

Predicting the mobilization of dissolved metals, organics and gas generation from aquifer sediments prior to in situ operations

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Summary

This study subjected three glacial aquifer sediments from the Cold Lake oil sands region to temperatures of 4°C, 60°C and 120°C under controlled laboratory conditions with the objective of gaining a better understanding of the mechanisms for gas production and the release of dissolved metals, metalloids, and organic compounds to groundwater. The results of chemical and mineralogical analyses showed similar concentrations of arsenic (As) in all three aquifer sediments and that pyrite was the main carrier of arsenic. There was a rapid release of dissolved As during the first week of heating. Although As concentrations were relatively low in the aquifer sediments, after 188 days of heating at 120°C, dissolved As concentration were 3.5 to 150 times higher in than their initial concentrations in the water. The dominant species of As released from the sediments was As(III). The heating experiments also showed releases of other dissolved elements including Ba, Li, Mo, and Al, suggesting that these elements could be useful for tracing thermal plumes in groundwater. In addition to metals and metalloids, organic compounds were also released during heating, with dissolved organic carbon and some organic acids released from all sediments heated at 120°C. During the experiments, gases, including CO₂, methane and reduced sulfur compounds were detected after 188 days. These heating experiments provide a method to assess the potential risks associated with heating specific geological units prior to oil sands development that can be incorporated into initial investigations at in situ operations.

Introduction

The Alberta oil sands deposits are estimated to contain approximately 1700 billion barrels of oil of which 170 billion barrels are recoverable with existing technology (Gosselin et al., 2010). Only 20 % of the oil sands are recoverable through surface mining. The remaining 80 % of the oil sands are located at depth below 80 m and must be extracted by in situ methods (Burrowes et al., 2010). At reservoir temperatures, bitumen is immobile, however when heated to 200°C, it approaches the viscosity of water (Fairbridge et al., 2012). To reduce the viscosity of bitumen for recovery, enhanced thermal recovery methods are used including steam-assisted gravity drainage (SAGD) and cyclic steam stimulation (CSS). The transport of steam into the bituminous reservoir requires the installation of injection wells from surface to the target formation, which may pass through unconsolidated sediments and non-saline groundwater aquifers. The transfer of radiant and advective heat from the injection well casing to the adjacent aquifer sediments may increase groundwater temperatures, increasing the solubility of some mineral phases. The dissolution of minerals or mobilization of poorly sorbed elements from the sediments may release arsenic and other metal(oid)s to the groundwater. These mobilized elements and heat may be transported down-gradient, away from the injector well, along groundwater flowpaths. A study by Fennell (2008) monitoring groundwater impacted by CSS operations found elevated dissolved arsenic concentrations associated with elevated groundwater temperatures down-gradient from the injection well. Similarly, a monitoring program by CNRL (2005) observed a plume of dissolved arsenic approximately 360 m down-gradient from CSS injectors.

This study subjected glacial fluvial aquifer sediments to elevated temperatures under controlled laboratory conditions with the objective of gaining a better understanding of the mechanisms for gas production and the release of dissolved metal(oid)s, and organic compounds to groundwater.

Methods

Aquifer sediments were collected from the Cold Lake Oil Sands Region in the Cold Lake-Beaver River Basin (CLBR) (Figure 1). Formations sampled from the CLBR basin included the Grand Centre (GC), Sand River (SR) and Bonnyville (BNV) aquifers. Discrete sediment samples were collected using an auger drill rig equipped with a split-spoon, sampling in advance of the drilled bore-hole. No fluids were used during drilling to ensure that samples were not contaminated. Sediment samples were sealed in plastic containers and immediately frozen on-site. Samples were stored at -20°C until analyzed. Water used for the heating experiments was sampled from monitoring wells installed in the bore-holes where sediments were collected.

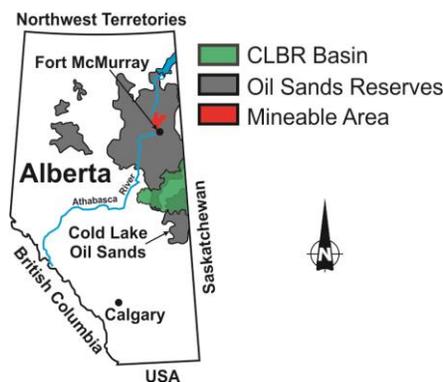


Figure 1. Location of the Cold Lake - Beaver River Basin (CLBR) and extent of the Alberta oil sands reserves.

Sediment and groundwater were added to 100 mL pressure vessels, prepared in sets of 9 and in triplicate, with one set used as a control (4°C) while the second and third sets were subjected to constant temperatures of 60°C and 120°C. Groundwater used for the experiment was purged with nitrogen gas to remove dissolved oxygen from the water following the method of Butler et al. (1994). Water and sediments were placed in an anaerobic glove box and purged with nitrogen gas. One-hundred millilitres of water was added to 10 g of sediment in each pressure tube and sealed. Water used for each sample corresponded to the aquifer from which the samples were collected. One set of samples from each location was refrigerated at 4°C and the second and third sets of samples were heated at a constant temperature of 60°C and 120°C, respectively. Vessels were maintained at temperature for 188 days, and sampled on days 0, 3, 6, 10, 16, 23, 37, 51, 73 and 188. Water samples were analyzed for routine parameters, dissolved metals and organic compounds, As speciation, stable isotopes of $\delta^{18}\text{O}$, $\delta^2\text{H}$, $\delta^{13}\text{C}$ -DIC, $\delta^{34}\text{S}$, $\delta^{18}\text{O}$ - SO_4 , and free gases. Mineralogical analyses of each sediment type were done before and after the thermal experiments. Organic profiling was conducted using Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (ESI-FTICR MS).

