



**Taking Nanotechnological Remediation Processes  
from Lab Scale to End User Applications  
for the Restoration of a Clean Environment**

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**WP2: Design, Improvement and Optimized  
Production of Nanoparticles -Zero-Valent  
Iron Nanoparticles – nZVI**

**DL2.1 Large Scale Production of nZVI**

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## 1 Summary

DL2.1 deals with up-scaling of the nZVI production process from the lab-scale (gram amounts) to semi-industrial (kg amounts) and large-scale (100 kg amounts). The optimized air stable nZVI products with oxide shells were scaled up and the production is prepared for quantities required for pilot testing at selected sites (about one ton of nZVI annually). UPOL tested the production process in the laboratory and together with NANO IRON were responsible for up-scaling. NANO IRON produced industrial quantities for testing and pilot application at VEGAS. The milling/grinding production was optimized as well. UVR-FIA was responsible for the schedule of the up-scaling production from the laboratory to industrial level including the design of the appropriate machinery and/or production process. CTM participated in the optimization of the production process. NANOIRON and UVR-FIA is prepared to produce and deliver at least 1.5 ton/a each. In both cases the quality of the products was compared with products developed on a laboratory scale, where all WP2 members participated. The nZVI particles in the developed form are offered on the market for outside applications.

## 2 Background of the large scale production

The deliverable “Large Scale Production of Nano Zero-valent Iron” is focused around two types of nZVI production:

- air-stable nZVI with a combined inorganic/organic shell
- nZVI based on grinding/milling

There are various types of nZVI materials available on the market supplied mainly in the form of an aqueous suspension. nZVI is gradually oxidized due to its reaction with water where the content of the active phase is significantly reduced in the product. Increased transport costs (due to the presence of water in the product) together with massive aggregation of nanoparticles tend to lead to poor migration properties and low reactivity, which are major problems, making the whole application significantly more expensive and less successful.

The development of an air-stable nZVI production technology with the possibility to control the thickness of the oxide shell has led to the possibility of transporting the nZVI product in the form of a chemically stable powder without any loss of the active phase.

Air-stable nZVI can be stabilized secondarily by a suitable environmentally friendly organic surfactant to reduce the degree of aggregation of material and ensure the appropriate migration properties in the aquifer, which is also the main focus of this research. The secondary organic modification, which sits on top of the stabilizing oxide shell, can be done directly at the site, just before the application, thereby ensuring perfect migration properties and high quality of injected nZVI (i.e. cumulative effects of the oxide and organic layers do not reduce nZVI reactivity significantly).

The application potential of such a technology is extraordinary because it simultaneously reduces the cost of application due to lower transport costs and higher efficiency of nZVI having following features:

- high Fe(0) content,
- air-stability over time,
- variable properties according to the application (control of the reactivity and migration properties of nZVI by shell thickness and choice of the organic surfactant),
- environmentally friendly material (iron oxide end products),

Second research direction was to prepare nZVI by less expensive technology, which is milling/grinding from larger zero-valent iron particles (microscopic Fe). If nZVI production is significantly cheaper, such technology can be competitive with air-stable nZVI even with worse nZVI properties for treatment of contaminant.

The WP2 members worked during the first period of the project on setting up large scale particle production and all supporting developments. The whole procedure can be mapped as follows: development of optimal particles for reactivity with chlorinated hydrocarbons and mobility in the aquifer on a laboratory scale, based on these results to set-up the production in a large scale, testing of production, nZVI characterization and comparison of nZVI produced in laboratory and large scales.

In close collaboration with the company NANO IRON, UPOL and TULib worked on up-scaling the production process of air-stable nZVI from laboratory to semi-industrial and large-scale; UVR-FIA, CTM and TULib collaborated on the large scale production of milled particles; UPOL, CTM, TULib and CNRS worked on nZVI characterization; TULib performed initial laboratory scale testing of particle reactivity and mobility and later particle testing for application in the field.

