Solution with HS⁻

HS⁻ → FeS → Fe²⁺ → Fe³⁺ → HS⁻

Bentonite
Investigating bisulfide sorption onto bentonite through laboratory batch experiments

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Abstract

Bentonite clay is a key part of the engineered barrier system of the deep geological repositories (DGRs), designed by many nuclear nations worldwide to safely house the used nuclear fuel. However, the copper coated used fuel containers (UFCs) may undergo corrosion due to bisulfide (HS-) transport through the bentonite towards the containers. Understanding the sorption behaviour of HS- is therefore critical in understanding the HS- transport dynamics and in assessing the long-term safety of the DGR. As such, this study investigated HS- sorption onto bentonite, through laboratory batch experiments and microscopic/spectroscopic analyses, under the influence of various experimental conditions, such as contact time (1-120 hours), temperature (10-40°C), liquid to solid mass ratios (L:S) (100-1000), initial HS- concentration (1-6 mg L⁻¹). The study results indicated that HS- sorption onto bentonite occurred faster and the equilibrium sorption capacity increased (by 3%) with increasing temperature (from 10°C to 40°C). Several established kinetic and isotherm models were applied to the experimental data to provide insight into the key processes driving HS- sorption onto bentonite. The desorption test results indicated that HS- was irreversibly sorbed on bentonite. The surface analyses of the bentonite test samples were conducted using scanning electron microscopy along with energy dispersive spectroscopy. These results suggested that the sorption might have occurred due to chemical reactions of HS- with the iron present in bentonite and subsequent formation of iron monosulfide (FeS). The findings of this study provided critical information to better understand the underlying sorption mechanism of HS- on bentonite, which can reduce HS- transport in the DGR.
Keywords

Deep geological repository; Sorption; Bentonite; Bisulfide; Desorption, Iron monosulfide.
1 Introduction

Due to the widespread use of nuclear power, used nuclear fuel management is a major challenge faced worldwide. The most preferred and internationally recognized approach for long-term storage of used nuclear fuel is isolation in deep geological repositories (DGRs) (Chen et al., 2018; Hall et al., 2021). Similar to many nuclear nations, Canada has been developing a national DGR since the early 1970’s (Baumgartner et al., 1996; Standish et al., 2016). The latest DGR concept proposed by the Nuclear Waste Management Organization (NWMO) is to encapsulate the used nuclear fuel in a steel container with an outer shell of copper and emplace these used fuel containers (UFCs) in either crystalline or sedimentary host rock at least 500 m below ground surface (Hall et al., 2021). In the host rock, the UFCs will be surrounded by highly compacted bentonite, which can suppress the migration of corrosive agents and prevent microbiological activity (Chen et al., 2018, 2019; Hall et al., 2021). The use of bentonite – a swelling clay – in DGRs is widely favoured because of its low hydraulic conductivity, high sorption potential, self-sealing ability, and good durability (Sellin and Leupin, 2014; Kaufhold and Dohrmann, 2016).

Copper has been chosen as an exterior of UFCs by several countries as it is thermodynamically immune to most corrosion processes that may occur within the anoxic conditions expected in the DGR (Chen et al., 2014; Martino et al., 2014). During the initial phase of the DGR life (i.e., within a few months or years), a limited quantity of trapped oxygen will be present due to repository excavation and emplacement. As such, the UFCs may undergo oxic corrosion over this initial period (Standish et al., 2016; King et al., 2017). Once all trapped O₂ is consumed by corrosion or
other reduction processes, the repository environment is expected to remain anoxic for the remainder of its life (i.e., many millions of years) (King et al., 2017).

During this anoxic period, microbiologically-influenced corrosion of copper may occur due to bisulfide (HS\(^-\)) in the DGR, produced primarily by sulfate-reducing bacteria (SRB). HS\(^-\) may be generated in a DGR via ‘far-field’ production from SRB within the host rock or at the host rock/bentonite interface, particularly within the excavation damaged zone or other cracks/fissures (Hall et al., 2021). The low water activity and high swelling pressure of bentonite with dry densities \(\geq 1.6 \text{ g cm}^{-3}\) has been proven to suppress microbial activity within the buffer material, including HS\(^-\) production from SRB (Stroes-Gascoyne et al., 2010; Stroes-gascoyne et al., 2011). As bentonite has very low permeability, anoxic UFC corrosion in the DGR is expected to be governed by HS\(^-\) diffusion through the bentonite towards the UFC surface and subsequent formation of very porous copper sulfide (Cu:2S) films following Eq. (1) (Briggs et al., 2017; Hall et al., 2021):

\[
2Cu(s) + HS^{-}_{(aq)} + H^+_{(aq)} \rightarrow Cu_2S(s) + H_2(g)
\]  

