A field and reactive transport model study of arsenic in a basaltic rock aquifer

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ABSTRACT

The use of geothermal energy as a source for electricity and district heating has increased over recent decades. Dissolved As can be an important constituent of the geothermal fluids brought to the Earth's surface. Here the field application of laboratory measured adsorption coefficients of aqueous As species on basaltic glass surfaces is discussed. The mobility of As species in the basaltic aquifer in the Nesjavellir geothermal system, Iceland was modelled by the one-dimensional (1D) reactive transport model PHRE-EQC ver. 2, constrained by a long time series of field measurements with the chemical composition of geothermal effluent fluids, pH, Eh and, occasionally, Fe- and As-dissolved species measurements. Di-, tri- and tetrathioarsenic species (As(OH)2− S2−, As2H4, As3− S2− and As(SH)2−) were the dominant form of dissolved As in geothermal waters exiting the power plant (2.556 μm total As) but converted to some extent to arsenite (H3AsO3) and arsenate (HAsO2−) oxyanions coinciding with rapid oxidation of S2− to SO4−2 and finally to SO4−2 during surface runoff before feeding into a basaltic lava field with a total As concentration of 0.882 μm following dilution with other surface waters.

A continuous 25-a data set monitoring groundwater chemistry along a cross section of warm springs on the Lake Thingvallavatn shoreline allowed calibration of the 1D model. Furthermore, a series of ground water wells located in the basaltic lava field, provided access along the line of flow of the geothermal effluent waters towards the lake. The conservative ion Cl− moved through the basaltic lava field (4100 m) in less than 10 a but As was retarded considerably due to surface reactions and has entered a groundwater well 850 m downstream in accordance to the prediction of the 1D model.

The 1D model predicted a complete breakthrough of arsenate in the year 2100. In a reduced system arsenate is not retained for about 1 ka.

1. Introduction

Geothermal areas frequently produce spring and stream waters with elevated As concentrations (Webster and Nordstrom, 2003). Utilisation of geothermal areas can increase the discharge of geothermal waters towards the surface with associated As and metal contamination (Olafsson, 1992; Baba and Armannsson, 2006; Gallup, 2007; Aksoy et al., 2009). Re-injection of spent geothermal fluids to deep aquifers is rapidly increasing around the world and is recommended as the standard procedure to avoid adverse impacts of geothermal utilisation (Baba and Armannsson, 2006).

Arsenic is believed to primarily enter crustal fluids during crystallising of deep plutons as hot volatile-rich magmatic fluids escape from the plutons and segregate into vapour and brine resulting in the formation of porphyry-style and epithermal ore deposits and fumarole activity in volcanic areas (Goldschmidt, 1954; Ballantyne and Moore, 1988). Arsenic concentrations in volcanic gases sampled between 400 and 900 °C often range between 1 and 10 ppm of the vapour condensates (Mambo et al., 1991) corresponding to As enrichment in the gas phase between 100 and 1000 with respect to the magma body suggesting an important transfer of As into the hydrosphere and atmosphere during magma degassing and volcanic eruptions (Pokrovski et al., 2002). Arsenic preferentially concentrates into the liquid aqueous phase in water dominated active hydrothermal systems below 350 °C (Ballantyne and Moore, 1988). Arsenic mainly occurs as As(III) hydrosilicate, primarily as As(OH)3 aqueous species and to lesser extent, the sulfide H4AsS4−, AsS3− S3− and to lesser extent, the sulfide H4AsS4− species in natural hydrothermal solutions depending on temperature, pH and H2S content (Akinfiev et al., 1992; Helz et al., 1995; Pokrovski et al., 1996). According to dissolution experiments, As occurs to a large extent in a soluble form in intermediate and silicic volcanics in New Zealand, probably as salts on mineral grain surfaces (Ellis and Mahon, 1964). The ratio of As to Cl in solution in deep aquifers in Iceland is similar to that of tholeiitic basalts indicating the As may be leached congruently from the rock surfaces as meteoric water reacts with those rocks in high-temperature geothermal systems (Giroud, 2009) or at lower depths in colder environments (Arnorsson, 2003).

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Arsenic has been reported to be highly mobile in shallow ground waters up to 90 °C in basaltic terrain (Arnorsson, 2003), however it may not be considered as conservative as Cl⁻ and B in hydrothermal solutions in Iceland (Giroud, 2009). It may be incorporated into secondary sulfide minerals such as pyrite (FeS₂), realgar (As₂S₃) and orpiment (As₂S₅) (Cleverley et al., 2003) depending on H₂S(aq) concentrations. As the hydrothermal solutions rise towards the surface and mix with cold ground waters at shallow levels the As may be effectively removed from the solution by coprecipitation with or adsorption onto ferric hydroxides (Giroud, 2009; Arnorsson, 2003) or sorbed on basaltic glass surfaces (Sigfusson et al., 2008).

