NANO-SCALE ZEROVALENT IRON FOR SUBSURFACE REMEDIATION: EXPERIENCES OF DEKONTA

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Abstract

This contribution relates to application of nanoscale zerovalent iron (NZVI) for the subsurface remediation. Results of experiments focused on objective comparison of both migration properties of various types of the NZVI in porous media and reactivity of NZVI with various contaminants are presented. Obtained results indicate that it might be a problem to keep good migration properties of NZVI in porous media together with its high reactivity.

Reactivity of NZVI up to two orders of magnitude higher than reactivity iron particles of normal size (chips, shavings) has been proven. Original design of mixing apparatus for NZVI aqueous suspension preparation and injection into the subsurface was developed and successfully tested.

Furthermore, results of NZVI in-situ application on chlorinated hydrocarbons contaminated site are presented. Chlorinated hydrocarbons concentrations were substantially lowered in groundwater after NZVI injection, however, rebound effect was observed. NZVI application can be recommended as an efficient method for in-situ remediation mainly at less-contaminated sites where source of contamination.

Introduction

The application of nano-scale zerovalent iron (NZVI) represents one of the innovative approaches in the field of subsurface remediation. This method started to be considered, studied and tested a few years ago by several research teams. The principle of the NZVI application consists in a strong reductive potential of the NZVI aqueous suspension which is given by nano-scale dimensions of metallic iron particles. The nano-size of the NZVI particles is expected to provide two main advantages: (1) substantially higher reactivity in comparison with the usual-sized particles of metallic iron (shavings, etc.) and (2) the ability to migrate with water through the subsurface porous environment as a true solution and thus, to react with contaminants in-situ. Despite that such theoretical advantages sound promising, practical experience and experimental results indicate that it is not always simple to achieve it.

Experimental part

The main idea of our migration experiments was to compare the migration properties of the commercially available samples of the NZVI in the highly-permeable model porous matrix and to check the possibilities of improving the migration properties through both addition of the stabilization agents and very fast mixing. The suggested experimental setup reflects an effort for simple but precise measuring which would allow objective evaluation of the migration ability of the NZVI samples including examination of various improving pre-treatment methods and their influence on the migration properties of the NZVI. Thus, measuring can also be understood as an indirect method for the characterization of the NZVI suspensions (from the "applied" point of view).

Samples of the NZVI tested

In this study, we examined the migration properties of the commercially available samples of the NZVI. Although we only want to show our independent experimental results achieved by our methodology (without preference of some supplier), we do not want to present the producers in order to prevent any senses of discrimination or harm.

Particular information about the NZVI samples tested is summarized in Table 1. The particle size information is enclosed in order to provide additional information, since the producers usually present particle size in tens of nanometers. However, the laser diffraction probably detects the created agglomerates, not primary solid particles (which might really have sizes in tens of nanometers).

Table 1: Samples of NZVI aqueous suspensions tested

sample	Fe^0 (% weight) (approximate values)	stabilization	particle size (median, µm)
1	11	water soluble polymer (3 %)	1.6 / 37
2	11	water soluble polymer (3 %)	1.7 / 55
3	17	inorganic modificator + organic stabiliser	3.0 / 48
4	17	inorganic modificator	3.2 / 5

In order to check the possibility of further improvement of the NZVI migration properties, a dose of an additional stabilization agent (carboxy-methyl cellulose, CMC) was tested.

Two mixing methods of the diluted NZVI suspensions before the migration experiments were tested: slow stirrer (~250 rpm) and disperser IKA (~9500 rpm). The particular combinations were chosen during the experiments based on the actual results, they are disclosed in the results part.

Experimental setup

All experiments have been carried out using the same apparatus and under identical conditions which allows a direct comparison of the results achieved by various NZVI suspensions. The experimental apparatus is displayed schematically in Figure 1.

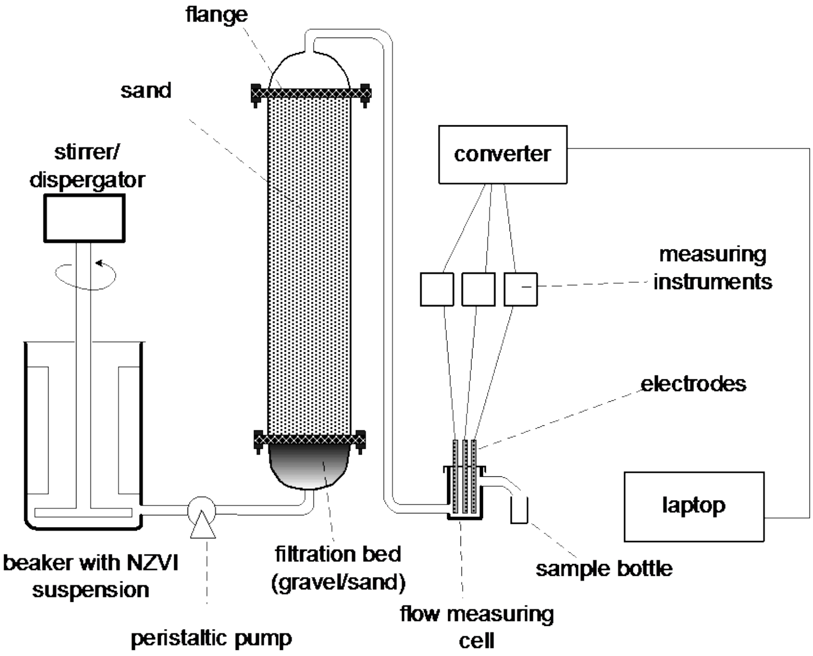

Figure 1: Apparatus for migration experiments (scheme and photo)

