POSSIBILITIES OF USING MAGNETIC SEPARATION TO RECOVER SELECTED METALS FROM THE ACTIVE MATERIAL OF Li BATTERIES

Jitka MALCHARCZIKOVÁ, Renata PALUPČÍKOVÁ, Ondřej STUDENKA

VSB - Technical University of Ostrava, Ostrava, Czech Republic, EU, jitka.malcharczikova@vsb.cz, renata.palupcikova@vsb.cz, ondrej.studenka.st@vsb.cz

https://doi.org/10.37904/metal.2025.5155

Abstract

Currently, the focus of the waste Li-ion battery processing is on better separation of individual material components of the batteries so that this process is as efficient as possible. This step is closely related to the success of the subsequent processing of the individual separated components. The active material (black mass) after separation contains a certain proportion of metals in the form of their compounds and graphite. The paper deals with the possibility of separating a portion of selected metals, such as cobalt and nickel, into a separated fraction of the black mass using magnetic separation. The active material was annealed at 900 °C, whereby some of the metals were converted into a ferromagnetic state. The subsequent leaching converted the soluble salts into solution. A wet magnetic separation method was then used to concentrate the selected metals into the separated fraction. From the process, a mass fraction richer in the content of selected metals, a fraction richer in graphite and, after drying the solution after leaching, a proportion of salts including lithium salts was obtained. The success of the process depends on a number of parameters during leaching of the material and subsequent magnetic separation. This process made it possible to obtain a metal concentrate containing up to 60-70 wt% of cobalt and 2-3 wt% of nickel. The problem is to achieve better separation of individual components from the Li active material. Finding the best way to process waste lithium batteries is important for sustainable electromobility.

Keywords: Lithium batteries, magnetic separation, metals recovery, cobalt, automotive sustainability

1. INTRODUCTION

Lithium-ion batteries (LIBs) have become a key technology for energy storage, enabling a revolution in portable electronics and supporting the growth of electromobility and stationary storage systems. The global Li-ion battery market is expected to double every five years. A significant demand for LIBs in the automotive sector is anticipated over the next decade [1]. However, with increasing utilization, the need for efficient recycling becomes more critical. Electrode material, also referred to as "black mass," will be classified as hazardous waste. As a result, it will become a more strictly regulated commodity, enabling improved utilization within the European Union [2]. Battery lifetime requirements are also rising, exceeding 10 years for automotive applications [3], Moreover, a complete transformation in the material composition of traction batteries is expected [4]. The processing and recycling of lithium-based battery waste is currently, and will continue to be in the near future, essential for ensuring the sustainability of electromobility. Spent LIBs can contain 5–20% of cobalt, 5–10% of nickel, 5–7% of lithium and other metals (copper, aluminum, iron), 15% organic compounds, and 7% plastics [5]. Waste lithium batteries contain not only valuable metals—previously targeted for recovery through direct pyrometallurgical [6], hydrometallurgical, and combined processes, but also a significant fraction of valuable graphite [7].

A major challenge in the processing of waste lithium batteries is the separation of anode and cathode materials, which tend to be intermixed in the electrode mass following mechanical battery treatment. The anode material

is graphite-based, whereas the cathode material consists of metal oxides such as Co, Ni, and Mn [4,8]. Both materials contain lithium. Graphite itself, along with all of the metals, represents a valuable and costly resource. Currently, efforts focus not only on the mechanical separation of casings (Fe, Al, polymers), current collectors (Al, Cu), and electrode mass, but also on the direct separation of graphite and metal-based components from the black mass. One possible approach involves thermal treatment of the electrode mass at elevated temperatures to induce a transition of the metal content (e.g., Co, Ni, and residual Fe) into a ferromagnetic state, enabling subsequent separation through leaching and magnetic separation.

