Testing on emerging nanoparticles for arsenic removal under real conditions on a pilot field site, in Asturias, Spain.

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Site description and case study approach

The Spanish test site is an abandoned 20Has brownfield site in Asturias (Northern Spain), used historically for the production of chemical fertilizers during 48 years (1950 – 1998). Contaminants include predominantly heavy metals both in soil and groundwater, associated to site's madeground.

It has been decided to focus the research on a single metal treatment, facilitating the interpretation of results and the technology validation: solved arsenic (As) in groundwater has been selected as the target contaminant, given its high concentration (5527,2ppb max., 1378,5ppb mean concentration) and the lack of field cases in the literature that pay attention to this element, which makes this field experiment particularly groundbreaking. The main source of As is related to the sulphuric acid production by arsenopyrite (FeAsS) burning. Pyrite ashes rich in As in the form of AsO4Fe resulting from this burning process were then uncontrolledly dumped on site as madeground.

Pilot test

A total of 3 injection points (IP-1/3) and 8 control points (CP-1/7+MW-1) conform Nanorem's Spanish pilot test. All wells were drilled down to bedrock (7m below ground level) into a semi-confined alluvial aquifer.

From the 23rd until 27th February 2016 a total of 250kg of dry nano-ZVI product (Nanofer Star®) have been injected at 8-12l/min rate and low pressure in the 3 injection wells making up a total of 17.000l of injected product in the aquifer. Together with the iron, Lithium (LiCl at 50mg/l) was also added as tracing element.

Before, during and 6 months after the injection application, real-time geochemical maesurements (pH, temperature, redox potential- ORP, electrical conductivity - EC and dissolved oxygen - DO) have been recorded and periodic groundwater samples have been taken in order to understand nZVI's effectivity and behavior under real conditions.

Figure 1. Nanofer Star® canisters

Figure 2. Spanish pilot test works execution

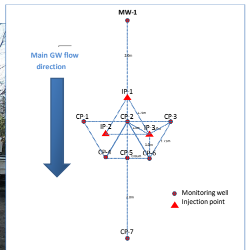
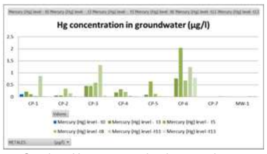


Figure 3. Pilot test layout

Preliminary Results – Potential risks

Potential risks associated to nZVI injection

- Dissolved total chromium (redox sensitive), mercury (redox sensitive) and lead (redox insensitive) levels increased immediately after the application of nZVI, exceeding their reference value for groundwater (Dutch intervention value). Last sampling campaigns concentrations for these metals (29.08.2016), were below their intervention reference value. It is considered necessary to investigate at lab-scale the effect of nano-iron application to mixtures of dissolved heavy metals, particularly when mercury is present.



Graph 1. Hg concentration in groundwater (Dutch Intervention Value: 0.3µg/l). In blue Hg concentration before nZVI application.

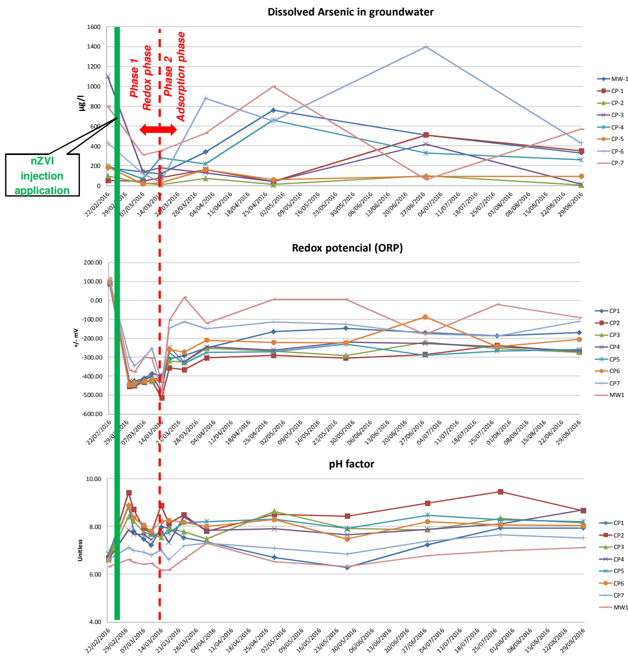
- The toxicity results with cultivable bacteria isolated before and after nZVI addition, show that a significant percentage tolerate the effect of nanoparticles.

Preliminary Results – Effectivity

According to literature, both arsenates As(V) and arsenites As(III) can be fully transformed into metalloid arsenic As(0) by reaction with nZVI. As(0) is insoluble, thermodynamically stable, and this reaction is not expected to be reversible.

Treatment efficiency

- Laboratory reactivity test results with groundwater samples from the site showed that concentration of solved arsenic decreases significantly in treatments using both goethite and nZVI, being the later one more efficient in terms of the presence of As in solution.
- According to field data, total dissolved As reduction in groundwater and therefore the technology efficiency has been explained in 2 phases:
  - **I. Geochemical phase 1: redox phase** (0w until 4w after NPs application): characterized by the presence of *lowest As concentrations, highest levels of Fe* (total and ferrous iron), *lowest values of ORP* (between -400 and -500mV), *lowest levels of DO and alkaline conditions, in all wells*. All this factors suggest that NPs in suspension are taking effect and the arsenic is being reduced, fully transformed into metalloid arsenic As(0), and captured in a growing oxide matrix, by reaction with nZVI.
  - **II. Geochemical phase 2: adsorption phase** (4w until 24w after NPs application): defined by *As level variations*, with not a clear trend for all wells, *ORP values below pre-injection conditions* (all wells show negative values opposed to positive original ones), *stable pH and higher than original* values and *minimal concentrations of dissolved total and ferrous Fe, in all wells*. During this chemical stage, NPs have been most likely oxidized and have precipitated shaping a reactive zone to which dissolved As gets adsorbed. The main source of As in the groundwater comes from the fill rich in pyrite ashes. Since dissolved As is uninterruptedly generating as rainfall recharges the aquifer, there is a counteracting effect of the active source against the effect of the reactive zone.



Graph 2. Dissolved Arsenic , redox potential and pH factor evolution in groundwater and geochemical phases boundary.

nZVI subsurface migration

- Fe particles are detected as total and ferrous iron in all (8) control wells, including CP-7 located 4m downgradient from the injection zone.

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

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