STUDY OF THE CRYOMILLING TECHNIQUE FOR THE PRODUCTION OF NANO ZERO-VALENT IRON (nZVI) PARTICLES

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NanoRem is a four year, €14 million research project funded through the European Commission FP7.

Introduction

Particle size reduction is still an important challenge to obtain zero valent iron nanoparticles suitable for the application in subsurface water remediation. To date, conventional milling has been limited by the high iron ductility. Typically iron milling at room temperature produces large flakes of several microns in width and a thickness of tens of nanometers [1] without any significant evolution with time or energy, e.g.: *Figure 1.* However, at cryogenic temperatures the iron ductility is dramatically reduced.

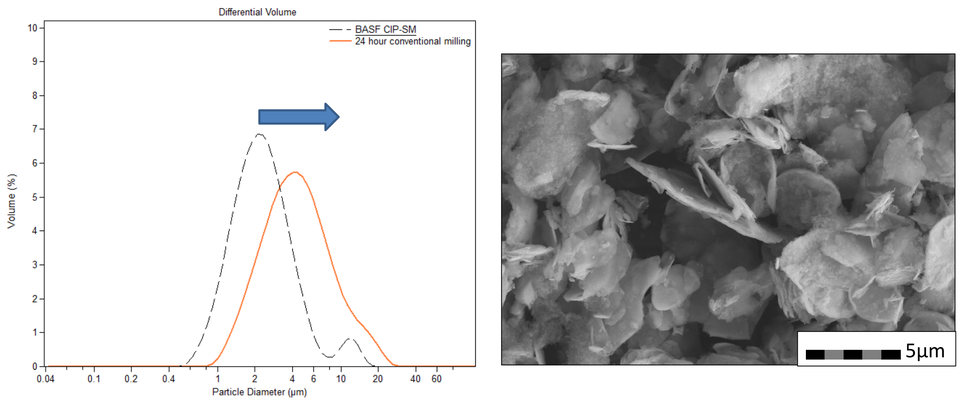

Figure 1. Size distribution (left) and SEM image of conventionally milled particles (right).

Materials and methods

Experimental Design

In order to figure out the evolution of the material through the process, four milling times were chosen: 20, 40, 60 and 90 minutes, respectively. 3 g of Iron powder CIP-SM from BASF GmbH were used in each assay. The temperature was maintained cryogenic (77 K) all the milling.

Feeding Iron

BASF GmbH CIP-SM iron was selected, these were the initial size characteristics, by volume: a mean of 2.8 µm and a 4.7% <1 µm.

Cryogenic Mill

The 6870 Freezer/Mill - SPEX SamplePrep mill was used. Magnetic coil moves a cylinder from face to face of the vial smashing the sample. The main advantage of this specific model is the complete immersion of the vial into liquid nitrogen ensuring always a cryogenic temperature and an inert atmosphere, *Figure 2.*

Figure 2. Magnetic coil surrounding the Vial (Top), Vial container (Bottom).

Particle characterization

All milled samples were manipulated in a glove box under nitrogen atmosphere (Jacomex 2P), then samples were stored in absolute ethanol.

For the Scanning Electron Microscope (SEM) studies, the samples were deposited and led to evaporate into the glove box over standard pins.

For size characterization, Laser Diffraction Particle Sizing (LDPS) was chosen. Samples were previously mixed in a ultrasonic bath and then immediately analyzed directly in ethanol. Finally, data was post processed with the Fraunhofer optical model.

Results and discussion

As SEM images shows, a diminution of particle size through time can be observed, but signs of aggregation were detected especially for longer millings. Interestingly no flakes were formed entailing a fragile behavior, *Figure 3*.

