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HIGH REACTIVE NANO ZERO-VALENT IRON PRODUCED VIA WET MILLING THROUGH ABRASION BY ALUMINA

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Abstract

The performance of new nano zero-valent iron (nZVI) particles produced by a promising new milling method in organic solvent was examined. The basic feature of the new process involves the addition of abrasive alumina particles having an average particle size of 5 μm during milling. The milled particles with alumina had a specific surface area exceeding $20 \text{ m}^2 \cdot \text{g}^{-1}$ as well as high percentages of Fe(0) content of 75-80%. The reactivity against Cr(VI), Trichloroethylene, and Tetrachloroethylene was determined and in all cases, the removal capacity of the milled particles was higher than that of commercial available nZVI particles. This high reactivity may be related to the absence of a thick and continuous oxide layer on the surface, the high disorder levels of the metallic structure and the large number of reaction sites. Sedimentation tests revealed very good suspension stability, while in mobility tests, the particles could be distributed throughout the column length. The results showed a low tendency to agglomerate in aqueous solution. This behaviour has been attributed to two factors related to the milling process: first, the high ζ -Potential found in the particles, which enhances electrostatic repulsion. The second factor is the significant decrease of saturation magnetization of the milled particles with alumina in comparison with the values of the commercial nZVI particles, leading to a reduction in magnetic interparticle interaction. This decrease may be related to the introduction of a significant carbon content in the iron particles (0.65-1.35 %wt., depending on the sample) and the presence of a highly deformed nanostructure.

Keywords:

Nano zero-valent iron (nZVI); nanoparticles; reactivity; milling; aggregation; mobility.

1. Introduction

Although it is a very promising technology in terms of remediating a wide range of contaminants [1], currently, nano zero valent iron (nZVI) is not a widespread commercial technology in Europe. This may be attributed to a variety of factors, including a cautionary attitude towards nanomaterials [2], performance concerns regarding mobility and passivation [3,4], the fact that the technology is unknown to most consultants, governments and site owners [2] and, finally, its high production costs [5]. Since nZVI manufacture represents a major portion of the application cost [6], and the physicochemical characteristics linked to the performance are related to the production method [7,8], it is important to study advantages and drawbacks of current manufacturing methods and develop new production approaches.

The introduction of a straightforward method of nZVI production for remediation research on a laboratory scale was published in 1997 [9]. This marked the onset of the nZVI field, leading to the introduction of nZVI in many research institutions, thereby advancing the field and assessing its potentials and limitations. The method consists of the reduction of iron (III) chloride hexahydrate using sodium borohydride by precipitating metallic iron spheres with a diameter of 1-100nm.

Unfortunately, the sodium borohydride reduction method cannot be scaled up for commercial applications, due to health and safety concerns involving the synthesis (and its cost) of sodium borohydride [6,10], and concern that residual boron in iron nanoparticles may leach into the aquifer [11]. Since new and reliable methods for large-scale and cost-effective production are crucial for the success of nZVI remediation technology [12], a range of new methods has been proposed [5-13]. Currently, the nZVI manufacturing methods can be classified as bottom-up or top-down. Bottom-up involves the atom-by-atom production of nanostructures, whereas top-down begins with large size, granular, or microscale materials.

Bottom up. Thermal reduction is the main process through which commercial nZVI is produced. This method is based on the reduction of iron oxide nanoparticles, pentacarbonyl, or aqueous Fe(II) by thermal energy (350–600 °C) using different gaseous reducing agents (H₂, CO₂, CO) [5,14]. Apart from thermal reduction, other bottom-up approaches (most of them on the laboratory scale) are used to obtain nZVI, including green synthesis [15,16], electrolysis [17], thermal [18] and sonochemical [19] decomposition of iron-containing complexes.

Top down. High energetic ball milling of iron in water [20] has been tested, but the use of an aqueous solution may lead to a major decrease in Fe(0) content due to oxidation [5]. However, pure iron [8] and pure iron together with activated carbon powder [21] has been ball milled in an inert grinding media without a significant loss of Fe(0). In these last cases, good reactivity was observed in the milled particles [8,21]. It is interesting to note that the use of ball milling enables the partial removal of the initial oxide layer of the powder, leading to an enhanced reactivity [22]. Recently, the ball milling technique has been used to form novel composites, such as Fe-C nanocomposites which combine the advantages of both materials in the elimination of TCE [21], and sulfidated microscale ZVI in which the Fe-S zones increase the effectivity of Fe(0) electrons in reducing TCE, making it more difficult for them to produce hydrogen in the outer iron oxide layer [23].

Of all of the mentioned methods, two of these have been successfully scaled up and commercialized for remediation in the European market: thermal reduction [24] and milling [8]. In the latter case, the particles are ball milled in an organic solvent to prevent oxidation and the final size falls within the micrometric range, due to the difficulties in breaking the iron flakes. Since pure iron is a ductile metal, initial powder particles are repeatedly deformed into very thin particles with a large surface but without breakage, hindering the production of iron with a smaller particle size [8].

In order to break the iron flakes during the milling of pure iron in a protective organic solvent such as Mono Ethylene Glycol (MEG), a novel milling technique was presented in a previous publication [25]. In this case, instead of using a very high milling speed [21], the technique consisted of introducing an abrasive material such as fine alumina powder during the milling process. As the amount of the introduced alumina was increased, a progressive shattering of the flakes was observed. An optimal concentration of alumina was found in which the large iron flakes were completely broken. Above this optimal concentration, the increase in pressure and temperature inside the vials resulted in leaks and an increased particle size. The particles produced in the optimal concentration revealed a good reduction in size, with a final average diameter of 1.1 μm . And they retained a large Fe(0) content of 92%, with an acceptable surface area for unit of mass (specific surface area) of 14.0 m^2g^{-1} [25].

It appears that this new procedure could combine the advantages of the milling approach (low cost and high throughput) with those of ZVI at the nanometric size (high reactivity and mobility). To achieve this, a greater reduction in particle size and further knowledge regarding the performance of the milled particles on key points of *in situ* groundwater remediation treatments, such as reactivity against different pollutants, suspension stability, and mobility, are needed. Therefore, the aim of this study was to present new advances in the reduction of particle size using the new procedure together with a characterization of the structure and composition of the milled particles. Furthermore, the reactivity of the new particles against Cr(VI), TCE and PCE was determined, and sedimentation and mobility tests were conducted. The performance of the new milled particles in all of these fields were compared with those of already commercialized nZVI products to see if the new milling procedure may offer an advance in the in-situ groundwater remediation processes.

