Abstract. Two novel materials have been developed and tested in initial studies for the \textit{in-situ} generation of sorption and sorption/reaction barriers for subsurface water treatment. With stable colloidal suspensions of activated carbon, an approved material of environmental technology is now applicable for injection into contaminated aquifers to form sorption barriers by controlled deposition on aquifer sediment directly in the flow passages. Based on these colloidal carbon particles, a second material has been developed which combines the sorption properties of the activated carbon carrier and the reactivity of the zero-valent iron deposits. This CARBO-IRON (20 wt-% zero-valent iron) proved its suitability as a dehalogenation reagent applicable for plume and source treatment.

During the last decade, intensive research has been carried out on the development of suitable materials for reactive barriers in subsurface application. In the usual approaches of this type for groundwater treatment, granular activated carbon (AC) is used as sorbent in reactors or permeable barriers. Another substance often applied in environmental technology is zero-valent iron (ZVI), which has been used in permeable reactive barriers for the remediation of groundwater contaminated with halogenated organic compounds (HOC) or heavy metals. Iron walls have already been constructed at more than 100 sites worldwide. Recently, the application of nano-sized particles has been advanced, because colloidal solutions of metal particles can easily be injected into the aquifer without the necessity of extensive underground work. Nano-sized metal particles have an additional advantage: their high surface-to-mass ratio allows very high reaction rates. However, pure nano-sized ZVI is not sufficiently mobile under aquifer conditions and is not well suited for source remediation.

Therefore, we decided to follow two alternative approaches. The goal is the \textit{in-situ} construction of treatment barriers at low cost by introducing sorbents or reagents via injection wells. Both approaches are based on finely-ground AC with a particle size of $D_{50} = 0.8 \, \mu m$ which is quasi-soluble, i.e. it forms stable colloidal solutions in water over a wide concentration range. With this agent a new remediation strategy can be followed – the \textit{in-situ} generation of a permeable AC sorption barrier in contaminated aquifers. A key property of \textit{in-situ} reagents is their mobility inside the aquifer. By adjusting to an optimum mobility the number of injections necessary for constructing a continuous treatment zone can be reduced. From the colloid filtration theory it is known that aquifer particles in the lower micrometer-scale have higher mobilities than those in the nanometer-scale. The characteristic curve of the so-called ‘single-collector-efficiency’ over the particle size has a minimum at around one to two micrometers, which is the same size range we chose for the colloidal AC particles. Laboratory and scale-up studies were carried out in order to investigate mobility and deposition characteristics of flushed-in colloidal AC suspensions into fixed beds of original aquifer material.
The experimental results showed that the colloids become less mobile with increasing ionic strength. In the presence of cations the electrostatic repulsion between the negatively charged surfaces of the mineral grains and the colloids is lower. The increase in the ionic strength of the solution also diminishes the electrostatic repulsion between the carbon colloids themselves, so that their agglomeration is favoured. The transport behaviour of AC colloids in the aquifer can widely be controlled, e.g. by variation of the ionic strength of the water. The construction of the barrier in the aquifer could be performed by injection of a suspension of colloidal AC in deionised water. The colloids are transported by the groundwater flow. Due to certain dissolution of aquifer material and spontaneous mixing with the saline groundwater in the border zones, the AC colloids are immobilised on the aquifer sediment, resulting in an aquifer zone enriched with activated carbon in the preferred groundwater flow passages – an effective sorption barrier. The sorption capacity of such a barrier can be increased by means of further injections of AC and can therefore be adapted e.g. to changes in the contaminant concentration of the groundwater or to prolonged periods of use.

However, AC can only create a sorption barrier. The second aim of our research is to expand the idea of the *in situ* flushed-in sorption barrier in the direction of a reactive sorption barrier. We gave the colloidal carbon material additional reactivity by impregnating it with iron salts followed by reduction at elevated temperatures with hydrogen. The procedure results in activated carbon with ZVI nano-clusters. We call this new composite material CARBO-IRON. With this reagent a new remediation strategy can be followed – the *in-situ* generation of a permeable sorption/reaction barrier in contaminated aquifers.

It could be shown that by modification of the AC with Fe not only the full sorption activity of the sorbent could be preserved; in addition, it could be shown in laboratory experiments that the sorbed pollutants are available at the Fe clusters and crystallites for reductive dechlorination. CARBO-IRON (20 wt-% ZVI) proved its dehalogenation activity for chlorinated and brominated C₁ and C₂ hydrocarbons in aqueous solution. Furthermore, the hydrophobic nature of CARBO-IRON permits its distribution in NAPL phases where dehalogenation can be performed without the application of additives. The surface properties of these novel bi-functional colloids are essential for their possible utilization in plume *and* source treatment - conventional ZVI does not have these properties, which can otherwise only be provided by expensive chemical additives (such as surfactants). Lifetimes of the material in the order of several weeks have already been achieved in laboratory studies. It is worthy of mention that CARBO-IRON showed similar activities in batch and column tests, indicating accumulation and successive supply of pollutant by the carrier.