During this process, chemical reactions occur between cobalt and lithium compounds and graphite [9,10]. According to thermodynamic calculations, $LiCoO_2$ first decomposes into Li_2O, CoO, and oxygen, with the theoretical decomposition temperature in air being approximately 813 °C. Carbon then reduces cobalt oxides to metallic cobalt, while itself oxidizing to CO or CO_2. These gases can further react with Li_2O to form lithium carbonate (Li_2CO_3). Other metals, including nickel, may also participate in similar redox reactions. In the subsequent separation steps, the ferromagnetic properties of cobalt, nickel, and residual iron are utilized. A leaching step is advantageous, where soluble non-magnetic compounds are transferred into the solution phase. Certain lithium compounds are water-soluble, allowing for their efficient separation. Upon crystallization from solution, lithium compounds form a white powder. Subsequently, the magnetic and non-magnetic fractions are separated from the solid portion on the basis of different magnetic properties. The magnetic fraction should contain Co, Ni, and Fe. Whereas the non-magnetic fraction is expected to retain Mn, Cu, Al from the monitored elements and mainly C. However, the efficiency of magnetic separation is hindered by the presence of polymeric binders and other organic compounds, which are difficult to remove by roasting.

2. DESCRIPTION OF THE EXPERIMENT

The basis of this experiment is the verification of the possibility of using the roasting of the electrode material from Li accumulators in air, converting part of the material into a ferromagnetic state and subsequent leaching of the treated material in an aqueous environment. During leaching, the non-magnetic soluble fraction should be transferred to the solution. After crystallization, this fraction should contain mainly lithium in the form of salts, which can also be of a more complex nature. The solid residue can then be separated into a non-magnetic (the largest proportion should be graphite) and a magnetic fraction (cobalt, nickel and their compounds, which are ferromagnetic) using the wet magnetic separation method.

2.1. Preparation of the experiment

Electrode mass from waste Li-ion batteries (LIB) was used as an input for the experiment after sieving and separating the magnetic fraction. The composition of the input material (LIB mass) is given in **Table 1**, material is marked as LIB IN. The content of selected elements was determined by the method ED-XRF (Energy Dispersive X-ray fluorescence) using the device Delta professional. This analysis is only indicative and was used to compare the content of selected metals for the experiment. This mass was annealed in air at 900 °C for 30 minutes (oxidative roasting). Annealing was carried out in two ways in electric resistance furnace Clasic. Firstly, the material was annealed in a larger volume (about 50 g, designated as LIB R1) and in a smaller volume for better roasting (about 20 g, designated as LIB R2). The content of selected elements in the annealed electrode mass was determined again by the method ED-XRF.

Table 1 Average content of selected elements in LIB mass after annealing - content of element (wt%)

	Co	Mn	Ni	Fe	Cu	Al
LIB IN	25.06±0.53	3.11±0.06	1.69±0.06	0.24±0.24	1.61±0.22	1.91±0.12
LIB R1	28.33±0.30	3.53±0.06	1.95±0.03	0.27±0.01	1.86±0.12	1.44±0.08
LIB R2	32.85±0.10	4.12±0.04	2.68±0.05	0.37±0.01	2.17±0.23	1.22±0.09

It is clear from **Table 1** that the element content increased because part of the organic and volatile components was removed during annealing. Roasting in a thin layer has a better effect for removing organic components and increasing the proportion of metals of interest Co, Ni, Mn, as can be seen in **Table 1**. In the LIB R2 sample, the Co content increased by 7 % compared to the original content. The weight loss during annealing was for the sample LIB R1 14,39 % and for LIB R2 23,01 %. After oxidative roasting under the given conditions, the material was ferromagnetic**. Figure 1** shows the electrode material after annealing (left) and then after crushing and sieving (right). This modified mass was used for subsequent experiments.

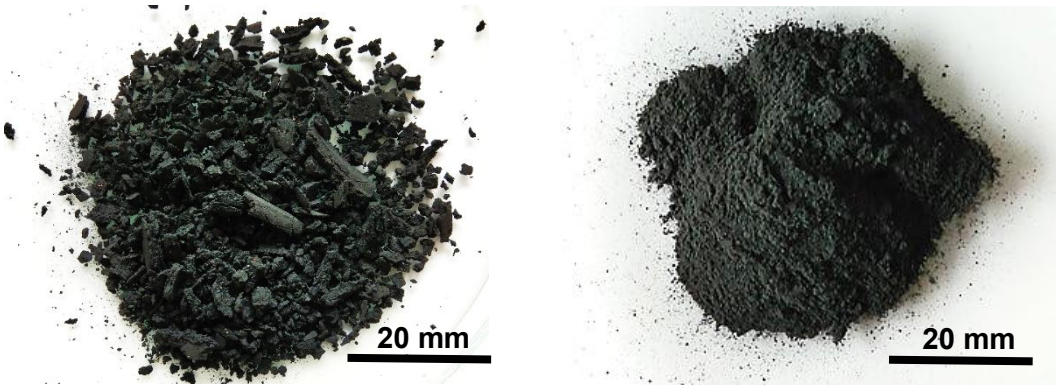

Figure 1 Black mass after roasting: left before and right after crushing and sieving