(1)

However, several studies suggest that bentonite has a retardation effect on HS\(^-\) transport (Bengtsson and Pedersen, 2016, 2017; Pedersen et al., 2017). Generally, any process that partitions the aqueous phase mass onto a solid phase surface (e.g., via adsorption, absorption, precipitation or other chemical transformations) is described as sorption (Kaplan, 1999; Limousin, 2007; Vinšová et al., 2008). Therefore, HS\(^-\) sorption onto bentonite is expected to limit HS\(^-\) flux towards
the UFCs and minimize the risk of copper corrosion. A schematic illustration of HS\(^-\) sorption onto bentonite anticipated in the DGR is presented in Figure 1.

**Figure 1.** Generic illustration of HS\(^-\) sorption onto bentonite (A and B indicates different generic molecules)

Given this background, the sorption phenomenon of HS\(^-\) onto bentonite can be an important aspect of additional DGR safety, but the dynamics are not well-understood. Only a few studies that investigated the adsorption of H\(_2\)S gases on bentonite found that bentonite exhibits significant adsorption capacity for hydrogen sulfide (H\(_2\)S) gas, particularly when bentonite was modified with iron (Fe) and copper chloride (Nguyen-Thanh et al., 2005; Stepova et al., 2009). In addition, Pedersen et al. (2017) reported the sulfide immobilization capacity of different types of bentonite clays (i.e., Wyoming MX-80, Asha, and Calcigel) was in the range of 40–90 μmole H\(_2\)S g\(^-1\) clay.
Pedersen et al., (2017) also suggested that the immobilization mechanism of sulfide at a pH level above 7 can be explained by the oxidation-reduction (redox) reaction of $\text{HS}^{-}$ with the ferric iron ($\text{Fe}^{3+}$) present in bentonite, and the resulting formation of ferrous sulfide ($\text{FeS}$) and elemental sulfur following Eq. (2) (Pedersen et al., 2017). The role of bentonite as a sink to immobilize the sulfide as solid iron sulfides has also been reported in several other studies (Wersin et al., 2014; Maanoja et al., 2020; Miettinen et al., 2022).

$$2\text{HS}^{-} + 2\text{Fe}^{3+} \rightarrow \text{Fe}^{2+} + S^{0} + \text{FeS} + 2\text{H}^{+} \quad (2)$$

Another experimental study on MX-80 bentonite and sulfide solutions conducted by Swedish Nuclear Fuel and Waste Management Company observed a decrease in concentration of the sulfide added in the solution due to presence of bentonite (Svensson and Wikberg, 2017). That study suggested that sulfide-bentonite interaction seemed to proceed quickly (within 1–2 hours), and sulfide seemed to be removed in the range of 1–10 kg per 1000 kg of bentonite (Svensson and Wikberg, 2017). However, this study did not provide insight into the sulfide loss mechanism (e.g., absorption/transformation/reaction), and a key knowledge gap persists.

In general, there is a lack of systematic studies that investigate the nature of $\text{HS}^{-}$ sorption onto bentonite (i.e., whether it is reversible physisorption or irreversible chemisorption or a combination of both). In addition, the effect of various DGR conditions (e.g., temperature, pH, redox conditions, $\text{HS}^{-}$ concentration) on the capacity of bentonite to sorb $\text{HS}^{-}$ has not been thoroughly investigated. This knowledge gap hinders the development of a reactive transport model of $\text{HS}^{-}$ in a DGR. To
address this knowledge gap, laboratory batch sorption experiments were conducted to evaluate the
effect of key factors (i.e., temperature, contact time, liquid to solid mass ratio, and HS− concentration) on the sorption behaviour of HS− onto MX-80 bentonite. In addition, the sorption
mechanism and the kinetic rate limiting processes were investigated by applying various kinetic
and isotherm models to the experimental data. Desorption tests and field emission scanning
electron microscopy and energy dispersive spectroscopy (FESEM/EDS) analyses were performed
to obtain further insight into the HS− interactions with bentonite. Although the study does not aim
to directly explore sorption in the compacted bentonite planned in the real DGR, it endeavours to
provide key information on the fundamental aspects of HS− sorption onto bentonite. The sorption
dynamics obtained from this study can be applied to develop a thermodynamic sorption model of
HS− onto bentonite, which will allow researchers to accurately model the reactive transport of HS−
in the DGR.

