

Carbon Isotopic Fractionation by Zero-Valent Iron: Influence of Surface Pre-treatment

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Reductive dechlorination of dissolved chlorinated ethenes by zero-valent iron metal has been of great interest to contaminant hydrogeology in recent years. Numerous studies have been carried out with the goal of understanding the mechanisms of reductive dechlorination of chlorinated hydrocarbons by zero valent iron and monitoring the extent to which dechlorination has occurred in the field. Much of this research has focused on the iron surface and the role of surface oxides in the reaction mechanism.

This study investigated the stable carbon isotopic behaviour of trichloroethylene (TCE) during reductive dechlorination of TCE by electrolytic iron and Peerless cast iron. In order to assess the influence of surface oxides on the isotopic fractionation during reductive dechlorination, both types of iron were pre-treated by either acid washing to remove surface oxides or autoclaving to increase surface oxidation. Strong isotopic fractionation of the residual TCE pool was observed in all experiments. This isotopic fractionation could be modelled with a Rayleigh model. Significant variation in isotopic fractionation was observed between acid washed and autoclaved electrolytic iron, whereas isotopic fractionation by cast iron was not significantly affected by surface pre-treatment. For experiments involving Peerless cast iron (acid washed and autoclaved) the enrichment factors were reproducible with a mean enrichment factor of -16.2 ± 1.0 permil. In contrast, the enrichment factors

for the electrolytic iron were -22.6 ± 3.2 permil for the acid washed iron and -18.0 ± 1.0 permil for the autoclaved irons. This contrast in isotopic behaviour of the electrolytic iron suggests that the presence of oxides on the surface of the electrolytic iron is significantly influencing isotopic fractionation. The enrichment factors of the autoclaved electrolytic iron are very similar to those of the cast irons. The mean enrichment factor for all experiments involving cast iron (acid washed and autoclaved) and autoclaved electrolytic iron is -16.9 ± 0.8 permil. This suggests that the energetics of reductive dechlorination of autoclaved electrolytic iron are similar to those of cast iron. This similarity in isotopic behaviour may be related to the presence of surface oxides and/or impurities affecting the energetics of the reductive dechlorination reaction.

The observation of a reproducible isotopic enrichment factor for all the cast iron and autoclaved electrolytic experiments suggests that this enrichment factor of -16.7 ± 0.8 permil may be a useful tool to monitor the extent of dechlorination of TCE by iron wall remediation schemes. This is supported by the observation that isotopic fractionation during reductive dechlorination in a column study using Connelly cast iron followed a Rayleigh curve with an enrichment factor of -16.9 permil. Using this mean enrichment factor and the change in isotopic composition of the TCE between two sampling points, it may be possible to monitor the extent of TCE degradation at a field site.