Development of a contaminant leaching model for aquifer storage and recovery technology

Abdulwahab Tuwati and Maohong Fan

Abstract: Due to the water shortage in the state of Wyoming as a result of the warm temperatures and relatively little precipitations, development of a contaminant-leaching model for aquifer storage and recovery (ASR) was considered as an alternative option to replace some other more expensive technologies. Therefore, ASR model using batch and continuous flow leaching tests was conducted under different conditions, and the associated leaching models were obtained. Results from this study have indicated that only 4 (Boron, Barium, Manganese, and Vanadium) of the total 15 metals present in the sandstone rocks were soluble and fall within the detectable range of the inductively coupled plasma calibration curve. The metals’ rates of dissociation are dependent on pH, water injection flow rate, and temperature variation. The kinetic study of leachable metal species fitted in a first-order kinetic model. The solubility product constants, $K_{sp}$, were measured over a specified temperature range in order to determine the thermodynamic quantities, enthalpies, $\Delta H$, and entropies, $\Delta S$, for the leachable elements.

Keywords: Earth Sciences; Environment & Agriculture; Environmental Studies & Management

1. Introduction

The state of Wyoming is considered a part of a semi-arid hydro-climatic region. It is ranked as the third driest state in the USA, and drought is a constant threat in this region. According to the National Climatic Data Center (McBeth, Reddy, & Skinner, 2003), Wyoming is placed as the 48th wettest in the USA, with annual precipitation average of 12.97 inches. In general, the state has limited sustainable
surface water available for use. Furthermore, Wyoming is one of the largest fossil fuel suppliers in the country (McBeth et al., 2003), with large quantities of water generated during production released either onto land or into nearby lakes or rivers with no beneficial use. Worldwide, the oil and gas industry generates more than 70 billion barrels of produced water per year. Within the USA alone, between 15 and 20 billion barrels of produced water are generated each year. This is equivalent to a volume of 1.7–2.3 billion gallons per day. Of the above total of produced water, the state of Wyoming has shown a share of approximately 2 billion barrels per year as reported in the year 2007 (Chris, n.d.). Accordingly, an environmentally friendly and relatively inexpensive method could be used to store this large volume of the co-produced water after a necessary partial or comprehensive treatment. An aquifer storage and recovery (ASR) injection method could be a feasible technology for conserving natural and/or produced water that would otherwise be wasted. Large quantities of water are stored deep underground, which reduces or eliminates the need for construction of large and expensive surface reservoirs. In addition to the above-mentioned driving force, the ASR technology can also be used to protect environment, aquatic, and terrestrial ecosystems. Most ASR storage zones are ranged in depth from 200 to 2,700 feet. Water is stored in different water-bearing geologic formations that may be in sand, clay sand, sandstone, gravel, limestone, dolomite, glacial drift, basalt, and other types of geologic settings.

The types of aquifers in North America are generally classified into the following groups: unconsolidated, semi-consolidated sand and gravel, sandstone, carbonate rock aquifers, aquifers in interbedded sandstone and carbonate rocks, and aquifers in igneous and metamorphic rocks (Lai, 2005). Sand and gravel, sandstone, carbonate rock, and interbedded sandstone and carbonate rock aquifers exist to some extent in the state of Wyoming. Regardless of the aquifer type, the injected water displaces the natural water that is present in the aquifer and causes a very large bubble around the well. This bubble is usually confined by overlying and underlying geologic formations that do not produce water. These bubbles have water storage capacities as small as about 13 million gallons in individual ASR wells to as much as 2.5 billion gallons or more in large ASR well fields (Water Treatment Solutions, Lenntech, http://www.lenntech.com/who-eu-water-standards.htm). However, in order for the ASR to be a successful technology for water storage, potential contamination should be addressed. The contamination might occur during water injection and storage as a result of the leaching of toxic metals.

The present study has been aimed to investigate continuous and batch leaching of heavy metals (National Primary Drinking Water Regulations, EPA, 2009) for the prediction of the potential leaching of contaminants into aquifers. The effects of varying certain parameters on the mobility of heavy metals through rocks, including pH and temperature, have been studied using both leaching processes. Flow rate was also used as a variable for continuous process studies. The work seeks to study mobility and investigate the leaching kinetics of several heavy metals that may be present in “sandstone” rock types. Sandstones are arenaceous sedimentary rocks composed mainly of feldspar and quartz, and exhibit different colors. They are broadly divided into three groups: arkosic sandstones, which have a high (>25%) feldspar content, quartzose sandstones, such as quartzite, which have a high (>90%) quartz content, and argillaceous sandstones, such as greywacke, which have a significant fine-grained element.

The term “heavy metal” refers to any metallic element that has a relatively high density, and typically refers to the group of metals and metalloids with atomic densities greater than 4 g/cm³ (Mortin & Hutt, 1997). Heavy metals are well known to be toxic to human beings and most other organisms when present in high concentrations in the environment (Mortin & Hutt, 1997). Table 1 lists the standard levels of these elements considered safe in water, according to World Health Organization (WHO) (Skousen, 1995) and the United States Environmental Protection Agency (EPA) (Gregg & Thomas, 2007).