2 Materials and Methods

2.1 Materials

All the experiments were conducted using MX-80 powder bentonite supplied by NWMO.
According to the X-ray diffraction (XRD) analysis results reported by Dixon et al. (2018) and
Dixon (2019), the MX-80 bentonite sample contains predominately montmorillonite (79-95%,
with an average of 87%) and some other minerals such as Calcite (2.2-3.6%), Quartz (1.6-3.5%),
Illite (0.3-7.1%), K-Feldspar (3-6.8%), Pyrite (0.6%), Gypsum (0.4%). In addition, some key
minerology related characteristics of MX-80 include cation exchange capacity of >75 cmol(+) kg\(^{-1}\), specific surface area of >500 m\(^2\) g\(^{-1}\), and specific gravity of 2.75 (Dixon et al., 2018; Dixon, 2019).

All solutions used in the study were prepared using ASTM Type 1 (18 MΩ-cm) ultrapure filtered and deionized (DI) water (Milli-Q® Direct 8/16, MilliporeSigma) deoxygenated by purging nitrogen gas. All chemicals used, e.g., sodium sulfide salt (Na\(_2\)S·9H\(_2\)O, ≥ 99.99% purity), bisulfide analysis reagents, sodium hydroxide salt (NaOH, 99.99% purity), hydrochloric acid (HCl, 36.5 to 38% assay) were analytical grade, purchased from Fisher Scientific and MilliporeSigma.

### 2.2 Sorption experiments

While designing the batch experiments, the study selected 4 independent variables, which were identified by others as some of the key factors influencing the sorption dynamics on bentonite (Xu et al., 2008; Zhao et al., 2008; Yang et al., 2009; CB. Gupt et al., 2019). Table 1 presents an overview of two sets of batch experiments conducted to observe the effects of the selected factors, such as: (i) contact time, (ii) temperature, (iii) liquid to solid mass ratio (L:S), and (iv) initial HS\(^{-}\) concentration on HS\(^{-}\) sorption onto bentonite. Temperature was selected as an important factor to understand sorption kinetics and thermodynamics, and due to its relevance in the DGR. The other parameters, such as: contact time, liquid to solid mass ratio (L:S), and initial HS\(^{-}\) concentration were selected primarily to determine their appropriate range to execute the batch experiments in the laboratory set up and to provide more information about the various sorption mechanisms. The
range of the values of the factors were selected considering the experimental constraints and anticipated DGR conditions (see rationale in Table 1).

**Table 1.** Batch experiment overview

<table>
<thead>
<tr>
<th>Experiment set no.</th>
<th>Independent variables</th>
<th>Rationale of selecting the range of values</th>
<th>Constant experimental conditions</th>
</tr>
</thead>
</table>
| 1.                 | Contact time = 1-120 hours | From experimental observation of the time required to reach equilibrium | pH = 9.5  
L:S = 100  
Initial HS\(_{-}\) conc. = 5 mg L\(^{-1}\) |
|                    | Temperature = 10, 22, 30, 40°C | The Canadian DGR is anticipated to experience elevated temperatures (10-80°C) (King et al., 2017; Hall et al., 2021), which will affect sorption kinetics and thermodynamics. The range (10-40°C) was chosen based on practical equipment limitations. | |
|                    | L:S = 200, 500, 1000 | Based on preliminary work performed to select the appropriate L:S for the study (discussed in detail in Section S.1 of supplementary information (SI)). | pH = 9.5  
Temp = 22±2°C  
Contact time = 28-30 hours |
| 2.                 | Initial HS\(_{-}\) Concentration = 1, 2, 3, 4, 5, 6 mg L\(^{-1}\) | A minimum of 1 mg L\(^{-1}\) initial HS\(_{-}\) concentration was required to maintain detectable aqueous HS\(_{-}\) after sorption onto bentonite  
Samples with higher initial HS\(_{-}\) concentration (> 6 mg L\(^{-1}\)) exhibited large measurement error. | |
2.2.1 Stock solution preparation

Bentonite stock solutions were prepared for all experiments at a liquid to solid ratio (L:S) of 20 by adding required amount (12.5 g) of dried bentonite powder in deoxygenated water (250 ml) and mixing with a probe sonicator (Qsonica Q700, 700 watts) for 1 hour at 40% amplitude. The ultrasonication helped to deagglomerate the bentonite particles and to ensure a homogenously dispersed bentonite slurry.

