16	Potassium Hydroxide Hydrate	KOH · H ₂ O
00-007-0155	16	Zinc Chloride Hydroxide Hydrate	Zn ₅ (OH) ₈ Cl ₂ · H ₂ O
00-039-0697	11	Potassium Oxide	KO ₂
00-028-1468	9	Zinc Manganese Oxide	ZnMn ₂ O ₄
00-022-0720	6	Manganese Chloride	MnCl ₂
00-042-1316	4	Manganese Oxide	MnO ₂
00-023-0064	1	Carbon	C

Tab. 2: Phase composition of black powder

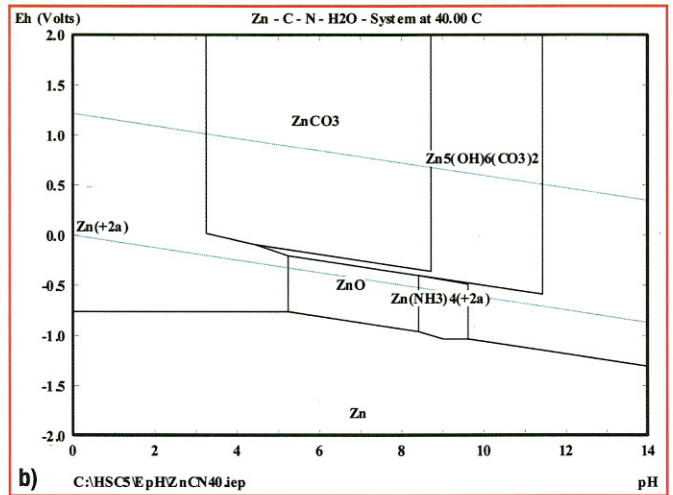
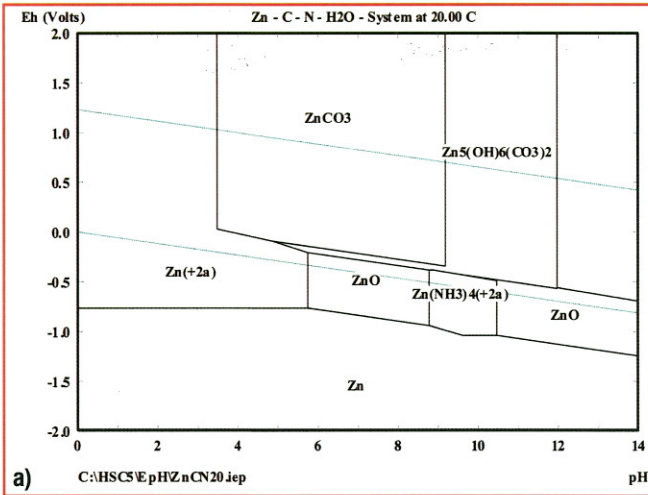


Fig. 4: Potential-pH diagram for Zn - N - C - H₂O system at temperature of 20 °C (a) and 40 °C (b)

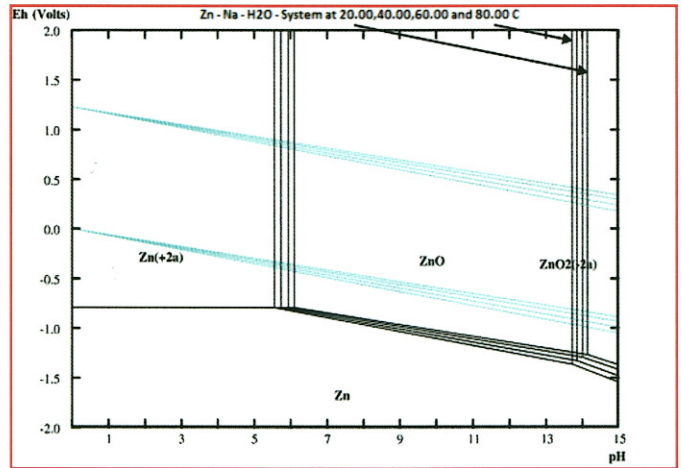
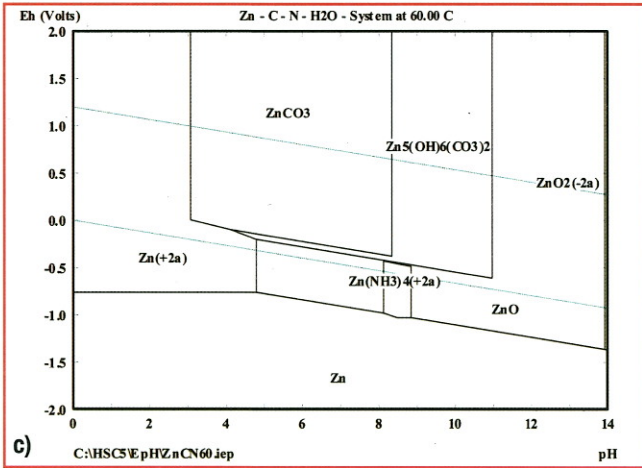