Hydrothermal fluids may rise towards the surface with limited interaction with cold ground waters, either naturally in the form of springs and fumaroles or through discharging boreholes utilised for geothermal power production. Recent advances in analytical techniques have made possible direct determination of thioarsenic species in geothermal waters either in the field (this study) or in the laboratory after preservation (Wallschlager and Roehl, 2001; Stauder et al., 2005; Planer-Friedrich et al., 2007). Planer-Friedrich...
et al. (2007) found that as the discharged waters from a sulfidic hot spring flowed on the surface, thioarsenates preferably transformed into arsenite with less thioarsenates transforming stepwise by ligand exchange to arsenate and finally the arsenite oxidised to arsenate as all thioarsenates and H$_2$S had disappeared.

From chromatographic methods, the As contained in alkaline sulfidic solutions can occur either mainly as thioarsenate or thioarsenite (Wilkin et al., 2003; Stauder et al., 2005; Planer-Friedrich et al., 2007), however, Beak et al. (2008) have pointed out that the chromatographic methods cannot independently determine the oxidation state of As and peaks generated by thioarsenates may also be explained by thioarsenite species. In any case, the thioarsenic species, incorporating the As in either oxidation state, break down under oxidised conditions at the surface in a series of kinetically controlled reactions (Planer-Friedrich et al., 2007). Therefore, the chemical composition of the water and the reaction time at the Earth’s surface determine the As speciation in the geothermal water once it runs on the surface or seeps back into the bedrock. An accurate quantification of the individual species may as a consequence, be detrimental for As transport prediction by geochemical modelling.

The transport of As in shallow groundwater aquifers has been studied extensively due to its toxicity, e.g. Charlet et al. (2007). The reduced form of As, arsenite (As(III)) is generally considered more toxic than the oxidised form, arsenate (As(V)) (Ferguson and Gavis, 1972). The harmfulness of arsenite is based on its reaction with SH-groups of proteins (Squibb and Fowler, 1983) and, therefore, Stauder et al. (2005) suggested the toxicity of As could be decreased by formation of thioarsenates (addition of SH-groups to As) from arsenite in sulfidic environments. The mobility of these As species depends on the chemical characteristics of the species themselves as well as the surface properties of the aquifer matrix. The surface of the aquifer in this contribution is primarily composed of basaltic glass. Sigfusson et al. (2008) measured sorption processes of arsenite and arsenate on basaltic glass and reported decreasing mobility of arsenite as pH increased from 3 to 10 whereas arsenate was immobile at pH 3 and highly mobile at pH 10. Stauder et al. (2005) predicted that thioarsenates should be less mobile than arsenite and arsenate on soil materials such as pyrite and goethite due to the shift from a neutral to weak anionic form to a strong anionic As complex as a result of thioarsenates. This would be the case under acidic conditions whereas the thioarsenates should be more mobile at alkaline conditions as encountered in the high-temperature geothermal fluids in the current contribution.

The aim of this study was to predict the transport of As in a basaltic aquifer within the Nesjavellir geothermal system in SW Iceland. To this end, laboratory measured adsorption coefficients of aquatic As species on basaltic glass surfaces were incorporated into the one-dimensional (1D) reactive transport model PHREEQC ver. 2 (Parkhurst and Appelo, 1999) constrained by 25-a long time series of field measurements of chemical composition of geothermal effluent fluids and ground waters, pH, Eh and occasionally Fe- and As-dissolved species measurements.

2. Geological setting and power production

2.1. Geological setting

The Nesjavellir geothermal power plant is a so called co-generation power plant, producing both 88 °C hot water by heat exchange, and electricity. It lies in the eastern rim of the Hengill...
### Table 1

Chemical composition of geothermal effluent, river and groundwaters.

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central volcano complex in south western Iceland (Fig. 1). The Hengill central volcano complex is the northernmost complex of the Western volcanic rift zone of Iceland that extends from the tip of the Reykjanes peninsula which then submerges to form the Mid Atlantic ridge (MAR). To the north of the Hengill central volcano, Lake Thingvallavatn fills a tectonic graben associated with WNW tectonic movement of the North American plate and the Hreppar micro plate which separates the North American and Eurasian plates in the area (Einarsson, 2008). The lake is primarily spring fed by shallow aquifers to the north and supports a relatively high productivity ecosystem for its latitude (Jonasson, 1992). The Nesjavellir power plant lies in the Nesjavellir graben extending from Hengill central volcano to Lake Thingvallavatn (Fig. 1). The bedrock topography is characterised by predominantly basaltic lavas formed at interglacial intervals or predominantly hyaloclastite ridges which are mostly basaltic glass, formed subglacially during glacial intervals (Tomasson and Saemundsson, 1967).

