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Production of purified spherical graphite

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Abstract

The University of Oulu produced a flotation concentrate using the Takkula graphite from the municipality of Pälkäne as source material. At GTK Mintec, the carbon content of the concentrate received (76 wt.%) was increased by sieving to 81 wt.% in the +26 µm size fraction. Approx. 15 kg of this material was dispatched to ProGraphite GmbH in Germany for spheroidization tests. First, flotation was carried out in five stages to increase the carbon content to ≥95%. Two fractions with D50-values of 23 µm and 14 µm were produced by micronizing. Both fractions were spheroidized twice, resulting in spherical graphite products with D50-values of 15 µm and 14 µm (SPG 15 and SPG 14). Alkaline purification and acid purification were tested, and both resulted in products with LOI of 99.97%. Finally, 500g of SPG 15 and 500g of SPG 14 were produced, with using the alkaline purification method, and sent to GTK.

Keywords
graphite, carbon, flotation, spheroidization

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1 INTRODUCTION

When graphite is applied as an anode material in Li-ion batteries, spherical form gives the best electrochemical values. This report details the spheroidization of graphite obtained in the Takkula graphite formation located in the municipality of Pälkäne, south-western Finland. The spheroidization was carried out by ProGraphite GmbH, Germany. The report is deliverable D3.1.4 of the BATCircle2.0 Project, funded by Business Finland.

2 SAMPLING OF THE TAKKULA GRAPHITE AND THE FLOTATION TESTS

The Takkula flake graphite deposit belongs to the early Proterotzoic Pirkanmaa Belt, which mostly consists of high grade migmatites with tonalitic and trondhjemitic leucosomes. The formation is relatively high in graphitic carbon, 11.75 wt.% C_g, and total sulfur averages 5.35 S_{tot}. Graphite flakes average about 150−400 µm (measures of long edges), varying from 50 µm to 1000 µm.

A big sample (8 000 kg) composed of graphitic mica schist was obtained by drilling and blasting in an outcropping area in the southern part of the Takkula graphite formation. The characterization of the feed for the graphite concentrate was carried out at GTK Mintec, Outokumpu (Korhonen et al. 2023). According to mineral liberation analysis (MLA), it is composed of quartz (25.5 wt.%), plagioclase (20.7 wt.%), graphite (13.1 wt.%), pyrite (12.7 wt.%) and biotite (10.6 wt.%), also potash feldspar (5.2 wt.%) and muscovite (5.1 wt.%). The analysis was performed using a pulverized feed (< 100 µm), which was the same material used in the flotation test.

Mining School Research Centre of the University of Oulu studied pilot-scale recovery of graphite using continuous flotation. Optimal flotation conditions for the Takkula graphite comprised of feed rate of 25 kg/h, particle size of flotation feed P80 % < 50 µm, pH > 10 and pulp density of 30% solids. The concentrate contained up to 81 wt.% C_{tot} with a graphite recovery of over 95%.

3 SAMPLE PREPARATION FOR SPHEROIDIZATION TESTS

The graphite concentrate received at GTK Mintec contained 76.1 wt.% graphitic carbon (Korhonen et al. 2023). During the preparation of the material for spheroidization test, the concentrate was first leached with water in a big bucket to reach a solids content of approximately 20% and thoroughly mixed. In order to upgrade the graphite content, about 30 kg of concentrate was sieved as wet with the Sweco vibrating sieve into two size fractions: +26 µm and -26 µm. The +26 µm fraction contained 81 wt.% of carbon, and approx. 15 kg of it was sent to ProGraphite for spheroidization tests.

4 SPHEROIDIZATION TESTS

The test work carried out by ProGraphite included micronizing, spheroidizing and purifying the material received from GTK in order to produce spherical graphite (ProGraphite 2023). Two types of spherical graphite were planned to be produced, a medium size one (D50 of 14−16 µm) and a coarse size one (D50 of 20−23 µm).

