LAB SCALE FABRICATION OF NANO ZERO-VALENT IRON (nZVI) PARTICLES FOR GROUNDWATER REMEDIATION BY MILLING

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Introduction

Nano Zero-Valent Iron (nZVI) particles are being used for contaminated groundwater remediation because exhibit an extreme reactivity **[1]** .

These nZVI particles can be produced by a borohydride chemical reduction of ferrous/ferric solution (bottom-up approach), the reduction of ferric iron oxides by hydrogen at a high temperature **[2-3]** and by milling from microscopic particles (top-down approach) **[4]**.

The present work includes the milling in ethanol and Mono Ethylene Glycol (MEG), a pre-treatment as hydrogen embrittlement and a mid-treatment using an abrasive.

Materials and methods

Milling in ethanol tests

In a first approach milling in ethanol was selected. The preparation of nanoparticles by wet milling in ethanol started from 1.5 g of microscale iron (< 18 µm) using steel and stainless steel (SS) shots in 250 ml stainless steel vials. The milling was performed under argon atmosphere in a Planetary ball mill (Fritsch Pulverisete-5) at 400 rpm.

Milling in MEG tests

Ethanol was changed to MEG due to the lower risk of flammability of MEG in contact with nZVI. An initial powder BASF GmbH CIP-SM iron was selected for MEG milling. The initial size characteristics, by volume has a mean of 2.8 µm and a 4.7% of the volume <1 µm. The milling was carried out in low-carbon steel grinding media and in a specially designed vials to avoid contamination, *Figure 1.*

Figure 1. H_2 Reactor.

Hydrogen embrittlement tests

The exposure of iron to hydrogen increases embrittlement of iron which could improve performance of milling. This is a known phenomenon and has the advantage to avoid contamination of iron. This operation was performed in a reactor (*Figure 2*) operating at 150 ºC and 40 atm for 1 week, that are the theoretical conditions that allow and absorption of 7 g H_2•Ncm^{-3} per each 100 g of iron.

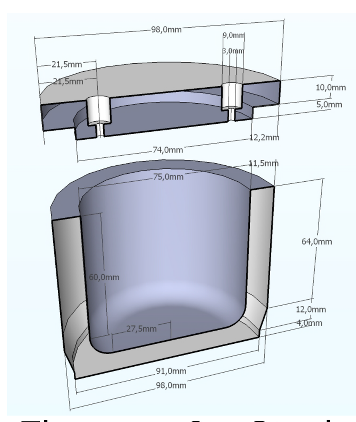

Figure 2. Steel Vial.

Abrasion with alumina tests

As post-treatment method, a first step of wet milling with MEG was combined with a second step in which alumina was added as abrasive (Al_2O_3).

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 by volume.

References

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Results and discussion

Milling in ethanol

SEM results showed that iron behaved as a ductile metal since very large deformation was produced. Substantial changes from spherical to large flakes shape were observed in the iron particles (*Figure 3*), in which lengths of several µm together with thickness of only 50 nm were measured.

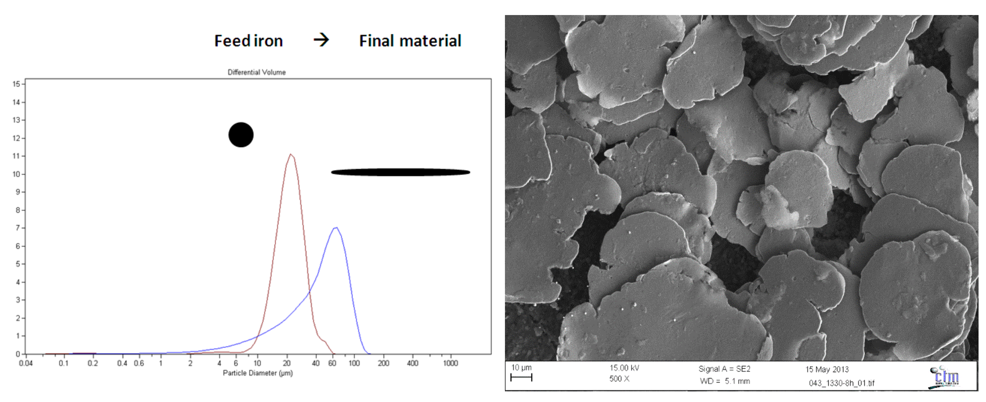

Figure 3. LDPS Evolution of particle size in milling of solutions of iron powder with ethanol. Final SEM picture

Table 1. Relevant tests with ethanol

Ref.					Laser Diffraction (by vol.)	
	Grinding media	Material	BPR	Milling time	Mean Ø	< 1 µm
				h	µm	%
NA 8	Cr/Ni 60	SS	166	16	43.1	2.7
NA 11	Cr/Ni 20	SS	166	16	7.09	3.3
NA 12	Cr/Ni 60	SS	166	16	46.7	0.1
NA 13	[⅔] Cr/Ni 60 [⅓] S110	SS	166	24	41.9	0.1
NA 16	Cr/Ni 60	SS	166	24	5.93	3.4
NA 17	Cr/Ni 60	SS	166	20	6.24	1.8
NA 18	Cr/Ni 60	SS	166	24	4.69	7.1

Once the flakes were formed, no significant evolution to smaller particles was found with time and different milling media. LDPS analyses showed that milled material had, in general, a scarce fraction of powder <1 µm (results not shown).