The area is one of the most active volcanic areas in Iceland. On the surface, Holocene lavas of variable age have flowed from eruption sites in the vicinity and extended far into the lake. Of the surface lavas, Stangarholshraun is the oldest and erupted in early Holocene (8 ka) from a crater row extending from westerly parts of Stangarholshraun toward the lake in a NE–SW direction (Figs. 1 and 2a). The lava flows in this area are of AA type with thick glassy scoria at the base and top of the lava flows facilitating fast groundwater flow at the base of the lavas. The lava is partially covered by the younger Hagavikurhraun (5.5 ka) which erupted from a crater row to the east of the Nesjavellir graben and flowed over the graben (Figs. 1 and 2a). The lava is composed of oxidised scoria at the top and base of the flow while the centre of the flow is more dense and crystalline. The youngest lava, Nesjahraun (2 ka), erupted near the Hagavikurhraun and covers a large portion of the older lavas as shown in Figs. 1 and 2a (Saemundsson, 1995). The lava primarily covers the eastern parts of the Nesjavellir graben between the power plant and Lake Thingvallavatn and extends 1 km into the lake to 40 m depth. A series of tectonic events occurred between the eruptions of the two youngest lavas leaving a series of faults in the Nesjavellir graben (Fig. 2a). The subsided area formed in these tectonic events was later filled with the Nesjahraun lava (Saemundsson, 1995). The Holocene lavas overlie the hyaloclastite rock formation consisting of basalt of variable crystallinity such as tuff, breccias, pillow lavas and pillow fragments, and glacial till can also be found in the bedrock (Hafstaðó et al., 2007) (Fig. 2a). Fig. 2a represents a lateral cross section extending along the main groundwater flow path. Fig. 2b depicts the proposed mass balance scheme for the As transport as described later.

2.2. Power production at the Nesjavellir site

The power plant was commissioned in September 1990. Initially, four wells were connected to the production line. Prior to electrical power production in 1998, the 198°C geothermal

![Fig. 3](image-url) Measured Cl, SO4, SiO2 and As concentrations from the springs along Lake Thingvallavatn shoreline from 1983 to December 2008. Sampling locations are displayed in Fig. 1. Black line in 1990 marks commission of the power plant, black line in 1998 marks the expansion of the power plant to electricity generation. All samples were collected by the research department of Reykjavik Energy, which also determined Cl, SO4, and SiO2 concentrations. Arsenic concentrations were measured from archived samples. (See separate file for grey tones version for print copy.)

![Fig. 4](image-url) Sample chromatogram for As and anion speciation from water measured at Site 6 × 1 min after sampling.
fluid was separated by gravity into its water and gas phase. The hot steam was used to heat the 4 °C ground water from the Grámelur (Site 13 in Fig. 1) to 88 °C. This low dissolved solid 88 °C heated water was then used for municipal district heating.

The brine was evaporated at atmospheric pressure and disposed of in the nearby Nesjavallalækur brook as shown in Fig. 1. Further downstream, this brook forms the pond Lækjarhvarf, which drains into the subsurface entirely. The separated steam phase was conducted to the power house where it was used for the heat exchange. The condensed steam produced during the heat exchange was disposed of into shallow wells adjacent to the power plant.

The geothermal power plant was redesigned to a co-generation plant for both hot water and electricity production in the summer of 1998. From then on, heat exchangers harnessed the energy of the high dissolved solid geothermal waters, while the steam was conducted to two turbine units for electricity production. Following 1998, increasing amounts of cold ground water were needed for municipal heating, which lead to dramatic increases in discharge from the Grámelur pumping station. The separated water phase was disposed of into the brook Nesjavallalækur, but since 2004 an increasing amount (initially 40 L s⁻¹) of separator water has been disposed of into 800 m deep wells near the power plant. In the beginning of 2009, 190 L s⁻¹ were disposed of into the wells along with a large proportion of the condensate while the remaining 50 L s⁻¹ are disposed of into the Nesjavallalækur brook.

3. Fluid geochemistry

3.1. Sampling sites

Samples for detailed chemical analysis were collected at 13 sites near the Nesjavellir power plant in March 2008 (Fig. 1 and Table 1). Furthermore, the research Department of Reykjavík Energy has sampled the water at Nesjavallalækur and Lækjarhvarf (Sites 1 and 7, respectively), at Grámelur (Site 15) and the shoreline of Thingvallavatn biannually since 1983 (Figs. 1 and 3a–d).

