



PROGRAMME

Konferens i Mineralteknik Conference in Minerals Engineering

7–8 February 2023

Mineralteknik/Mineral Processing

itu.se/minpro

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LULEÅ
TEKNISKA
UNIVERSITET

MINERALS ENGINEERING 2023

Wednesday, February 8, 2023

Session 3 – Industrial projects

Session chair: Laurindo de Salles Leal Filho

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|---------------|---|
| 08.45 – 09.15 | Mohammad KHOSHKHOO, BOLIDEN MINERAL AB
<i>Bioleaching: A Promising Option for Recovery of Valuables from Sulphidic Residues</i> |
| 09.15 – 09.45 | Ulrika HÅKANSSON, LKAB MINERALS
<i>Circular Production of Phosphorus and Rare Earth Elements</i> |
| 09.45 – 10.15 | Mohammad JOOSHAKI, GTK
<i>Digitization and Automation of GTK's Mineral Processing Pilot Plant and Research Laboratories – for Improving Productivity and Customer Experience</i> |

10.15 – 10.45	Coffee break
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Session 4 – Particles and simulation

Session chair: Jan Rosenkranz

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| 10.45 – 11.15 | Per SVEDENSTEN, NMS RESEARCH CENTER
<i>New Crusher Simulation Model for Improved Flowsheet Simulation Accuracy</i> |
| 11.15 – 11.45 | Magnus EVERTSSON, CHALMERS
<i>Characterization of Single Particle Breakage for Improved Energy Efficiency in Comminution</i> |
| 11.45 – 12.15 | Raimon TOLOSANA-DELGADO, HZDR
<i>Particle-based process understanding and geometallurgical testing</i> |

12.15 – 13.15	Lunch at Bistron
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Session 5 – Battery technology

Session chair: Saeed Chelgani

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|---------------|---|
| 13.15 – 13.45 | Mohamed ELSADEK, LTU
<i>Recovery of Valuable Metals from Spent LIBs Black Mass Using Thermal Treatment</i> |
| 13.45 – 14.15 | Allan GOMEZ-FLORES, HANYANG UNIVERSITY
<i>Simulating the Separation of Black Mass Particles Using CFD</i> |
| 14.15 – 14.45 | Gilsang HONG, HANYANG UNIVERSITY
<i>Direct Separation of Cathode and Anode Active Materials of Spent Lithium Ion Batteries</i> |

14.45 – 14.50	Conference closing
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15:00 (15:20) LLT-buss till Luleå Airport (Linje 4)/LLT-bus to Luleå Airport (Nr 4)

Avgård var 20:e minut / Departure every 20th minute

DIRECT SEPARATION OF CATHODE AND ANODE ACTIVE MATERIALS OF SPENT LITHIUM-ION BATTERIES

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ABSTRACT

There is increasing interest and demand for electric vehicles (EVs) over internal combustion engine vehicles in the carbon economy industry. EVs use secondary batteries like lithium-ion batteries (LIBs) that can be charged and discharged. The demand for LIBs is also increasing along with the demand for EVs, and it is expected that many secondary batteries will be needed in the next decade. Recycling of spent LIBs is necessary because a stable supply of batteries is essential for a stable EV market. Recycling of spent LIBs through pyrometallurgical and hydrometallurgical methods to recover valuable metal with relatively high economic value has been in progress, but these methods have environmental and economic disadvantages due to high energy consumption and the use of strong acids. Therefore, research on direct recycling, which directly recovers components without decomposing the chemical structure, is actively being conducted. In particular, the flotation process is mainly used for the separation of cathode and anode materials in direct recycling. However, the separation of these materials is not straightforward due to the presence of impurities such as organic binders (e.g., PVDF) and solid electrolyte interphase (SEI), making it difficult to separate the two materials. Therefore, this presentation will discuss a preliminary study on the pretreatment of spent LIBs as well as the flotation behavior of cathode and anode active materials.

1 Introduction

Efforts towards carbon neutrality are being made globally to address the climate crisis. To achieve carbon neutrality, efforts are needed in various fields such as industry, transportation, and construction. In the transportation field, there is a transition from internal combustion engine vehicles to eco-friendly vehicles. The European Union (EU) has announced a plan to ban the sale of internal combustion engine vehicles by 2035 to reduce carbon emissions, and other countries have also announced regulations on the production and sale of internal combustion engine vehicles. US President Biden has also stated that by 2030, half of new cars will consist of electric vehicles, hybrid vehicles, and fuel cell. An executive order has also been issued to convert all federal transportation vehicles, including car and trucks, to EVs by 2035. The Republic of Korea will also ban new registration of internal combustion engine vehicles by 2035 and promotes the transition to eco-friendly vehicles. As a result, sales of EVs, which are representative eco-friendly vehicles, are continuously increasing. According to Canalys estimates, about 50% of all new cars sold in 2030 will be EVs.

