FACT SHEET NANO PRODUCTS

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Umwelt Bundes Amt
Für Mensch und Umwelt

Use of nanoscale iron for the remediation of groundwater damages

1 Description of the area of application

Need for remediation

The applicability of a number of nanomaterials[1] for the remediation of environmental damages is being examined and tested. Preliminary experiences suggest that they allow the better, faster and more cost-efficient remediation of environmental damages. The use of nanoscale iron for the remediation of groundwater damages represents an innovative remediation method. At present, it is still in development in Germany and has only been used in individual cases in the past. For this reason, the experience with this approach is still relatively low.

Groundwater damages can be caused for instance by the inappropriate handling of environmentally hazardous materials, disasters or improper handling and disposal of waste. The so-called pump and treat method was the method of choice for the remediation of groundwater damages in the past. It involves the transport of the contaminated groundwater through remediation wells and the purification in an on-site system.

Alternative solutions have been developed because of the often long remediation times associated with hydraulic remediation methods and the inherent high operating costs. In Germany, they have already been used directly in the underground (in situ) since the 1990s. They include purifying walls that allow the contaminated groundwater to flow through and in which e.g. granular metallic iron is used as environmentally friendly, cost-efficient reduction agent.

Nanoparticles, in which zerovalent iron acts as electron donor for the decontamination process, are jointly referred to as nanoscale iron below. It can occur in different formulations. The differences are mainly the result of the manufacturing process and the combination with other materials.

Mode of action and treatable pollutants

Elementary iron is a powerful reduction agent which oxidises to Fe(II) during the reduction of the reaction partner. Oxides (magnetite, hematite), hydroxides (limonite, goethite), carbonates (such as siderite) and sulfides (such as pyrite) which precipitate can be created in the process.

[1] Nanomaterials consist of definable structural components with a size range of 1 - 100 nanometres (1 nm = 10^{-9} m) in at least one dimension. Nanoparticles are a subset of the nanomaterials and have the size range mentioned above in all three dimensions (see also the recommendation of the commission (2011/696/EU) dated 18/10/2011 concerning the definition of nanomaterials).

Because of its small size and large specific surface, nanoscale iron is 10 to 1000 times more reactive than granular iron. Since nanoscale iron particles readily agglomerate and exhibit strong absorption properties with the soil matrix, they are extremely short-lived and possess a limited reach. To enable the transport of nanoscale iron to the harmful substances in the underground and to help improve the remediation efficiency, it has to be modified. This can be achieved for instance by treating the surface or by coating the particles, by placing nanoscale iron particles onto colloidal (micro)-activated carbon, with emulsification, with hydrophobisation of nanoscale iron by merging it into a mixture of oil and tensid or with the manufacture of stabilised aqueous suspensions.

A broad range of materials can be treated with nanoscale iron. It is mainly used for groundwater damages caused by volatile and not easily volatized chlorinated hydrocarbons. These substances are in part persistent, toxic or carcinogenic. The reaction of nanoscale iron with the chlorinated hydrocarbons achieves their dechlorination.

Conduct of the in situ groundwater remediation

Legal framework and requirements

On an international level, the process of coordinating legally binding regulations with respect to nanotechnology is still in development. ISO[2] and OECD[3] represent the most active forums aimed at advancing uniform testing, evaluation and regulation processes on a global scale. So far, the EU has not been regulating the use of nanoscale iron for groundwater remediation.

In 2011, the NanoKommission of the German Federal Government tabled proposals to regulate the handling of nanomaterials. These proposals are general in nature and are not specifically addressing the environment-related use of nanoscale iron.

In Germany, the remediation of harmful alterations of the soil and hazardous waste at abandoned contaminated sites as well as the pollution of waters caused by harmful alterations of the soil or hazardous waste at abandoned contaminated sites is governed by the Federal Soil Protection Act[4] and the Federal Soil Protection Directive[5]. The competent agency decides whether and how such groundwater contamination should be remediated.