<table>
<thead>
<tr>
<th>Table 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Instrument setup for the detection of arsenic oxy- and thioanions by AEC–HG-AFS.</td>
</tr>
<tr>
<td><strong>Anion exchange chromatography (AEC) separation</strong></td>
</tr>
<tr>
<td>Instrument</td>
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<tr>
<td>Column</td>
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<tr>
<td>Eluent</td>
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<tr>
<td>Gradient</td>
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<tr>
<td>Sample volume</td>
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<tr>
<td>Typical retention times</td>
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<tr>
<td>Arsenite</td>
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<tr>
<td>Arsenate</td>
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<tr>
<td>Monothioarsenite</td>
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<tr>
<td>Dithioarsenite</td>
</tr>
<tr>
<td>Trithioarsenite</td>
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<tr>
<td>Tetrathioarsenite</td>
</tr>
<tr>
<td><strong>Suppression</strong></td>
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<tr>
<td></td>
</tr>
<tr>
<td><strong>Hydride-generation atomic fluorescence spectroscopy (HG-AFS) detection</strong></td>
</tr>
<tr>
<td>Instrument</td>
</tr>
<tr>
<td>Reductant</td>
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<tr>
<td>Carrier gas</td>
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<tr>
<td>Gas/liquid separator</td>
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<tr>
<td>Air dryer</td>
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</table>

Fig. 5. The relationship of B and total As with the conservative ion Cl⁻. Measured Cl, B and As concentrations represented as dots. Dashed line represents the reaction path for basalt leaching by the local precipitation.
3.2. Sampling methodology

Samples were pumped directly from the respective source (borehole, spring or stream) by a peristaltic pump (Cole Parmer Masterflex E/S portable sampler) through a High Density Polyethylene (HDPE) cooling loop followed by a 0.2 μm cellulose acetate (CA) filter (Advantec MFS) enclosed in a HDPE housing. Samples from boreholes were extracted 2 m below the water table. All bottles were pre-rinsed with filtered water prior to sample collection. The sample for As and anion speciation was directed into a 10 mL gas tight syringe and injected into a Dionex ICS-2000 ion chromatograph (IC) coupled to a PSAnalytical hydride-generation atomic fluorescence spectrophotometer (HG-AFS) immediately on sampling as the analytical equipment was field deployed. An example chromatogram is shown in Fig. 4. Then the sample was directed through the cooling loop into a pH/Eh flow-cell and pH and Eh recorded (Cole Parmer combination gel filled electrode for pH and Pt-electrode with saturated KCl calomel as a reference for Eh with Eutech pH200 displays). The temperature of the pH/Eh flow-cell was set as close as possible to 25 °C by adjusting the sample flow rate through the cooling loop. Then 60 mL for total carbonate C (TCC) were pumped into an amber glass bottle, which was filled completely before being sealed with an air tight cap. The sample was then pumped into a 50 mL HDPE bottle and 0.5–7.5 mL of sample pipetted into a 15 mL HDPE bottle for determination of H2S. The remainder in the 50 mL bottle was preserved 6 N

![Calibration of the groundwater model assuming Cl acted conservatively](image)

Fig. 6. Calibration of the groundwater model assuming Cl acted conservatively (a). Lækjarhvarf water was mixed with pristine ground water from Grámelur. This mixture flowed through the model and the duration of each time shift in the transport model was iterated until the modelled curve corresponded to the data prior to 2000. After 2000, the Cl data from Grámelur displayed increased scatter due to extensive pumping from the groundwater system leading to increased influx of surface rain and melt-waters along with geothermal water (Werner and Wallquist, 2008). Figures b–e represent measured total As concentrations at the shoreline of lake Thingvallavatn and Grámelur.
HCl, to 1%, for the determination of Fe(II) and Fe(III). Another 50 mL HDPE bottle was filled and sample pH raised to 10 by the addition of 1.0 N NaOH followed by the addition of 0.5 mL of 30% H2O2. After 30 min, HCl was used to acidify the sample to pH < 2 (Beak et al., 2008). After that, a 50 mL HDPE bottle was filled and acidified to 0.5% by concentrated HNO3 for the analysis of major constituents and selected minor constituents. Finally, a sample for further As-speciation analysis was pumped into two 15 mL HDPE bottles which were immediately frozen in dry-ice.