HS\textsuperscript{-} stock solutions were prepared at desired HS\textsuperscript{-} concentrations by dissolving sodium sulfide nonahydrate (Na\textsubscript{2}S\textperiodcentered9H\textsubscript{2}O, MilliporeSigma, ≥ 99.99% purity) salt in deoxygenated water following the standard method 4500-S\textsuperscript{2-} A. (APHA, 2017).

2.2.2 Sample and blank preparation

Sample solutions were prepared in 50 mL Pyrex® glass centrifuge tubes (Fisher Scientific) by mixing the required amounts of bentonite and HS\textsuperscript{-} stock solutions and diluting with deoxygenated DI water to obtain the desired L:S and HS\textsuperscript{-} concentration (as shown in Table 1). The initial pH values of the samples were found in the range of 8-10. As HS\textsuperscript{-} is the dominant sulfide species at pH > 9 (Lewis, 2010; Ahlatci et al., 2016; Neto et al., 2018), the pH values of the samples were adjusted at ≈9.5 (by adding 0.1 M NaOH and/or 0.1 M HCl) to avoid loss of HS\textsuperscript{-} due to H\textsubscript{2}S gas formation.

For each experimental condition, two different types of experimental blanks were prepared: type (i) with HS\textsuperscript{-} but no bentonite and type (ii) with bentonite but no HS\textsuperscript{-}. Type (i) blanks were used to
determine the loss of HS\(^-\) due to experimental effects other than sorption onto bentonite (e.g., adsorption of HS\(^-\) on the centrifuge tube walls). Around 2-10% loss of HS\(^-\) was observed from type \((i)\) blank analysis. In addition, type \((ii)\) blanks were used to measure the background absorbance resulting from the combined effect of bentonite particle (< 0.2 µm) interference and presence of background HS\(^-\) in bentonite (type \((ii)\) blank analyses are discussed in detail in Section S.1 of supplementary information (SI)). The stock, sample, and blank solutions were prepared in an anaerobic chamber (Coy Laboratory Products) to minimize the loss of HS\(^-\) due to oxidation and to ensure the anoxic conditions expected in the DGR.

### 2.2.3 Measuring the HS\(^-\) concentration \((C_t)\)

After sample and blank preparation, the centrifuge tubes were placed in a tube rotator (MX-RD-Pro, SCILOGEX) and shaken at 60 rpm for the required contact time (as shown in Table 1). To vary temperature, the rotary shaker was placed in a dual incubator/refrigerator (MaxQ 6000, Thermo Fisher Scientific) and the tubes were shaken at four different temperatures controlled at 10, 22, 30 and 40°C. After shaking, the solid and aqueous phases were separated by centrifuging the solutions at 2100 rpm for 1 hour and sequentially filtered with 1.2 and 0.2 µm hydrophilic polytetrafluoroethylene (PTFE) syringe filters (Fisher Scientific). Finally, the HS\(^-\) concentration in the aqueous phase was measured using the standard methylene blue method (4500-S\(^2\)-D) with a spectrophotometer (Hach DR 3900, Hach) at a wavelength of 665 nm (APHA, 2017). The method detection limit for HS\(^-\) was determined as 0.02 mg L\(^{-1}\). The experiment blanks were also analyzed using the same protocol followed for the test samples.
2.3 Desorption test

Desorption test samples (prepared with bentonite and HS\textsuperscript{-} at L:S = 100 and 1000 and an initial HS\textsuperscript{-} concentration of 6 mg L\textsuperscript{-1}) were shaken at room temperature (22±2°C) for more than 24 hours to reach sorption equilibrium, as determined from Experiment set 1. Then, the phases were separated by centrifugation and the aqueous phases were removed as much as possible. The volume of solution removed was replaced by an equal volume of deoxygenated DI water without HS\textsuperscript{-} at a pH ≈ 9.5. The new mixtures were then shaken for 24, 48, 72, and 96 hours at 22 and 40°C, centrifuged, and filtered. The remaining aqueous phases were then analyzed to determine whether any HS\textsuperscript{-} had desorbed from the bentonite.

