Production of abrasive milling nZVI and activation of air stable nZVI as methods to improve groundwater remediation

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INTRODUCTION AND OBJECTIVES

nZVI is a very promising in situ new technology which can achieve the degradation of a broad range of contaminants. The purpose of this study is to help to overcome some of the challenges that limit a widespread implementation of this technique, such as the lack of a cost-effective straightforward production method and uncertainness on the reactivity governing factors.

Two approaches to increase the reactivity of nZVI against Cr (VI) and Chlorinated Aliphatic Compounds were developed.

- A new milling method for nZVI production with abrasive at lab scale
- An activation method to decrease oxide shell in commercial particles

nZVI PRODUCTION THROUGH ABRASIVE MILLING

The addition of micronized alumina during the milling process lead to the production of particles at the nanoscale. Abrasion of the grinding media and breakage of flakes were the main mechanisms for the nZVI production. *(Fig. 1)*.

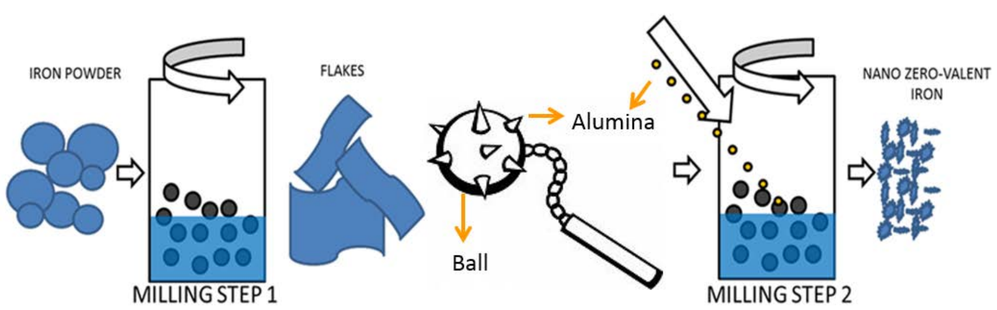


Fig. 1 Working principle

The optimization of the milling parameters were Ø 0.5mm shots composed of high carbon steel (0.80-1.20% C) and an alumina concentration of 80.4 g·l^{-1}.

A detailed characterization of the produced nZVI was performed. The results were compared to other commercial products.

The developed particles showed excellent properties in all studied parameters, highlighting reactivity and suspension stability. The NA 84 sample had a mean particle diameter of 0.16 µm (by SEM), a specific surface area (SSA) of 29.6 m2·g-1. *(Fig. 2 and 3)*.

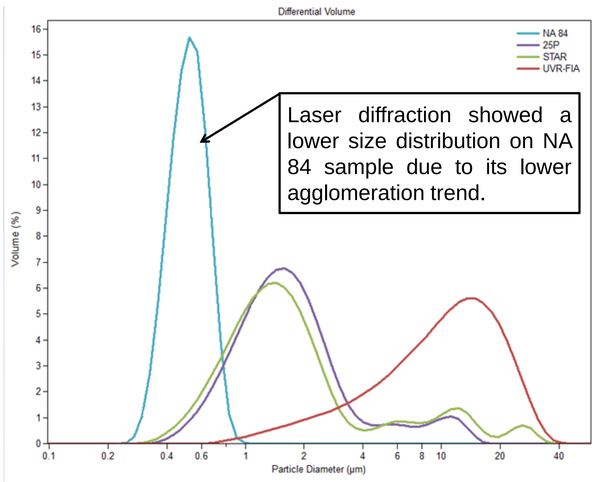


Fig. 2 Granulometry (laser diffraction)

Reactivity of developed particles (NA74 and NA84) showed to be several times higher than the commercial nZVIs, also when it was related to SSA and Fe (0). *(Fig. 4)*

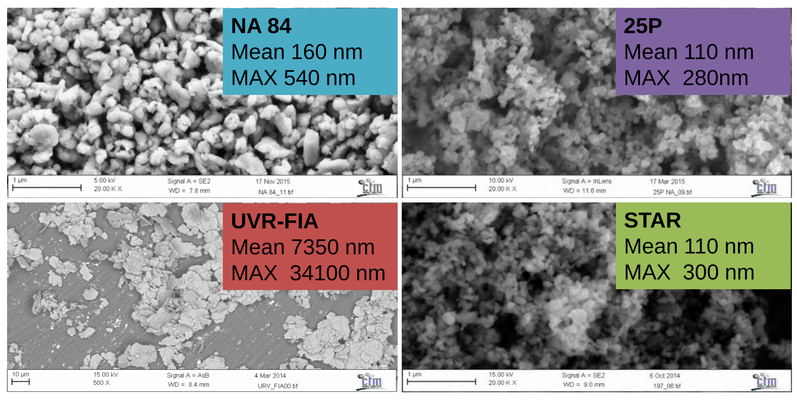
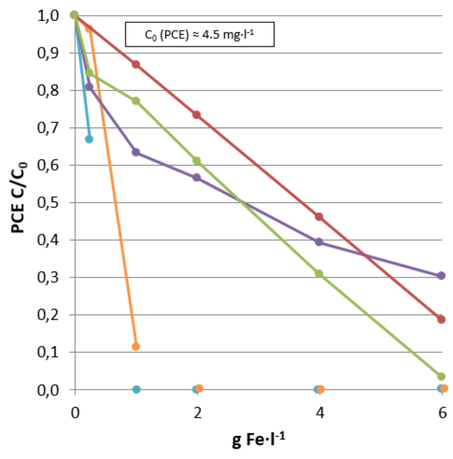