3.3. Analytical methods

Major and some minor constituents were measured with a Spectro Ciros Vision Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES). Arsenic species, arsenite (H3AsO3), arsinite (AsO2), mono-, di-, tri- and tetrathioarsenate, (As(OH)2, As(OH)3, As(OH)3−, As3H7+, AsS32− and As(SH)4) and the anions F−, Cl−, SO4, S2O2−, S2O− were separated according to Planer-Friedrich et al. (2007). Briefly, a Dionex ICS-2000 with self generated AEC separated and detected, anionic species and the HG-AFS detected species that contained As (Table 2). The As concentration for each individual species was quantified with HG-AFS as opposed to ICP-MS, as the instrumentation was field deployed. Total As was measured by HG-AFS according to PSAnalytical (1997). Total dissolved inorganic C was measured by AEC according to (Stefansson et al., 2007). DOC was measured by persulfate UV-oxidation followed by infrared detection of generated CO2 (LABTOC-Pollution and Process Monitoring). Iron speciation was carried out with Metpac™ PCDA eluent on a Dionex ICS-3000 (LABTOC-Pollution and Process Monitoring). Iron speciation was pumped into two 15 mL HDPE bottles which were immediately frozen in dry-ice.

3.4. Thermodynamic data

Results from chemical analysis were inserted into the computer code PHREEQC ver. 2 (Parkhurst and Appelo, 1999) where speciation calculations were carried out. The waterq4f.dat (with PHREEQC ver. 2.15) was amended with equilibrium constants for thioarsenic from Wilkin et al. (2003).

3.5. Fluid composition

Results for aqueous chemical analysis are given in Table 1. The temperature and pH of the geothermal outlet brine at Site 4 was 65.5 °C and 9.00 (measured at 25 °C), respectively, and had reduced to 22 °C and pH 8.64 at Site 7 were surface water disappeared under the lava. Similarly the Eh shifted from −234 to +22 mV. Ferric iron was the dominant Fe species in the groundwater wells whereas more Fe(II) was detected in some surface waters.

The pH drop in the brook is a consequence of H2S oxidation to SO4 2− (Table 1), silica polymerization (Gunnarsson and Arnorsson, 2008) and dilution with surface runoff as indicated by the Cl−/B ratio of these waters (Fig. 5). The mixed Nesjavallalækur (Site 5) was a 2:1 mixture of the outlet water (Site 4) and Nesjavallalækur (Site 1) based on Cl− concentrations. The high C concentration at Site 6 was due to surface runoff from Site 2 (heated groundwater rich in carbonate (1.45 mM)) which mixed with the Nesjavallalækur brook to give a carbonate concentration of (1.16 mM).

Arnorsson and Andredottir (1995) showed that the Cl−/B ratio of geothermal waters could be explained by leaching of basaltic rocks and that both components were highly conservative in solu-

\[ \begin{align*}
\text{Site 4:} & \quad \text{As(III)} = 50 \%, \text{As(V)} = 50 \% \\
\text{Site 5:} & \quad \text{As(III)} = 60 \%, \text{As(V)} = 40 \%
\end{align*} \]

As-speciation analysis was pumped into two 15 mL HDPE bottles which were immediately frozen in dry-ice.
the current contribution and it may be inferred that those waters are products of leaching of basaltic rock with local precipitation. The outlet of the power plant has the highest Cl\textsuperscript{−} and B concentrations while the NL-11 water from the flank of the rift valley (Fig. 1) has the lowest concentrations and most samples lie on a line between those two end members. The Cl\textsuperscript{−}/As ratio on the other hand shows depletion of As compared to Cl\textsuperscript{−} and B in the groundwater flow but Cl\textsuperscript{−} concentration increased in Varmagjá (Site 14), Eldvík and Sigguvík (Fig. 1) shortly after the commission of the power plant whereas the total As peak was maintained to some extent throughout the study period. The same As increase was not observed in Varmagjá or Grámelur (Fig. 6c and d), which lie in the course of the main streams of the groundwater flow in the lava field (Kjaran and Myer, 2005).