2.4 Bentonite surface analysis

Surface analyses via field emission scanning electron microscopy (Thermo Fisher Scientific Quanta 3D 20KV voltage) coupled with energy dispersive spectroscopy were performed on selected test samples (bentonite with HS\textsuperscript{-} at L:S = 1000 and initial HS\textsuperscript{-} concentration 6 mg L\textsuperscript{-1}) and type (ii) blank samples (i.e., only bentonite, no HS\textsuperscript{-}). For FESEM/EDS analysis, the solid phase samples, which were separated via centrifugation, were dried in the anaerobic chamber upon a 2-3 cm bed of drierite. The samples were then crushed into a fine powder using a pestle and sieved through 200 mesh (75 μm) USA Standard sieve. The samples were then mounted on aluminum stubs over carbon tape followed by compressed air spraying (to obtain a bounded monolayer) and coated with 2-3 nm of platinum plasma using a sputter coater.
3 Calculations

3.1 Sorption% and sorption capacity

From the measured concentration of HS⁻, the sorption percentage of initial HS⁻ concentration $C_i$ (mg L⁻¹) added in the solution was calculated using the following equation:

$$\text{Sorption\%} = \frac{C_i,\text{corr} - C_t}{C_i,\text{corr}} \times 100\%$$

where $C_{i,\text{corr}}$ is the corrected initial HS⁻ concentration (mg L⁻¹). In this study, the type (i) blank concentration at each experimental condition was used to determine $C_{i,\text{corr}}$ to account for the experimental losses of HS⁻ other than sorption on bentonite. $C_t$ is the HS⁻ ions aqueous phase concentration at time $t$ (mg L⁻¹). The absorbance from type (ii) blank was subtracted from $C_t$ to account for the interference from small bentonite particulates and background HS⁻.

In addition, sorption capacity, i.e., mass of HS⁻ sorbed per unit mass of bentonite at any time ($t$), $q_t$ and at equilibrium, $q_e$ were calculated using the following equations:

$$q_t = \frac{(C_{i,\text{corr}} - C_t)V}{m}$$

$$q_e = \frac{(C_{i,\text{corr}} - C_e)V}{m}$$
Where $C_e$ is the HS–aqueous phase concentration at equilibrium (mg L$^{-1}$). $V$ is the solution volume (ml), and $m$ is mass of bentonite (g). The masses of the liquid and bentonite define the liquid to solid mass ratio (L:S) in each experiment.

### 3.2 Kinetic, isotherm and thermodynamic studies

To investigate the rate-limiting mechanisms and the nature of HS–sorption onto bentonite, three different kinetic models were explored, i.e., (i) Pseudo–first-order (PFO), (ii) Pseudo–second-order (PSO), and (iii) Weber’s intraparticle diffusion (IPD) model. While PFO and PSO models assume chemisorption to be the rate-limiting mechanism, the Weber and Morris kinetic model is applicable if intraparticle diffusion limits the rate of the sorption (Ho and Mckay, 1998; Tsibranska and Hristova, 2011; Rani and Mahajan, 2016). In addition, two common isotherm models were explored i.e., (i) Langmuir and (ii) Freundlich models. The Langmuir isotherm model describes monolayer sorption occurring on distinct localized sorption sites with uniform energies, whereas the Freundlich isotherm describes multilayer sorption occurring on heterogeneous surfaces and active sites with different energies (Edet and Ifelebuegu, 2020). The corresponding equations (Eqs. (S1-S13)) and implications of the kinetic and isotherm models are discussed in detail in Section S.4 of SI.

In addition, the thermodynamic parameters were determined following the Eqs. (S14-S15) as presented in Section S.4 of SI.
4 Results and discussion

4.1 Effect of contact time and temperature

The resulting sensitivities in HS⁻ sorption capacity of bentonite with contact time and temperature from Experiment set 1 (Table 1) are presented in Figure 2. The sorption % results are presented in Figure S.3 (Section S.2 of SI).