Fig. 5: Potential-pH diagram for Zn - N - C - H₂O system at 60 °C

Fig. 6: Potential-pH diagram for Zn - Na - H₂O system in the temperature range 20 - 80 °C

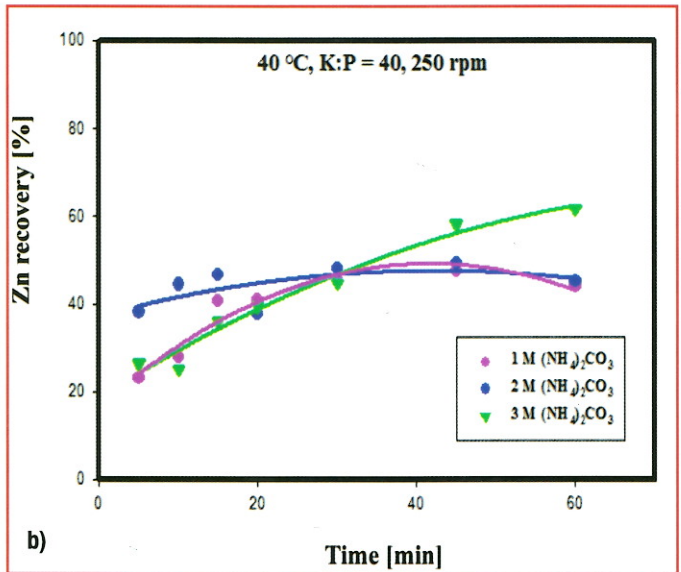
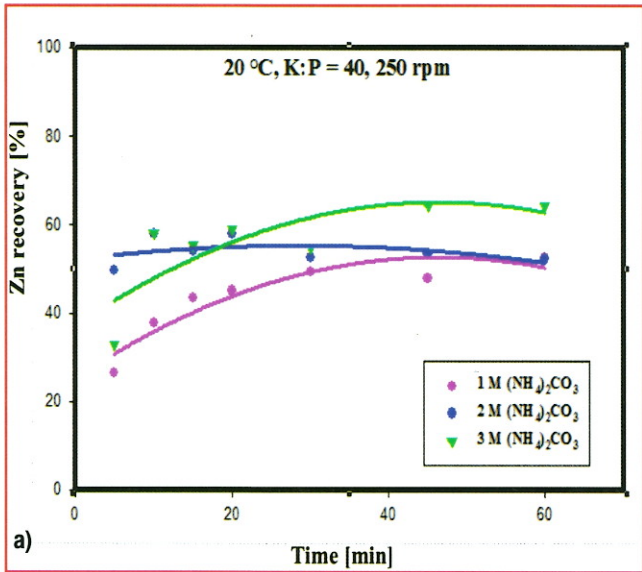


Fig. 7: Kinetics curves of zinc extraction at temperatures 20 °C (a), and 40 °C (b) with (NH₄)₂CO₃ concentrations 1, 2, and 3 M.

results in zinc passing into the solution (64 %).

Series of experiments was conducted by leaching black powder in 2 M (NH₄)₂CO₃

with addition of NH₄OH as reductant as depicted in Fig. 9.

From results shown in Fig. 9, clear increase of zinc recovery (89 %) after adding 10 ml

of NH₄OH can be seen. Addition of 20 ml of agent led to 100 % Zn extraction.

In Fig. 10 and Fig. 11, there are shown kinetics curves of zinc extraction in the tempera-

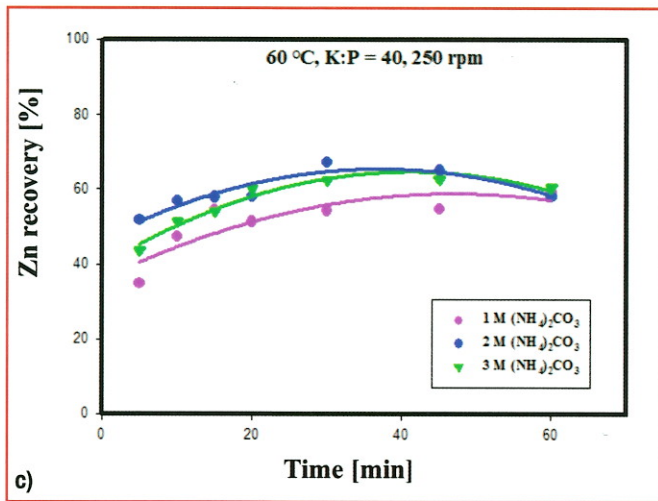


Fig. 8: Kinetics curves of zinc extraction at temperature of 60 °C with $(\text{NH}_4)_2\text{CO}_3$ concentrations 1, 2, and 3 M.