### 3.6. Arsenic speciation of surface and ground waters

Heated ground water (Site 2) is mainly directed into shallow wells at the power plant but some fraction enters the Nesjavellir Brook as is evident from the high C concentration in Site 6. The water at Site 2 had a small amount of arsenate (mainly as HAs\textsuperscript{V(OH)2}) and Site 3 is a condensed steam which is also mainly directed into wells but at the time of sampling a small proportion of this water entered the Nesjavellir Brook. The main As-species was arsenious acid (H\textsubscript{2}As\textsubscript{2}O\textsubscript{4}\textsuperscript{−}) with less dihydrogen arsenate and monohydrogen arsenate (H\textsubscript{2}As\textsubscript{3}O\textsubscript{6}\textsuperscript{−}) and no thioarsenites were detected. The current instrumental setup could not distinguish between thioarsenites and thioarsenates, but the thioarsenite species As(\textsubscript{OH})\textsubscript{2}(SH), As(\textsubscript{OH})\textsubscript{2}S\textsuperscript{−}, As(\textsubscript{OH})\textsubscript{2}S\textsubscript{2}\textsuperscript{−}, As\textsubscript{2}H\textsubscript{2}O\textsubscript{2}−, As\textsubscript{2}S\textsubscript{3}O\textsubscript{3}\textsuperscript{−} and As(\textsubscript{SH})\textsubscript{4}\textsuperscript{−} proposed by Wilkin et al. (2003) were used in all calculations (Fig. 5). At the power plant outlet (Site 4) the abundance of As-species in the separator water decreased through the thioarsenite species As:S 1:2 > 1:3 > 1:4 followed by the arsenite species (Table 1). The power plant effluent was immediately mixed at Site 5 with surface runoff of the Nesjavallalækur (Site 1) where the HS\textsuperscript{−} concentration decreased from 1 mM in the outlet to 0.3 mM in the mixture associated with a ~25% dilution of the conservative components Cl\textsuperscript{−}, B, F and Na. At Site 5, the thioarsenite species were still the most important As-species (Table 1). The brook flowed approximately 500 m before the next sampling Site 6 (Fig. 1). At Site 6, HS\textsuperscript{−} had decreased from 0.3 mM to 0.01 mM without significant increase in S\textsubscript{2}O\textsubscript{3}\textsuperscript{2−} and SO\textsubscript{4}\textsuperscript{2−} (Table 1) whereas the total As concentration had lowered. The tetra-thioarsenite was no longer detected and monothioarsenite had formed as well as arsenate (Fig. 7, Table 1). At Site 7 (the surface inlet solution for the groundwater model) the HS\textsuperscript{−} had decreased to 0.002 mM with associated increases in S\textsubscript{2}O\textsubscript{3}\textsuperscript{2−} and SO\textsubscript{4}\textsuperscript{2−} and a small decrease in total As.

### Table 3

<table>
<thead>
<tr>
<th>Column properties</th>
<th>Background</th>
<th>Lækjarhvarf</th>
<th>Input mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of cells</td>
<td>41</td>
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<td></td>
</tr>
<tr>
<td>Cell Length</td>
<td>100 m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liquid in each cell</td>
<td>5 liters</td>
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<td></td>
</tr>
<tr>
<td>Hydraulic conductivity, K</td>
<td>5.86E−04 m s\textsuperscript{−1}</td>
<td></td>
<td></td>
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<tr>
<td>Dispersivity</td>
<td>14 m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>=&gt; Column timestep</td>
<td>70,00,000 s</td>
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<td></td>
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<tr>
<td>=&gt; one Pore Volume (PV)</td>
<td>79722.22 h</td>
<td></td>
<td></td>
</tr>
<tr>
<td>=&gt; shifts in each year</td>
<td>Five shifts</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Solution composition**

| pH  | 7.71 | 8.64 | 8.62 |
| pe  | 1.54 | 0.36 | 1.1  |
| HS\textsuperscript{−} | 0     | 0.002 | 0.165 mmol L\textsuperscript{−1} |
| SO\textsubscript{4}\textsuperscript{2−} | 0.085 | 0.486 | 0.165 mmol L\textsuperscript{−1} |
| CO\textsubscript{2}\textsuperscript{−5} | 0.699 | 0.862 | 0.73 mmol L\textsuperscript{−1} |
| F   | 0.005 | 0.033 | 0.011 mmol L\textsuperscript{−1} |
| Cl  | 0.264 | 2.243 | 0.66 mmol L\textsuperscript{−1} |
| Si  | 0.389 | 5.77  | 1.467 mmol L\textsuperscript{−1} |
| Na  | 0.454 | 3.712 | 1.108 mmol L\textsuperscript{−1} |
| K   | 0.0274 | 0.395 | 0.101 mmol L\textsuperscript{−1} |
| Ca  | 0.219 | 0.206 | 0.217 mmol L\textsuperscript{−1} |
| Mg  | 0.217 | 0.113 | 0.196 mmol L\textsuperscript{−1} |
| As  | 0     | 0.882 | 0.1765 mmol L\textsuperscript{−1} |
| Fe(2) | 0    | 236   | 72.3 µmol L\textsuperscript{−1} |
| Fe(3) | 1000 | 2263  | 1300 µmol L\textsuperscript{−1} |
| Al  | 2.48 | 32.2  | 8.43 µmol L\textsuperscript{−1} |
| B   | 83   |       | 16.6 µmol L\textsuperscript{−1} |