With the increasing demand for EVs, the use of secondary batteries, which are the heart of EVs, is also rapidly increasing. It is expected that a large number of secondary batteries will be needed in the next decade. Since a stable supply of batteries is essential for a stable EV market, battery recycling is necessary. Lithium-ion batteries (LIBs), one of the various types of secondary batteries, are mainly used in EVs due to their long storage life, high energy density, low self-discharge, and safe handling. LIBs, which typically consist of an anode, cathode, separator, and electrolyte, are made of valuable materials such as lithium (Li), nickel (Ni), cobalt (Co), manganese (Mn), and graphite (C).

Currently, the recycling industry for LIBs focuses on hydrometallurgy (chemical leaching, extraction, and bioleaching) and pyrometallurgy methods (melting or burning components at high temperatures). However, these methods have environmental problems and high costs due to the use of strong acids, and the focus is on recovering valuable metals with high economic value. To overcome these disadvantages, there is growing interest in direct recycling research, in which battery components are directly recovered, recycled, and reused without decomposing the chemical structure. A separation process is essential for direct recycling.

The flotation process is a representative separation method used to separate cathode and anode active materials. It involves separating particles that can attach to bubbles from particles that cannot attach by using the difference in hydrophobicity of the particles. The flotation process is suitable for separating a cathode active material (e.g., lithium oxide) with a hydrophilic surface and an anode active material (e.g., graphite) with a hydrophobic surface. However, pretreatment is required due to impurities such as organic binders used in the manufacturing process of batteries and the solid electrolyte interphase (SEI) layer generated during initial charging. In this study, we focused on establishing optimal pretreatment conditions for the separation of cathode and anode active materials and confirmed the degree of separation of the active materials through flotation according to pyrolysis pretreatment.

2 Materials and Methods

2.1 Materials

Spent LIBs in the form of black powder were obtained from SungEel HiTech Co., Ltd. The black powder was a mixture of various NCM-type batteries. After a pyrolysis procedure, active materials from the metal foil (Al and Cu) were separated using dry sieving with a 100-mesh screen ($\sim 150\ \mu\text{m}$), obtaining liberated active materials.

2.2 Pyrolysis procedure

The pyrolysis process was conducted in a muffle furnace, where the atmosphere can be controlled. The black powder was placed in a crucible inside the furnace, and the atmosphere was changed to a vacuum using a vacuum pump. Then, high purity nitrogen gas was introduced at a rate of 2L/min.

2.3 Pyrolysis Sample characterization

A field emission scanning electron microscope (FE-SEM) with energy dispersive x-ray (EDX) spectrometry, particle size analyzer, goniometer, thermogravimetric analyzer (TGA), X-ray diffractometer (XRD), and X-ray photoelectron spectrophotometer (XPS) were used to analyze

the characteristics of the pyrolysis black powder. The contact angle of the black powder was measured using the sessile drop method on compressed pellets. The crystal structure, surface atom configuration, and interatomic bonding state of the black powder were studied using both XRD and XPS analyses.

2.4 Froth flotation

Flotation tests were conducted on black powder at room temperature using a lab-scale flotation machine (Metso D-12, Metso:Outotec, Finland) with a pulp density of 20 g/L and an impeller speed of 1800 rpm. Kerosene (Sigma-Aldrich, USA) was used as a collector at a dosage of 300 g/t and methyl isobutyl carbinol (MIBC, 98%, Sigma-Aldrich, USA) was used as a frother at a dosage of 150 g/t.

3 Results and Discussions

3.1 Removal of current collector in black powder

The black powder is made from spent LIBs by removing the case and grinding the remaining materials. It consists of active materials as well as current collectors like Cu and Al foils. The particle size analysis of the black powder revealed two normal distributions (**Figure 1**). Most of the larger particles were believed to be current collectors, and the elements of black powder were confirmed through ICP analysis to determine the exact content (**Table 1**). The black powder contained about 3.5% current collectors (Cu and Al). To remove the current collectors, a sieving process was performed using a 100-mesh screen, reducing their amount to about 1%. To minimize impurities during flotation of active materials, screening tests were conducted after pretreatment of all samples, regardless of conditions.