### **3 NZVI produced by solid-state thermal reduction of iron oxide powder**

#### **3.1 Particle development and large scale production**

Pure nZVI powder without surface treatment (pyrophoric Fe) was taken as a basis for production of air-stable nZVI powder. During the first project period (M 1-18) WP2 intensively worked on the development and further optimization of the nZVI preparation procedure, which is based on solid-state thermal reduction of iron oxide powder. The layer of the iron oxide shell stabilizes the surface of the nanoparticles and prevents their rapid oxidation (burning). A combination of various parameters during synthesis (appropriate mixture of N<sub>2</sub>, Ar and O<sub>2</sub> gases, temperature and time) affects the resulting thickness of the iron oxide shell and thus the resulting product properties. Alternatively, it is possible to prepare nanoparticles of elemental iron coated with other inorganic phases, but this process was not tested in large scale. The proportion of the magnetite/maghemite phase increases during the passivation process of the nZVI surface. The passivating oxide shell on the surface of the nanoparticles has been studied using transmission electron microscopy – the layer thickness varies from 4 nm to ~ 20 nm depending on the passivation conditions. The shell thickness influences the stability, reactivity and also the agglomeration of nanoparticles. The 4 nm layer is adequate for most situations.

This research activity led to the development of a new generation of nZVI with an inorganic shell (i.e. with a shell formed by iron oxides) of a controlled thickness and turned the nZVI particles into an air-stable product capable of subsequent anchoring of the outer organic shell. This production was firstly tested on a laboratory scale, then the procedure was transferred to a semi-industrial scale at NANO

IRON and finally to an industrial scale. The actual production capacity of air-stable powder of 200 kg/month can be easily increased by a multi-shift operation or by using multiple devices.

These nanoparticles were subsequently covered by secondary environmentally friendly organic stabilizers, namely polymers etc. – e.g., carboxymethylcellulose (CMC), polyethyleneimine (PEI), polysterene sulfonate (PSS), polyacrylamide (PAM), guar gum (GG), polyacrylic acid (PAA) in order to enhance the aggregation stability, reactivity and mobility of the nZVI particles.

The production of nZVI with a combined shell is carried out in two steps: Firstly, the dry air-stable powder (NANOFER STAR) is produced by solid-state thermal reduction of iron oxide powder with final stabilization by addition of oxygen. Secondly, selected organic substance is incorporated into the solution and the solution is dispersed in order to obtain a homogeneous suspension and break up agglomerated nanoparticles. The second step can be performed days or week later and on site as well.

Recommended slurry composition for organic stabilization:

- 20% wt. of dry nanoparticles
- 80% wt. of solution with an organic substance (0.01-3% of organic substance, 99.99-97% of water)

### 3.2 Particle characterization

Subsequently, the selected materials (produced in a large scale by NANO IRON) were characterized in detail to confirm the properties of the nZVI particles prior to disseminating them to NanoRem partners, with detailed measurements of the thickness of the developed oxide shell on the nZVI particles. For the nZVI characterization, different methods were employed, including X-ray powder diffraction, <sup>57</sup>Fe Mossbauer spectroscopy, BET surface area measurements and scanning/transmission electron microscopy. Three samples were prepared in a quantity of 20 kg each for testing (the smallest amount for large scale production). The sample STAR\_224 was prepared exactly according to the up-scaled procedure, while the other two charges were purposely prepared with a thicker and thinner oxide shell. These experimental charges were prepared to check whether the changes in procedure parameters and subsequent nZVI properties are possible also during large scale production.

#### 3.2.1 X-ray powder diffraction

X-ray powder diffraction (Fig. 1) together with Mossbauer spectroscopy (Fig. 2) was used to check Fe(0) content in the sample produced at a large scale. The results were compared with the sample developed at a laboratory scale to confirm good up-scaling of the process. Different laboratory samples consist of 75-80% of elementary Fe, which is in very good agreement with the large scale production, which showed 74% of Fe(0), 8% of FeO and 18% of Fe<sub>3</sub>O<sub>4</sub>.