Site-related information and parameters must be available in order to make a decision about the eligibility of an in situ approach for groundwater remediation. With respect to the use of nanoscale iron, they include specifically:

- Geological, hydrogeological and hydrochemical characteristics,

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[2] ISO: International Standards Organisation

[3] OECD: Organisation for Economic Co-operation and Development

[4] Law for the protection against harmful alterations of the soil and the remediation of hazardous waste at abandoned contaminated sites dated 17 March 1998 (Federal Law Gazette I, p. 502), last amended with Article 3 of the law dated 9 December 2004 (Federal Law Gazette I, p. 3214)

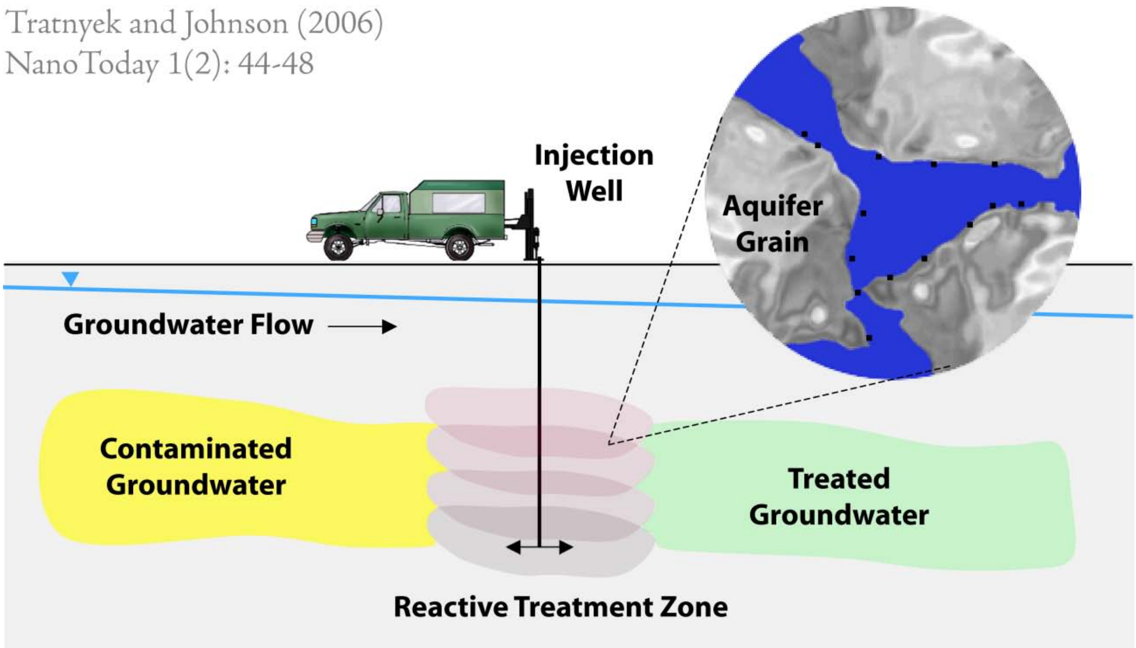
[5] Federal Soil Protection and Hazardous Waste Directive dated 12 July 1999 (Federal Law Gazette I, p. 1554), amended with Article 2 of the Directive dated 23 December 2004 (Federal Law Gazette I, p. 3758).

- Extent and localisation of the pollution sources and highly contaminated sites,
- Nature, concentration, mass and distribution of the pollutants as basis for the determination of the mass of nanoscale iron required to reduce them,
- Factors which determine the mobility of nanoscale iron in the underground, such as composition and properties of the soil matrix, hydraulic properties of the aquifer,
- Environmental conditions and groundwater composition.

Introduction into the saturated soil zone

The use of specially treated, highly-reactive nanoscale iron in the form of an aqueous suspension offers the option of a targeted injection into the underground. The suspension should be introduced into the aquifer such that the nanoscale iron is optimally distributed in the contaminated groundwater and reacts with the pollutants (Figure 1). Among other things, the distances between the injection levels are based on the grain size of the soil matrix and usually range between one and several meters.

Figure 1: Injection of nanoscale iron for groundwater remediation (according to Tratnyek, Johnson, 2006)



The effectiveness of the method is dependent on other criteria (e.g. the properties of the nanoscale iron particles, the quantity of pollutants present at the injection site, the composition and properties of the suspension as well as the hydrogeological and hydrochemical properties of the site).