Examples

Aquifer sediments from the GC, SR, and BNV were mainly composed of quartz, calcic plagioclase, K-feldspar, and carbonate minerals including calcite and ankerite-dolomite. The BNV sediment also contained traces of siderite. Pyrite was present in trace concentrations in all samples, occurring as individual and semi-aggregates of framboids. The textural features of the framboidal pyrite grains suggest that it is a neo-mineral formed within the sediments post deposition. Arsenic concentrations in the framboidal pyrite were

typically higher than the detection of 100 ppm and reaching concentrations up to 1550 ppm, suggesting that pyrite represents an important As carrier in the sediments. Total digestion of the aquifer sediments found that arsenic concentrations were similar, between 1.9 and 2.7 µg/g, similar to that of Moncur et al., (2015), that found the average arsenic content from 216 sediment samples from the CLBR basin to be 6 µg/g, ranging from 0.3 to 17 µg/g. These As concentrations are typical of the range of concentrations found in glacial deposits (Smedley and Kinniburgh, 2002).

Dissolved As concentration measured in groundwater from the three aquifers was less than 3 µg/L (Table 1). Arsenic was mainly in the oxidation state of As(III) in the SR groundwater and As(V) in the BNV groundwater. The GC groundwater had a similar As(III)/As ratio (Table 1). During the experiments where sediments were maintained at ambient groundwater temperatures of 4°C, minimal changes in As concentrations were observed. Heating the sediments to 120°C showed a rapid release of As during the first week. After 188 days of heating at 120°C, dissolved As concentrations were 3.5 to 150 times higher than initial concentrations. Speciation showed that As(III) was the dominant oxidation state in the GC and SR waters and the As(III)/As ratio increase in the BNV waters. Framboidal pyrite grains observed in the pre-heated sediments showed no signs of alteration. However, after 188 days of heating at 120°C, some framboidal grains showed features such as surficial pitting and tarnishing which might be indicative of early-stage sulfide oxidation. In the BNV sediments, secondary goethite was observed that resembled former framboidal pyrite grains, suggesting complete oxidation of some pyrite may have occurred. These observations are supported by depleted $\delta^{34}\text{S}$ and $\delta^{18}\text{O}\text{-SO}_4$ values after the heating experiments, showing strong fractionation towards sulfide oxidation.

Table 1. Dissolved arsenic concentrations prior to heating (day 0) and at the end of the thermal experiments (day 188).

| Formation | Day | As | As | As | As(III)/As |
|--------------|-----|------|------|-------|------------|
| | | 4°C | 60°C | 120°C | 120°C |
| | | µg/L | µg/L | µg/L | % |
| Grand Centre | 0 | 0.5 | 0.5 | 0.5 | 46 |
| Grand Centre | 188 | 1.9 | 7.2 | 70 | 90 |
| Sand River | 0 | 2.0 | n/a | 2.0 | 80 |
| Sand River | 188 | <0.6 | n/a | 6.9 | 84 |
| Bonnyville | 0 | 2.8 | 2.8 | 2.8 | 12 |
| Bonnyville | 188 | 1.1 | 46 | 22 | 41 |

When the sediments were heated to 120°C Ba, Li, Mo, and Al were also released, suggesting that these elements could be useful for tracing groundwater thermal plumes. Dissolved organic carbon was also released from all of the sediments during the 120°C experiments, and their composition was profiled using ESI-FTICR MS. The organic profiling showed increases in the number of homologues detected in the groundwater after heating (e.g. 1834 homologues were present in the SR groundwater at the beginning of the experiment, and 2202 homologues were detected at the end of the experiment). The gases generated during the 188 day experiment included CO₂, methane and some carbon and reduced sulfur compounds.

Conclusions

The heating experiments were successful in identifying differing potential for release of dissolved metals, organics and gases from different sediment types. The experiments were able to simulate the range of temperature and redox conditions present in aquifers impacted by thermal in situ operations. The experimental design and monitoring program also included sufficient parameters to identify potential sources and mechanisms for the release of different metal(oid)s. For example, increased concentrations of

dissolved Ba, Li, Mo, Al and more diversified assemblages of organic compounds were detected after the heating experiments. These results suggest that these parameters could be used as thermal tracers. In particular, monitoring pH, Eh and the As speciation were necessary to identify potential controls on As release and mobility. Although As concentrations were relatively low in the aquifer sediments, dissolved As concentration in the water after 188 days of heating at 120°C were 3.5 to 150 times higher than initial concentrations, depending on the sediment. This methodology can be used during the planning and operational phases at in situ facilities to better evaluate the potential sources of metal, organic and gas mobilization and so that potential risk can be identified and mitigated. The information from these thermal tests is capable of identifying the aquifers with the greatest potential for impacting water quality or releasing gases, which would allow these aquifers to be targeted for more intensive monitoring and risk assessment.

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