2. Materials and methods

2.1. Commercial zero-valent iron nanoparticles

Three types of commercial nZVI particles were studied for direct comparison with the milled particles with alumina: pyrophoric 25P, air-stable STAR but in the activated state [4] and wet milled A01 particles in mono-ethylene glycol. Details of particles and suspensions preparation are showed in supporting information file (SI). The three commercial particles 25P, STAR and A01 were extensively characterized and, in general, the results agreed with previous literature [8,26-29]

2.2. nZVI production through wet milling

NZVI particles were produced by milling in two steps. In the first step, conventional ball milling was conducted. Here, the iron particles were deformed and flattened, producing very thin flakes. In the second step, with the introduction of alumina in the milling, the flakes were broken and smaller iron particles were obtained [25]. The initial iron powder was Carbonyl Iron Powder (CIP-SM, BASF), having an iron content of >99%, a carbon content of $\leq 0.1\%$, and a narrow size distribution with a $d_{50}=2.34 \mu\text{m}$ (BASF SE). The millings were done in a planetary ball mill (P-5, Fritsch) using AISI 1085 steel (0.80-0.93 wt.% C) vials with a 250 ml capacity in order to minimize cross metallic contamination from the vials.

In the first step, the vials were filled with 100 ml of MEG, 1.5 g of iron powder, and a 250 g grinding media load (low-carbon steels balls or high-carbon steel shots). The vials were purged with argon gas so as to create a protective atmosphere inside the vials. The rotating speed was 400 rpm and the milling cycle consisted of 30 min of attrition followed by 30 min of stand-by periods to allow the vial to cool down. The effective milling time was 24 hours. In the second step, the vials were opened in a

glove box and irregular alumina powder (Ref. 12015, PRESI GmbH) having an average diameter of 5 μm was introduced. The vials were once again purged and the milling was extended for 24 hours under the same conditions as those described in the first step. Following the milling process, the slurry was sieved at 150 μm to remove the grinding medium.

In order to determine the effect of the grinding media and the alumina content in the final size of the particles, two different milling media were used with an increasing alumina content. The first was low-carbon steel balls (AISI 1010, 0.08-0.13% wt.% C) measuring 5 mm in diameter and the second was high-carbon steel shots (0.80-1.20% wt.% C) (Ref. S110, Pometon) 0.5 mm in diameter. The variation of the final size of the iron particles for both grinding media with increasing amounts of alumina content is shown in Fig. 1. In this figure, the results from [25] have been included, since here, medium-carbon steel shots (0.80-1.20% wt.% C) (Ref. S660, Pometon) of 2 mm diameter were used as grinding media. It may be seen that the largest reduction in iron particle size was obtained with the smallest grinding media (S110, 0.5 mm). On the other hand, increasing amounts of alumina caused a gradual reduction of final particle size. The minimum values were achieved with 54 and 80 $\text{g}\cdot\text{l}^{-1}$, depending on the case. At higher alumina contents, a slight increase in the iron particle size was observed, along with a great increase in the vials' internal pressure leading to frequent leaks.

The best samples for each of the grinding media were selected for extensive characterization: for low-carbon steel balls (0.08-0.13% wt.% C) of 5 mm diameter, the sample with 53.6 $\text{g}\cdot\text{l}^{-1}$ of alumina (labelled NA64), and for high-carbon steel shots (0.80-1.20% wt.% C) of 0.5 mm in diameter, the sample with 80.4 $\text{g}\cdot\text{l}^{-1}$ of alumina (labelled NA84).

2.3. General particle characterization

All of the particles included in the reactivity and mobility studies (25P, STAR, A01, NA64 and NA84) were extensively characterized. For a better characterization of the milled iron particles NA64 and NA84, they were separated from MEG and alumina in the following cases: determination of particle size, specific surface area and analyses with Transmission Electron Microscopy. The separation process was carried out by placing the slurry near a permanent magnet (720g of NdFeB, Grade N42) to concentrate iron particles. Supernatant liquid was poured off and particles were re-suspended in pure ethanol. This procedure was repeated five times and the resulting samples were labelled NA64(5x) and NA84(5x). Subsequent analysis of alumina concentration showed that with this procedure, the total amount of remaining alumina in NA64(5x) and NA 84(5x) samples was approximately 40%, and that with successive washings of up to 15 times, a little more than 30% of alumina was still present in the milled samples (Fig. S1).

Particle size distribution was determined using Laser Diffraction Particle Size Analysis (LD) (LS 13320, Beckman Coulter) in an absolute ethanol solution. Before the LD measurements, samples were dispersed using an ultrasonic bath for 5min. In addition, during the measurements, samples were continuously stirred in the cell by an internal recirculation pump set at 70%. All of the results were calculated by particle volume mode. The Brunauer-Emmett-Teller (BET) specific surface area (SSA) was determined from N₂ adsorption using a BET surface area and porosity analyser (ASAP 2020 Micromeritics). Degassing was carried out for several hours at a maximum temperature of 100°C.

For electronic microscopy characterization, samples were prepared in a glove box, maintaining oxygen concentration below 5 ppm. Samples were re-suspended by mixing them vigorously in absolute ethanol. The morphology of the particles and elemental composition was examined with Scanning Electron Microscopy (SEM) (Gemini ultra plus, Zeiss) equipped with Energy-Dispersive

X-ray Spectroscopy (EDS) (X-MAX 50 mm², Oxford Instruments); samples were deposited and were left to evaporate over copper pins in a glove box. Particle structure was observed with Transmission Electron Microscopy (TEM) (JEM-2100, JEOL) equipped with High-Angle Annular dark-field imaging (STEM-HAADF). For TEM observation, a droplet of the ethanol suspension was placed on a 300 copper mesh grid with a supporting film made of holey carbon. Samples were transferred to microscopes over a surface of liquid nitrogen contained in box to reduce contact with oxygen [4].

