

Modification of iron nanoparticles for ground water remediation



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Introduction

Since some years, iron nanoparticles (so called nanoscale zero-valent iron, nZVI) have been used to treat ground water and rock environment for the decomposition of chlorinated hydrocarbons, heavy metals, radionuclides and other contaminants.

The method is based on injection of Fe(0) nanoparticles to ground water through drill holes. Due to nanodimensional character and suitable surface stabilization, the injected nanoparticles can migrate through the rock environment, where they induce reduction reactions with pollutants dissolved in the ground water.

It was experimentally confirmed that by this way, it is possible to eliminate or significantly reduce the activity or the content of many toxic substances.

Aims and Concept

This work is a part of the NAPASAN project, which is dedicated to the development of ferrous nanoparticles for the treatment of contaminants. The particles are modified in such a way that transport in the groundwater zone can take place and contact with contaminants can be achieved to ensure degradation.

The tendency of iron nanoparticles to aggregate after getting in contact with the soil and groundwater is the problem to be solved.

Our primal aim within this project is to develop appropriate coatings, starting with synthesized nanoparticles and proceed with milled nanoparticles.

For further information visit the homepage : www.napasan.de

Synthesized Iron Nanoparticles

A method for the formation of iron nanoparticles covered by surface active agents was developed.

The nanoparticles can be coated during their formation process.

The function of this coating is to diminish aggregation / precipitation of the dispersed nanoparticles and also to increase their stability.

Fig. 1 shows a scheme of a nanoscale iron particle covered by a surface active agent.

Some PEG-derivatives and some carboxylic- or phosphonic acids (see Fig. 2) were found to significantly increase the stability of aqueous dispersions from iron nanoparticles.

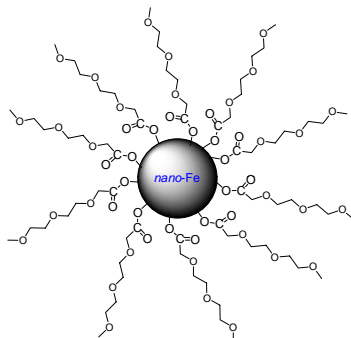


Fig. 1 : Scheme of a nanoscale iron particle covered by Methoxyethoxyethoxyacetic acid (MEEA)

Iron nanoparticles were synthesized by reduction of FeCl₂ with NaBH₄ in ethanol-water solution in the presence of stabilizing molecules (in most cases PEG derivatives, see Fig. 2).

Light scattering particle size measurements showed particle size distributions usually in the range between 20 nm and 250 nm with maximum values between 60nm and 90nm. Particle size distribution and apex sizes are depending on the reaction parameters and on the type and concentration of the used coating molecules (see Fig. 2).

In several cases aqueous nZVI dispersions could be obtained by this method, which were stable up to two weeks in the absence of oxygen or diluted salts.

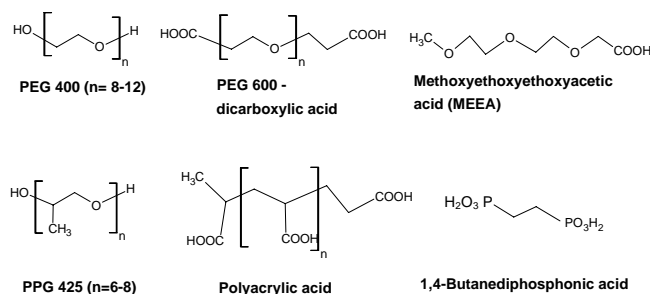


Fig. 2 : Coating molecules which were successfully tested to improve the stability of aqueous nZVI dispersions (inhibition of aggregation of iron nanoparticles)

Milled Iron Nanoparticles

For safety reasons ethanol was an unsuitable solvent for nZVI production by milling (produced at project partner UVR-FIA). Therefore ethylene glycol (EG) was found suitable to dissolve nZVI produced by milling process.

EG-MEEA-nZVI-suspensions are stable over several weeks but once the particles get in to contact with oxygen or salts (e.g. drinking water or ground water) precipitation starts immediately.

Sodium dodecyl sulfate (SDS) was found to give EG-MEEA-nZVI additional stability against precipitation caused by oxygen and salts.

Aggregation of EG-MEEA-nZVI in presence of SDS is inhibited and dispersions in drinking water are stable for several hours (see Fig. 3).



Fig. 3 : SDS-EG-MEEA-nZVI (left) and EG-MEEA-nZVI (right) 30 minutes after addition of drinking water Both samples were stored under nitrogen atmosphere

Measured particle size distributions of several SDS-EG-MEEA-nZVI batches were in between 13–200 nm with an average maximum value of 57nm.

2 hours after adding drinking water (hardness grade ca. 17–21°dH) to a SDS-EG-nZVI-sample a particle size distribution in between 50nm–615nm was measured with a maximum value of 90nm.

The same SDS-EG-nZVI-sample was aerated and decanted into a beaker. 4 hours later the suspension still was existing and 18 hours later the particles were oxidized and precipitated (see Fig. 4).



Fig. 4 : SDS-EG-MEEA-nZVI after aeration. The left image shows the sample 4 hours after aeration and the right image shows the sample after 18 hours aeration

Summary and Outlook

Aggregation of iron nanoparticles can be strongly reduced by adding stabilizing molecules during the formation process. However, the lifetime of the coated

iron nanoparticles is still limited, especially in the presence of air/oxygen or salts (e.g. calcium or magnesium salts in the ground water).