2.2 Wet magnetic separation of LIB mass

The wet magnetic separation method was used to separate cobalt and nickel from the annealed electrode mass. The process produces three separated fractions – a solid magnetic fraction (based on metals Co, Ni, Fe – (M)), a solid non-magnetic fraction (graphite and metals Al, Cu, Mn, … - (N)) and a liquid fraction (Li and other metals in soluble form – (S)). It is assumed that lithium in the annealed mass under the above conditions is in the form of slightly soluble Li_2CO_3.

Samples of the annealed electrode material were leached in 200 ml of distilled water and stirred for a given time on a magnetic stirrer. For experiment 1, mass LIB R1was used, for experiments 2-5 mass LIB R2. The weight was 2 or 1 g of mass, the ratio of solid to liquid phase S:L was 1:200 or 1:100. The leaching time was varied in the range 3-48 h. After the end of the process, the magnetic fraction (M) was taken out by permanent magnet using in magnetic stirrer and the liquid and solid fraction were subsequently filtered. The leachate was heated to cause crystallization for several hours (days) until completely dry. For the separated fractions (M, N, S), the content of selected metals was determined using the ED-XRF method and their proportion to the input was determined. Lithium and other elements cannot be determined by this method, however, from the analysis it is possible to evaluate how the metal content changes in each fraction after separation and whether it is present or not in the given fraction. Basic information about the leaching conditions is given in **Table 2**. From the results in **Table 2**, it follows that the proportion of the obtained magnetic fraction is within the range 10-27 %, non-magnetic fraction 50-74 % and crystallized 14-20 %. **Figure 2** shows the separated fractions from the LIB mass. The losses after separation are not listed in the **Table 2**.

Table 2 Basic information about leaching conditions, proportions of obtained fractions

Sample	m_{LIB} (g)	S:L	Time (h)	M		N		S	
				(g)	(%)	(g)	(%)	(g)	(%)
1	2.14	1:100	25	0.44	20.56	1.33	62.15	0.36	16.82
2	1.01	1:200	3	0.28	27.72	0.51	50.50	0.21	20.79
3	2.02	1:100	30	0.22	10.89	1.44	71.29	0.31	15.35
4	2.08	1:100	30	0.23	11.06	1.54	74.04	0.29	13.94
5	2.00	1:100	48	0.32	16.00	1.35	67.50	0.28	14.00

The determined contents of selected metals in the magnetic, non-magnetic and crystallized fractions are given in **Table 3**. It is clear from **Table 3** that during the experiments, Co and Ni were redistributed between the magnetic and non-magnetic fractions at longer leaching times. This process made it possible to obtain a metal concentrate containing up to 60-70 wt% of cobalt and 2-3 wt% of nickel in magnetic fraction. The increase in the content of Mn, Cu and Al in the non-magnetic fraction is not entirely obvious. A positive finding is that of the selected metals, only aluminum passes into solution. The aluminum content may be distorted, however, it is likely that aluminum will also form soluble compounds with lithium. The purity of the obtained fractions, respectively the efficiency of the separation, is important, therefore analysis was also carried out by the SEM method (scanning electron microscopy).