Table 2: Several key parameters of the experimental apparatus

apparatus volume (column+tubes+measuring cell)	~530 mL	sand grain size fraction	< 1 mm
pore volume of sand layer	~270 mL	hydraulic permeability	~ 10^{-2} – 10^{-3} m/s
suspension flow rate	40 - 42 mL/min	volume of sand in the layer	~590 mL
solution retention time	10 – 12 min	sand total porosity	40 - 45 %

Results and discussion

In total, about 20 migration experiments have been carried out. Since, the outputs from each of them involve records of effluent pH, ORP and conductivity during the test, mass balance of iron passed through the sand layer and photos, it serves no purpose to display them all. We would like to present two results achieved with the NZVI samples #1 and #2 since the results will demonstrate the differences in the NZVI behavior, although the samples look identical (both optically and from preliminary characterization). The initial concentration of iron in the inlet diluted suspension was 723 and 800 mg/L, respectively. No additives were used and the suspensions were dispersed under 9500 rpm prior to pumping into the column. The results are displayed in Figure 2.

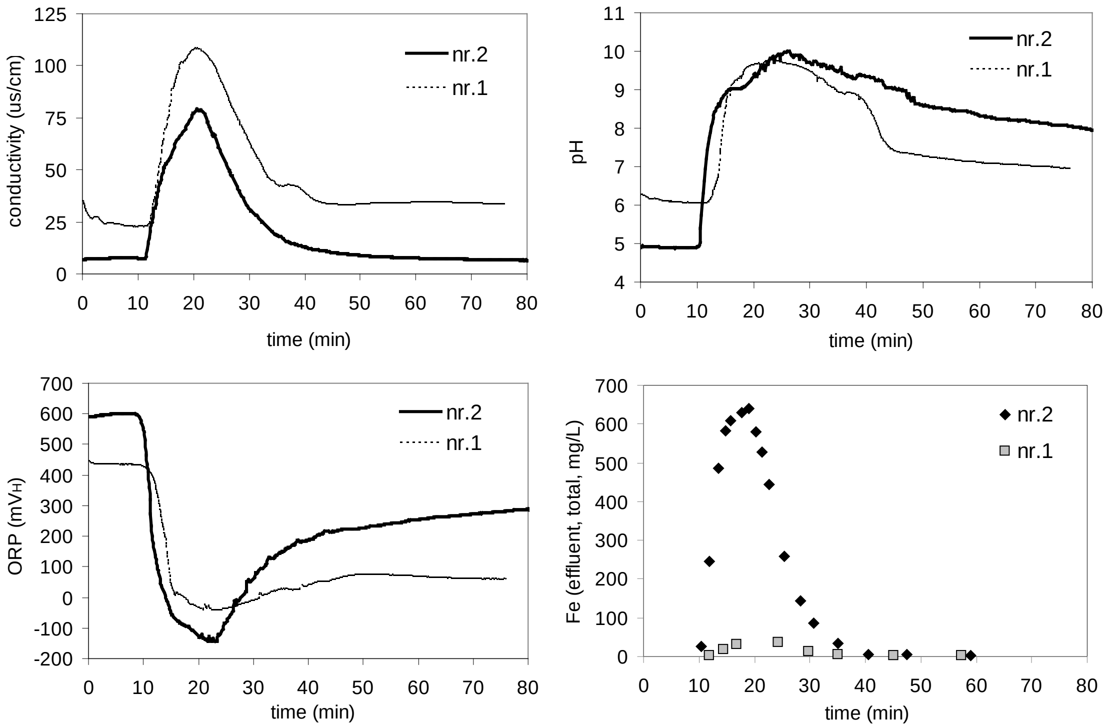

Figure 2: Comparison of results achieved for two samples of NZVI. The graphs represent values in the column effluent during identical migration experiments.

There is a difference in behavior of the two samples (#1 and #2), which is most clear from the concentrations of the iron in the effluent. The peak iron effluent concentration is relatively close to its initial value in the case of suspension #2 (such samples were also black and turbid). On the other hand, the peak concentration of #1’s effluent of only about 30 mg/L was very low. The mass balance difference is even more evident: in the case of #1, only 7 % of the iron passed through the column, while for #2 we achieved migration of 87 %. Migration of 7 % of the iron in case of the #1 implies that only a portion of the iron originally dissolved (ions) in the supplied NZVI product passed through the sand (in addition, the samples of the effluent were optically non-turbid). Finally, we can conclude that the NZVI #2 provides substantially better migration properties than #1.