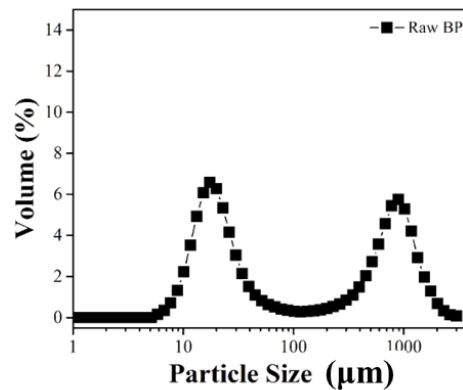


Figure 1. Black powder particle size distribution

Table 1: Element weight percentage of before and after screening (100 mesh)

Element	Cu	Al	Ni	Co	Mn	Na	K	Zn	Fe
Before (%)	1.28	2.19	15.11	8.57	7.97	0.18	0.02	0.07	0.03

After (%)	0.33	0.69	15.30	8.86	8.25	0.17	0.02	0.07	0.02
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3.2 Effect of pyrolysis on characteristics

The pyrolysis process was conducted at three temperatures: 400 °C, 500 °C, and 600 °C, over a period of 12 hours in a nitrogen atmosphere.

The results of the particle size analysis of the black powder, screened with a 100-mesh screen, after pyrolysis treatment at each temperature showed that the medium diameters were 11.5 μm , 10.5 μm , 10.9 μm , respectively. The medium diameter of the sample without pyrolysis was 20.1 μm . Except for the raw black powder, similar size distributions were identified. The raw sample showed a relatively large particle size distribution because the organic binder and the active material were not well liberated (**Figure 2**).

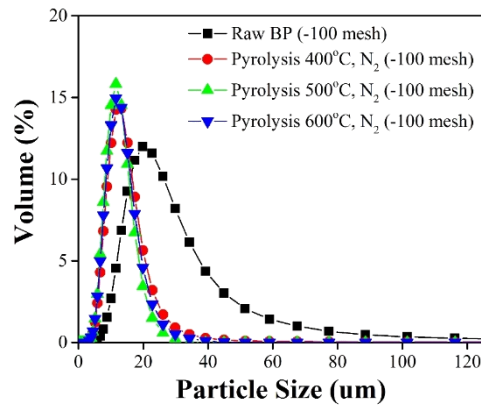


Figure 2. Black powder particle size distribution before and after pyrolysis

The surface morphology and degree of liberation of black powder after pyrolysis were observed using a FE-SEM. The content of the organic binder, polyvinylidene fluoride (PVDF), was also measured using EDX (**Figure 3**). The results showed that, regardless of the pyrolysis temperature, large agglomerations were reduced and active materials existed as individual particles. The content of PVDF also decreased significantly compared to the initial black powder, but there was no difference due to temperature.

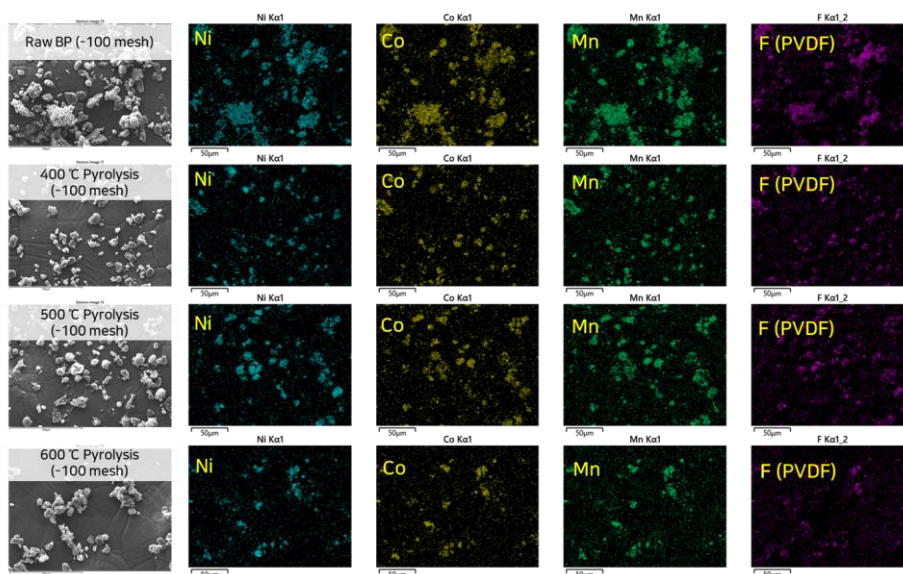


Figure 3. FE-SEM-EDX analysis of before and after pyrolysis

The contact angle, a measure of hydrophobicity, also decreased from 87.48° to around 30° after pyrolysis. (**Figure 4**). However, it is difficult to determine the optimal pretreatment temperature.