Table 3 Average content of selected metals in separated fractions after leaching

Sample/ Fraction	Content of element (wt%)					
	Co	**Ni**	**Fe**	**Mn**	**Cu**	**Al**
1-M	62.54±8.92	4.05±0.83	0.57±0.10	2.99±0.32	3.21±0.51	1.06±0.11
2-M	36.25±1.93	1.99±0.15	0.29±0.02	3.63±0.18	4.81±0.12	2.32±0.09
3-M	61.32±0.61	4.09±0.14	0.54±0.01	4.15±0.02	2.35±0.21	1.94±0.04
4-M	70.98±8.69	3.36±0.36	0.48±0.05	2.60±0.22	3.37±0.95	2.10±0.09
5-M	64.02±6.00	3.00±0.28	0.41±0.03	2.47±0.14	2.70±0.10	1.71±0.08
1-N	18.10±1.25	1.56±0.14	0.23±0.04	4.56±0.25	1.67±0.06	2.58±0.07
2-N	25.06±0.76	1.87±0.06	0.26±0.00	3.83±0.05	1.33±0.06	1.63±0.05
3-N	29.97±0.20	2.70±0.01	0.38±0.01	4.60±0.05	2.55±0.06	2.61±0.25
4-N	28.03±0.75	2.71±0.16	0.36±0.02	4.80±0.12	2.60±0.67	1.95±0.11
5-N	24.15±0.21	2.56±0.06	0.33±0.01	4.94±0.03	1.99±0.13	2.09±0.10
1-S	ND	ND	ND	ND	0.0017±0.0003	4.67±0.35
2-S	ND	0.0050±0.0015	ND	0.0114±0.0022	0.0038±0.0017	2.26±0.71
3-S	ND	0.0016±0.0002	ND	ND	0.0084±0.0004	9.12±1.15
4-S	ND	0.0028±0.0003	ND	ND	0.0042±0.0005	7.71±1.39
5-S	ND	0.0049±0.0008	ND	0.0096±0.0015	0.0037±0.0007	4.02±0.45

ND – The element content is below the detection limit.

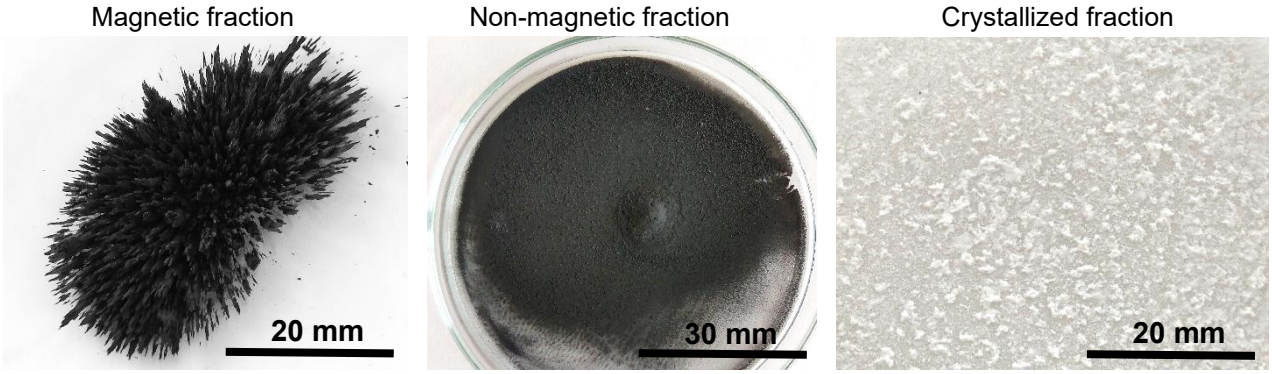

Figure 2 Black mass after process of wet magnetic separation – magnetic, non-magnetic, crystallized fraction

2.3 SEM analysis of separated fractions

A detailed characterization of selected experimental samples was conducted, including elemental analysis. Scanning electron microscopy (SEM) combined with energy-dispersive X-ray spectroscopy (EDX) was performed using an ESEM FEI Quanta FEG 450 microscope equipped with an EDAX EDS analyzer. Representative elemental analysis was carried out for both the magnetic and non-magnetic fractions. Although this method is not fully suitable for analyzing the crystallized fraction, an EDX analysis was performed for this sample as well. Sample 1 was selected as a representative example, and all separated fractions—1M

(magnetic), 1N (non-magnetic), and 1S (crystallized)—were documented. The measurement results were compared with the results obtained by the ED-XRF method listed in the **Table 3**. Enrichment of the 1M fraction in cobalt was confirmed, with relatively low contamination by other elements. **Figure 3** (left) shows a SEM image (BSE – back scattered electrons) of fraction 1M. Bright particles rich in metals, mainly cobalt, are clearly visible, intermixed with darker particles, which are presumed to be residual graphite. **Figure 3** (right) presents the SEM image of fraction 1N. Fraction 1N contained mainly carbon (dark particles) and small light particles based on metals. Both images in **Figure 3** indicate that complete separation of the fractions was not achieved, which corresponds to the values listed in **Table 3**. **Figure 4** displays a SEM image (SE – secondary electrons) of the crystallized fraction 1S. The image reveals a heterogeneous mixture of crystalline particles. Unfortunately, from the results of the elemental analysis, it is not possible to distinguish with certainty what compounds are involved. Lithium could not be determined by this method, however, it was found that this fraction does not contain metals such as Co, Ni or Fe. The analysis therefore showed that only a small amount of aluminum, passes into this fraction.