The leaching of heavy metals occurs naturally, as in the case of sulfide minerals in rocks that are oxidized upon contact with water and atmospheric oxygen, resulting in the formation of sulfates that generate the so-called “acid rock drainage” and “metal leaching” (ARD-ML). ARD-ML is usually characterized by high concentrations of metals and sulfates in solution and lower pH values (2–4), which lead
to the accelerated release of certain metals into the aquifers (Batchelor, 1998; Sun, Xie, Li, Xu, & Chen, 2006). The mobility of arsenic (As) as a toxic element in the presence of pyrite in ASR has been reported in various studies as an example of such leaching, and geochemical modeling has examined the stability of pyrite in limestone during the injection into wells of surface water (Ludwig, Khanna, Prenzel, & Beese, 2005). The goal of those modeling studies was to stabilize pyrite under certain conditions in order to alter the high leaching of As levels into ASRs. Another leaching model investigated interactions among immobilization reactions and transport mechanisms affecting the overall leaching of the contaminants (Batayneh, 2010), and a characteristic leaching procedure for assessing the toxicity of soils contaminated with heavy metals has been reported elsewhere (Banat, Howari, & Al-Hamad, 2005). In addition, several reports have been cited for the release of heavy metals from sources such as fly ash (Mendez-Ortiz, Carrillo-Chavez, & Monroy-Fernandez, 2007), water springs (Chen et al., 2006), soil (Clemente, Escolar, & Bernal, 2006), mine waste material (i.e. tailings) (Maskall & Thornton, 1998), acidic sandy soil amended with dolomite phosphate rock fertilizers (Bettinelli, Baroni, & Pastorelli, 1987), and contaminated calcareous soil (Chen et al., 2006) into the groundwater.

All of these reports indicate the mobility of heavy metals in soil to some extent under various amendment conditions. Further, it has been reported that the addition of organic material could result in the fixation of metals such as zinc (Zn) and lead (Pb) in soil, which in turn might help to reduce leaching of these metals into the aquifers (Hazardous Substances Data Bank, [HSDB], 1998). The study of metal leaching from various fly ash samples (Mendez-Ortiz et al., 2007) showed different behavior patterns. The chemical partitioning of lead (Pb) and zinc (Zn) in soils, clays, and rocks has been documented (Maskall & Thornton, 1998), with their migration showing an increase under low pH conditions. In the present study, we found it both necessary and useful to design and develop leaching models to study the kinetics of each individual contaminant species; to investigate the potential leaching of some of these heavy metals from sandstone rocks using both continuous and batch leaching processes; and to measure the effects of varying parameters such as pH and temperature of the leachate on both leaching processes, as well as the effects of flow rate on the continuous leaching process.

2. Materials and methods

2.1. Leaching kinetics of heavy metals

Heavy metal leaching models were derived using a batch system. Assuming that the leaching of contaminant species, \( i \), follows a first-order kinetic model, its leaching kinetics can be written as

<table>
<thead>
<tr>
<th>Table 1. WHO/EU drinking water standards</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Element</strong></td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>Arsenic (As)</td>
</tr>
<tr>
<td>Barium (Ba)</td>
</tr>
<tr>
<td>Beryllium (Be)</td>
</tr>
<tr>
<td>Boron (B)</td>
</tr>
<tr>
<td>Cadmium (Cd)</td>
</tr>
<tr>
<td>Chromium (Cr)</td>
</tr>
<tr>
<td>Copper (Cu)</td>
</tr>
<tr>
<td>Iron (Fe)</td>
</tr>
<tr>
<td>Lead (Pb)</td>
</tr>
<tr>
<td>Manganese (Mn)</td>
</tr>
<tr>
<td>Nickel (Ni)</td>
</tr>
<tr>
<td>Selenium (Se)</td>
</tr>
<tr>
<td>Silver (Ag)</td>
</tr>
<tr>
<td>Zinc (Zn)</td>
</tr>
</tbody>
</table>
\[
\frac{dC_i}{dt} = k_i [C_{e,i} - C_i] 
\]  \hspace{1cm} \text{(E1)}

or

\[
-\frac{d[C_{e,i} - C_i]}{dt} = k_i [C_{e,i} - C_i] 
\]  \hspace{1cm} \text{(E2)}

where \( k_i \) is the leaching rate constant of species \( i \), \( C_{e,i} \) is the leaching concentration of contaminant \( i \) at leaching equilibrium state, and \( C_i \) is the concentration of species \( i \) at any time \( t \).

With the boundary condition, \( C_i|_{t=0} = 0 \), the integral form of E1 is:

\[
-\ln \left( C_{e,i} - C_i \right) = k_i t. 
\]  \hspace{1cm} \text{(E3)}

Rearranging E3, we have

\[
-\ln\left( \frac{C_{e,i} - C_i}{C_{e,i}} \right) = k_i t. 
\]  \hspace{1cm} \text{(E4)}

The left side, \(-\ln \left[ C_{e,i} - C_i \right] \), in E4 can be plotted against time \( t \). If the experimental data fit the plot, then the assumed leaching rate order (first order) is correct. Otherwise, an alternative leaching rate order needs to be assumed and checked until the experimental data fit the associated kinetic model.

2.2. Experimental section

2.2.1. Sample collection and preparation

Sandstone rock samples were collected from an open pit (Figure 1) operated by Black Butte Coal and Mining Company, and located about 170 miles west of Laramie, Wyoming. The samples were obtained from an adjusted depth of about 169–214 feet, as shown in Table 2.

The samples were transported to UW lab in containers, and upon arrival, their surfaces were cleaned with water and left to dry at room temperature. After drying, all samples were crushed with a jaw crusher and screened with a sieve (mesh opening of 0.185 inch). The retained particles were then mixed several times to obtain representative samples and kept in closed containers until use.
2.2.2. Sample analysis

An adapted procedure (Maskall & Thornton, 1998) was partially followed for rock sample digestion in order to screen for the following elements: Ag, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Ni, Pb, Se, V, and Zn. The first step of the digestion method involved the addition of 5-mL aqua regia (1:3 v/v, HNO₃: HCl) and 2-mL hydrofluoric acid (HF) to a 0.2-g fine powder of sandstone rock sample in a Teflon beaker. The sample mixture was then placed on a hotplate and heated at 100°C until dry. Another 5-mL aqua regia was then added to bring the dissolved metals back to the solution. The resulting mixture was then filtered with Whatman 2 filter paper (pore size: 8 μm) and rinsed with deionized (DI) water. The filtrate was then transferred into a 50-mL plastic vial and diluted to its mark. The digestion method was performed thrice. The final solutions were analyzed by an ICP-OES spectrometer (ICAP 6000 series, Thermo Scientific).