The final carbon content of the milled particles was analysed with combustion infrared analysis (CS-200, LECO). Total iron concentration was assessed, firstly, by digesting the suspensions with 2:1 HNO₃:H₂O₂, and then by analysing it with Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), (Optima 3200, Perkin-Elmer). Fe(0) content was analysed in triplicate through the hydrogen production method [30] using specific hardware (nZVI Tester, Nanoiron).

For X-Ray Diffraction analysis (XRD), the solid samples (25P, STAR) or a drop of the suspension (A01, NA64 and NA84) were placed on a zero background silicon sample holder (pw1817/32) of a PANalytical X'Pert PRO MPD powder diffractometer, using Cu K α radiation at 45 kV with a step size of 0.033° 2 θ and measuring time of 100 seconds per step (15 repeated scans).

Magnetic measurements were performed with a Quantum Design MPMS XL5 instrument with a superconducting interference device (SQUID) detector working at a temperature of 300 K under external magnetic fields ranging from -5 to +5 T. The experimental data were corrected for the diamagnetism of the sample holder and alumina.

The ζ -Potential is the electrical potential difference between the dispersion medium and the last stationary layer attached to the dispersed particle. The ζ -Potential sign affects the electrostatic

interaction of the particles and its absolute magnitude influences the stability of the particles suspended in a solution. Initially, the ζ -Potentials of the nZVI particles and the initial alumina powder samples were determined using electrophoretic light scattering (ZetaSizer Nano ZS, Malvern). The $1 \text{ g}\cdot\text{l}^{-1}$ suspensions from dried particles at 0.01 M NaCl ionic strength were prepared for each sample, and then the pH of the suspensions was left to evolve for a few minutes until a stable measure was obtained. At this point, the suspensions were immediately analysed. The entire process was performed in an inert atmosphere (Ar).

2.4. Reactivity characterization

To compare the reactivity of the nZVI particles produced in this work with commercial particles, dose (different nZVI concentrations) – response (contaminant depletion) tests were set in batch mode using deionized water. In the tests, hermetic bottles of 250 ml with a very small headspace were used, and they were vertically rotated at 2 rpm (Reax 20, Heidolph) in order to prevent the particles from settling and sticking to the glass. The pH for initial water was 7.71 and the ORP 175 mV. For these reactivity experiments, three harmful substances, extensively reported for nZVI remediation, were selected: Cr(VI), Trichloroethylene (TCE) and Tetrachloroethylene (PCE).

In the case of the reduction of Cr(VI) to Cr(III), an initial Cr(VI) concentration of $50 \text{ mg}\cdot\text{l}^{-1}$, prepared from dried potassium chromate ($\geq 99.5\%$, Panreac) was chosen. Seven reaction batches were prepared for each type of nZVI, spiking each iron sample to a final concentration of 0.1, 0.25, 0.5, 2.0, 2.5, 4.0, and $8.0 \text{ g}\cdot\text{l}^{-1}$. To observe the effect of alumina and MEG, blanks with the amount of both products in the milled samples NA64 and NA84 were also prepared. Batches were analysed after 24h, given that the preliminary Cr(VI) batch tests revealed that Cr(VI) depletion took place mainly within the first hours (Fig. S2). This fast reaction kinetics was exposed in [25] and it was also reported previously in several publications [4,31,32]. The collected samples were ultrafiltered by

using a nylon syringe Agilent 0.2 μm RC. The Cr(VI) concentration was determined colorimetrically (DR3900, Hach Lange) via diphenylcarbazide reaction in acid solution (US EPA method 7196A). For TCE and PCE reduction, the batches were set with an initial TCE ($\geq 99.5\%$ Sigma Aldrich) concentration of $2.0 \text{ mg}\cdot\text{l}^{-1}$ together with a PCE ($\geq 99.97\%$ Scharlab, Spain) concentration of $4.5 \text{ mg}\cdot\text{l}^{-1}$, simulating a real polluted site. Each nZVI sample was spiked to a final iron concentration of 0.25, 1.0, 2.0, 4.0, and $6.0 \text{ g}\cdot\text{l}^{-1}$ plus blanks without iron but with the same amount of alumina and MEG than in the milled samples NA64 and NA84. All of the tests were duplicated and the CAHs batches were left to react for 14 days (Fig. S2), ensuring that most of the reaction took place. In this case, to avoid reactions of chlorinated compounds with plastic, magnetic separation using glassware was employed to remove iron from solutions.

TCE, PCE, and their chlorinated transformation products (1,1-Dichloroethylene, cis-Dichloroethylene, trans-1,2-Dichloroethene and Vinyl Chloride) in aqueous phase were quantified by Head Space (HS 7694E, Agilent) - Gas Chromatography (HP6890, Hewlett Packard) – Electron Capture Detector (μECD G2397A, Agilent). The GC was equipped with a split/splitless injector operated at a 1:200 ratio and the column (DB-624, Agilent) was $25 \text{ m} \times 0.2 \text{ mm} \times 1.12 \mu\text{m}$. The system was calibrated using a volatile halocarbon mix (48001, Sigma-Aldrich) with all analytes included. Concerning analyte volatilization, batches were sampled at 4°C with a 1 ml gastight micro-syringe and were introduced into the bottom of a 20 ml vial containing 10 ml of cold water. The vial was immediately sealed with a PTFE/rubber septum. Dibromomethane (41097, Sigma-Aldrich) was used as an internal standard for all analyses.

It is important to note that in all of the tests the milled nZVI particles were injected without removing the MEG or alumina as they are intended for use in field applications. In order to evaluate possible side effects of MEG and alumina such as an advantageous dispersant action, additional control tests

with 25P nanoparticles were performed at $1 \text{ g}\cdot\text{l}^{-1}$. In one case, the same MEG and alumina concentration were used and in another case Guar Gum (Sigma Aldrich) was added. In all of these tests, a significant drop in the reactivity of 25P particles was observed as compared to the case in aqueous solution. The main reason for this loss of effectiveness of the 25P particles is the particle shielding that prevents pollutant interaction, as stated in the literature [28,31].

2.5. Suspension stability, and migration set up

Suspension stability was measured through the sedimentation rates using a (TurbidScan LAB, Quantachrome) at $1 \text{ g}\cdot\text{l}^{-1}$ in deionized water. The sedimentation tests were performed by monitoring the transmission of monochromatic light through the suspension at a wavelength of 880 nm. The transmission data were collected during 1 hour and during the entire depth of the samples suspension [28]. The suspensions were placed in an ultrasonic bath for 10 minutes prior to the sedimentation tests.