Fig. 3 Granulometry (SEM)

This good reactivity could be produced thanks to: absence of an oxide layer, great amount of superficial irregularities forming a great number of reactive sites and the presence of a very fine nanostructure.



	Removal capacity	Removal capacity by SSA and Fe(0)
	mg PCE·g Fe	mg PCE·g Fe^{-1}·m^{-2}
NA 74	-4.24	-0.11
NA 84	-8.25	-0.28
25P	-0.54	-0.02
STAR	-0.62	-0.04
UVR-FIA	-1.04	-0.06

TCE, trans-1,2 DCE; cis-1,2 DCE; 1,1 DCE; VC **NOT DETECTED**

Fig. 4 PCE reactivity test

ACTIVATION PROCESS OF AIR STABLE nZVI

The thick and compact oxide shield of surface-passivated nZVI particles significantly decreases their reactivity compared to non-stabilized nZVI particles. The introduction of a simple activation process consisting of an aging of dense nZVI slurry in water (0.2 w/w iron to water ratio) for 36h led to a partial recovery of the nZVI reactivity.

Three types of nZVI particles with different oxide shell thicknesses (25P 1.8 nm, Star 197 3.4 nm and STAR 400 6.5 nm) have been tested for Cr(VI) removal. Particles with an oxide shell thickness of 3.4 and 6.5 nm increased their reactivity by a factor of 4.7 and 3.4 after activation (A), *(Fig. 5)*. Additional tests with chlorinated compounds confirmed the increase in the degradation rate by activated nZVI particles.

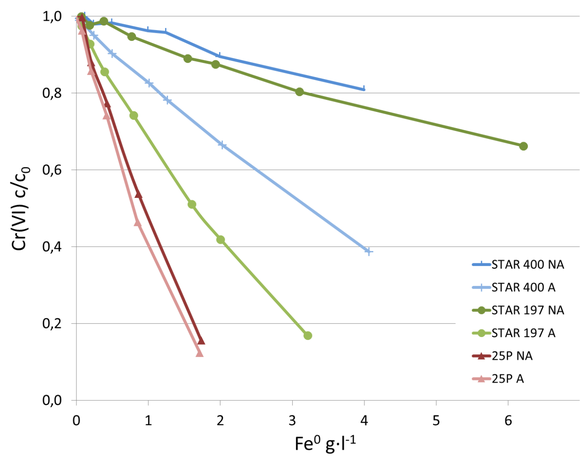


Fig. 5 Cr (VI) reactivity test. A Activated, NA Non-activated

The improvement in reactivity in this second approach is related mainly to the degradation of the oxide shell, which enhances electron transfer and leads secondarily to an increase in the specific surface area of the nZVI after the activation process. *(Fig. 6)*.

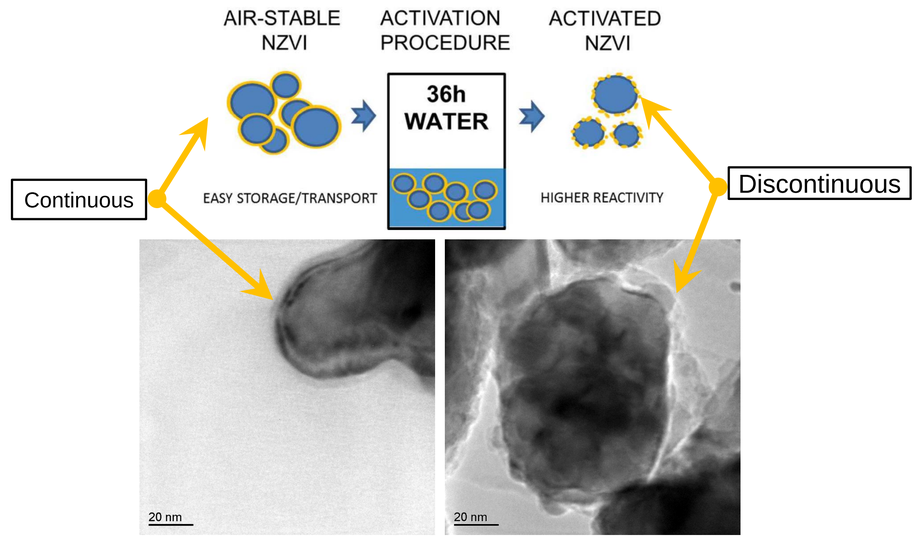


Fig. 6 Activation working principle

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