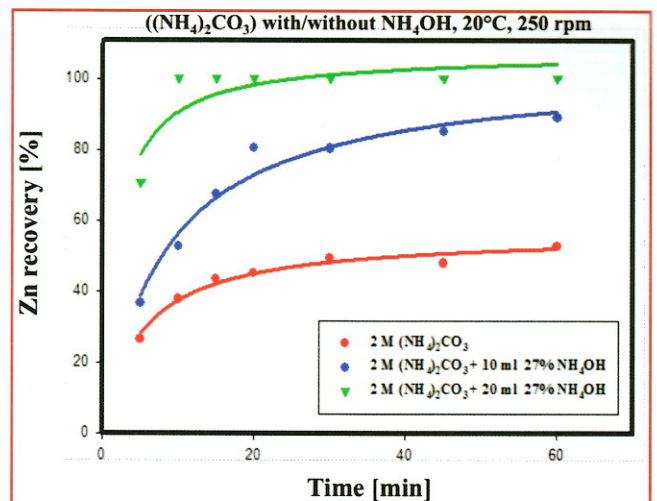


Fig. 9: Kinetics curves of zinc extraction at temperature of 20 °C with $(\text{NH}_4)_2\text{CO}_3$ concentration 2 M with or without addition of NH_4OH .

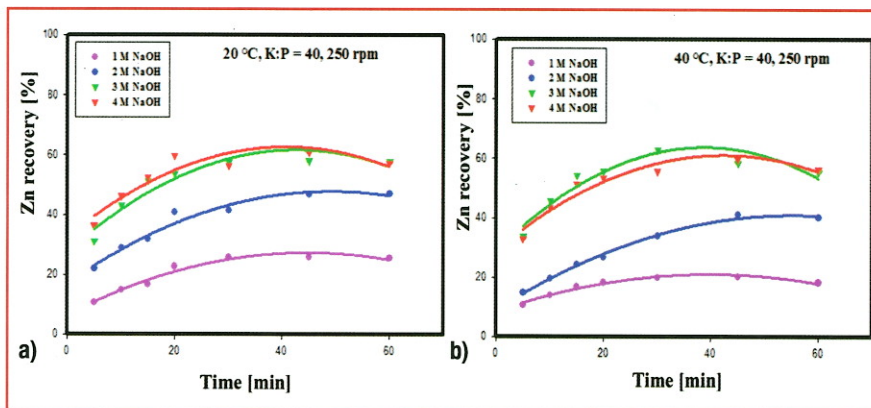


Fig. 10: Kinetics curves of zinc extraction at temperatures 20 °C (a) and 40 °C (b) with NaOH concentrations 1, 2, 3 and 4 M.

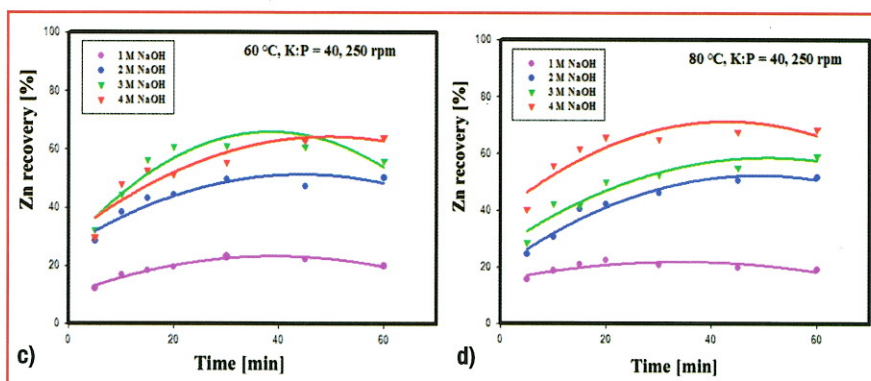


Fig. 11: Kinetics curves of zinc extraction at temperatures 60 °C (c) and 80 °C (d) with NaOH concentrations 1, 2, 3 and 4 M.

ture range 20 – 80 °C in hydroxide sodium with concentrations 1,2,3, and 4 M. The extraction of zinc increases with increased concentration of leaching

medium hydroxide sodium. Significant effect of temperature was not observed. Practically, zinc cannot be completely leached out in time periods in the present

leaching medium. The use of concentrated leaching medium (4 M) at high temperature (80 °C) results in 68 % zinc extraction.