So far, no mobilisation of the pollutants and displacement into other media has been observed after the injection. As well, there was no evidence for an accumulation of chlorinated decomposition products due to incomplete decomposition of chlorinated hydrocarbons. Under suitable framework conditions, the groundwater remediation with nanoscale iron can achieve a considerably greater effectiveness within a significantly shorter period of time compared to traditional methods and have a positive effect on the remediation costs.

Control and monitoring of the remediation

The remediation process is controlled at representative groundwater measuring points (monitoring wells). The decomposition of pollutants can be demonstrated by monitoring a variety of parameters. Specifically, this includes the change in nature and quantity of the decomposition products. If a relevant residual contamination of the underground remains after the remediation, the sustainability of the remediation outcome should be monitored.

2 Environmental behaviour and environmental impact

Behaviour in the soil and groundwater

In the literature, the mobility of untreated nanoscale iron in the saturated soil zone is estimated to be low because of its poor dispersing ability, rapid agglomeration/aggregation as well as adsorption on the soil matrix. Nanoscale iron which was modified to improve the remediation efficiency possesses a higher stability and greater mobility.

Once treated nanoscale iron reacts with the groundwater, the pollutants and other contents, it loses its reactivity after several weeks. It is oxidized and precipitates as iron hydroxide (rust) and iron oxide. Iron occurs naturally in the majority of soil types (in the form of hydroxides, oxides and sulfides) as well as in groundwater. The iron concentration of the suspension only results in a local increase of the natural iron content. Insofar, we consider the incorporation of nanoscale iron as being unproblematic. However, an undesirable effect is induced if agglomerated nanoparticles obstruct the pores of the soil matrix, thus preventing the contaminated groundwater from flowing through.

Whether the use of nanoscale iron for the in situ remediation actually does induce environmental risks can only be assessed tentatively. No validated analytical methods are yet available to detect nanoscale iron separately from naturally occurring iron. For this reason, the behaviour and persistence of technically engineered nanoscale iron in the environment cannot be monitored conclusively.

Ecotoxicology

Only a limited number of studies have been conducted so far to investigate the ecological effects of nanoscale iron and nanoscale iron oxide[6]. In the past, the main focus was on the examination of harmful effects on microorganisms. In the bacterium *Escherichia coli*, nanoscale iron can induce dose-dependent cytotoxic effects. Recent studies examining the influence of nanoscale iron on the population density, composition and biochemical activities of microbial communities did not reveal any harmful effects. As well, no inhibition of the bioluminescence and biogas production of bacteria by nanoscale iron oxide has been demonstrated.

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In experiments with Japanese rice fish (*Oryzias latipes*) embryos and adults, nanoscale iron caused an impairment of the defence system used to reduce oxidative stress. Histopathological alterations were observed on the gills and in the intestine. Furthermore, an additional study demonstrated that nanoscale iron can have a lethal effect on the sperm of mussels. This effect increased when nanoscale iron was stabilised with a polyacrylate coat.

Even though the available data stock is limited, we consider the likelihood low that nanoscale iron spreads to aboveground bodies of water after being introduced into the contaminated groundwater, thus resulting in an exposure to effect-relevant levels of aquatic organisms such as invertebrates or fishes. Due to the short lifetime of nanoscale iron, we consider the risk of an impact on aboveground bodies of water via groundwater pathway and hence the potential damage of water organisms residing there as being low.

In the highly unlikely event of exposure via exposure pathway groundwater to aboveground bodies of water, sediment organisms would also have to be included in the ecotoxicological evaluation of nanoscale iron. As long as no ecotoxicological data on the potential effect of nanoscale iron on sediment organisms is available, we discourage the in situ remediation of contaminated sediments with nanoscale iron.

It is difficult to assess the relevance of the ecotoxicological findings, because it is hard to bring the exposure levels examined in the studies into perspective with the nanoscale iron quantities injected at the remediation site. Due to the lack of experience with nanoscale iron materials, it is impossible to predict whether a relevant exposure of the organisms is taking place.

So far, information about the environmental long-term effects is scarce. On the basis of available studies, we consider the acute ecological harm as being low. The ecotoxicological relevance of nanoscale iron and nanoscale iron oxides should be contrasted and evaluated with the expected benefit for the environment achieved with the remediation of groundwater damages.