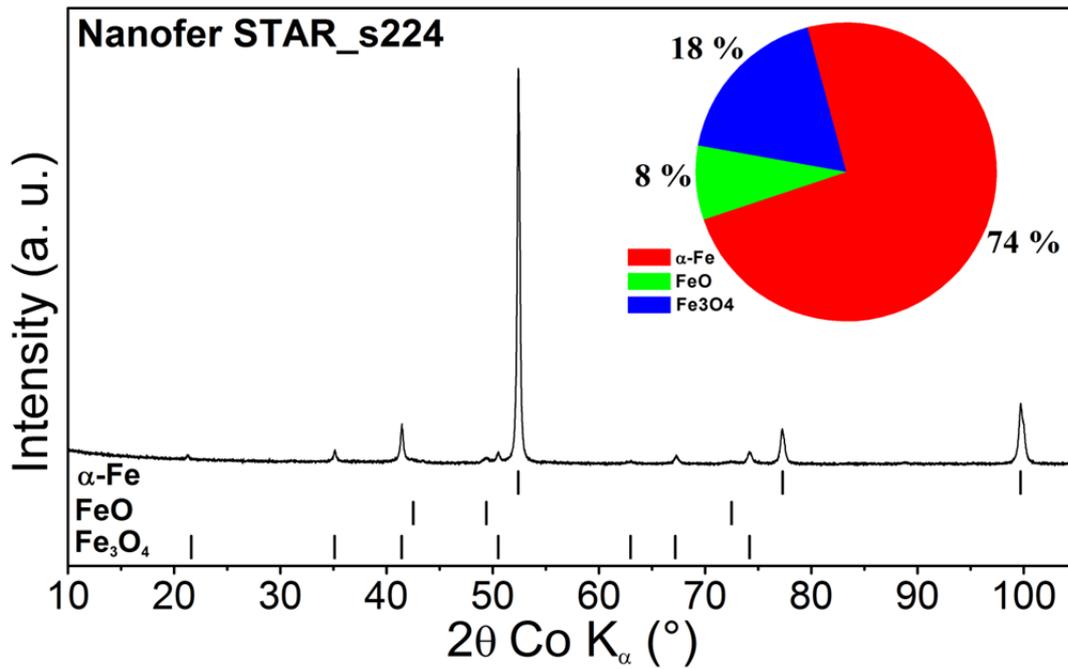


Figure 1: X-ray powder diffraction of STAR sample

### 3.2.2 <sup>57</sup>Fe Mössbauer spectroscopy

While X-ray powder diffraction is able to specify crystalline forms of Fe, Mossbauer spectroscopy identifies the amorphous phases as well, because the technique is based on counting Fe atoms in different oxidation states. The results (area of the appropriate peaks in Fig. 2) confirm 74% of Fe(0) in the sample ( $\alpha$ -Fe), which shows there is no amorphous phase in any significant quantity. The amount of FeO was slightly smaller (area of 5%) compared to the large amount of Fe<sub>3</sub>O<sub>4</sub> (area of 21%). These differences are not significant.