From the conditions of *Table 1*, it was noticed by SEM-EDX an increase of the powder fraction <1 µm in stainless steel Cr/Ni vials and balls. This means the breaking of the flakes was observed due to an embrittlement of the iron by Cr alloying.

Milling in MEG

In the case of MEG milling (*Figure 4*), with increasing milling times (24 to 96 hours) there was a reduction in the size of iron particles and a slight increase of the number of iron particles below 1 µm.

However, the flake form was the dominant morphology as in the case of ethanol.

In order to increase the yield of nZVI particles, pre-treatment and post-treatments were tested to facilitate the breaking of the large flakes formed due to the ductile behaviour of iron. measured.

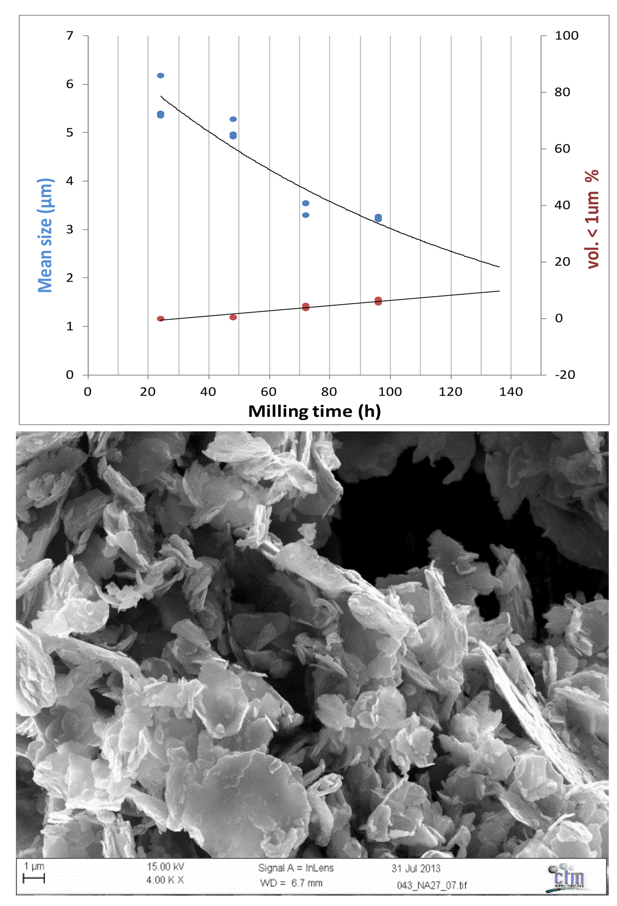

Figure 4. Evolution of particle size in milling of solutions of iron powder with MEG

Pre-treatment

After hydrogen embrittlement pre-treatment no significant differences were observed comparing milling between the untreated and the treated iron, thus, this option was discarded.

Mid-treatment

Abrasion tests have shown good preliminary results with more than 40% of NPs bellow 1 µm (see *Figure 5*) and open further study of this alternative. Confirmation of homogeneous milling and repeatability and reproducibility of the process must be checked, together with the study of the effect of residual alumina on the elimination of contaminants.

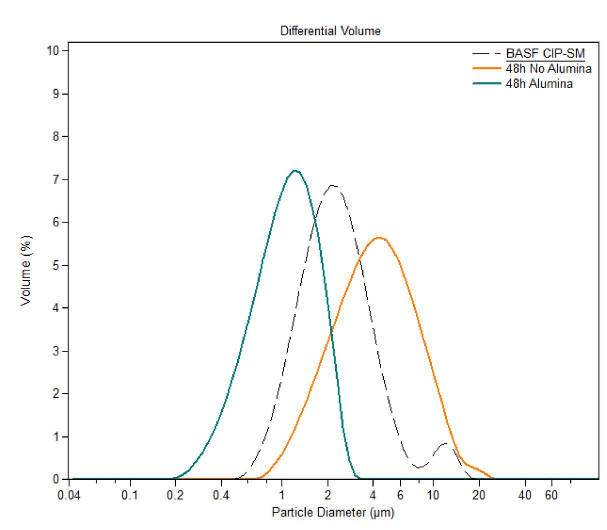

Figure 5. Same conditions with/without alumina.

Conclusions

As a conclusion, the use of ethanol and MEG allowed to obtain non oxidized iron in flake form, with a thickness that matches to the definition of nanoparticle but a flat dimension higher than the starting material. New mid-treatment approaches with abrasives allow to obtain smaller nZVI particles to improve its mobility and reactivity in groundwater.

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