Figure 2. Effect of contact time and temperature on sorption capacity, \( q_t \) (mg kg\(^{-1}\)) related to HS⁻ sorption on bentonite (experimental conditions: L:S = 100, \( C_i = 5 \) mg L\(^{-1}\), pH = 9.5). All data presented are the average of duplicate or triplicate tests, with error bars showing the standard deviation.
Figure 2 suggests that similar sorption behaviour was observed for temperatures of 22, 30, and 40°C. At these temperatures, the sorption capacity increased sharply until 8 hours, and then gradually approached equilibrium in 24 hours at 22 and 30°C, and in 16 hours at 40°C. In contrast, slower sorption was observed at 10°C and it required much longer contact time (i.e., around 96 hours) to reach equilibrium at this lower temperature.

As shown in Figure 2, the sorption capacity values at the equilibrium conditions slightly increased from 442.5±1.71 to 455.8±0.85 mg kg\(^{-1}\) (about 3% increment) with increasing temperature from 10 to 40°C. To investigate whether this variation is significant or not, a single factor ANOVA (analysis of variance) test was performed (using Microsoft Excel) on the equilibrium sorption capacity values (i.e., from triplicate measurements, Table S.1, SI). From the ANOVA analysis test results (Table S.2 presented in Section S.3 of SI), the F-Statistic value (85.57) was found higher than F-Critical value (7.59, at 99% level of confidence), which suggested this small increase in equilibrium sorption capacity with temperature was statistically significant (Kazerouni, 2009). Altogether, these findings show that HS\(^{-}\) sorption onto bentonite was faster and the equilibrium sorption capacity increased slightly with increasing temperature.

According to several studies (Saeed and Ahmed, 2006; Boparai et al., 2011), this type of sorption trend (i.e., increase in sorption capacity with increasing temperature) indicates an endothermic chemisorption process, which involves the breaking of hydration bonds and formation of new bonds with the active sorbent sites (Saeed and Ahmed, 2007). To investigate the rate limiting
process of HS− sorption onto bentonite three kinetic models were applied and discussed in Section 4.2.

4.2 Sorption kinetic models

The linearized and non-linear forms of Pseudo-first-order (PFO), Pseudo-second-order (PSO) and Intraparticle diffusion (IPD) models were used to investigate the rate limiting mechanism of HS− sorption on bentonite. While the sorption kinetics in these experiments are complicated because of various consecutive processes, e.g., film/external diffusion, intraparticle diffusion, surface interaction by physisorption or chemisorption (Can, 2015; Nguyen et al., 2017; Sahoo and Prelot, 2020; González-lópez et al., 2022), these simplified kinetic models are commonly used to initially understand sorption processes in various contexts – including bentonite sorption studies (Galambos et al., 2013; Gomdje et al., 2015; Dada et al., 2019; Pająk et al., 2019). Figure 3 and Table 2 presents the key results from comparing the non-linear plots of the applied kinetic models, as many recent studies recommend non-linear methods provide improved insight and reduced method bias than linearized methods (Zafar et al., 2015; Simonin, 2016; Nguyen et al., 2017; Moussout et al., 2018; Bujdák, 2020; Revellame et al., 2020; González-lópez et al., 2022). Moreover, as per the recommendations of these studies, the chi-squared (χ², Eq. (S12), SI) values were calculated alongside the coefficients of determination (R², Eq. (S13), SI) to evaluate the fit of each model (Table 2). The linearized plots of the sorption kinetic models and their associated parameter values are presented and discussed in Section S.5 of SI.
Figure 1: Model fittings of pseudo-first-order (a), pseudo-second-order (b), and intraparticle diffusion (c) for different temperatures.
Figure 3. Non-linear plots of Pseudo-first-order, Pseudo-second-order, and Intraparticle diffusion models for HS\(^-\) sorption on bentonite (Experiment set 1 conditions: L:S = 100, initial HS\(^-\) concentration = 5 mg L\(^{-1}\), pH = 9.5). Points represent experimental data and dotted lines represent non-linear fit of models to the experimental data.