**Basaltic glass**

| Mass in each cell | 10 | kg |
| Specific surface area | 1.5 | m\textsuperscript{2} g\textsuperscript{−1} |
| Surface sites | 4 | sites nm\textsuperscript{−2} |

**Arsenic surface reactions on BG (Sigfusson et al., 2008)**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>log K (25 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As(III)</td>
<td></td>
</tr>
<tr>
<td>2Glass-\textsubscript{OH} + H\textsubscript{2}AsO\textsubscript{4} = (Glass-\textsubscript{O})\textsubscript{2}AsOH + 2H\textsubscript{2}O</td>
<td>4.7</td>
</tr>
<tr>
<td>Glass-\textsubscript{OH} + H\textsubscript{2}AsO\textsubscript{4} = Glass-\textsubscript{H}AsO\textsubscript{4}</td>
<td>2.78</td>
</tr>
<tr>
<td>As(Y)</td>
<td></td>
</tr>
<tr>
<td>Glass - \textsubscript{OH} + H\textsubscript{2}AsO\textsubscript{4} = Glass - O\textsubscript{2}AsO\textsubscript{2} + 2H\textsubscript{2}O</td>
<td></td>
</tr>
<tr>
<td>2Glass - \textsubscript{OH} + H\textsubscript{2}AsO\textsubscript{4} = (Glass - O\textsubscript{2}AsO\textsubscript{2} + H\textsubscript{2}O</td>
<td>2.3</td>
</tr>
<tr>
<td>2Glass-\textsubscript{OH} + H\textsubscript{2}AsO\textsubscript{4} = (Glass-O)\textsubscript{2}AsOOH + 2H\textsubscript{2}O</td>
<td>4.3</td>
</tr>
</tbody>
</table>
concentration, of which dithio- and trithioarsenite were the only detected species (Table 1). The concentration of As dropped markedly from the surface waters to the ground waters and no arsenite or thioarsenite species were detected in groundwater wells (Sites 8–13), the spring (Site 14) in Thingvallavatn and Grámelur (Site 15) and arsenate was the only species detected at these sites (Fig. 7).

The occurrence of thioarsenite species down the brook flowpath was clearly kinetically controlled. According to thermodynamic calculations thiarsenites should be the dominant species in the outlet and the mixture at Site 5, however, down the flow path at Sites 6 and 7 the dominant species should be arsenite due to the low concentration of HS (Wilkin et al., 2003) (Fig. 5). Speciation calculations in PHREEQC ver. 2 highlighted the sluggishness of the thioarsenite breakdown although no thioarsenites were detected in the shallow groundwater wells down-flow from Site 7 representing the termination of the brook. The residence time of the groundwater was counted in days to months (Table 3) compared to hours in the brook.

4. Groundwater flow model

A mass balance scheme, as proposed by Werner and Wallquist (2008) for the fate of CO2 in the groundwater system, was used in the present study to determine input and fate of As in the groundwater system (Fig. 2b). The system boundary was chosen to frame the disappearance of the geothermal wastewater at Laekjarvarf (Site 7, Figs. 1 and 2a) into an unconfined aquifer with a gradient of 0.86 m/km leading to the Grámelur pumping station (Site 15, Figs. 1 and 2a) close to the shoreline of Lake Thingvallavatn. Groundwater flow rate was calibrated against changes in measured Cl− concentrations in the Grámelur pumping station.

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Fig. 8. Predicted breakthrough of arsenite and arsenate at Grámelur pumping station if all effluent water would have been disposed off into Lækjarvarf (a). Predicted traverse of arsenite and arsenate in January 2009, circles represent total As measurements (b). Predicted traverse of arsenite and arsenate in the year 2050 assuming all effluent water is disposed off into Lækjarvarf (dashed lines) and assuming all effluent water is disposed off into deep wells after 2010 (lines) (c). Predicted traverse of arsenite and arsenate in the year 2100 assuming all effluent water is disposed off into Lækjarvarf (dashed lines) and assuming all effluent water is disposed off into deep wells after 2010 (lines) (d).
lowing assumptions were made:

1. Chloride acted as a conservative ion in the groundwater (Gíslason and Eugster, 1987; Arnorsson and Andresdottir, 1995).
2. The water pumped up in Grámelur during the years 1991–1997 was assumed to be “pristine” ground water without the influence of anthropogenic geothermal effluents from the power plant (Figs. 3a and 5a).
3. The water pumped up in Grámelur from 1998 onwards had increasing effluent signature (Cl− concentration) with a complete breakthrough of the effluents in July 2000 (Fig. 5a). As a result, one pore volume in the system was replaced in 3320 days (9 years and 36 days).
4. The inlet solution for the reactive transport modellings was produced by mixing Lækjarhvarf and pristine Grámelur waters in 1:4 ratio to produce the Cl− concentrations measured at Gráme- lur after one PV had been replaced in the system.