Looking at the graphs, it might be a bit surprising that a 20 times higher concentration of iron (in addition, the solution was turbid and black) caused only a slightly more efficient decrease of ORP in comparison with #1, however, the higher initial value of the ORP in case of #2 should also be considered in this case. Nevertheless, these results indicate that #2 could provide a relatively lower reactivity in comparison with #1, which was partly confirmed by our reactivity experiments (but this is not a subject of this contribution).

The migration experiments results are simply summarized in Table 3. The most important result is the mass balance of the iron portion which has passed through the column. Although the median value of #2's samples particle size in Table 1 seems to be almost the same as #1, the migration properties differ substantially. This fact promotes our experience with the effort of the NZVI suspensions characterization, where we found out that the interpretation of such characterizations (using various methods) may result in inaccurate conclusions. For example, based on laser diffraction measuring, similar migration properties of #1 and #2 would be expected due to the similar particle size. Thus, the behavior of the NZVI is probably more complicated in reality than during measuring of some available characteristics.

When considering the results, it is very useful to mention what the on-line measured parameters of the initial suspension were before its pumping into the column. The ORP, pH and conductivity in case of NZVI #1 and #2 diluted suspensions before the introduction into the column were approximately: -250 mV, 11 and 600 µS/cm, respectively. For #4 the values were: -200 mV, 9 and 14 µS/cm, respectively, while for #3: -370 mV, 8 and 14 µS/cm. However, the ORPs are only approximate values due to the strong influence, especially by dissolved oxygen content, which is non-defined (it depends, for example, on how fresh the distilled water is, etc.)

The only NZVI which, in our methodology, provided proven migration abilities was #2. At least 90 % of iron passed through the sand, independently on the sample age (within 3 months).

The portion of the iron passed through the column achieved for #1 was, in all cases, about 5 – 8 %, except the tests influenced by preferential pathways (which, however, resulted in an increase of balance only to 20-30 %, which was also unsatisfactory). Thus, the migration abilities of #1 were poor.

Table 3: Summary of the results achieved in the frame of the migration experiments

sample of NZVI (#) (+ additive)	concentration of iron in diluted susp. (mg/L)	mixing (rpm) (9500 – disperser; 250 – stirrer)	lowest effluent ORP achieved (mV_H)	iron passed (%)
0	***1***	***2***	***3***	***4***
1	121	9500	220	7.4
1	723	9500	-40	6.9

0	*1*	*2*	*3*	*4*
1 + CMC (3 g/L)	830	9500	-60	22.8
1 + CMC (3 g/L)	906	250	-210	30.1
1 + CMC (3 g/L)	790	250	0	6.2
1 + CMC (3 g/L)	840	9500	-10	4.9
3	1026	9500	300	< 1
4	776	9500	150	< 1
2	800	9500	-150	87,3
2	795	9500	-120	>95
2	725	9500	100	87.7
2	798	9500	100	87.8
3	1047	9500	120	< 1

as in a frame of three months. Thus, the prospective influence of ageing was checked.

Related to the NZVI #3 and #4, its migration properties looked very poor. In addition, no (or only a very negligible) decrease of effluent ORP was observed, although the initial ORP was minus hundreds mV. It is different behavior than #1, where, despite that almost no migration was observed, the ORP decreased to negative values (except one experiment with a too low NZVI dose). Such results indicate that #1 and #2 samples do not release some reductive species into the water and the decrease of ORP is directly conditioned by the presence of solid (nano)particles, which might be complicated to explain. An explanation of such a behavior would require more research work, but from an applied point of view the results are convincing.

The last thing related to samples #3 and #4 refers to its reactivity. We would like to mention that during our reactivity tests, these samples provided the best results. Such observations suggest that it is not possible to have both migration properties and reactivity at once. In fact, this balance between achievable properties might correspond with theoretical principles: highly-reactive (e.g. non-polar, yet) particles could be expected to agglomerate more than the less-reactive, more polar iron particles (and vice versa).

Results are disclosed in the Table 4.

Table 4: Summary Results of the reactivity tests

sample (#)	Iron capacity (mg/g of product) *(associated with „product weight")* *-Depends on Fe(0) content in sample* *(of NZVI suspension)*	Iron capacity (mg/g) *(associated with pure Fe(0) content)*
1	5.5 - 7.5	35 – 45
2	2 – 4.1	15 – 29.6
3	13 – 18.4	80 – 113.5
4	18.6 – 24.3	80 - 105
Fresh NZVI $NaBH_4$ reduction	120 – 125* * - excess of $NaBH_4$ not removed by decantation	50-60* * - fast ageing during decantation
Iron sawdust (1 – 3 mm)	1-2	1-2

Conclusions

This contribution tried to objectively compare the migration properties of commercially available NZVI suspensions. The main aim was to identify the most migrating type using standardized column experiments.
It was proven that migration through sand provides the sample of NZVI #2, although its laser diffraction has not shown lower particle sizes. Furthermore, the NZVI #3 and #4 provided the worst migration, but on the contrary, their reactivity has been found as the best between the samples examined. Finally, it is important to answer a question what the key desired property is (which property we want to employ in a practical application), because the results indicate that it is a problem to achieve both good migration and high reactivity.

Acknowledgements

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