2.2.3. Leaching apparatus

Two schematic diagrams of continuous and batch percolation extraction set-ups are shown in Figures 2 and 3, respectively. The columns are clear PVC columns approximately seven-feet long with an outside diameter of 2.5 inches. Each is sufficiently high to contain about 5-kg rock sample (particle size of 0.185 inch), with additional height to contain applied water in the event of poor percolation. A sampling point at the bottom of the column was used for sampling collection. A cotton filter medium was placed near the sampling point for easy sample withdrawal. Each column has a

Table 2. Drill hole lithology

<table>
<thead>
<tr>
<th>Raw depths (feet)</th>
<th>Adjusted depths (feet)</th>
<th>Lithology type</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00–5.00</td>
<td>0.00–5.05</td>
<td>Soil</td>
<td>Yellow-brown</td>
</tr>
<tr>
<td>5.00–22.00</td>
<td>5.05–22.21</td>
<td>Sandstone</td>
<td>Grey-brown</td>
</tr>
<tr>
<td>22.00–25.00</td>
<td>22.21–25.24</td>
<td>Siltstone</td>
<td>Brown</td>
</tr>
<tr>
<td>25.00–29.00</td>
<td>25.24–29.27</td>
<td>Sand</td>
<td>Grey</td>
</tr>
<tr>
<td>29.00–56.00</td>
<td>29.27–56.53</td>
<td>Siltstone/mudstone</td>
<td>Grey</td>
</tr>
<tr>
<td>56.00–61.00</td>
<td>56.53–61.58</td>
<td>Siltstone</td>
<td>Grey</td>
</tr>
<tr>
<td>61.00–74.00</td>
<td>61.58–74.70</td>
<td>Mudstone</td>
<td>Grey</td>
</tr>
<tr>
<td>74.00–83.00</td>
<td>74.70–83.78</td>
<td>Siltstone</td>
<td>Grey</td>
</tr>
<tr>
<td>83.00–85.00</td>
<td>83.78–85.80</td>
<td>Mudstone</td>
<td>Grey</td>
</tr>
<tr>
<td>85.00–93.00</td>
<td>85.80–93.88</td>
<td>Siltstone</td>
<td>Grey</td>
</tr>
<tr>
<td>93.00–98.00</td>
<td>93.88–98.92</td>
<td>Mudstone</td>
<td>Grey</td>
</tr>
<tr>
<td>98.00–129.00</td>
<td>98.92–130.22</td>
<td>Siltstone</td>
<td>Grey</td>
</tr>
<tr>
<td>129.00–135.00</td>
<td>130.22–136.27</td>
<td>Mudstone</td>
<td>Grey</td>
</tr>
<tr>
<td>135.00–143.00</td>
<td>136.27–144.35</td>
<td>Siltstone</td>
<td>Grey</td>
</tr>
<tr>
<td>143.00–144.00</td>
<td>144.35–145.36</td>
<td>Mudstone</td>
<td>Grey</td>
</tr>
<tr>
<td>144.00–150.00</td>
<td>145.36–151.42</td>
<td>Sandstone</td>
<td>Grey</td>
</tr>
<tr>
<td>150.00–153.20</td>
<td>151.42–154.65</td>
<td>Mudstone</td>
<td>Grey</td>
</tr>
<tr>
<td>153.20–155.00</td>
<td>154.65–156.46</td>
<td>Coal</td>
<td>Black</td>
</tr>
<tr>
<td>155.00–158.70</td>
<td>156.46–160.20</td>
<td>Carbonaceous mudstone</td>
<td>Brown</td>
</tr>
<tr>
<td>158.70–160.00</td>
<td>160.20–161.51</td>
<td>Coal</td>
<td>Black</td>
</tr>
<tr>
<td>160.00–168.00</td>
<td>161.51–169.58</td>
<td>Mudstone</td>
<td>Grey</td>
</tr>
<tr>
<td>168.00–212.00</td>
<td>169.58–214.00</td>
<td>Sandstone</td>
<td>Grey</td>
</tr>
<tr>
<td>212.00–240.20</td>
<td>214.00–241.20</td>
<td>Coal</td>
<td>Black</td>
</tr>
<tr>
<td>240.20–245.00</td>
<td>241.20–245.68</td>
<td>Carbonaceous mudstone</td>
<td>Brown</td>
</tr>
<tr>
<td>245.00–247.50</td>
<td>245.68–248.01</td>
<td>Coal</td>
<td>Black</td>
</tr>
<tr>
<td>247.50–255.00</td>
<td>248.01–255.00</td>
<td>Sandstone/mudstone</td>
<td>Grey</td>
</tr>
</tbody>
</table>

Source: Black Butte Company.
punch plate and punch plate support, with the bottoms sealed tightly with bubble caps. An adjustable metering pump was used in the continuous leaching model to ensure a constant flow rate of extraction fluid (water). In the continuous leaching model, containers to hold both influent and effluent liquids were used during extraction.

2.2.4. Operation procedure

2.2.4.1. Continuous leaching method: A 5-kg dry rock sample was loaded in increments into the PVC column. In order to minimize particle segregation and compaction, the sample increments were carefully loaded without shaking or tamping. Cotton filter medium was inserted into the column near the sampling point in order to withdraw sample effluents using a syringe during the extraction process. Deionized water (DI) was pumped from a container holding a minimum of six liters into the column at a specified flow rate using a diaphragm-type metering pump (series 100/150). The initial temperature and pH of the leachate water, as well as the date and starting time of the leaching
process, were recorded in accordance with ASTM D 1293 (Hazardous Substances Data Bank, 1998). Extraction sample of about 10-mL was collected in plastic vials from the sampling point at different time periods. Collected leachate samples were then analyzed for leachable metals using an ICP-OES spectrometer (ICAP 6000 series, Thermo Scientific). The same procedure was used under different experimental conditions, including flow rate and pH.
2.2.4.2. Batch leaching method: With the exception of the use of a metering pump, the procedure largely similar to method (I) was used to assess the batch leaching method. DI water (~1,800 mL) was added to the column at the start of the leaching process and the amount was adequate to saturate the sample, and small aliquot samples (10 mL) were withdrawn and poured into 15-mL vials every 8 h over a period of 40 h (unless otherwise specified) from the column sampling point. Procedure was repeated at different pH and temperatures.