The migration tests were performed in a column with a length of 2 m and an inner diameter of 20 mm, filled with standard silica sand with an average grain size (d_{50}) of $930 \mu\text{m}$ and a 94.2% of the sand between $630\text{--}1250 \mu\text{m}$. The column was filled as homogeneously as possible using a funnel and afterwards, the sand was carefully compacted and positioned vertically between two holders. In order to delay oxidation processes, the column was flushed with nitrogen and saturated with degassed water against the direction of gravity. After saturation and stabilization, the nZVI sample was injected at a concentration of $10 \text{ g}\cdot\text{l}^{-1}$ with the flow maintained at $100 \text{ m}\cdot\text{d}^{-1}$ throughout the test. A specifically designed magnetic susceptibility scanner monitored the transport of the iron slurry during injection. The column was scanned up to 1.8 m every 10 min up to 90 min (shown results) where no further movement could be seen. A porosity of 0.413 was calculated with a tracer assay. The 90 min value corresponds to 3.5 pore volumes.

3. Results and discussion

3.1. Characterization of the particles milled with alumina.

Fig.2 shows the SEM images obtained for the NA64 and NA84 samples using secondary and backscattered electrons to identify iron and alumina particles. In both cases, it is evident that the presence of alumina particles is important. The elemental analysis made by EDS basically reveals the presence of iron, aluminium and oxygen together with a significant presence of C in both samples, not detected in the initial iron. As mentioned in section 2.3, attempts were made to remove the alumina by magnetic separation, but a significant alumina content was still observed after five washes in NA64(5x) and NA84(5x) (Fig. S3).

The analyses of iron and carbon concentration in the final slurries helped to increase the understanding of the mechanisms involved in the particle production by milling. The final total iron concentration in both NA64 and NA84 samples was $96.7 \text{ g}\cdot\text{l}^{-1}$ and $148.3 \text{ g}\cdot\text{l}^{-1}$, respectively, higher than the expected concentration due to the initial iron powder introduced in the vials ($15.0 \text{ g}\cdot\text{l}^{-1}$). This result demonstrates a large iron abrasion from the grinding media and contradicts the main mechanism indicated in the introduction, which was based on the breaking of the large iron flakes by the action of micronized alumina acting as micro-grinding medium. Furthermore, the SEM image in backscatter mode of the recovered alumina after milling in Fig. S4 reveals iron debris adhering to the edges, reinforcing the existence of an abrasion mechanism in the production of the present milled particles.

The analysis of carbon concentration also coincides with the idea of an abrasion mechanism, since the values found in the milled samples, 0.65 %wt. for NA64 and 1.35 %wt. for NA84, were higher than those of the initial iron (≤ 0.1 %wt.) and helps to explain the presence of a significant carbon signal in the EDS analysis. This final carbon content of the milled samples is closely related to the composition of the grinding medium: in the case of NA64, the final carbon content is lower since the carbon content of balls (AISI 1010 steel) is low and only the vials (AISI 1085 steel) have a larger carbon content. On the other hand, in the case of NA84, the final carbon content is clearly higher (1.35 wt.% C) due to the higher level of carbon in the S110 balls (0.85 – 1.2% C). At this point, it should be noted that in both cases, the weight loss of the balls and vials after milling was measured and in the case of the NA84 samples, a substantial weight loss was detected in S110 balls, reinforcing the idea of their presence in milled particles.

The possibility of producing metallic nanoparticles through the wear of balls in a powder-free ball milling process has been previously reported [33]. In that study, tungsten carbide vials were used and no hard abrasive material such as alumina was introduced. In this case, the vials were made of a softer material (AISI 1085) and the action of hard alumina must be taken into account. Therefore, a larger quantity of material can be produced by wear and the obtained nZVI may be formed by a mixture of initial iron, fragments of balls and vials due to the repetitive breaking and soldering of the milled particles during high-energy milling when the flakes are broken [34].

3.2. General particle characterization

3.2.1. Particle size, Specific surface area and Fe(0) content.

Size characterization is a significant feature since mobility and reactivity have a strong dependence on this parameter [3]. Fig. 3 shows the SEM images for the two types of milled particles after partial

alumina separation (NA64(5x) and NA84(5x)) and the three commercial nZVI particles studied in this work. As for the NA64(5x) and NA84(5x) milled particles, after the second step with alumina, both samples revealed no presence of flakes (Figs. 3A and 3B). Moreover, the different grinding balls render distinct particle sizes. In the case of NA64(5x), in which 5-mm AISI 1010 steel balls were used, the counting of individual particles in SEM revealed an average size of 0.47 μm . For NA84(5x), in which high carbon steel balls ten times smaller in diameter were used, the average size of the individual particles was 0.16 μm . Furthermore, NA84(5x) appears to have a more homogeneous particle size. On the other hand, 25P and STAR nanoparticles have a smaller size, since individual particles were clearly smaller (Fig. 3C and 3D). These nanoparticles also appear to be quite homogeneous in size, but with a certain degree of agglomeration. Finally, the AO1 flakes (Figs. 3E) were clearly within the micrometric range.

The different degrees of agglomeration of nanoparticles in liquid solution are reflected in the results obtained with LD studies. This effect is not very large for milled particles (1.01 μm for NA64(5x) and 0.52 μm for NA84(5x)), but when compared to the individual value, a significant increase in size is observed for 25P and STAR nanoparticles (2.35 μm for 25P and 3.31 μm for STAR). This may be understood by examining Fig.S5, in which the distribution of particle diameter for all the nZVI particles is presented. In the case of 25P and STAR a long tail of larger agglomerates may be observed. In contrast, the AO1 particles are larger in size (10.9 μm).

Regarding SSA, the milled particles show good results with 20.0 $\text{m}^2 \cdot \text{g}^{-1}$ for NA64(5x) and 29.6 $\text{m}^2 \cdot \text{g}^{-1}$ for NA84(5x). This high SSA for milled particles may be explained by the large number of defects produced by the milling action, such as cracks, folds, wrinkles, and internal voids, as will be seen later in section 3.2.2. An interesting detail is the pronounced difference between 25P and STAR, (26.1 versus 14.6 $\text{m}^2 \cdot \text{g}^{-1}$), taking into account the similar particle size distribution. In this case, a

possible explanation is the welding between aggregates during the STAR passivation process [4].