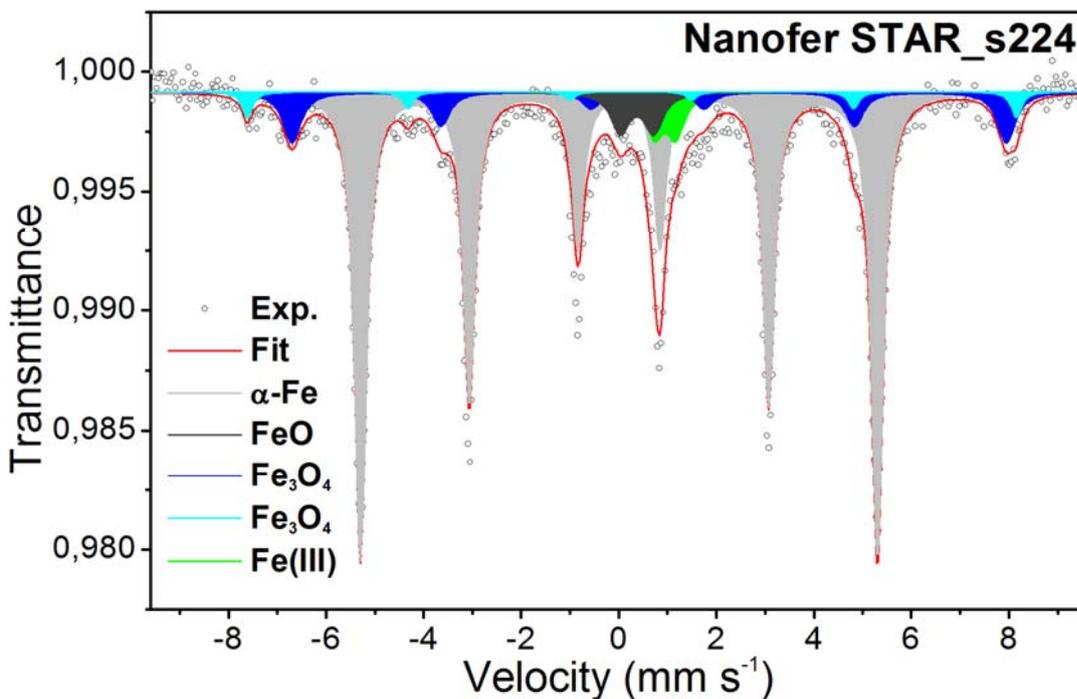


Figure 2: Mossbauer spectroscopy of STAR sample

### 3.2.3 Transmission electron microscopy

TEM was used to see the shape, size distribution and oxide layer thickness of the nZVI (Fig.3). The pictures (two different spots on the STAR\_224 sample) show no significant variations in nZVI size, narrow size distribution, mean particle size of around 50 nm and thickness of oxide layer between 4-5 nm (Fig.4), which is again in very good agreement with samples determined in the laboratory in small quantities.