3. Results and discussion

3.1. Reference sample analysis

Table 3 lists (in mg/kg) the results of heavy metal concentrations potentially present in sandstone rock samples. Because of the chemical composition, matrix complexity and insolubility of the rock type in mild acidic media (due mainly to a high silica content of approximately 95–97% and various other resistant mineral constituents), the fine powder sample was treated under harsher acidic conditions to ensure complete elemental extraction into the aqueous solution. The method used for the sample dissolution is outlined in Section 2.2.2. In order to minimize errors due to the varying distribution of elements within different rocks, the concentrations shown in Table 3 are based on an average of three representative sandstone samples. The reported data are based on the average of three independent runs with a calculated relative standard deviation of ~2%. The sandstone samples were found to contain a total of 13 heavy metals at various concentrations, all within the calibration curve and the inductively coupled plasma (ICP) detectable range. Compared to the remaining elements, barium (Ba) and manganese (Mn) concentration levels were observed to be highest. However, Ba and Mn are considered less harmful contaminants, and their levels in the sample were far below the allowable limits set by the WHO and EPA for standard potable water. Other, more toxic elements such as Cd, As, Be, Co, Cu, Ni, Pb, and Se were present as well, but with lower ppm-range concentrations. The remaining elements (Cr, Zn, and V) showed moderate ppm concentration levels. Iron appeared to be present in high quantities, but showed inconsistency (possibly from the jaw crusher's blades) among the samples, and so was not included in this study.

In order to get some clue about the chemical composition of the sandstone sample, approximately 4-g finely ground sample was pressed into a solid pellet and scanned by XRF (PANalytical Axios XRF analyzer, PANalytical Inc., Almelo, the Netherlands). Table 4 illustrates the concentrations of some major constituents that are present in the sample. Elements in the actual sandstone rocks are tabulated as “metal oxides” and were reported in weight percent (W %) with absolute errors less than 0.080%. It can

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration in ppm (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic (As)</td>
<td>5.51</td>
</tr>
<tr>
<td>Barium (Ba)</td>
<td>206.81</td>
</tr>
<tr>
<td>Beryllium (Be)</td>
<td>0.93</td>
</tr>
<tr>
<td>Cadmium (Cd)</td>
<td>0.85</td>
</tr>
<tr>
<td>Cobalt (Co)</td>
<td>4.97</td>
</tr>
<tr>
<td>Chromium (Cr)</td>
<td>18.09</td>
</tr>
<tr>
<td>Copper (Cu)</td>
<td>8.68</td>
</tr>
<tr>
<td>Manganese (Mn)</td>
<td>275.84</td>
</tr>
<tr>
<td>Nickel (Ni)</td>
<td>6.19</td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td>7.55</td>
</tr>
<tr>
<td>Selenium (Se)</td>
<td>5.44</td>
</tr>
<tr>
<td>Zinc (Zn)</td>
<td>33.37</td>
</tr>
<tr>
<td>Vanadium (V)</td>
<td>38.91</td>
</tr>
</tbody>
</table>
be seen that, alumina “aluminum oxide” (Al$_2$O$_3$) and silica “silicon dioxide” (SiO$_2$) are predominantly present due to the fact that the rock used in the study is of sandstone type. Other metal oxides are present with lower concentrations.

### 3.2. Effect of flow rates on metal leaching

Variations in flow rate were examined in order to determine any effects they might have on the fractionation or the desorption of metals from the sandstone rocks and the dissociation from their counter anions. Aliquots were collected every 8 h from the column’s sampling point over a period of 40 h and analyzed by ICP. Other experimental parameters such as temperature and pH were kept constant at 21°C and 6, respectively. Water was introduced from the top of the column and percolated downward through the sandstone particles at four specified constant flow rates. The water flow rates used in the study ranged from 11.67 to 33.33 mL/min. Figures 4–8 represent (in ppb) concentrations of soluble metals in the leachate, tending toward mobilization through the sandstone particles at various flow rates from the bottom column’s sampling point; these were collected at specified sampling periods.

The results obtained were generated from the average of three independent experiments. Regardless of the flow rate applied, only 5 of the 13 elements were observed to have any desorption capability through rocks and dissociation from their minerals under the specified conditions. Their easy fractionation might be attributed to their weak physical or chemical adsorption bonding in their minerals or might instead be due their solubility tendency relative to the other heavy elements.

The majority of the other heavy metals in the studied rock particles did not show any leaching under the given conditions. Their immobility might possibly owe either to their chemical bonding interactions with the rock’s particle surfaces or to the formation of complexes with the rock’s

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### Table 4. The concentrations of major oxides in rock sample (sandstone)