3 Health-related aspects

In the past, not much attention has been paid to the possible absorption of nanoscale iron and nanoscale iron oxide particles in the human body. The influence of the particle shape and size on the toxicity of nanoscale iron oxide particles is less significant than the chemical composition of the particles in the cover (e.g. iron oxide) and the core (e.g. elementary iron). The coating of nanoscale iron oxide particles e.g. with silicate or dextran can further reduce their acute or subacute toxicity.

On inhalation, the target organ for harmful effects is predominantly the lung. Even a short inhalative absorption of moderate particle concentrations can induce effects involving the lung. Moreover, effects indicating inflammatory foci in the organism have been observed.

Due to its basic properties (pH value = 11), the aqueous nanoscale iron suspension can have an irritating effect on the eyes and skin. For this reason and because of the high reactivity of nanoscale iron, the respective latest material safety data sheets as well as other special safety instructions must be observed when transporting and handling the material.

The risk of direct exposure of humans is extremely low if the nanoscale iron suspension is handled properly before and after the introduction into the aquifer, if the dosing is appropriate and based on the properties of nanoscale iron.

4 Conclusion

The experience relating to the behaviour and effect of nanoscale iron in the environment is still limited. After evaluating the available information, the Federal Environment Agency believes that the use of nanoscale iron for the remediation of groundwater damages does not pose a relevant nano-specific risk. No relevant acute harmful effects on the living environment induced by the use of nanoscale iron are expected. However, nanoscale iron preparations may potentially contain harmful substances as blending components.

The environmental compatibility of nanomaterials is a crucial aspect for the Federal Environment Agency when evaluating the benefits and risks of this new technology. This is especially true if nanomaterials are specifically released into the environment, such as is the case with in situ groundwater remediation.

In principle, any new applications should be examined extensively based on individual case tests in accordance with the precautionary principle, before making a decision on their general introduction into the practice. A concern can only be excluded or at least reduced to a reasonable extent by means of a comprehensive risk assessment. With respect to the current lack of information, precautions are necessary to ensure that nanoscale iron and its reaction products are not expanding beyond the localized application site in connection with groundwater remediations and in particular that they do not reach other aquifers.

We recommend the development of special methods for measurement and analysis which allow a better risk assessment and monitoring of the procedure. The use of nanoscale iron for groundwater remediation should be monitored and the sustainability of the remediation outcome ensured.

Furthermore, in situ remediation procedures should be compared with established remediation procedures in terms of their effectiveness as well as in terms of their potential to relieve the environment. In so doing, the method-related use of energy and raw materials, produced waste, emission of environmentally hazardous substances as well as possible negative impacts on other subjects of protection, affected third parties and future uses should also be taken into account. The Federal Environment Agency will continue to track the development of products containing nanoscale iron and which are used for remediation purposes.

The information exchange between researchers, product developers, remediation experts and decision makers should continue, including for the sake of nature conservation.

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P.O. Box 14 06
06813 Dessau-Roßlau
Ph.: 0340/2103-0
Fax: 0340/2103 2285
E-mail: info@umweltbundesamt.de
Internet: http://www.umweltbundesamt.de

Authors: The fact sheet was compiled by the "Nanotechnology" working team of the Federal Environment Agency. Notably, the following persons have contributed:

Petra Apel (II 1.2 – Toxicology, Health-related Environmental Monitoring)
Dr. Heidi Becker (II 1.2 – Toxicology, Health-related Environmental Monitoring)
Dr. Wolfgang Dubbert (III 2.1 – General Aspects, Chemical Industry, Combustion Plants)
Barbara Kabardin (II 2.6 – Soil Protection Measures)
Dr. Bettina Rechenberg (III 2 – Sustainable Production, Resource Conversation and Material Cycles)
Dr. Katrin Schwirn (IV 2.2 – Pharmaceuticals, Washing and Cleaning Aspects, Nanomaterials)
Dr. Doris Völker (IV 2.2 – Pharmaceuticals, Washing and Cleaning Aspects, Nanomaterials)
Christine Winde (III 2.5 – Monitoring Methods, Waste Water Management)