Table 2. Kinetic parameter values obtained from non-linear fitting of kinetic models

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameters</th>
<th>Temperature (C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>Pseudo-first-order model</td>
<td>q&lt;sub&gt;e,exp&lt;/sub&gt; (mg kg(^{-1}))</td>
<td>442.538</td>
</tr>
<tr>
<td></td>
<td>q&lt;sub&gt;e,cal&lt;/sub&gt; (mg kg(^{-1}))</td>
<td>431.831</td>
</tr>
<tr>
<td></td>
<td>k&lt;sub&gt;1&lt;/sub&gt; (h(^{-1}))</td>
<td>2.581</td>
</tr>
<tr>
<td></td>
<td>R(^2)</td>
<td>0.551</td>
</tr>
<tr>
<td></td>
<td>χ(^2)</td>
<td>1.33</td>
</tr>
<tr>
<td>Pseudo-second-order model</td>
<td>q&lt;sub&gt;e,exp&lt;/sub&gt; (mg kg(^{-1}))</td>
<td>442.538</td>
</tr>
<tr>
<td></td>
<td>q&lt;sub&gt;e,cal&lt;/sub&gt; (mg kg(^{-1}))</td>
<td>440.231</td>
</tr>
<tr>
<td></td>
<td>k&lt;sub&gt;2&lt;/sub&gt; (kg mg(^{-1}) h(^{-1}))</td>
<td>0.019</td>
</tr>
<tr>
<td></td>
<td>R(^2)</td>
<td>0.903</td>
</tr>
<tr>
<td></td>
<td>χ(^2)</td>
<td>0.551</td>
</tr>
<tr>
<td>Intraparticle diffusion model</td>
<td>C&lt;sub&gt;in&lt;/sub&gt; (mg kg(^{-1}))</td>
<td>413.237</td>
</tr>
<tr>
<td></td>
<td>k&lt;sub&gt;in&lt;/sub&gt; (mg kg(^{-1}) h(^{1/2}))</td>
<td>3.099</td>
</tr>
<tr>
<td></td>
<td>R(^2)</td>
<td>0.679</td>
</tr>
</tbody>
</table>

Figure 3 and Table 2 suggest that the PSO model showed better fit (with higher R\(^2\) [0.903-0.950] and lower χ\(^2\) values [0.001-0.561]) to the experimental data than the PFO and IPD models at all temperatures studied. The PSO model derived q<sub>e</sub> values were found to be close to the experimentally determined q<sub>e</sub> values (442.5±1.71 to 455.8±0.85 mg kg\(^{-1}\)) and an increasing trend
in second-order rate constants \( (k_2) \) values (from 0.019 to 0.032 kg mg\(^{-1}\) h\(^{-1}\)) was observed with increasing temperature from 10 to 40°C. In contrast, the non-linear PFO model provided lower \( R^2 \) (0.551-0.891) and higher \( \chi^2 \) values (0.269-1.45), indicating a poorer fit to the experimental data than the PSO Model. Furthermore, no trend in the first order rate constant \( (k_1) \) values was obtained from the PFO model.

Like the PFO model, the IPD model also showed a poorer fit \( (R^2 \text{ values } [0.450-0.755]) \) to the experimental data than the PSO model. For all the temperatures, the IPD model plots did not pass through the origin (Figure 3); which indicates that intraparticle diffusion was not the only rate-limiting step, but some other sorption mechanisms likely occurred simultaneously (Crini et al., 2007; Li et al., 2007; Tsibranska and Hristova, 2011).

Overall, the model results in Figure 3 reveal that pseudo-second order kinetics best described the sorption dynamics, which suggests that chemisorption appears to be the principal rate-limiting process of HS\(^-\) sorption on bentonite (Ho and Mckay, 1999; Senthilkumaar et al., 2006; Crini et al., 2007; Boparai et al., 2011; Falahian et al., 2018; Zbair et al., 2019). However, due to the limitations of the applied kinetic models (Nguyen et al., 2017; Bujdák, 2020), the following sections provide additional analyses to better understand the underlying sorption mechanisms of HS\(^-\) onto bentonite.
4.3 Effect of L:S and initial HS\textsuperscript{-} concentration

To evaluate the effect of L:S and initial HS\textsuperscript{-} concentration on sorption, Experiment set 2 varied these parameters between 200 to 1000 and 1 to 6 mg L\textsuperscript{-1}, respectively. For these experiments, all samples and blanks were shaken at ambient temperature (22±2°C) for more than 24 hours (28-30 hours) to ensure equilibrium (as found from Experiment set 1 results, discussed in Section 4.1). However, Experiment set 1 results show that L:S = 100 resulted in high sorption\% at equilibrium (around 97-99\%, Figure S.3, SI). As such, Experiment set 2 was conducted with higher L:S ratios (i.e., 200 to 1000) so the $C_e$ values were well-above the method detection limit (0.02 mg L\textsuperscript{-1}).

