Sulfidation of nZVI Particles for Improved Performance in Groundwater Treatment Technologies: Laboratory versus Field Experiences

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Background. Over the past 15 years zero-valent iron nanoparticles have been used for reductive in situ groundwater remediation contaminated primarily with chlorinated hydrocarbons, hexavalent chromium, other organic substances and potentially risk elements. The success of the decontamination processes is significantly related to: i) ability of nZVI particles to migrate within groundwater at the treated site, and ii) the rate of nZVI reaction with targeted compound(s) (i.e., related mainly to the selectivity of nZVI eliminating unwanted side-reactions). Therefore, many researchers are focusing on the improvement of nanoparticles through surfactants, various chemical modifications and development of a broad range of nanocomposites where nZVI particles are deposited on inorganic substrates (carbon black, clay minerals, nanoscale TiO_2, etc.) in order to enhance product properties and prolong storage time and application effect. Out of many different approaches to enhance above-mentioned aspects of nZVI functionality, the chemical modification of nZVI particles by sulfur turned out recently to be technologically simple, cheap and environmentally acceptable.

Approach. In this study, the preparation and applicability of sulfidated nZVI particles will be summarized and improved reactivity/migration of sulfidated nZVI will be demonstrated on laboratory-scale experiments, as well as on results from field-scale pilot tests. The key characteristics of modified nZVI particles were evaluated by robust combination of XRD, XPS, HR-TEM with elemental mapping, ^{57}Fe Mössbauer spectroscopy, SQUID magnetometry, and by BET surface area and Zeta-potential measurement. Mobility was tested in 1D geometry (glass columns filled with quartz sand), along with monitoring of toxicity, evaluation of long-term stability and characterization of oxidation products. Subsequently, reactivity tests were designed for removal of CHC and CrVI from model solutions and from real contaminated water. The validity of experimental observations was then verified in field-scale pilot treatment of locality with aquifer contaminated by mixture of PCE, TCE (as a main contaminant) and DCE where non-sulfidized nZVI was used as a reference.

Results. Generally, results from all experiments proved independently good migration ability, high selectivity towards TCE degradation and increase of long-term stability of sulfidized-nZVI suspension (both in laboratory-scale testing and in pilot-scale verification). Moreover, sulfidation process does not significantly alter the key characteristics of nZVI particles (metallic iron content, particle size and other physical parameters). The suggested modification method (i.e., surface sulfidation of pre-formed nZVI particles) turned out to be highly-promising and inexpensive way how to significantly enhance nZVI performance in technologies of groundwater treatment.