Finally, the SSA of A01 is surprisingly high ($18 \text{ m}^2 \cdot \text{g}^{-1}$) [8] taking into account the particle size. This may be caused by the flake morphology which confers a high aspect ratio. As for the relative content of Fe(0), all samples had an Fe(0) content that exceeded 75-80% except for 25P, having an Fe(0) content of 93%.

3.2.2. TEM and XRD analysis.

TEM studies were carried out on NA64(5x) and NA84(5x) milled particles, which rendered similar results. The representative images for both milled particles are presented in Fig.4. On the one hand, dark field TEM images reveal that the particles are made up of very small crystal lattices of 5-10 nm in both cases (Fig. 4A). This nanostructure with a large number of defects is due to the milling action. Expanding the analysis to a larger number of particles, the STEM-HAADF image in Fig. 4B shows that a significant number of Al_2O_3 particles are present as individual particles or are integrated within more complex iron- Al_2O_3 particles. On the other hand, no clear signs of continuous and thick iron oxide layers are observed in any of the examined samples (Fig. 4C and 4D). The presence of oxide layer cannot be excluded since it can be thin and then difficult to be observed.

Previous works have examined the presence and thickness of the external oxide layer in 25P and STAR nanoparticles in the activated state [4], following the same procedure and using the same equipment as in this work. Images of these have been included in Fig. 4 for direct comparison. The TEM observations in the A01 particles were not successful given the large particle size. The 25P nanoparticles showed a very thin ($\sim 1.8 \text{ nm}$) but continuous oxide layer (Fig. 4E), whereas STAR particles in the activated state had a larger oxide shell (initially around $\sim 3.5 \text{ nm}$) although in this case, this layer appears to be broken or detached frequently (Fig. 4F).

The XRD patterns of initial iron, alumina, NA64, NA84, A01, 25P and STAR are shown in Fig. 5.

The initial iron pattern shows no presence of other constituents and it is highly crystalline, just like α - Al_2O_3 . In the NA64 and NA84 milled samples a strong reduction of the height as well as an increased width of the iron peaks can be observed. This is typical of mechanical milling processes, given the high reduction of the crystallite size and the microstrain introduced in the lattice [22,35]. The peaks of α - Al_2O_3 can be distinguished based on their intensity and interaction with iron signals, but in both samples, the presence of alumina is very clear. There were no signs of iron oxides. After mechanical milling, most of the oxides present in the initial particles usually give no signal in XRD studies [35,36]. Another possibility is that the formed oxides were amorphous [7]. If that were the case, that layers should be thin since there has been no clear signal of them in TEM observations. Finally, the presence of cementite has been detected by the peaks at 42.3° and 48.7° (2θ). These peaks are more intense in NA84 as compared to NA64, coinciding strongly with their corresponding carbon content. Since the initial iron did not show these cementite peaks, their presence reinforces the proposed mechanism of formation of the particles in NA64 and NA84 as a mixture of fragments of initial iron and steel grinding medium.

As for commercial particles, the XRD pattern for A01 also shows a decrease in the relative intensity and a broadening of the diffraction peaks of iron, but to a lesser extent than in the NA84 and NA64 samples. Although all of these particles were produced by a ball milling process, in the case of A01 the flakes have been not broken (Fig. 3E) and the degree of microstrain and reduction in grain size should be less intense than that of the particles milled with alumina. The peaks for cementite have higher intensities, revealing that the carbon content of these particles is clearly larger than that of NA64 and NA84 [29]. No peaks of magnetite (Fe_3O_4), maghemite ($\gamma\text{-Fe}_2\text{O}_3$), wüstite (FeO) or oxy-hydroxide phases have been detected, in accordance with the results of the other milled samples. It is interesting to note that the presence of a small percentage of magnetite was confirmed in similar

samples from the same company in [29], but in this case the samples were dried before the test and therefore, a higher amount of oxidation in the surface is expected. Regarding 25P and STAR samples, slender peaks of iron may be observed in both cases, corresponding with high crystallinity, and a crystal size that corresponds with the particle size [27]. The presence of magnetite is confirmed, with a small presence of wüstite [4], in agreement with the oxide layer observed in TEM observations.

According to the TEM and XRD results, there was no evidence of thick and continuous oxide layer on the surface of NA64 and NA84 particles, unlike 25P and STAR. The high deformation along with the high number of fractures and cold-welding processes in the powder particles during ball milling in MEG solution appear to be capable of destroying and detaching the initial oxide layer in many sites, in more efficient manner as the degree of milling increases. Furthermore, the solution seems to be able to control oxidation since the new oxide layers are difficult to identify by TEM observation. These issues have been examined in microscale ZVI (mZVI) aluminium, mechanochemically sulfidated mZVI iron (S-mZVI) and Fe-C composites [21-23]. In these cases, no sign of oxide layer was observed by XRD, but X-ray photoelectron spectroscopy (XPS) detected the presence of oxygen in the surface of ball milled particles. A similar situation, only with no flakes was observed in the case of S-mZVI. On the other hand, in the case of FeC composites, it has been reported that an increase of oxidation was detected by XRD in milled samples in propylene glycol. These cases offer a clear evidence that the oxide layer is only partially eliminated by milling and subsequent oxidations are not discarded, although no TEM observations were made [22,23], or they were not focused in the study of the oxide layer [21]. Therefore, according to the consulted literature, a continuous and thick oxide layer is not expected, which agrees with the TEM observations of the milled particles NA64(5x) and NA84(5x).

3.2.3. Magnetization and ζ -Potential analysis.

The saturation magnetization (M_s) was determined from the magnetic curves for all of the examined nZVI particles (Fig. S6). In the case of the 25P and STAR particles, the M_s values were 180 and 168 emu/g, respectively. These results are similar to those that were previously reported for similar materials [27]. According to Kaslik et al. in [27], the decrease of M_s is directly related to the increase in the thickness of the oxide layer. Therefore, 25P, which has high crystalline iron with a very thin oxide layer has higher M_s , whereas STAR, which has a thicker oxide layer shows a small reduction in M_s . Both particles have a very small individual size and are considered single domain structures, having a lower value of magnetic moments as compared to larger multi-domain particles [37].