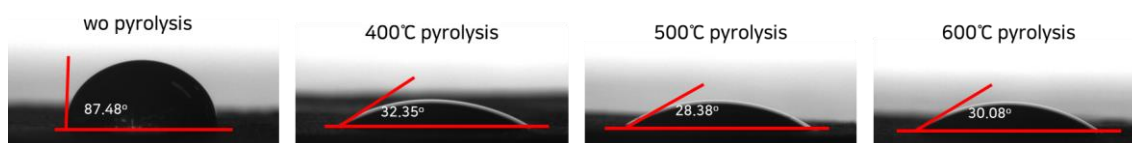


Figure 4. Contact angle of black powder with before and after pyrolysis

TGA analysis was performed to determine the amount of removed binder and remaining fixed carbon after pyrolysis in a nitrogen atmosphere (**Figure 5**). The weight decrease and removal of organic binders were similar at 400 °C, 500 °C, and 600 °C. The untreated black powder showed a 4.3% reduction in organic binders under oxygen conditions. The weight of the black powder increased slightly at the 600 °C pyrolysis condition, potentially due to a phase change, which was confirmed by XRD and XPS analyses. The fixed carbon content of the black powder after pyrolysis was 37.89%, 36.71%, and 33.23% at 400 °C, 500 °C, and 600 °C, respectively, with the highest amount of graphite (anode active material) present at 400 °C.

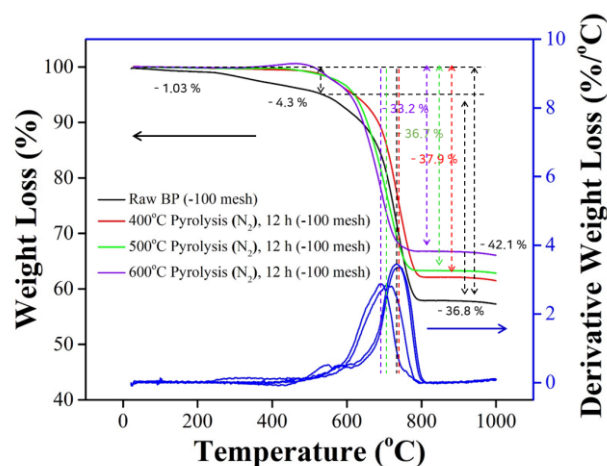


Figure 5. TGA analysis of black powder with before and after pyrolysis

The crystal structure of the active material after pyrolysis treatment was examined using XRD analysis. The results showed that the crystal structure was not different from the original black powder after 400°C and 500°C pretreatment, but a new crystal structure was created at 600°C. This is consistent with the results from the TGA analysis, which showed an increase in weight at 600°C. The weight change is attributable to the presence of NiO (**Figure 6**). However, since the 600°C pretreatment changes the crystal structure, it is not suitable for direct recycling.

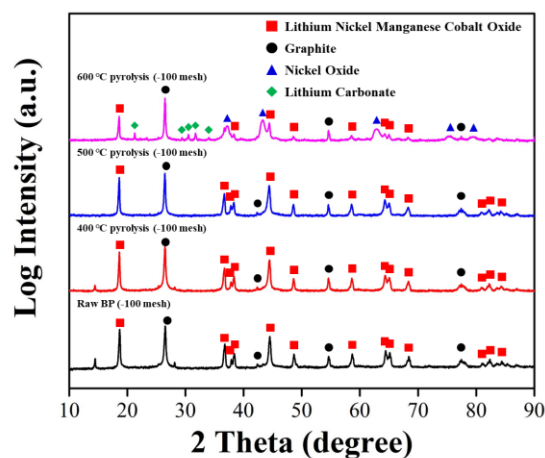


Figure 6. XRD analysis of black powder with before and after pyrolysis

The bonding state between atoms on the surface was confirmed through XPS analysis. In the XRD analysis, since 600 °C was not suitable as a pretreatment condition, only XPS analyses with 400 °C and 500 °C pyrolysis pretreatment were performed. The percentage of F, which is a relative results value, was 7.96% without pretreatment. However, after 400 °C and 500 °C pyrolysis treatment, F content was reduced to less than 1%. Moreover, all F-C bonds present in the initial black powder disappeared with pyrolysis treatment, but F-metal bonds were still present even after pretreatment. The existing F-metal bond is LiF, and it may dissolve when it interacts with liquid in the flotation pulp and will not affect the separation. Interestingly, a new peak of O-Ni

bond was observed at 500 °C in the O1s spectrum. The O-Ni spectral area at 500 °C occupied a relatively small distribution at 3.16% (**Figure 7**). Spectrum distribution refers to the relative amount of bonds. Since it was produced in such a small amount, it would not have been detected in XRD analysis. At a pretreatment temperature if a new bond is formed even at a small amount, it is inadequate for direct recycling.