<table>
<thead>
<tr>
<th>Compound name</th>
<th>Concentration in weight (%)</th>
<th>Absolute error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$O$_3$</td>
<td>16.997</td>
<td>0.035</td>
</tr>
<tr>
<td>BaO</td>
<td>0.074</td>
<td>0.001</td>
</tr>
<tr>
<td>CaO</td>
<td>3.290</td>
<td>0.0095</td>
</tr>
<tr>
<td>CeO$_2$</td>
<td>0.023</td>
<td>0.001</td>
</tr>
<tr>
<td>Cl</td>
<td>0.033</td>
<td>0.001</td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td>0.005</td>
<td>0.0005</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>2.708</td>
<td>0.005</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>2.763</td>
<td>0.0065</td>
</tr>
<tr>
<td>MgO</td>
<td>1.549</td>
<td>0.01</td>
</tr>
<tr>
<td>MnO</td>
<td>0.054</td>
<td>0.001</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>1.122</td>
<td>0.025</td>
</tr>
<tr>
<td>Nb$_2$O$_5$</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>NiO</td>
<td>0.007</td>
<td>0.001</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>1.886</td>
<td>0.0065</td>
</tr>
<tr>
<td>Rb$_2$O</td>
<td>0.011</td>
<td>0.001</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>0.266</td>
<td>0.0025</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>68.595</td>
<td>0.08</td>
</tr>
<tr>
<td>SrO</td>
<td>0.011</td>
<td>0.001</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.554</td>
<td>0.0035</td>
</tr>
<tr>
<td>Y$_2$O$_3$</td>
<td>0.003</td>
<td>0.001</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.007</td>
<td>0.001</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>0.040</td>
<td>0.001</td>
</tr>
</tbody>
</table>
minerals. Another explanation could be that some might have leached or desorbed out but formed complexes with minerals in the rock and, as a result, showed no solubility toward water. However, as evidenced by its high concentrations at all flow rates and collection times, one of the leached species, boron (B), showed the highest mobility of all the elements. All plots show that concentrations of B exhibited a direct relationship with flow rate, indicating that its migration or desorption increased as it contacted the water flow. By contrast, the fractionation of other leached elements within the run showed somewhat less mobility based on flow rate variation.

Figures 4–8 also show desorption of these metal species with respect to sampling time. It can be observed that prolonged water contact with the particles’ surfaces significantly impacted the
metals’ mobility. Maximum concentration levels of leached metals occurred at the first sampling collection time (8 h); leachate collected at later sampling times (i.e. 16, 24, 32, and 40 h) showed lower concentrations of leachable metals. Prolonged contact with the water flow caused desorption within shorter time periods due either to solubility or the weak physical bonding of these species with the rock surface. It is worth noting that all of the leached metals’ concentrations at all flow rates were observed to be below the WHO/EPA drinking water standard limits (Table 1). From these findings, it was determined that to complete the remaining task of determining the effect of pH on metal leaching, a lower flow rate would be recommended in order to minimize desorption of the leachable metals (especially, B and Mn).

3.3. Continuous vs. batch leaching

A comparison of continuous and batch processes for the leachable heavy metals is presented in Figures 9 and 10, with levels of the extracted amounts shown in ppb concentrations. The concentrations are plotted against collection sampling time periods of 8, 16, 24, 32, and 40 h. Experiments were conducted at a constant temperature of 21°C and a pH of 6. A water flow rate of 6.33 mL/min was used in the continuous leaching. In the case of batch leaching, a quantity of water (about 1,800 mL) was added from the top of the column sufficient to immerse the 5-kg sandstone particles at the beginning of the process. Samplings were taken periodically every 8 h. Only four metals (B, Ba, Mn, and Zn) appeared to have any mobility in either leaching process. The amounts of Ba and Zn leached were comparable regardless of the leaching process. Steady water contact with the particle surfaces in batch leaching did not cause any noticeable desorption enhancement of the leached metals, rendering extracted metal concentration levels similar to those of the continuous process. However, B was an exception to this finding, evincing a slightly higher mobility in the continuous process compared to the batch process. The reason for this might be due to the flow of water moving downward through the particles, causing greater mobility of B. By contrast, the behavior of Zn was opposite to that of B due perhaps to the physical interaction or bonding of Zn to the particle surface. Finally, water contact and flow rate were not shown to have any significant effect on leaching of the metals.

Figure 7. Effect of flow rate on metal leaching (collection time 32 h).

Figure 8. Effect of flow rate on metal leaching (collection time 40 h).
remaining elements present in the studied rock material. V was not detected as in the previous plots and this could be attributed to the uneven metal’s distribution within the rocks.

### 3.4. Effect of pH on the heavy metals mobility

Figures 11–14 represent leaching of some of the heavy metals that showed their tendency to dissociate or desorb from their minerals and their dependency on pH change. Samples were taken every 12 h over 10 sampling times. Results obtained in the study showed that only 4 out of the total 13 heavy metals present in the sandstone rocks were soluble and fall within the detectable range of the ICP calibration curve. These are namely boron, barium, manganese, and vanadium. The concentrations of these cations and their degree of pH dependency have some similar trends. All four metals have a higher solubility at lower pH. An increase in the pH tends to gradually decrease their solubility, and, as a result, they become more immobile and hence less leachable. The lower mobility
could be attributed to their precipitations and formation of insoluble (i.e. aluminum oxides or iron hydroxides) complexes in the basic media. Prolonged contact did not seem to cause significant effect on the rate of the dissociation of the metals, and particularly in the case Mn and V, whereas B indicated some solubility rate increase with contact time. The solubility profiles are not perfectly graphed, which is mainly due to the heterogeneity and the less uniform distribution of the heavy metals within and between the rock samples. Due to the above reason, Zn was not present in any of the plots.
and this could be due to its concentration variation among the rocks or the possibility of its precipitation with iron hydroxides media of higher pH.

3.5. Determination of inorganic anions in the leachate

Table 5 lists all possible anions present in the leachate that were collected from the different pH solution media and analyzed via Ion Chromatography (Metrohm 792 IC). In Table 5, sulfate ion has the highest concentrations (441–560 mg/L) among all the anions. This may indicate that most of the leached heavy metal cations originally bonded with sulfate in minerals. However, Ba tends to have low solubility in the presence of sulfate which forms BaSO₄, but the presence of chloride ion as the second major ion in the leachate (28–45 mg/L) and nitrate ion (4–17 mg/L) would indicate that Ba could be fractionated or desorbed from minerals that contain chloride or nitrates. BaCl₂ and Ba(NO₃)₂ are known to be more soluble, and the presence of high levels of chloride ion may enable sulfate-rich water to retain more Ba in the solution. In the case of Mn, it was mentioned that most of its salts are readily soluble in water, with the exception that its carbonate and phosphate have low solubilities in water (Hazardous Substances Data Bank, 1998). Boron salts are generally soluble, although some boron salts such as boron nitrite are completely insoluble in water. Boron halides are soluble in water, which would suggest that boron could be fractionated or desorbed from chloride mineral complexes. The major anions in the leachate are listed in Table 5.