In the case of A01, a small reduction of M_s is observed (160 emu/g). In this case, the deformation introduced in the particles during the milling process causes a broadening of the iron peaks in the XRD pattern, resulting in a decrease in crystallite size and greater disorder. We should here note that the loss of ordering in iron causes a reduction in its magnetic moment [38], and thus, it is expected that an amorphous iron has lower values of M_s than a crystalline one. This is the case for nZVI particles prepared following the borohydride reduction method. These particles are amorphous and have M_s levels of 105 emu/g [39]. Therefore, the deformation introduced by milling may be the cause of the observed decrease of M_s . Moreover, the presence of cementite is also associated with a reduction of the magnetic susceptibility in steels [40] and thus a decrease in magnetization values should be expected from this part. On the other hand, A01 particles are very large as compared to the 25P and STAR particles, and they should not have any reduction in the magnetic moment by size effect. The same factors may be applied in the analysis of M_s for NA64 and NA84 samples (138 and 118 emu/g, respectively). These low values may be first related to the very small crystallite size (5-10 nm) in the highly-deformed particles, as can be seen in TEM images (Fig. 4A) and in the large

broadening and reduction in height of the diffraction peaks. Together with the weak crystallinity of the samples, the presence of cementite may help to reduce the magnetic moment of samples, especially in NA84, with its higher carbon content.

The ζ -Potential values for the studied particles are shown in Table 1. It can be seen that NA64, NA84, and STAR have values close to or above ± 30 mV. Specifically, NA64 and NA84 have high positive values and high evolved pH. On the other hand, A01 and 25P have values that are closer to zero at lower evolved pH. These ζ -Potential values for NA64 and NA84 in the +25-30 mV range are in concordance with the micro ZVI prepared by a top-down approach [41] and nZVI particles freshly prepared in water by bottom-up methods [32,42]. In order to determine if the presence of alumina could result in increased ζ -Potential values as in the case of a nZVI coated with a $\text{Al}(\text{OH})_3$ thin shell [39], additional ζ -Potential determinations were made in initial alumina and in NA64 and NA84 samples after 5 and 15 magnetic separations. These measurements are shown in Fig. S7 and it is evident that ζ -Potential values for NA64 and NA84 are not sensitive to changes in the amount of alumina, exhibiting values of approximately +25-30 mV. On the other hand, alumina has a Point of Zero Charge (PZC) that ranges from 7.9 to 9.4 [43]. The trend is for the ζ -potential variation to decrease with increasing pH [44,45]. This means that the measurement taken in this paper ($+7 \pm 6$ mV at pH=9.2) is very close to PZC and, at a pH of approximately 9.5-10 (as in the case of NA64 and NA84 pHs), a weak negative ζ -potential is expected. These results would explain the low influence of alumina on NA64 and NA84 ζ -Potential values.

3.3. Chemical and reactivity characterization

Fig. 6 shows the depletion of Cr(VI) in a solution with the amount of nZVI used in reactivity tests, while the calculated Cr(VI) removal capacity is presented in Table 2. The Cr(VI) removal capacity of NA64 and NA84 was high compared with the other tested particles. This superior Cr (VI) removal

capacity of NA64 and NA84 is maintained when it is normalized to SSA and Fe(0) content, and it should be noted that NA64 particles are more effective than NA84 ones. As for commercial nZVI samples, they all have similar performance, with only very slight differences in the normalized values.

The results of the reactivity tests with chlorinated compounds (TCE and PCE) are shown in Fig. 6 and Table 3. In all cases, dechlorinated products such as 1,1-Dichloroethylene, cis-Dichloroethylene, trans-1,2-Dichloroethene, and Vinyl Chloride were found to be below the quantification level in all samples ($25 \mu\text{g}\cdot\text{l}^{-1}$), as seen in the example of Fig. S8. This is in agreement with the literature, since it has been reported that unlike the biological pathway, in the reactions of chlorinated ethylene and chlorinated acetylene with Fe(0) particles, β -elimination prevails over α -elimination. β -elimination is 10-100 times faster and prevents the formation of the previously mentioned daughter products [46-48]. The same mechanism has also been observed when sulfidated-mZVI was tested. [23,49]. As in the case of Cr(VI), once again, the most reactive particles by weight and normalized by SSA and Fe(0) were NA84 and NA64. In contrast with the Cr(VI) reduction, the TCE/PCE elimination capacity values for NA84 were significantly higher than those for NA64. In all cases, in the blanks of NA64 and NA84 containing the same amount of alumina and MEG than in the milled samples, no concentration changes in Cr(VI), TCE and PCE were observed, which indicates that alumina is not active in the elimination of these pollutants.

All of these experiments concluded that the developed milled particles were effective in removing different pollutants and that in all the cases they performed better than all of the commercial products that were tested. The good reactivity of SSA and Fe(0) with normalized values may be related to certain special features of the milled products. One of these is the absence of a continuous and thick oxide layer in the particles. The presence of a thick oxide layer results in a drop in the reactivity

against the present pollutants in contrast to particles with thinner oxide layer [3,27,50]. However, the absence of a continuous and thick oxide layer is also expected for A01 particles [8] and the oxide layer in 25P nanoparticles is fairly thin [24], therefore other factors should be considered.

The first of these factors is the large number of irregularities found on the surface of the milled particles. It has been reported that an increase in the density or reactive sites on the surface will increase reactivity [29,51] and that the new surfaces formed by a fracture process offer more reaction sites [8,20]. As described in Section 3.1, the final milled particles are mainly formed by the joining of small fragments of the iron flakes and worn particles from the vials and the grinding balls. All of these particles contain fracture surfaces that remain partially free in the final surface of the mixed particles (Fig. 4). It is important to note that this rough morphology is not found in the other nZVI studied, or in A01, since in those particles, the flakes have been not broken.

A second point is the large number of defects in the nanocrystalline structure of the milled particles. As seen in Fig. 4, the iron particles are made up of very fine crystals of less than tenths of nanometres in size. Since it has been reported that the reactivity of highly disordered nZVI is higher than that of nZVI particles obtained by thermal reduction of iron oxides [22,30,52], better reactivity of the milled particles as compared with the 25P and STAR nanoparticles is expected. In the case of A01, although they have been produced by a milling process, the degree of deformation has to be much lower than in the case of the NA64 and NA 84 samples. Therefore, the reactivity of A01 should also be lower.