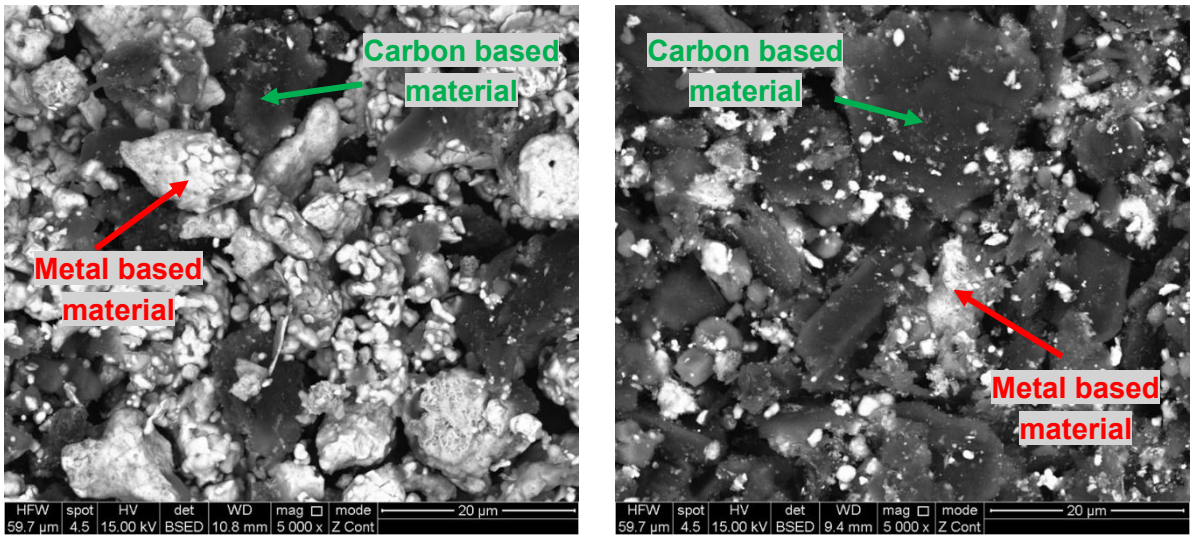

Figure 3 SEM-BSE images of magnetic (left) and non-magnetic (right) fractions

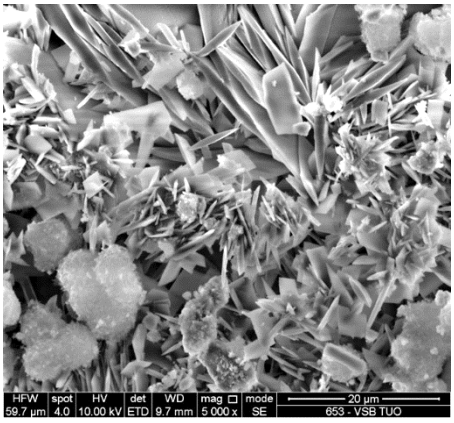

Figure 4 SEM-SE image of the dissolved and subsequently crystallized fraction

The wet magnetic separation technology is suitable for processing electrode mass with higher Co and Ni contents. The obtained results show that the separation method is applicable to increase the efficiency of processing LIB mass. However, the success of the method is influenced by a number of parameters and it is also appropriate to bring the solution closer to real conditions for recycling Li-Ion batteries. The authors of some articles achieved higher separation efficiency, but pure materials were used for the experiments [9,10]. For our experiment, the used material was derived from the processing of real Li batteries, which contain a

number of other elements. Flotation technology [11] and other procedures are also being tested to solve the separation of components from LIB material. At the moment, there is an effort to completely change the principle of Li accumulators used in electric vehicles so that their reuse, refurbishing or direct recycling is possible (recrystallization, reactivation) [1,3,12].