3.6. Determination of the desorption order of leachable heavy metals

A batch leaching run is presented in Figure 15. Rate of leaching of each individual metal varies with time. B and Mn have similar leaching profiles, where the concentrations show a direct increase with time. Similar leaching behaviors were observed for Ba and V. Leaching rates of Ba and V were almost constant, regardless of the sampling time. The concentrations of each leached species were plotted against time. If the leaching data of contaminant species $i$ fit a first-order kinetic model, then plot of $-\ln (C_i - C_j) \sim t$ should be linear with a high regression coefficient. Figures 16–19 are used to establish the

<table>
<thead>
<tr>
<th>Sample (mg/L)</th>
<th>pH 6</th>
<th>pH 7</th>
<th>pH 8</th>
<th>pH 9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluoride</td>
<td>1.5</td>
<td>1.7</td>
<td>1.7</td>
<td>1.7</td>
</tr>
<tr>
<td>Chloride</td>
<td>28.4</td>
<td>29.1</td>
<td>30</td>
<td>45</td>
</tr>
<tr>
<td>Nitrite as N</td>
<td>1.7</td>
<td>2.0</td>
<td>0.30</td>
<td>2.2</td>
</tr>
<tr>
<td>Nitrate as N</td>
<td>5.7</td>
<td>4.4</td>
<td>4.9</td>
<td>17.4</td>
</tr>
<tr>
<td>Bromide</td>
<td>0.2</td>
<td>0.2</td>
<td>0.10</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Phosphate</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Sulfate</td>
<td>484</td>
<td>443</td>
<td>441</td>
<td>560</td>
</tr>
</tbody>
</table>

Figure 15. Batch leaching (total volume 2 L).
reaction orders of B, Ba, Mn, and V. Generally speaking, the leaching of the four species follows a first-order kinetic model. However, the regression values \( R^2 \) for all plots are not very high, which could be attributed to the uneven distribution of heavy metal within the rock particles. Dissociation or desorption rate constant \( k_i \) in E1–E4) for each leached metal can be obtained from the slope of the corresponding plot and they are presented in Table 6.

3.7. Effect of temperature on the desorption of heavy metals
The depth of an aquifer is another indirect factor to be considered when it comes to the storage of water. Temperature within the Earth increases with depth. It has been reported that the increase is about 25°C per km of depth in most of the world (MadScience Network, 2002). As a result, it is
important to examine the effect of temperature on the desorption of the heavy metals from their minerals. In this study, the temperature variations over the range of 5–55°C were tested to find out their effects on the desorption of the heavy metals. The investigations in this study have shown that only four metals have been desorbed to some degree and dissolved in water regardless of temperature. However, the dissolution of these leached metals has shown an increasing trend with temperature. Tables 7–10 represent the average concentrations of triplicate independent runs of B, Ba, Mn, and V at specified temperatures. A noticeable increase of the concentration was observed for each metal within each table as going down (as temperature increases) the tables regardless of sampling.
times. However, the horizontal trend shows no major concentration variations between sampling times, rather a constant rate of leaching and therefore a dynamic status.

### 3.8. Determination of solubility-product constant, $K_{sp}$

The solubility product constant, $K_{sp}$, is the equilibrium constant for a solid substance dissolving in an aqueous solution. It represents the level at which a solute dissolves in a solution. This constant can be applied in this study for the leachable metals to check their degree of desorption, and hence their solubility in water. The general adsorption/desorption equation of the leaching metals can be written as:

$$M_A(s) \rightleftharpoons x M^+ + y A^{-}$$  \hspace{1cm} (R1)

where $M_A(s)$ represents the undissolved solid or mineral complexes in the rock particle that have shown some tendency to dissolve and dissociate in contact with water to give $M^+$ and $A^-$. $M^+$ is the leached metal cations such as B, Ba, and Mn dissolved in water. On the other hand, $A^-$ is the counter part of the cations (anions listed in Table 5). Since the cations’ and anions’ concentrations are measured and known, the equilibrium constants ($K_{sp}$) for the desorbed species can be found by the following equation:

$$K_{sp} = [M^+]^x[A^-]^y$$  \hspace{1cm} (E5)

where $K_{sp}$ is the product of the concentration of the ions that are present in the saturated water solution. Tables 11–13 present the $K_{sp}$ values for the data collected at day 6 at temperatures of 5–55°C for the expected low soluble compounds along with their corresponding literature values. As it can be seen from these tables, the experimental $K_{sp}$ values turned out to be slightly different than that of the ones reported in the literature. The difference may be contributed to the matrix complexity and the chemical composition of the minerals present in the rock. Hence, these metals are not purely dissociated from their counter ions species i.e. $H^+$, $SO_4^{2-}$ and $OH^-$, but rather from other minerals. Another reason for this inconsistency could be due to the presence of some precipitating metals or oxides which altered the solubility of these compounds. No $K_{sp}$ values have been found in the literature for Vanadium compounds, and as a result the experimental $K_{sp}$ values were not included in