After leaching procedure the solid residue was submitted to XRD analysis. The result is shown in Tab. 3.

XRD analysis showed that the residual Zn is present in ZnMn_2O_4 compound also called hetaerolite. It follows that Zn leached out from the black powder into the solution from the phases like ZnO a $\text{Zn}(\text{OH})_2$. Sample was submitted to annealing at temperature of 600 °C, 700 °C and 850 °C. The sample after annealing can be seen in Fig. 12. The temperature of 850 °C led to decomposition of hetaerolite phase as showed in Tab. 4.

Conclusion

The following conclusions can be drawn from this study:

1. Using of leaching medium NaOH had no positive effect on high zinc extraction.
2. Using of leaching medium $(\text{NH}_4)_2\text{CO}_3$ did not result in high zinc extraction.
3. The optimal conditions for selective 100 % zinc extraction are: leaching in 2 M $(\text{NH}_4)_2\text{CO}_3$ with addition of 20 ml NH_4OH as reductant at temperature 20 °C, within 10 minutes.
4. Effect of leaching temperature was negligible using both leaching media.
5. Effect of concentration on zinc extraction was observed.
6. The hetaerolite (ZnMn_2O_4) phase presented in solid residue can be decomposed by annealing at 850 °C within 1 hour.

Ref. Code	Score	Compound Name	Scale Factor	Chemical Formula
00-025-0284	33	Carbon	0.730	C
01-071-2499	22	Zinc Manganese Oxide	0.706	ZnMn_2O_4

Tab. 3 The result of XRD phase analysis of the solid residue from leaching in NaOH.

Ref. Code	Score	Compound Name	Scale Factor	Chemical Formula
01-075-0625	60	Manganese Oxide	0.727	MnO
00-026-1077	46	Carbon	0.487	C
01-079-0208	22	Zinc Oxide	0.081	ZnO
00-006-0540	13	Manganese Oxide	0.058	Mn ₂ O ₃

Tab. 4: The results of XRD phase analysis of annealed sample

7. Zinc presented in the black powder is leached out mainly from phase ZnO and Zn(OH)₂.

Acknowledgements

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Fig. 12: Annealed sample

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Mittelfristig weiterhin Defizite am Zinkmarkt möglich – DERA veröffentlicht Studie

Trotz neuer Bergbauprojekte weltweit können kurz- bis mittelfristig Defizite am Zinkmarkt auftreten. Der Grund: Nicht alle zusätzlichen Kapazitäten werden voraussichtlich rechtzeitig den Markt erreichen, um Bergwerksschließungen aufzufangen und gleichzeitig eine starke Nachfrage abzudecken. Die Versorgungslage bei Zink ist aufgrund der zahlreichen neuen Projekte langfristig jedoch unkritisch. Zu diesem Ergebnis kommt die Deutsche Rohstoffagentur (DERA) in der Bundesanstalt für Geowissenschaften und Rohstoffe (BGR) in ihrer neuen Studie „Rohstoffrisikobewertung – Zink“.

Der Rohstoff wird im Wesentlichen zum Verzinken von Stahl als Korrosionsschutz eingesetzt, beispielsweise in der Automobil- und Bauindustrie. Bei Feinzink, Zinklegierungen und Zinkstaub zählt Deutschland zu den größten Nettoimporteuren weltweit. Einen wichtigen Beitrag für die Verfügbarkeit von Zink leistet auch das Recycling. Weltweit liegt die Recyclingrate für Zink aus Endprodukten bei über 50 %, in Europa sogar bei 70 %. Wichtigster Treiber der globalen Zinknachfrage ist China. Gleichzeitig ist das Land weltweit bedeutendster Produzent

von Zinkerzen und -konzentraten sowie Zinkmetall. Trotz der chinesischen Dominanz ist der Zinkmarkt derzeit noch vergleichsweise gut diversifiziert. Ein Szenario zur zukünftigen globalen Marktdeckung bis 2020 kommt zu folgendem Ergebnis: Eine jährliche Nachfragesteigerung von etwa 2,2 % könnte bis 2020 – unter Berücksichtigung der derzeit am weitesten fortgeschrittenen Bergbauprojekte – gerade noch abgedeckt werden. Studie: www.deutsche-rohstoffagentur.de/DERA/DE/Downloads/studie_zink_2015.pdf?__blob=publicationFile&v=3