COMPARISON OF MIGRATION AND REACTIVATION PROPERTIES OF NEW TYPES OF IRON NANOPARTICLES

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Abstract

The submitted work presents the results of comparative laboratory tests focussing on a comparison of the reactive and migration properties of new types of iron nanoparticles (nZVI). Specifically, the results of batch tests and column tests of a new type of non-pyrophoric iron powder STAR with additional surface modification using various organic stabilizers were compared a standard, commercially available nanoiron product called NANOFER 25S (N25S) from the manufacturer NANO IRON s.r.o. The test results show the different character of the powders in terms of reactivity and migration, which is given by the different method of preparation, whereby the surface of the resulting particles is coated by an oxide layer and has a higher mean size. In general, it can be stated that the STAR powder is slower to react than N25S due to the gradual breakdown of the surface shell of the oxides and has slower migration properties due to the lack of smaller fractions with high mobility.

INTRODUCTION

Research is underway in the framework of the project NANOBIOWAT, aiming to develop new types of iron nanoparticles for the remediation of the rock environment that are stable in air and do not have to be stored in an inert atmosphere. This greatly simplifies handling of the material during remediation (transport and preparation onsite). The pyrophoric properties of these nanoparticles are suppressed by stabilizing their surface using an inorganic shell, which prevents rapid oxidation (degradation) on contact with air. The aim is to achieve similar or better quality parameters (reactivity and migration in the rock environment) than the standard product supplied i.e. NANOFER 25S.

In terms of reactivity, STAR achieves good results, which are comparable with N25S, without any additional surface modification. However, it displays a delay in the onset of the reactivity of the material due to the gradual breakdown of the inorganic shell and the subsequent exposure of the reactive surface of the iron. The migration properties of the suspension with STAR nanoiron, however, are very limited, therefore it is very desirable to study their surface stabilization without decreasing reactivity, which is the aim of the submitted work.

1. MATERIALS TESTED

NANOFER STAR zero-valent iron nanoparticles were used for the tests in the form of aqueous suspensions, which differ in the preparation process (see the description in Table 1). Suspensions were prepared from powdered products in distilled water with a ratio of 1: 4 immediately before application in the laboratories of TUL using an LD laboratory dissolver. The reactivity and migration of the prepared suspensions were compared with the migration of the commercial product N25S prepared on an industrial disperser.

Table 1: Overview of the tested materials

| Name	Reaction solutions	Powder
STAR-Ax.	Organic modifier (Axilát)	NANOFER STAR
STAR-MSJ	Organic modifier (combination of hydrated alkali metal salts and aliphatic carboxylic acids)	NANOFER STAR
STAR-CMC	Organic modifier (Sodium carboxymethyl cellulose)	NANOFER STAR
STAR	Inorganic modifier	
STAR/BASF	Organic modifier (Polyethilenimine)	NANOFER STAR + µBASF
N25S	Organic modifier (Axilát)	NANOFER 25P

2.   LABORATORY TEST METHODOLOGIES

Batch tests

Kinetic batch tests were conceived using chlorinated ethene (CLE). The tests were carried out in 500 ml glass reagent bottles with lids sealed with Teflon-lined septa. To prevent volatilization, sample containers were prepared separately for each measurement point. At the start of the test, 500 ml of contaminated water (CLE) was added to each sample container, to which the appropriate amount of nZVI was dispensed using an automatic pipette. The concentration of iron in the stock suspension was measured before dosing using an ICP-OES instrument (Perkin Elmer Optima 2100 DV), at which time the iron sample for analysis was dissolved with hydrochloric acid and hydrogen peroxide or further diluted with distilled water. Subsequently, the sample was placed in a vertical turret shaker and subsequently analysed at specific times for CLE content by GC/MS (Varian 3800/Saturn 2800) and pH and ORP measurements were also taken using a WTW 343i multimeter with the respective electrodes. The natural rate of volatilization of the sample was evaluated based on the analysis of control samples.

Column tests

For the column tests, 22 cm long glass cylinders with an inner diameter of 2 cm, vertical orientation and washing against the direction of gravity were used. A 2 cm gravel filter was placed from the bottom of the column, on which was applied saturated glass quartz sand with a grain size of 0.5-2 mm, and hydraulic conductivity of 1×10^{-3} m/s, simulating the rock environment. Washing of the column was provided by two peristaltic pumps: circulation pump (PCD825, Pumps Kouřil) - providing the main water flow in the system (the water also passes through a MAD-02 degasser, REGOM INSTRUMENTS s.r.o.) and dosing pump (PCD21, Čerpadla Kouřil) - for continuous dosing
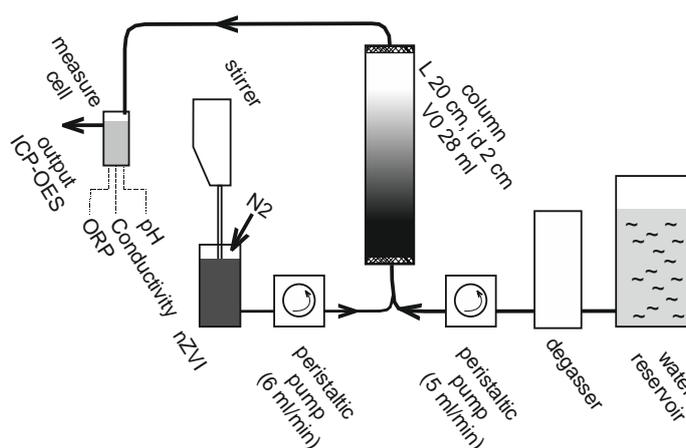
Fig. 1: Block diagram of the column test