At first, the material was examined in the laboratory and found to be a fine concentrate with a carbon content of approx. 80%. The particle size distribution roughly corresponds to the commercial grade "- 100 mesh". Further analysis revealed that the material has a normal moisture and volatile content and that the oxidation properties are positive. The specific surface area is slightly increased in relation to the particle size distribution, whereas the tap and bulk density are slightly lower than expected. All in all, the material properties make it seem suitable as a raw material for the production of spherical graphite when the carbon content is increased to 95%.

Flotation was carried out to increase the carbon content. With five cleaner flotation stages, a concentrate was produced with 95.8% LOI. By using an attrition mill, the particle size distribution could be kept almost unchanged. The resulting concentrate thus corresponded to the commercial grade "-195", which is usually used as feed material to produce spherical graphite.

The particle size of the feed material is reduced close to the desired final size of the spherical graphite by micronizing. For this purpose, micronizing tests were carried out with the impact mill. Then two samples with an average particle size (D50-value) of 23 µm and 14 µm were produced in larger quantities. These served as feed material for the spheroidization test.

The next step is to shape the micronized particles into spherical particles. The spherical shape is required as it increases the density of the graphite, which results in a higher amount of carbon in a given space. The aim of the spheroidization step is to produce round graphite particles with high tap density, high yield of coarse products and a low ratio of D90:D10.

The results from the first pass of the spheroidization were not particularly good: the particle size distribution was too broad, and the tap density achieved was quite low. These properties were the same for both grades. Interestingly, the spheroidization of the coarser material (feed D50 of 23 µm) led to significant comminution, the spheroidized products obtained had a D50 value of 17.5 µm. On the other hand, the finer feed material (feed D50 of 14 µm) led to a product with D50 value of 15.5 µm.

To improve the properties of the products, the material was reprocessed to increase the rounding time. The resulting two spheroidized graphite fractions showed D50 sizes of 14.9 µm and 14.4 µm. In both cases, this measure made it possible to achieve a significant improvement in the physical properties of the spheroidized graphite. In particular, the particle size distribution was very good after the second pass; a very narrow particle size distribution could be achieved. The tap density was also increased and reached a quite acceptable value of 0.92 kg/l for the coarser product. For the fine product the tap density was at 0.9 kg/l, which is still a bit too low. The specific surface area for both products was also relatively high, which is not desirable. The yield was good for both grades at around 50% even though double spheroidizing was applied. This corresponds to the normal values that are achieved with a batch spheroidizer.

Various SEM pictures were taken of the spherical graphite (Figure 1). The pictures show that the material consists mainly of very well-rounded graphite spheres. The range of different particle sizes is rather narrow, and the product looks very homogenous.

For the purification test work, two methods were investigated: alkaline purification and acid purification. Good results were achieved in both cases. The LOI measured was 99.97% for both methods, which is well above the specification limit for battery graphite of 99.95%. Practically all impurity-elements are at low levels after the purification. Especially the critical values for use in batteries, such as Fe, Cr and Cu were measured well below the typical specification limits. With the alkaline purification, only the value for sodium was increased. Sodium is very likely a residue from the NaOH digestion and can presumably be reduced significantly by further optimization of the purification. In the acid purification, the only element which was found in a slightly higher concentration as usual was calcium and it is not clear why the value is increased. Presumably, with higher water quality or a modified acid treatment the Ca value could be lowered. This should be achievable without great efforts.

It was decided to produce larger quantities of the spheroidized purified graphite using the alkaline method. A total of 500g of SPG 15 (spheroidized product with D50 size of 15 µm) and 500g of SPG 14 were produced and sent to GTK in August 2023.

In summary it can be said that the material from GTK was easy to upgrade by flotation to a level of above 95% carbon. Two SPG grades were produced, which show rather typical SPG values, but do not belong to the top group of the SPG. The material has a few physical properties of its own. The material could be easily purified to battery quality with both alkaline and acid purification. Nevertheless, there is good potential for modifications to produce spherical graphite with better physical properties.