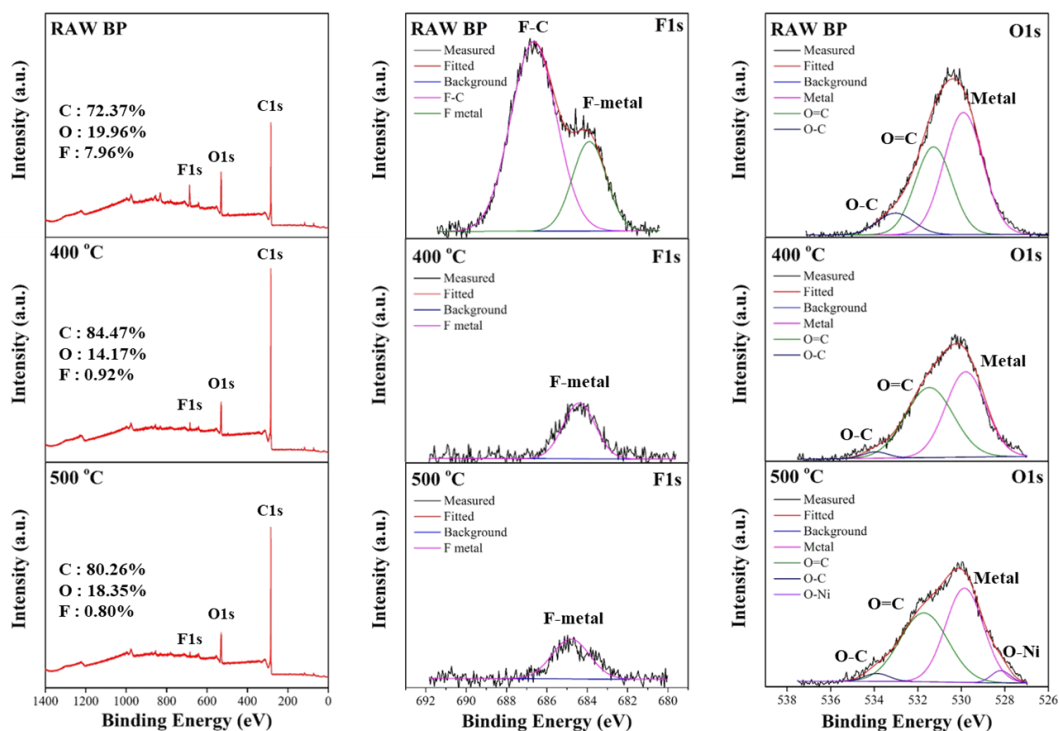


Figure 7. XPS analysis of black powder with before and after pyrolysis : (left) survey spectrum, (middle) F1s spectrum, (right) O1s spectrum

Although the F content was lowest at 500 °C (0.8%), the formation of a new bond (O-Ni bond) made it an inadequate pretreatment temperature. Consequently, the pyrolysis treatment at 400 °C was chosen as the optimal pretreatment condition for separation due to the removal of sufficient impurities (organic binders) and the absence of new structures.

3.3 Flotation test

The flotation tests performed on the black powder after pyrolysis treatment at 400°C showed improved results in terms of grade and recovery of anode materials, with 87.9% grade and 96.8% recovery. However, these results are not sufficient for the material to be used as a battery grade material and additional scavenging and cleaning flotation will be necessary in the future.

Table 2: Flotation result of froth product

Condition	Yield (%)	Grade (%)	Recovery (%)
wo pyrolysis	48.6	43.2	50.7

400 °C pyrolysis	44.5	87.9	96.8
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4 Conclusions

A study was conducted to apply spent LIBs used for recycling in Korea to direct separation. Pyrolysis pretreatment was used to remove impurities present on the surface of the active material for separation. Particle size analysis and FE-SEM images showed that the active material agglomerations combined with the organic binder were separated after pyrolysis. The median diameter of particles decreased from 20 μm to about 10 μm . In addition, the reduction of organic binder was observed through contact angle measurements and TGA analysis. No difference in particle size distribution and hydrophobicity was observed due to changes in pretreatment conditions. However, in XRD and XPS analyses, the formation of a new crystal structure such as NiO was observed above 500 °C. Therefore, in this study, a pretreatment condition of 400 °C was selected as the optimal condition in which sufficient impurity removal was achieved without the formation of new structures. Flotation performed under the optimal pretreatment condition showed improved results. Additional flotation and post-treatment are required.

5 Acknowledgements

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