Another point deserving attention is the potential influence of alumina in the reactivity of the NA64 and NA84 milled samples, since some alumina particles seem to be closely connected with the nZVI particles (Fig. 4B). As previously described, the sulfidation of nZVI (by different methods) increases the reactivity of nZVI since the FeS located in the surface inhibits the reaction of Fe with water and

enhances reactivity with TCE [23,49]. The fact that FeS is a good electron conductor enables the process since the flow of electrons from iron moving through FeS is feasible [53]. In this case, alumina has a large electron resistivity, and then the flow of electrons through alumina particles is more difficult. In order to elucidate this possible effect of alumina, new reactivity tests with Cr(VI) and TCE were carried out using NA64 after 15 cycles of magnetic separations, in which alumina content was highly reduced as compared to the initial NA64, and to the initial alumina. As seen in Fig. S9, alumina cannot remove Cr(VI) or TCE from solution, whereas after 15 washes, the NA64 solution revealed similar effectiveness as that of NA64. Therefore, at the alumina-tested concentrations, the presence of alumina has no effect on the reactivity of milled iron using a mechanism similar to the sulfidated nZVI.

3.4. Sedimentation rates and migration

The results of the mobility tests for the studied particles are shown in Fig. 7. These mobility tests were considered qualitative since, although the injected nZVI amount was the same, the total area observed was different. When considering the distances travelled and the concentration profiles along the column length, two types of behaviour are observed. On the one hand, 25P and STAR particles accumulated on the initial section of the column and then, a sharp decrease to zero concentration took place. Conversely, NA84, NA64, and A01 concentration profiles were almost steady, showing a constant mobility all across the column, especially in the case of NA84.

The Sedimentation Rates (SR) are also presented in Table 1 and it can be seen that milled particles NA64 and NA84 had a much higher resistance to settling as compared to the STAR (similar behaviour is expected for 25P) and even more so with the A01 particles. These results are directly related to the size of the different particles in solution as measured by LD, but not with the individual size of the particles. As the aggregate size increases, an increase takes place in sedimentation rates. The most relevant cases are the 25P and STAR nanoparticles, which have the smallest individual

size. In solution, these particles have a strong trend to agglomerate and there is a significant increase in size and thus, an increase in sedimentation rate.

The good performance of the milled particles with alumina in the mobility and stability tests reveals a significant resistance to aggregation in aqueous solution. In this case, due to the absence of surfactants and viscous liquids related to steric and shear-thinning stabilization [54] the electrostatic stabilization of the particles seems to play an important role. Electrostatic interaction is governed by the ζ -Potential, and it is believed that the ζ -Potential values above ± 30 mV produce stable dispersions due to the strong repulsion between particles of like charge [55,56]. In the light of the results of ζ -Potential presented in Table 1, the milled particles of samples NA64 and NA84 are very close to this threshold value, and this may partially explain the good stability and mobility of milled particles in aqueous solution.

Another important feature of nZVI particles that affects their dispersion stability is their high magnetic susceptibility. According to Phenrat et al. [56], the iron nanoparticles have a permanent magnetic moment even when no magnetic field is applied, implying strong attractive forces between them [56,57]. As a result, aggregation due to magnetic attraction occurs quickly despite favourable values of ζ -Potential or size [54,58]. Therefore, a decrease in the trend of agglomeration is expected with a decrease of the magnetization saturation (M_s) in nZVI particles, and new techniques have been developed to reduce M_s of the nZVI particles [39,41]. As discussed in section 3.2.3, the M_s of NA64 and NA84 samples was significantly reduced comparing with the other nZVI particles, which should cause a reduction of the magnetic attractive forces between particles. This reduction should be more important in the case of NA84, since this sample has the greatest reduction in M_s .

The reduction of magnetic attraction and the electrostatic repulsion between the milled nZVI NA64 and NA84 particles may explain the small tendency to aggregate that is observed and therefore, the good results of both samples in mobility tests.

4. Conclusions

- The new milled nZVI particles are formed by milled iron and small fragments of vials and grinding balls as a result of the breakage of iron flakes and the abrasion produced by hard micronized alumina. The final particles have a very fine nanostructure in which the presence of alumina and some carbon contamination have been confirmed.
- The produced particles have shown an excellent reactivity against chromium, TCE, and PCE, being several times superior as compared to commercial ones. The absence of a continuous and thick oxide layer in the milled particles, the presence of a large number of irregularities in the surface, and the high density of defects in the highly-deformed nanostructure of the milled samples help to explain this high reactivity.
- Stability and mobility of the new particles were much higher than those of commercial ones. This behaviour appears to result from large ζ -Potential values and low saturation

magnetization that result in a reduction of the interparticle attraction. These results suggest a very promising field mobility and enhance the potential of the milling process in the manufacture of nZVI particles for water remediation.

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ACCEPTED MANUSCRIPT

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TABLE 1

Results for sedimentation and ζ -Potential tests. Sedimentation rates, evolved pH for the 1 g·l⁻¹

¹ suspensions, ζ -Potential lectures, and replicates performed by an external laboratory.

	NA 64	NA 84	25P	STAR	A01
Sedimentation rates (mm·h ⁻¹)	5.64	1.39	-	42-89	1116 ¹
Evolved pH	9.78	9.57	7.87	7.90	7.13
ζ-Potential (mV)	+29.3	+24.5	+0.40	-31.6	-4.91
Rep. ζ-Potential (mV)	+30.2	+25.0	---	--	---

¹ [28].

TABLE 2

Reactivity against Cr(VI): Slope (S), R^2 of regressions from Cr(VI) tests, mass-based specific

Cr(VI) removal capacity by Fe(0), and SSA-mass-based specific Cr(VI) removal capacity by

Fe(0).