of aqueous suspension with dispersed nZVI from a stirred tank, which was purged with argon to suppress oxidation of nZVI. The water from the column passes through a closed measuring cell, in which basic physico-chemical parameters (pH, ORP, conductivity) were automatically measured using a WTW 343i multimeter with the respective electrodes. Samples of output water were taken from the column every 100 ml

(equivalent of approximately 3 pore volumes) during the injection of the nZVI. The concentrations of total Fe were measured in these samples using an ICP-OES instrument (Perkin Elmer Optima 2100 DV). A block diagram of the measurement system is shown in Fig. 1. After the experiment, the column was frozen and divided into samples of approximately equal size, from which the concentration of total Fe was measured. Breakthrough curves of each type of nZVI and distribution curves of the nZVI in the columns were then evaluated and compared with each other.

3. RESULTS

Batch tests

The batch tests were carried out in two stages. During the first stage, the reactivity of STAR/BASF and N25S in real water contaminated with CLE was tested. A concentration of 5 g/l nZVI (corresponding to the measured concentration of total Fe) was chosen for STAR/BASF, and a final concentration of 1 g/l nZVI was used for N25S. The test was conducted over 55 days. During the second stage, the reactivity of STAR, STAR-Ax., STAR-MSJ and STAR -CMC was tested in water artificially spiked with tetrachloroethane (PCE). A concentration of 1.6 g/l nZVI was chosen and the test was conducted over 89 days.

Fig. 2 shows the time course of the degradation of the total amount of CLE. Losses due to volatilization are approximately 20%. After compensation for the natural volatilization of CLE the lowest efficiency was recorded for STAR-Ax. (3%) and STAR/BASF (18%). Almost 52% of the original amount of CLE was removed within 7 weeks using N25S. This result is comparable to the reactivity of STAR and STAR-CMC, when approximately 52% of the original amount of CLE was degraded after 13 weeks. The effect of the material containing STAR took place later than N25S, in relation to the gradual removal of the surface stabilized shells of the Fe nanoparticles (0).
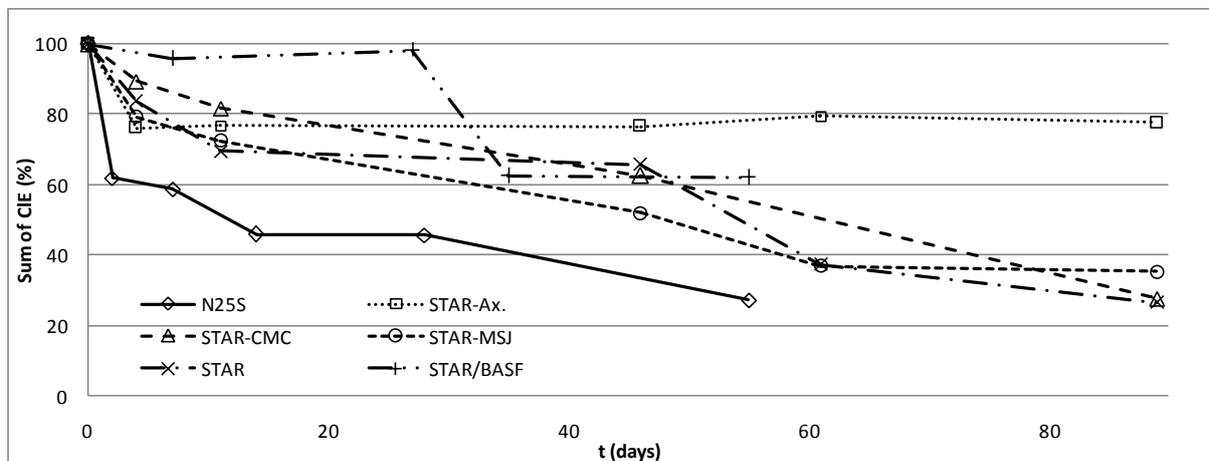

Fig. 2: Comparison of the time dependence of the breakdown of the sum of CLE for each material

Based on the batch test and a comparison of the effects of the suspensions prepared from STAR nZVI in different reaction solutions it is clear that after nearly 13 weeks the suspensions STAR, STAR-CMC and STAR-MSJ removed about the same volumes of CLE as N25S. The resulting efficiency of these nZVI based on the amount of applied Fe is approximately half (for suspensions with nZVI, a 1.6 times greater quantity of nZVI was dosed). The lower reactivity, however, is accompanied by a longer period of time during which the nZVI are reactive, which may be beneficial for certain applications. Typically, the onset of the reactivity due to the breakdown of the oxide shell can be after a week of migration in the rock environment.