<table>
<thead>
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<th>Day/temperature (°C)</th>
<th>Day 1</th>
<th>Day 2</th>
<th>Day 3</th>
<th>Day 4</th>
<th>Day 5</th>
<th>Day 6</th>
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<td>5</td>
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<td>6.4</td>
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<td>4.8</td>
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<td>11.4</td>
<td>9.8</td>
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<td>26.9</td>
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<td>13.3</td>
<td>32.3</td>
<td>14.3</td>
<td>40.7</td>
<td>60.8</td>
<td>58.4</td>
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<td>29.7</td>
<td>39.9</td>
<td>78.8</td>
<td>120.7</td>
<td>86.9</td>
<td>68.2</td>
</tr>
<tr>
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<td>41.5</td>
<td>108.3</td>
<td>84.9</td>
<td>124.0</td>
<td>120.9</td>
<td>134.2</td>
</tr>
<tr>
<td>55</td>
<td>192.9</td>
<td>252.8</td>
<td>272.6</td>
<td>296.9</td>
<td>291.2</td>
<td>296.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Day/temperature (°C)</th>
<th>Day 1</th>
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<th>Day 3</th>
<th>Day 4</th>
<th>Day 5</th>
<th>Day 6</th>
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<td>138.6</td>
<td>127.6</td>
<td>128.3</td>
<td>128.3</td>
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<td>150.3</td>
<td>144.8</td>
<td>143.4</td>
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<td>137.8</td>
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<td>161.1</td>
<td>149.7</td>
<td>147.5</td>
<td>157.0</td>
<td>149.7</td>
<td>154.6</td>
</tr>
<tr>
<td>45</td>
<td>169.5</td>
<td>150.5</td>
<td>153.1</td>
<td>148.7</td>
<td>151.2</td>
<td>151.8</td>
</tr>
<tr>
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<td>159.4</td>
<td>166.6</td>
<td>173.5</td>
<td>165.4</td>
<td>169.6</td>
<td>162.9</td>
</tr>
</tbody>
</table>
the study. Vanadium has been reported to exist as vanadyl and vanadate ions with the chemical formulas (VO$_2^+$ and VO(OH)$_2^+$) and ($H_2VO_4^-$ and $HVO_2^-$) (Bernhard & Werner, 1989). These two forms are found to be soluble and easily transferable from geological sediments to water. However, the concentration of vanadium was not high in the water and this is due to the fact that both compound species are known to bind strongly to some minerals and cations (such Al$_2$O$_3$, TiO$_2$) and some organics (ethylenediaminetetraacetic acid and acetylacetonate), and are either adsorbed or form complexes.

### 3.9. Determination of enthalpies ($\Delta H$) and entropies ($\Delta S$) for the leachable elements

Determination of the thermodynamic quantities, i.e. $\Delta H$ and $\Delta S$, for the leachable elements can be obtained by measuring $K_{sp}$ over a specified temperature range. These thermodynamic quantities can be expressed by the following equation as:

### Table 11. B(OH)$_3$ solubility product constants

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Concentration of B (ppb)</th>
<th>Concentration of B(OH)$_3^-$ (mol/L)</th>
<th>Concentration of H$^+$ (mol/L)</th>
<th>Experimental $K_{sp}$</th>
<th>Literature $*K_{sp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>211.6</td>
<td>1.9573 x 10$^{-5}$</td>
<td>5.0118 x 10$^{-3}$</td>
<td>9.8094 x 10$^{-14}$</td>
<td>5.80 x 10$^{-10}$</td>
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<tr>
<td>15</td>
<td>245.1</td>
<td>2.2671 x 10$^{-5}$</td>
<td>5.0118 x 10$^{-3}$</td>
<td>1.1362 x 10$^{-13}$</td>
<td>5.80 x 10$^{-10}$</td>
</tr>
<tr>
<td>25</td>
<td>385.5</td>
<td>3.5658 x 10$^{-5}$</td>
<td>5.0118 x 10$^{-3}$</td>
<td>1.7871 x 10$^{-13}$</td>
<td>5.80 x 10$^{-10}$</td>
</tr>
<tr>
<td>35</td>
<td>606.5</td>
<td>5.6100 x 10$^{-5}$</td>
<td>5.0118 x 10$^{-3}$</td>
<td>2.8116 x 10$^{-13}$</td>
<td>5.80 x 10$^{-10}$</td>
</tr>
<tr>
<td>45</td>
<td>800.2</td>
<td>7.4017 x 10$^{-5}$</td>
<td>5.0118 x 10$^{-3}$</td>
<td>3.7096 x 10$^{-13}$</td>
<td>5.80 x 10$^{-10}$</td>
</tr>
<tr>
<td>55</td>
<td>877.9</td>
<td>8.1204 x 10$^{-5}$</td>
<td>5.0118 x 10$^{-3}$</td>
<td>4.0698 x 10$^{-13}$</td>
<td>5.80 x 10$^{-10}$</td>
</tr>
</tbody>
</table>

*Literature values at 25°C.

### Table 12. BaSO$_4$ solubility product constants

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Concentration of Ba$^{2+}$ (ppb)</th>
<th>Concentration of Ba$^{2+}$ (mol/L)</th>
<th>Concentration of SO$_4^{2-}$ (mol/L)</th>
<th>Experimental $K_{sp}$</th>
<th>Literature $*K_{sp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>30.0</td>
<td>2.1846 x 10$^{-7}$</td>
<td>5.04 x 10$^{-3}$</td>
<td>1.1007 x 10$^{-9}$</td>
<td>1.10 x 10$^{-10}$</td>
</tr>
<tr>
<td>15</td>
<td>40.1</td>
<td>2.9200 x 10$^{-7}$</td>
<td>5.04 x 10$^{-3}$</td>
<td>1.4713 x 10$^{-9}$</td>
<td>1.10 x 10$^{-10}$</td>
</tr>
<tr>
<td>25</td>
<td>50.4</td>
<td>3.670110$^{-7}$</td>
<td>5.04 x 10$^{-3}$</td>
<td>1.8492 x 10$^{-9}$</td>
<td>1.10 x 10$^{-10}$</td>
</tr>
<tr>
<td>35</td>
<td>65.3</td>
<td>4.7551 x 10$^{-7}$</td>
<td>5.04 x 10$^{-3}$</td>
<td>2.3958 x 10$^{-9}$</td>
<td>1.10 x 10$^{-10}$</td>
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<tr>
<td>45</td>
<td>70.9</td>
<td>5.1629 x 10$^{-7}$</td>
<td>5.04 x 10$^{-3}$</td>
<td>2.6013 x 10$^{-9}$</td>
<td>1.10 x 10$^{-10}$</td>
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<td>55</td>
<td>75.4</td>
<td>5.4905 x 10$^{-7}$</td>
<td>5.04 x 10$^{-3}$</td>
<td>2.7664 x 10$^{-9}$</td>
<td>1.10 x 10$^{-10}$</td>
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</tbody>
</table>

*Literature values at 25°C (Generalic, 2015).