3. CONCLUSION

The fractions from the LIB mass were separated using the wet magnetic separation method. The active material was annealed at 900 °C, whereby some of the metals were converted into a ferromagnetic state. The subsequent leaching converted the soluble salts into solution. From the process, a mass fraction richer in the content of ferromagnetic metals, a fraction richer in graphite and, after drying the solution after leaching, a proportion of salts including lithium salts was obtained. This process made it possible to obtain a metal concentrate containing up to 60-70 wt% of cobalt and 2-3 wt% of nickel. The success of the process depends on a number of parameters during separation process and the problem is to achieve individual components from the Li active material with sufficient purity.

ACKNOWLEDGEMENTS

This article was created with the contribution of project SP2025/076 "Material and technological properties of construction materials in relation to their production method, processing and the effect of degradation mechanisms". This paper was created as part of the project No.CZ.02.01.01/00/22_008/000463. Materials and technologies for sustainable development within the Jan Amos Komensky Operational Program financed by the European Union and from the state budget of the Czech Republic.

REFERENCES

[1] AYDIN, Aslihan Örüm, et al. Lithium-ion battery manufacturing: Industrial view on processing challenges, possible solutions and recent advances. *Batteries*. 2023, vol. 9, no. 11. DOI: 10.3390/batteries9110555.

[2] Directorate-General for Environment. *New battery-related waste codes will boost circular management of batteries and their critical raw materials*. [online]. 2025 [viewed: 2025-05-14]. Available from: https://environment.ec.europa.eu/news/battery-related-waste-codes-update-set-boost-circular-economy-2025-03-05_en.

[3] MASIAS, Alvaro, et. al. Opportunities and challenges of lithium ion batteries in automotive applications. *ACS Energy Letters*. 2021, vol. 6, no. 2. DOI: 10.1021/acsenergylett.0c02584.

[4] WANG, Yuqing, et al. Recent progress on the recycling technology of Li-ion batteries. *Journal of Energy Chemistry*. 2021, vol. 55, pp. 391-419. DOI: 10.1016/j.jechem.2020.05.008.

[5] NEUMANN, Jonas, et all. Recycling of lithium-ion batteries - current state of the art, circular economy, and next generation recycling. *Adv. Energy Mater*. 2022, vol. 12, 2102917. DOI: 10.1002/aenm.202102917.

[6] MALCHARCZIKOVÁ, Jitka, et al. The possibilities of recovery of selected metals from lithium batteries by pyrometallurgical way. In: *28th International Conference on Metallurgy and Materials*. Brno, 2019, pp. 1615-1620. DOI: 10.37904/metal.2019.948.

[7] TAKACOVA, Zita, et al. Cobalt and lithium recovery from active mass of spent Li-ion batteries: Theoretical and experimental approach. *Hydrometallurgy*, 2016, vol. 163, pp. 9-17. DOI: 10.1016/j.hydromet.2016.03.007.

[8] LEE, Churl Kyoung, RHEE, Kang-In. Preparation of LiCoOsub2/sub from spent lithium-ion batteries. *Journal of Power Sources*. 2002, vol. 109, no. 1, pp. 17-21. DOI: 10.1016/S0378-7753(02)00037-X.

[9] VISHVAKARMA, Shubham a DHAWAN, Nikhil. Recovery of cobalt and lithium values from discarded Li-Ion batteries. *Journal of Sustainable Metallurgy*. 2019, vol. 5, no. 2, pp. 204-209. DOI: 10.1007/s40831-018-00208-4.

[10] LI, Jia, WANG, et al. Environmentally-friendly oxygen-free roasting/wet magnetic separation technology for in situ recycling cobalt, lithium carbonate and graphite from spent $LiCoO_2$/graphite lithium batteries. *Journal of Hazardous Materials*. 2016, vol. 302, pp. 97-104. ISSN 0304-3894. DOI: 10.1016/j.jhazmat.2015.09.050.

[11] YU, Jiadong, et al. A promising physical method for recovery of $LiCoO_2$ and graphite from spent lithium-ion batteries: Grinding flotation: Grinding flotation. *Separation and Purification Technology*. 2018, vol. 190, pp. 45-52. DOI: 10.1016/j.seppur.2017.08.049.

[12] WU, Chaofan, et al. Crystallization of battery-grade lithium carbonate with high recovery rate via solid-liquid reaction. Particuology. 2024, vol. 92, pp. 95-105. DOI: 10.1016/j.partic.2024.05.001.