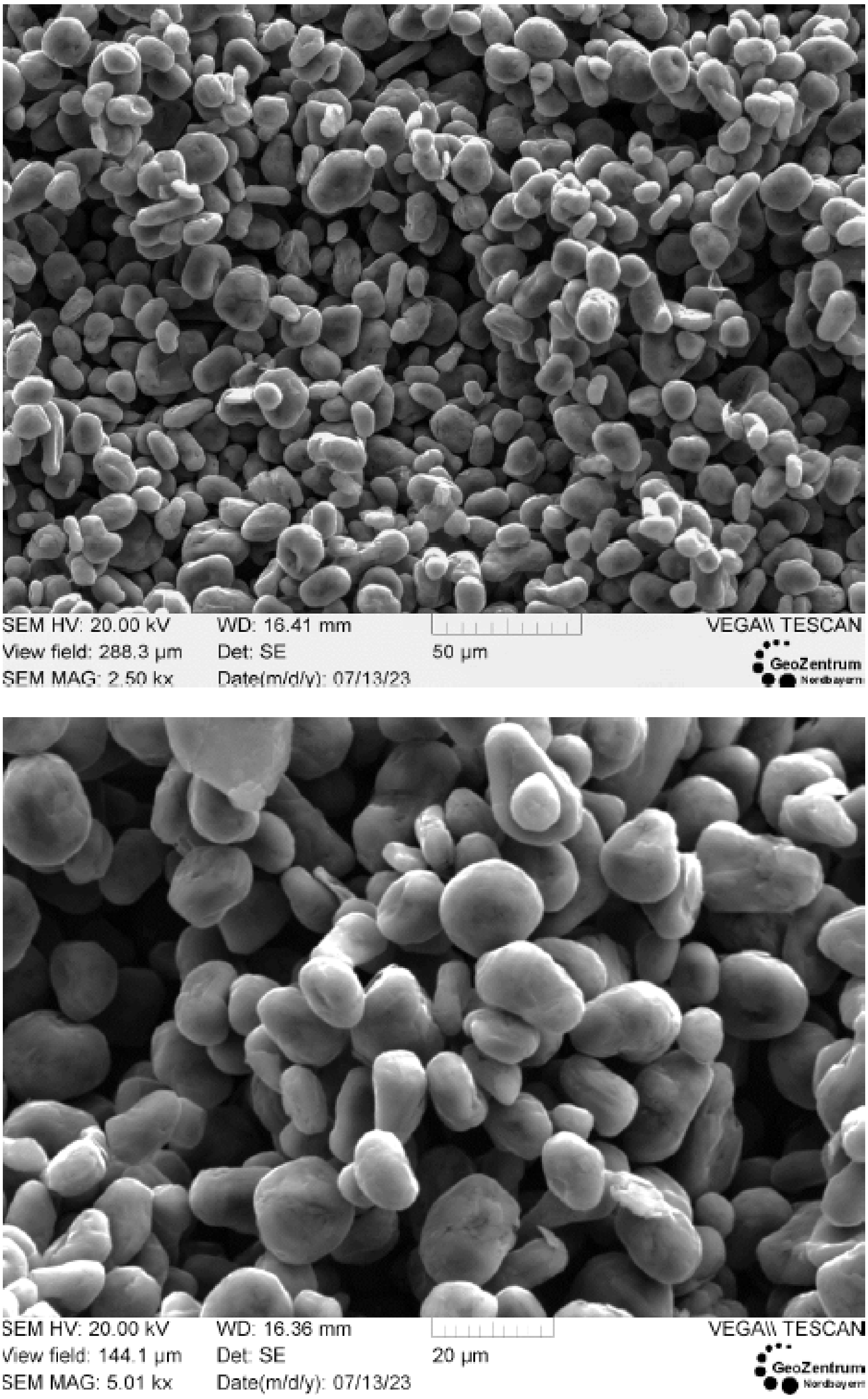

Figure 1. SEM picture of the spheroidized graphite SPG 14 in two magnifications.

5 ANODE GRAPHITE FOR BATTERY TEST

Spherical graphite is the most applied shape of graphite in Li-ion battery anodes, because the packing of round form results in the highest energy density. The material received from ProGraphite was dispatched to Kokkola University Consortium Chydenius to carry out the battery test within Task 4.3.2 of the BATCircle2.0 Project. In addition, graphite fines resulted as by-product from the spheroidization were dispatched to VTT to be further studied in the context of Task 4.3.4 of the BATCircle2.0 Project.

6 REFERENCES

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