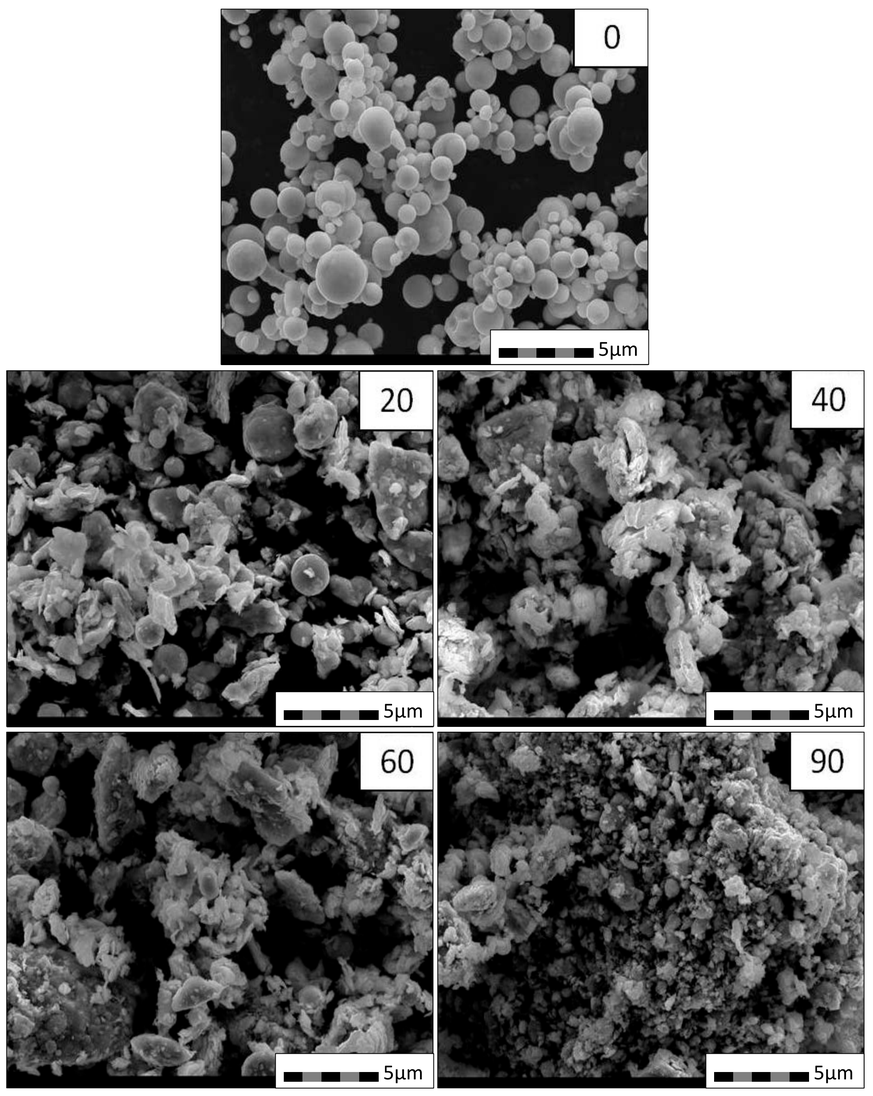

Figure 3. SEM images: 0 (initial powder), 20, 40, 60 and 90 min milling.

Analysis by LDPS, *Figure 4*, stated that the bonding in the aggregated particles was soft and an important percentage of small particles come off from the surface after ultrasonic pretreatment. By volume, there was an initial period in which a raise in mean particle size was observed but increase in particle fraction of <1 µm started to grow at 40 min. With increasing milling time, the overall particle size decreased and a growth in sub-micron fraction was incremented, with a value of 36.2% and a mean of 2.3 µm at 90 min.

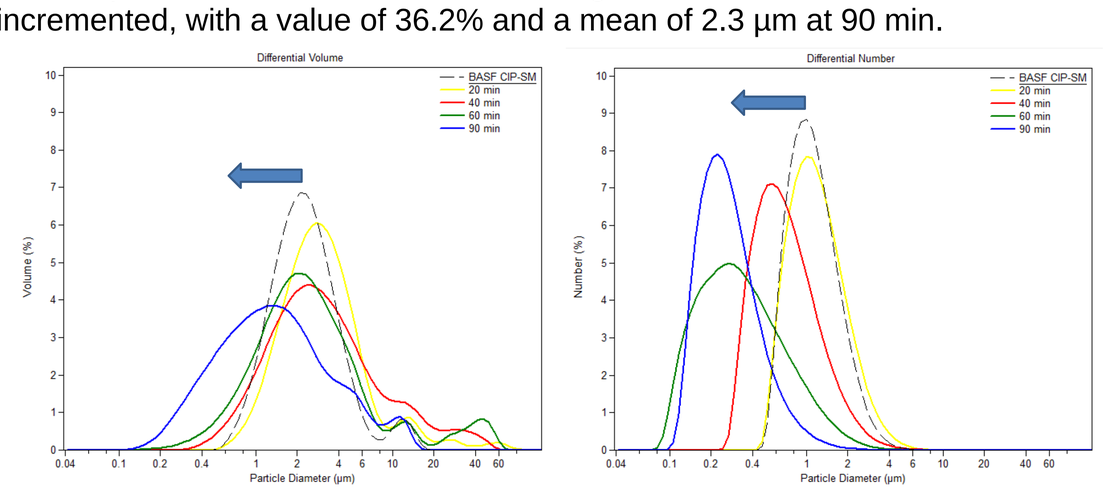

Figure 4. Particle size distribution by volume (left) and by number (right).

Conclusions

The use of cryomilling allows to obtain dry milled powder with a clear reduction of the particle size due to the brittle behavior of iron at cryogenic temperatures. In comparison with room temperature milling, the final particle size is high improved taking into account the small running times.

References

1. Köber, R., Hollert, H., Hornbruch, G., Jekel, M., Kamptner, A., Klaas, N., ... & Braun, J. (2014). Nanoscale zero-valent iron flakes for groundwater treatment. Environmental Earth Sciences, 72(9), 3339-3352.

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This project received funding from the European Union Seventh Framework Programme (FP7 / 2007-2013) under Grant Agreement No. 309517.