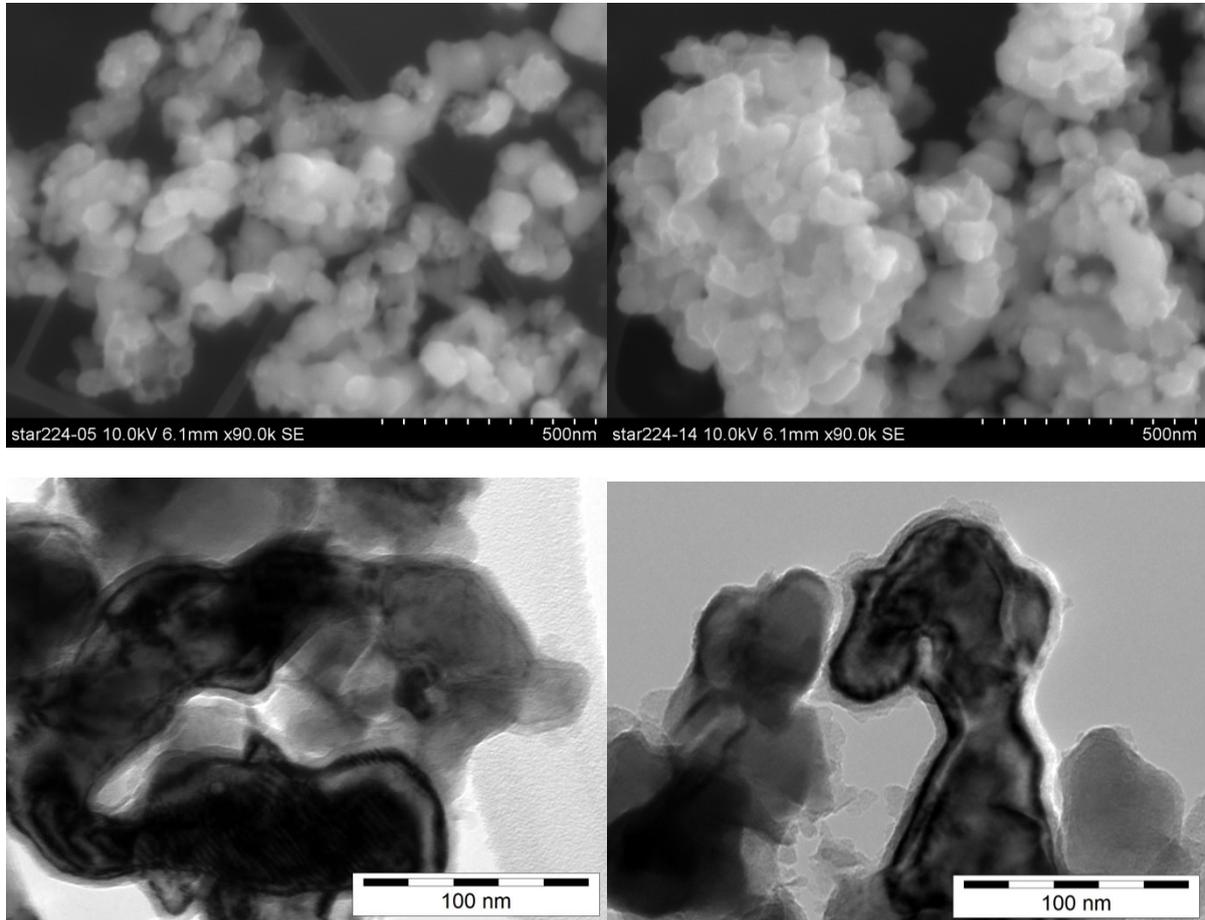


Figure 3: TEM pictures of STAR sample

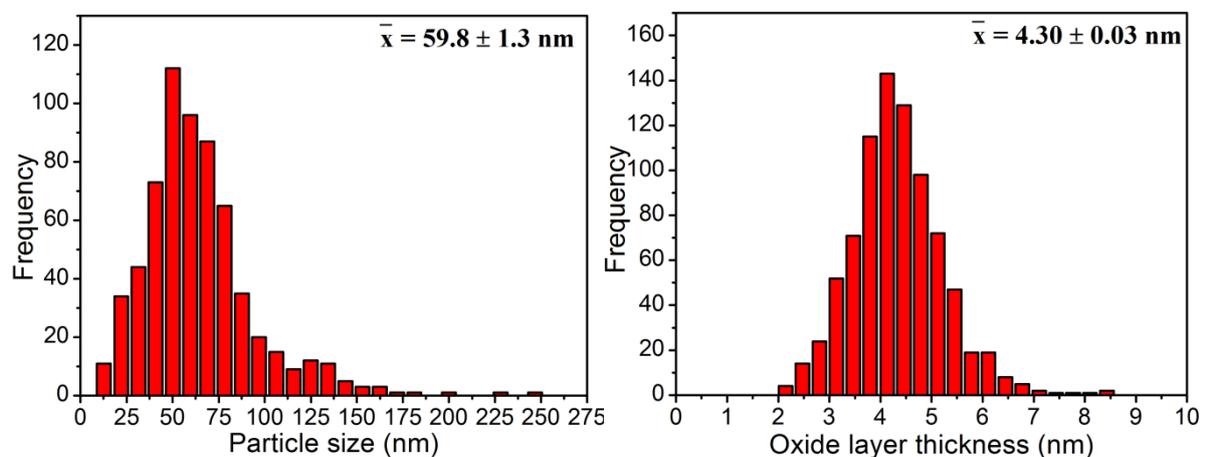
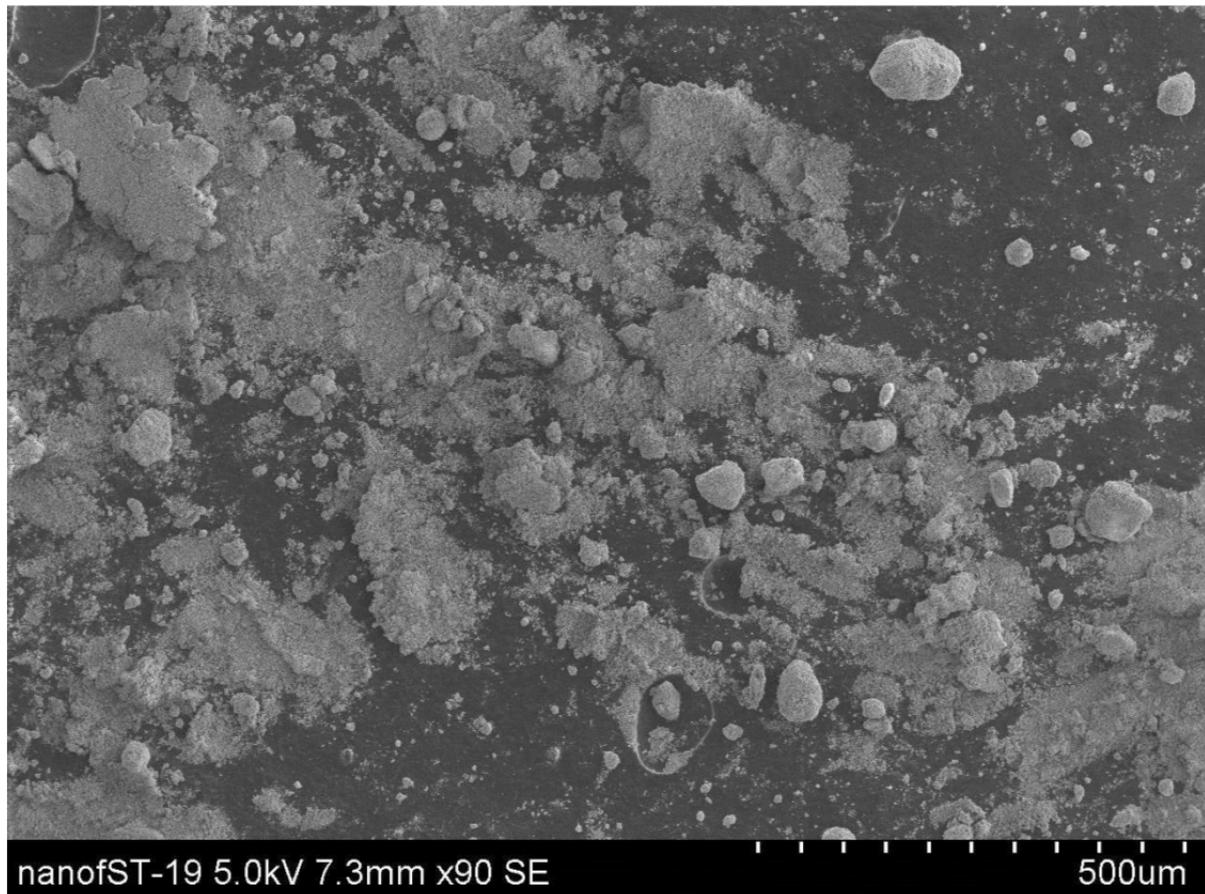