Column tests

Four column tests were performed with variously modified nanoiron (see Tab. 1) – the column tests were not performed for nZVI STAR and STAR/BASF, due to their very poor migration properties. The total flow of water in the column tests was set at 11.1 ml/min (5.1 ml/min circulation pump, 6 ml/min dosing pump), whereby the concentration of nZVI at the input to the column was in all cases very similar, i.e. 1.1 – 1.4 mg/l. Tab. 2 shows the overall balance and input concentrations of nZVI for each column, the pore volume determined by drying the entire length of the column and the sand bed (including the input gravel filter) simulating the rock environment. Graphs of the normalized input concentrations of Fe and the corresponding distribution of Fe in the columns after the completion of the column tests are presented Fig. 3.

Table 2: Overall balance of nZVI.

Type of nZVI >>	N25S	STAR-Ax.	STAR-CMC	STAR-MSJ
Fe$_{in}$ (mg/l)	1181 mg/l	1433 mg/l	1164 mg/l	1272 mg/l
Total **Fe on the output** (mg) *(%)*	574 mg *(29 %)*	494 mg *(19 %)*	24 mg *(1 %)*	191 mg *(9 %)*
Total **Fe in the column** (mg) *(%)*	1433 mg *(71 %)*	2084 mg *(81 %)*	1839 mg *(99 %)*	1971 mg *(91 %)*
Length of sand bed (cm)	21.5	21.5	20.5	21.3
Pore volume of the column (ml)	26.3	26.7	21.2	26

As expected, the graph on the left of Fig. 3 shows that N25S nanoiron has the best migration properties, as nanoparticles can be observed on the output of the column practically from the beginning of the experiment. STAR-Ax nanoiron, however, shows very similar behaviour. The behaviour is different for the remaining two STAR nanoiron surface modifications with the migration of particles being significantly slower. For the modified CMC the output Fe concentration is practically zero throughout the experiment, while the output from the column was only 1% of the total injected nZVI (this behaviour corresponds to unmodified STAR and STAR/BASF nZVI). Modified MSJ has a virtually zero Fe concentration output up to approximately one 25th of the pore volume, after which there is a sharp increase in concentration up to 35% of the input concentration. This behaviour indicates the existence of larger particles with good surface stabilization, which migrate through the rock environment slowly but steadily over a longer period of time due to their size. These findings also correspond to the distribution of Fe in the column (see Fig. 3 right) where the nZVI with the best migration has the least Fe in the rock environment and a more uniform distribution.
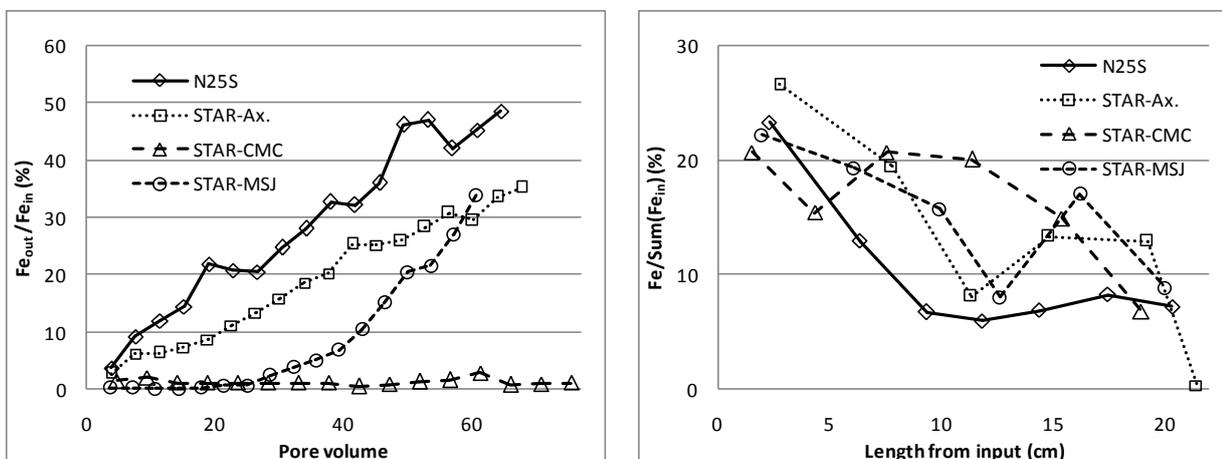

Fig. 3: Left: normalized input concentrations of Fe; right: distribution of Fe in the columns.

CONCLUSION

The results of the tests show that the additional surface stabilization of the suspension with STAR nanoiron, whose surface is coated with an inorganic shell, dramatically affects the migration characteristics in the rock environment. In terms of migration, the best results for surface modification were achieved using Axilát; however, it does not show good reactive properties. The best compromise in terms of the migration and reactive properties appears to be a combination of hydrated alkali metal salts and aliphatic carboxylic acids (abbreviated to MSJ). This still exhibits slightly lower reactivity and migration than the commercial product N25S, but it can be active in the rock environment approximately 2x times longer. This modification may represent a beneficial alternative for certain real-world applications.

ACKNOWLEDGEMENTS

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