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Arsenic speciation and transfer through basaltic glass

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Dissolution of arsenic from volcanic rocks can be a considerable problem in high temperature geothermal systems. Central volcanoes are often composed of poorly chrystalline pyroclastic rocks with relatively high dissolution rates. The combined effects of high temperature and unstable mineral lattice of the pyroclastic rocks can lead to elevated arsenic levels in geothermal water. The mobility of arsenic is primarily controlled by the speciation of arsenic, the surface characteristics of the aquifer particles and saturation state of As-minerals. The aim of this research was to predict As (III and V) movement within groundwater aquifers in volcanic regions. To this end, batch kinetic and isotherm studies were carried out in conjunction with dynamic column experiments.

Batch studies were carried out by shaking arsenic solution of known speciation with basaltic glass up to 24 hours. Samples were centrifuged after equilibration time and the As speciation of supernatant measured immediately using FIA-HG-AAS. Column studies were carried out by injecting four pore volumes of As solution onto a equilibrated basaltic glass column. Arsenic (III) in outlet solution was measured continuously by HG-AAS while samples for total As analysis were sampled by autosampler followed by analysis in HG-AAS. A conservative tracer as well as pH and Eh of outlet solution were monitored continuously. All experiments were carried out at with N2 purged solution at pH 3, 6.3, 8, 9 and 10 and constant ionic strength (0.01 M). The material was Stapafell basaltic glass (125-250 μm) from Iceland.

For all pH treatments (exept pH 6.3 treatment) sorption sites were saturated of As(III) within eight hours with less than 40% As(III) sorption. Sorption sites were saturated of As(V) within eight hours at pH 3, 9 and 10 whereas adsorption was not completed at the end of experiment at pH 6.3 and 8. Total sorption of As(V) in kinetic experiments increased with decreasing pH.

Adsorption isotherm data were analysed using Freundlich and Langmuir adsorption expressions. The maximum adsorption of As(III) was calculated as 0,084 mg g^{-1} and 0.0127 mg g^{-1} by Freundlich and Langmuir isotherms respectively at pH 8. The maximum adsorption of As(V) was calculated as 0.46 mg g^{-1} and 0.40 mg g^{-1} by Freundlich and Langmuir isotherms respectively at pH 3 but sorption was not observed at pH 10.

Column experiments give a measurement of species retention and sorption in a dynamic environment. Arsenic (III) showed highest retention at pH 9 followed by 10 then $8 \approx 6.3$ and at pH 3 the retention was limited. The opposite was true for As(V) where retention and adsorption increased from pH 10 to 8 but As(V) was nearly all sorbed at pH 6.3 and 3 so retention could not be estimated accurately. Arsenic (III) desorbed slower than As(V) at all pH's.

The overall conclusion of this research is that As(III) was mobile in contact with basaltic glass at pH 3 but less so as pH increased to 10. The opposite was true for As(V) where the mobility was highest at pH 10 whereas As(V) was almost entirely sorbed below pH 6.3.