### Table 13. Mn(OH)$_2$ solubility product constants

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Concentration of Mn$^{2+}$ (ppb)</th>
<th>Concentration of Mn$^{2+}$ (mol/L)</th>
<th>Concentration of OH$^-$ (mol/L)</th>
<th>Experimental $K_{sp}$</th>
<th>Literature $*K_{sp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>6.4</td>
<td>1.1650 x 10$^{-7}$</td>
<td>1.9952 x 10$^{-6}$</td>
<td>4.6377 x 10$^{-13}$</td>
<td>1.9 x 10$^{-13}$</td>
</tr>
<tr>
<td>15</td>
<td>26.9</td>
<td>4.8964 x 10$^{-7}$</td>
<td>1.9952 x 10$^{-6}$</td>
<td>1.9493 x 10$^{-15}$</td>
<td>1.9 x 10$^{-13}$</td>
</tr>
<tr>
<td>25</td>
<td>58.4</td>
<td>1.0630 x 10$^{-6}$</td>
<td>1.9952 x 10$^{-6}$</td>
<td>4.2319 x 10$^{-15}$</td>
<td>1.9 x 10$^{-13}$</td>
</tr>
<tr>
<td>35</td>
<td>68.2</td>
<td>1.2414 x 10$^{-6}$</td>
<td>1.9952 x 10$^{-6}$</td>
<td>4.9421 x 10$^{-15}$</td>
<td>1.9 x 10$^{-13}$</td>
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<td>9.7248 x 10$^{-15}$</td>
<td>1.9 x 10$^{-13}$</td>
</tr>
<tr>
<td>55</td>
<td>296.1</td>
<td>5.3897 x 10$^{-6}$</td>
<td>1.9952 x 10$^{-6}$</td>
<td>2.1457 x 10$^{-17}$</td>
<td>1.9 x 10$^{-13}$</td>
</tr>
</tbody>
</table>

*Literature values at 25°C (Generalic, 2015).
\[ \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \]  
(E6)

where \( \Delta G^\circ \) is the free energy change in a reaction. It can also be related to \( K_{sp} \) for the reaction by the equation,

\[ \Delta G^\circ = -RT \ln(K_{sp}) \]  
(E7)

Substitution of the left side of E6 with the right side of E7 yields E8.

\[ -RT \ln(K_{sp}) = \Delta H^\circ - T \Delta S^\circ \]  
(E8)

Rearrangement of E8 can lead to the following form, E9;

\[ \ln(K_{sp}) = -\frac{\Delta H^\circ}{R} \frac{1}{T} + \frac{\Delta S^\circ}{R} \]  
(E9)

Equation E9 is well suited for finding \( \Delta H^\circ \) and \( \Delta S^\circ \) by linear regression. Plotting \( \ln(K_{sp}) \) vs. \( 1/T \) as illustrated in Figures 20–22 would give the quantities of \( \Delta H^\circ \) and \( \Delta S^\circ \) from slopes \( (m = -\Delta H^\circ/R) \) and intercepts.
Table 14. Leachable metals’ thermodynamic values, $\Delta H^o$, $\Delta S^o$, and $\Delta G^o$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta H^o$ [kJ/mol]</th>
<th>$\Delta S^o$ [kJ/(K mol)]</th>
<th>$\Delta G^o$ [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>B(OH)$_3$</td>
<td>26.15</td>
<td>155.93</td>
<td>−20.34</td>
</tr>
<tr>
<td>BaSO$_4$</td>
<td>16.32</td>
<td>112.55</td>
<td>−17.23</td>
</tr>
<tr>
<td>Mn(OH)$_2$</td>
<td>52.12</td>
<td>160.74</td>
<td>41.93</td>
</tr>
</tbody>
</table>

($b = \Delta S^o/R$). The experimental thermodynamic values $\Delta H^o$, $\Delta S^o$, and $\Delta G^o$ for each leachable species are presented in Table 14.

4. Conclusions
Contaminant leaching model for ASR technology has been investigated in this study. The first part of the study was focused on a number of factors that could contribute or enhance the mobility of metals. These factors included pH, water injection flow rate, and temperature variation. The second part of the study examined the kinetic and thermodynamic properties of the leachable metals. The fractionation or the desorption of the leached metals from the studied sandstone rock samples were examined under the above-mentioned conditions. However, only 4 metals out of the 15, initially present in the rock samples, desorbed and appeared to show minimal concentrations in the water leachate compared to that of the reference samples. These concentrations were also found to be significantly below the WHO/EU standard limits for drinking water. Due to the very small contaminants found in the leachate, this puts the ASR as a promising and an alternative technology that may be used as way to replace some other highly expensive methods such as surface reservoirs.

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Author details
Abdulwahab Tuwati$^1$
E-mail: atuwati@uwyo.edu

Maohong Fan$^{1,2}$
E-mail: mfan@uwyo.edu

$^1$ Department of Chemical and Petroleum Engineering, University of Wyoming, Laramie, WY 72071, USA.
$^2$ School of Energy Resources, University of Wyoming, Laramie, WY 72071, USA.
$^3$ School of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA.

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