

Reactivity of nanoscale zero-valent iron particles used for *in situ* groundwater remediation

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Nanoscale zero-valent iron (nZVI) is a powerful reducing agent and has therefore been proposed as a tool for *in situ* groundwater remediation [1]. It has a high potential for transformation of a broad range of contaminants, including chlorinated solvents, redox active toxic metals/metalloids and radionuclides, chemical warfare agents, and pharmaceuticals [2,3,4]. The effectiveness of this remediation technique depends on the reactivity of nZVI particles, which is influenced e.g., by particle properties, hydrochemical conditions, and nature of the contaminants.

The aim of this study is to investigate the reactivity of two commercially available nZVI using iopromide in batch and column reactors under pH values typically found in groundwater (pH 7 and 8). Iopromide is a halogenated X-ray contrast media and serves as a model contaminant.

The investigated nZVI included polyelectrolyte-coated nZVI and non-coated nZVI, both in aqueous suspension (NANOIRON s.r.o., Czech Republic). All experiments were carried out under anoxic conditions with the same molar ratio of Fe⁰ and iopromide.

First results show that the degradation of iopromide with both nZVI studied follows a pseudo-first order kinetics. Non-coated nZVI appeared to be more reactive. Both types of nZVI were able to fully degrade iopromide in nearly ten minutes under the applied laboratory conditions. The surface area normalized reaction rate constant (K_{SA}) depends on the pH value and the type of nZVI. The non-coated nZVI reacted 2–3 times faster than the polyelectrolyte-coated nZVI. At the pH of 7 the K_{SA} increases from 330 L m⁻² h⁻¹ for coated nZVI to 940 L m⁻² h⁻¹ for non-coated nZVI. At a pH value of 8 the K_{SA} values are 3–4 times lower, varying from 110 L m⁻² h⁻¹ for coated nZVI to 240 L m⁻² h⁻¹ for non-coated nZVI.

Further experiments will be conducted in column reactors under similar hydrochemical conditions and iopromide concentrations in order to simulate the nZVI-mediated iopromide reduction in groundwater and to compare the reaction rate constants with these obtained in batch reactors.

[1] Karn *et al.* (2009): *Envir. Health Perspect.* 117, 1823–1831. [2] Zboril *et al.* (2012): *Hazard. Mater.* (211–212), 126–130. [3] Zhang, W. (2003): *J. Nanopart. Res.* 5, 323–332. [4] Stieber *et al.* (2011): *ES&T* 45 (11), 4944–4950.

Alpine metamorphism of the Pan-African gneiss basement in the Menderes/Çine massif, SW Turkey, revealed by garnet Lu-Hf geochronology

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The Menderes Massif is one of the large Alpine metamorphic complexes of Turkey. Its southern part, precisely the Çine submassif, is described as a high-grade gneissic core of Precambrian basement covered by a lower-grade series of Paleozoic schists and Cenozoic-Mesozoic marbles. The geochronology of the gneiss basement in this complex so far highly depends on U-Pb ages of zircons, which yield protolith ages between 560 to 540 Ma. Its metamorphic period has been constrained at Alpine ages between 63 and 25 Ma using Ar/Ar and Rb-Sr geochronology. However garnet, one of the most abundant minerals in schists of this region, has yet to be the focus of geochronological work. Here we present the first Lu-Hf ages of garnet crystals from garnet-biotite schists of the southern margin of the Çine submassif. Lu-Hf analysis have been performed on 4–6 cm sized euhedral garnet crystals by the use of a micro-sampling technique, which permits the analysis of the isotopic composition of cores and rims of garnets, and a set number of intermediate radii. Different zones of these garnet crystals were recognized based on trace element distributions in core to rim profiles. The Lu-Hf results so far reveal at least two events, i.e. the beginning of garnet growth represented by a garnet core age of ca. 60 Ma, and an age of ca. 40 to 38 Ma at an intermediate radius of the garnet crystal ($r \sim 50\%$), which also corresponds to a pronounced change in the distribution of heavy to medium rare earth elements. The Fe, Mg, Mn and Ca as well as the heavy rare earth element distributions in the garnet crystals indicate the preservation of a classical growth zoning pattern, i.e. bell-shaped Mn, constant decrease in Fe/(Fe+Mg), and HREE enrichment in garnet cores. Therefore it is clear that the Lu-Hf analysis yield growth ages rather than retrograde overprinting, hence the evidence for the Alpine metamorphism of the Çine submassif.