	$S = \frac{\Delta c/c_0}{\Delta [Fe]}$	R^2	Mass-based Cr(VI) removal capacity by Fe(0) mg Cr(VI)·g Fe ⁻¹	SSA-mass-based Cr (VI) removal capacity by Fe(0) mg Cr(VI)·g Fe ⁻¹ ·m ⁻²
NA 64	-0.586	0.97	29.30	1.81
NA 84	-0.611	0.90	30.86	1.41
25P	-0.432	0.99	20.39	0.89
STAR	-0.212	0.99	10.00	0.88
A01	-0.257	0.99	11.75	0.88

TABLE 3

Reactivity against TCE and PCE: Slope (S), R^2 of regressions from CAH tests and mass-based specific TCE/PCE removal capacity by Fe(0) and SSA-Mass-based specific TCE/PCE removal capacity by Fe(0).

	$S = \frac{\Delta c/c_0}{\Delta [\text{Fe}]}$	R^2	Mass-based TCE/PCE removal capacity by Fe(0) mg TCE/PCE·g Fe ⁻¹	SSA-mass-based TCE/PCE removal capacity by Fe(0) mg TCE/PCE·g Fe ⁻¹ ·m ⁻²
	TCE			
NA 64	-1.031	0.98	2.55	0.16
NA 84	-3.884	1.00	11.76	0.54
25P	-0.917	0.99	2.20	0.09
STAR	-0.600	0.99	1.47	0.13
A01	-0.174	0.93	0.56	0.04
	PCE			
NA 64	-0.446	0.95	2.26	0.14
NA 84	-1.131	0.98	8.25	0.38
25P	-0.101	0.85	0.54	0.02
STAR	-0.136	0.98	0.62	0.05
A01	-0.153	0.98	1.04	0.07

Fig. 1. Variation of the final average size of milled particles with alumina content for the different types of balls used as grinding media.

Fig. 2. SEM images for the initial milled particles. A and B) NA84. C) and D) NA64. In

B) and D), Fe particles are coloured in pink, and alumina particles in green.

Fig. 3. SEM images of all studied particles: a) NA64(5x), b) NA84(5x), c) 25P, d) STAR, e1) and e2) A01.

Fig. 4. TEM images of the nZVI particles . a) Bright-field, dark field and selected area diffraction (NA64(5x)). b) STEM (above) and STEM-HAADF (below) images showing the presence of alumina particles (NA84(5x)). C) Detail of iron nanoparticles surface (NA64(5x)) and D) Detail of iron nanoparticles surface (NA84(5x)). E) 25P particles, with a mark in the oxide layer [4] and F) STAR particles [4].

Fig. 5. XRD patterns for initial iron, alumina, 25P, STAR, A01 and milled particles NA64 and NA84.

Fig. 6. Depletion curves of Cr(VI), TCE, and PCE for the produced nanoparticles NA64, NA84 and the commercial reference irons 25P, STAR and A01.

Fig. 7. nZVI distribution over the column length at 90 min of NA64, NA84 and the commercial particles 25P, STAR and A01.

SUPPORTING INFORMATION

For

HIGH REACTIVE NANO ZERO-VALENT IRON PRODUCED VIA WET MILLING THROUGH ABRASION BY ALUMINA

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2.1. Commercial zero-valent iron nanoparticles

Commercial particles obtained from gas reduction of iron oxides (STAR and 25P) were supplied by NANOIRON, Czech Republic. STAR nanoparticles are air stable due to a surface passivation process that is typically performed by allowing the free atmosphere to slowly and progressively come into contact with pristine particles, building a protective oxide layer [4]. This oxide layer reduces reactivity but it may be degraded or detached by simply submerging the particles in water for some time. With this procedure, called the activation process, the nanoparticles significantly increase their reactivity [4]. In this case, the activation was carried out in a nitrogen atmosphere in a glove box (2P, Jacomex SAS). This consisted of preparing a 20% (by weight) iron/deionized water suspension that was dispersed with an energetic mixer (MICCRA D-9 ART) at 11,000 rpm, following a 60s on - 60 off - 60s on sequence. Then the solution was stored for 36 h at 5°C and at the end it was once again re-suspended [4]. Finally, it was immediately introduced into reaction batches. The 25P nanoparticles, on the other hand, are pyrophoric and very reactive. They have been used in several full-scale field remediation cases [26]. 25P nanoparticles were also dispersed in a 20% (by weight) iron/deionized water suspension into the glove box following the above protocol but without storage during the 36h activation process and therefore they were used immediately.

Commercial milled ZVI flakes (named A01) supplied by UVR-FIA, Germany, were also tested. These particles are produced by wet milling in mono-ethylene glycol (MEG) and are supplied in this MEG slurry. It consists primarily of iron flakes having a lateral size of several micrometres. In order to precisely dose these particles in reactivity tests, they were separated from the MEG using absolute ethanol rinses and were subsequently dried in a glove box.

Fig. S1. Evolution of alumina concentration in milled samples NA64 and NA84 with the number of magnetic washes.

Fig. S2. Two example of kinetics plots done with STAR nanoparticles at similar iron concentrations for Cr(VI) reactivity tests (above) and TCE/PCE reactivity tests (below).

Fig. S3. SEM images in Backscattered electrons imaging for A) NA84 and B) NA64 after 5 magnetic washes. Fe particles are coloured in pink and alumina particles in green.

Fig. S4. Alumina (pale) and Iron (bright) SEM image in backscattering mode.

Fig. S5. LD particle size distribution by volume of: NA64(5x), NA84(5x), 25P, STAR and A01.

Fig. S6. Magnetic field dependent magnetization for 25P, STAR, A01, NA64 and NA84 particles.

Fig. S7. Variation of Z-potential with the number of magnetic washes of NA64 and NA84 milled samples. The value for pure alumina is included for comparison.

Fig. S8. Chromatogram for the 2.5 mg·l⁻¹ standard in which TCE and PCE signals are marked together with the signals of the trans-1,2-DCE, cis-1,2-DCE, 1,1-DCE and VC daughter products for monitoring and quantification of final concentrations in batches. On the right the chromatograms for A01 and NA64 are exposed showing that any of these daughter products were observed.

Fig. S9. Depletion curves of Cr(VI) and TCE for the produced nanoparticles NA64 and the same sample after 15 magnetic washes NA64(15x).

Graphical abstract

Highlights

- Milled NZVI particles with Al_2O_3 have high reactivity against Cr(VI), TCE and PCE.
- High suspension stability and mobility comparing with commercial nZVI.
- The particles have a highly deformed structure with a thin oxide layer.
- High positive values of ζ -Potential and low saturation magnetization.