Figure 4: TEM determined particle size distribution and oxide layer thickness of STAR sample

The TEM picture also shows particle aggregation. Similarly, various sizes of agglomerates can be determined on a picture with smaller magnification (Fig.5). Therefore, agglomerated particles need to be broken up by an addition dispersing process prior to injection to the aquifer.



**Figure 5: Microscopic image of NANO FER STAR (smaller magnification)**

#### **3.2.4 Specific area according to BET**

The specific surface area according to BET is an important parameter for the determination of the nano-scaled iron particles. A method by adsorption of nitrogen; single-point differential method according to Haul and Dümbgen was used, which enables a simple and prompt determination of the specific surface area according to DIN EN ISO 9277.

For this analysis the particles must be in a dry state and oxidation must be avoided. A separate method was developed. The fluid phase of the suspension was removed at first and the particles were coated with methanol to prevent the oxidation. Before each BET measurement, the surface of the samples has to be degassed to avoid contamination. The degassing takes place in a separate thermostat controlled heating device at a temperature of 105 °C and the methanol evaporates.

Fig. 6 shows resulting isotherm of nitrogen absorption which was used for calculation of surface area. The result (19.4 m<sup>2</sup>/g) is again in very good agreement with the measurements from the laboratory scale sample (between 15 and 22 m<sup>2</sup>/g).