Once boundary conditions for the groundwater flow had been established a 4100 m 1D column was defined by a series of forty-one 100 m long cells as shown in Fig. 2b. The column was a scaled up column from Sigfusson et al. (2008) maintaining identical physical characteristics such as specific surface area, solid/solution ratio and dispersivity. All cells had the same physical properties (Table 3). A prediction of As movement was then carried out based on adsorption coefficients generated from laboratory experiments on the interaction between basaltic glass and dissolved arsenite and arsenate (Table 3) (Sigfusson et al. 2008) into the one-dimensional (1D) reactive transport model PHREEQC ver. 2 (Parkhurst and Appelo, 1999) (Fig. 8). Thermodynamic calculations and measurements showed that all As in the ground waters was in the arsenate (As(V)) form. In other words, all As that had reached the first groundwater well NK-1 was either arsenate when it entered the subsurface or was converted to arsenate from other species during the transport from Site 7 to the well.

Insufficient access to the aquifer prevented establishment of the kinetic coefficients of these reactions at this specific field site. However, since As is anticipated to exist as arsenite in geothermal waters which are immediately disposed of into the ground after utilisation without flowing on the surface, predictions were made for arsenite by blocking (increasing the log K for arsenite reduction to 100) the oxidation of the arsenite from the inlet solution in the model. At the pH conditions encountered in the model (pH 8.5–8.6) arsenate in Grámelur would be close to that of the inlet mixture towards the year 2100 whereas arsenite bound more strongly to the basaltic glass surface and would still be very low (Fig. 8a).

Predicted As concentrations in a cross section of the groundwater system for the year 2009 indicated the concentration of arsenate in well NK-1 (Site 8) should be 0.09 μM compared to the measured concentration of 0.031 μM (Table 1). The heterogeneity of the aquifer is clear from these figures and shows that some part of the effluent waters travels through crevasses with limited contact with the aquifer matrix (Figs. 5b–e and 8b) although the As was retained compared to Cl− (Fig. 7a and d). Two sets of calculations were done for cross sections for the years 2050 and 2100, one assuming continued disposal of all effluents into Lækjarhvarf (dashed lines) and the other assuming a complete disposal of effluents into deep wells (Fig. 8c and d). Continued injection of geothermal wastewater would result in saturation of the aquifer matrix surface soon after the year 2100 with the arsenate concentration at the lake shoreline as high as the concentration in the inlet mixture. An identical flow scenario for arsenite would result in complete breakthrough of arsenite in about 900 a. Therefore, the disposal of geothermal wastewaters into the subsurface prior to oxidation of arsenite to arsenate is advised to prevent fast distribution of As away from geothermal power plants. Since the adsorption coefficients of thioarsenic species onto basalt surfaces are not known the occurrence of H2S in geothermal water may increase the mobility of the aqueous As by the formation of mobile thioarsenic species or decrease the mobility by formation of insoluble Fe–As sulfides adjacent to injection wells. In any case, the oxyanion arsenate is more mobile than the thioarsenic ions under current conditions since arsenate was the only species detected in well NK-1 indicating that prevention of As conversion to arsenate is always advised to prevent high mobility of As in basaltic ground water systems. Disposal of the effluents into deep wells as opposed to disposal to the surface is a clear advantage since the As peak from the 20-a seepage period commencing in 1990 would smear out resulting in lower eluted concentrations at the lake shoreline as may be inferred from comparing the arsenate peaks in Fig. 8c and d. The arsenate already adsorbed at the proximal end of the column, will elute slowly into the groundwater but the concentrations will always be low as opposed to continued effluent seepage into Lækjarhvarf.

5. Conclusions

The Nesjavellir geothermal power plant has been in operation since 1990. During this time an increased proportion of the separator water has been directed into deep wells. Prior to deep well injection, the majority of the effluent waters with elevated Si, Cl− , SO4 2− and As concentrations seeped into a lava field in close proximity to the power plant. These effluent waters mixed with the ground water and flowed trough faults and crevasses and as matrix flow towards Lake Thingvallavatn. The As in the geothermal effluents existed primarily as thioarsenic species with decreasing As:ratios as the water flowed from the source. Although dithioar- senic and tri-thiolsenic were the main As species in the seepage water to the lava field, arsenate was the only As species measured in the ground waters towards Lake Thingvallavatn indicating either higher mobility of arsenate compared to thioarsenic species or a complete degradation of these species in the aquifer. According to the 1D model, arsenate travels approximately nine times faster than arsenite in the basaltic rock aquifer.

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References