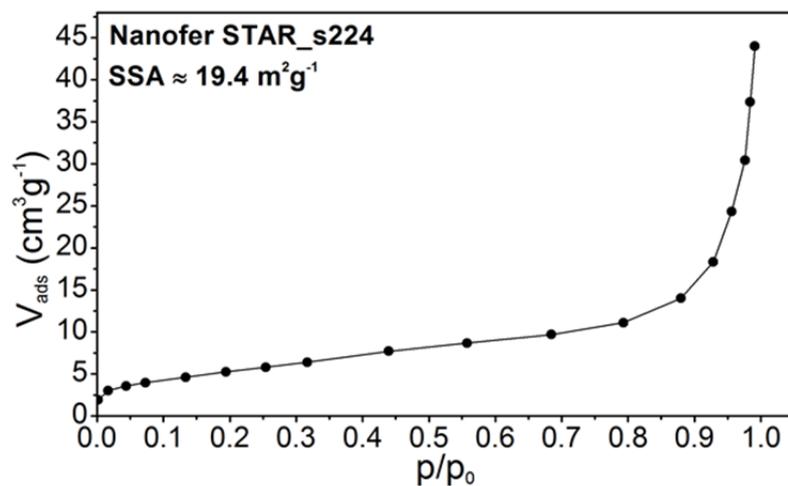
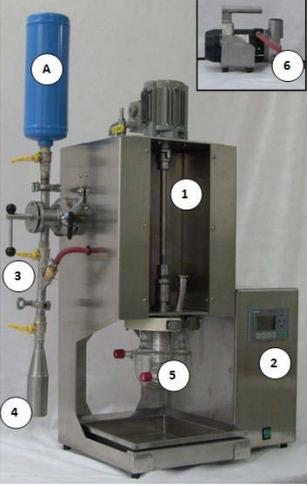


Figure 6: Result of BET measurement of STAR sample

In the project, we also performed detailed studies of the aging of the nZVI particles; test its non-toxic nature and providing the possibility of biodegradation of the organic shell in the contaminated water. Finally, the particles were tested with samples of contaminated water from the pilot sites to ensure nanoparticle degradation potential.

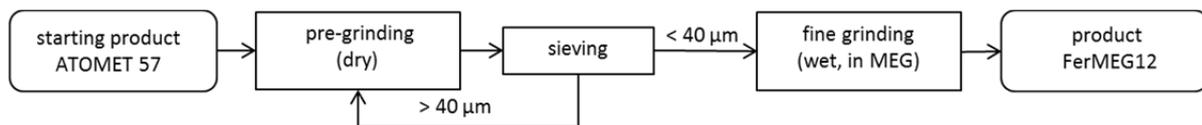
Table 1: Tested dispersing methods (equipment)

Type of device		Production capacity (slurry)
<p><b>Laboratory dispersing unit (NANO IRON)</b></p> <p>It is designed for direct manufacturing of aqueous suspension from any dry powder. The equipment provides manufacturing capacity of 500 grams of slurry in one batch. This unit is equipped with vacuum pump and can work under protective atmosphere, it is also possible to connect cooling or heating liquid to the mixing reactor. See <a href="http://www.nanoiron.cz">www.nanoiron.cz</a></p>		2kg/hour
<p><b>Industrial dispersing unit (NANO IRON)</b></p> <p>It is an upscaled laboratory dispersing unit having high production capacity using improved dispersing process leading to low size of agglomerates.</p>		80kg/hour
<p><b>Laboratory high-shear mixer (IKA Ultra Turrax, etc.)</b></p> <p>It is recommended to perform the mixing in a closed system (bottle) to minimize access of fresh air to the slurry during mixing.</p>		3kg/hour

## 4 Milled particle production

### 4.1 Milled particle development and large scale production

UVR-FIA GmbH has developed a method to produce nZVI in a two-stage top-down process (Fig. 7). At the start of the practical work various commercial iron powders (carbonyl iron; sponge iron) were tested. Various grinding equipment, grinding additives and milling times were investigated as well. As a basic raw material ATOMET 57 was selected, a coarse, high purity granulated iron powder from Rio Tinto, Quebec Metal Powders Ltd. The first step involves dry grinding with inhibitors as corrosion protection up to a particle size of  $< 40 \mu\text{m}$ . Wet grinding, the second process step, was at the beginning very problematic because of the formation of hydrogen. The milled particle development simultaneously took place at CTM, where different conditions and liquids were tested. This problem was ultimately solved by grinding with mono ethylene glycol (MEG) as the grinding liquid and by the addition of a surfactant. With this technology nano-structured, flake-shaped particles with thicknesses less than 100 nm are obtained.



**Figure 7: Flow chart**

UVR-FIA GmbH is able to process 60 kg of pre-grinded iron per fine grinding process. For the production a ball mill (Fig. 8) with the following parameters is used:

- diameter of the grinding chamber: 800 mm
- length of the grinding chamber: 2000 mm
- volume of the grinding chamber: 1000 l

Sieving is performed at Dreßler type of sieve (Fig.9) in dry process prior the fine wet grinding.

Final product, FerMEG12 is designed for the application in the reduction technology of groundwater remediation. Monoethylene glycol is water-dilutable and breaks down in a few weeks. Production is set to 500 kg, which is the amount planned for applications at the pilot sites during 2015.



**Figure 8: Filling operation of the ball mill**



Figure 9: Sieving of milled particles after dry milling, Dreßler type (400 x 600 mm)

## 4.2 Milled nZVI characterization

### 4.2.1 Scanning electron microscopy

For the analysis of the particle size, shape, surface and structure a Phenom electron microscope was used as a supplementary investigation. The raw material consists of flakes, spherical and irregular particles (Fig. 10, left). The pre-milling product contains small, compact particles. The surface of some of the particles is enlarged by small particles, which seem to be forged (Fig. 10, centre). The shape of the nano-structured final product is platelet-like only (Fig. 10, right).

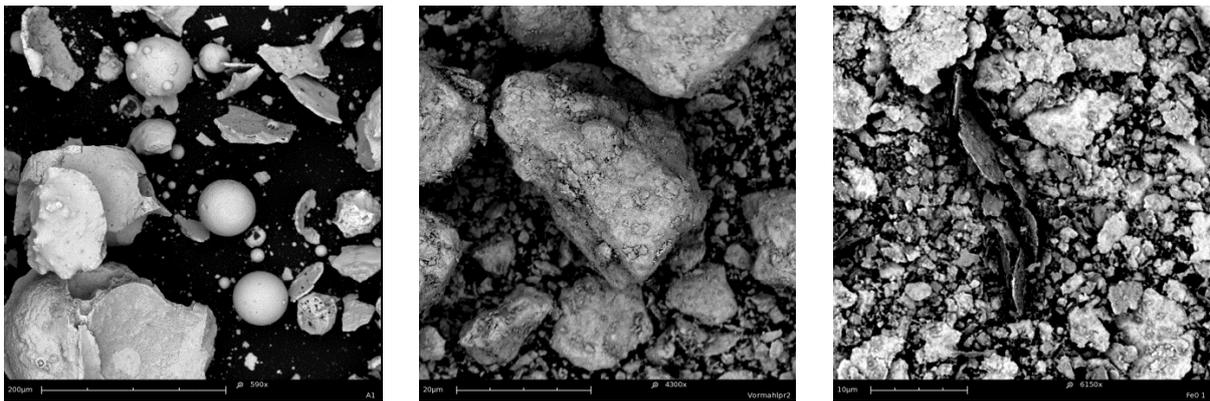


Figure 10: SEM picture of milled particles: left - starting product ATOMET57, centre - pre-milling product, right – FerMEG final nZVI

### 4.2.2 nZVI content

The measurement of nZVI content in a slurry or as a powder is based on the measurement of hydrogen volume, which is released during the chemical reaction of zero-valent iron and sulphuric acid. The volume of hydrogen is directly proportional to the amount of zero-valent iron, the amount of iron-oxides does not influence the volume of generated hydrogen; it only slows down the reaction

speed. The weight content of iron particles in MEG is about 25 – 30 %.

#### 4.2.3 Specific area according to BET

The specific surface area according to Brunauer–Emmett–Teller theory (BET method) ranges from 12– 18 m<sup>2</sup>/g.

## 5 Conclusions

- Currently, all of the products developed and tested in WP2 are available in large amounts from industrial production.
- NANOIRON distributed samples of NANOFEAR 25S (slurry), NANOFEAR 25P (pyrophoric Fe) and NANOFEAR STAR.
- During the past few months, NANOIRON improved the stabilization process and the dispersing technology provides a higher production capacity and better stabilization. On-site stabilization of NANOFEAR STAR is also available for a real remediation quantity.
- Large scale production of milled particles (UVR-FIA) is also set and manufacturing of 500 kg of FerMEG12 particles is under preparation (ball pre-milling is performed, sieving down to 40 µm).
- The particles will be produced according to the pilot site injection plans in 2015. The samples were also delivered to the project partners for further tests.

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