Figure 4 presents the sorption capacity, $q_e$ (mg kg\textsuperscript{-1}) sensitivities to L:S and initial HS\textsuperscript{-} concentration. In addition, the effects on sorption\% are presented in Figure S.5 (discussed in Section S.6 of SI).
Figure 4. Effect of L:S and initial HS\textsuperscript{-} concentration on HS\textsuperscript{-} sorption capacity of bentonite (condition: pH = 9.5, temperature = 22±2°C, contact time = 28-30 hours). All data presented are the average of duplicate or triplicate tests, with error bars showing the standard deviation.

Figure 4 shows that the sorption capacity (mg kg\textsuperscript{-1}) increased with increasing L:S and initial HS\textsuperscript{-} concentration. These results are consistent with other sorption studies performed using bentonite (Xu et al., 2008; Yang et al., 2009; C. B. Gupt et al., 2019). Gupt et al. (2019) attributed the reason for the lower sorption capacity of bentonite at higher solid content to its expansive behaviour. The study reported that the expansiveness of bentonite results in gel-like consistency at low L:S values, which may inhibit interactions between the ions and adsorbent. However, this inhibition reduces considerably as the L:S is increased. Although no gel-like consistency was observed at the studied L:S values (i.e., 200 – 1000), the trend observed (i.e., increasing sorption capacity with increasing L:S) may be explained by the fact that increasing L:S induced better bentonite dispersion, which minimized the effects from bentonite expansion. Therefore, the experiments with L:S = 1000 exhibited the least interference due to bentonite expansion and facilitated better interaction of HS\textsuperscript{-} with bentonite surface resulting in higher HS\textsuperscript{-} sorption on per unit mass of bentonite than the experiments using L:S = 200 and 500. However, further study into this phenomenon would be valuable.

Under the combined effect of both L:S and initial HS\textsuperscript{-} concentration considered in Experiment set 2, the maximum sorption capacity was observed at around 2564 mg kg\textsuperscript{-1} at the highest L:S and initial HS\textsuperscript{-} concentration used (i.e., L:S of 1000 and HS\textsuperscript{-} initial concentration of 6 mg L\textsuperscript{-1}).
However, since the maximum capacity did not reach any plateau at the conditions investigated (Figure 4), it might increase further if the initial condition increased.

4.4 Sorption Isotherms

Many researchers have used Langmuir and Freundlich models to understand the adsorption of organic and inorganic substances onto clays like bentonite (Xu et al., 2008; Zhao et al., 2008; Yang et al., 2009; Dawodu et al., 2012; Shahmohammadi-Kalalagh et al., 2015; Derakhshani et al., 2016; Emilio Alvarenga et al., 2016; C B Gupt et al., 2019; He et al., 2022). Still now, Langmuir and Freundlich models are the most extensively used models to analyze equilibrium sorption data. Therefore, the equilibrium data from Experiment set 2 were fitted to Langmuir and Freundlich isotherm models to obtain a preliminary understanding of the nature of HS⁻ sorption onto bentonite.

Figure 5(a) and 5(b) shows the non-linear fit of the data to the models. The good model fits in this figure shows that sorption over the experimental conditions investigated could be reasonably described by either Freundlich or Langmuir models. However, multiple features of HS⁻ sorption onto bentonite precludes the strict application of either model (see full discussion below). While neither model is suitable to fundamentally describe HS⁻ sorption onto bentonite, some observations from these models can provide helpful clues regarding the underlying sorption mechanisms. For example, the “n” values (> 1) from the Freundlich model (Table S.4, SI) indicate that the sorption process was favorable, and HS⁻ had a high sorption affinity towards bentonite (Raihan Taha et al., 2004; Boparai et al., 2011). However, the model results reported in Table S.4 (SI) indicate that both models fitted the experimental data with high R² (0.96-0.99) at all L:S values studied.
Therefore, it is not clear if the sorption was mono- or multi-layered, as similar $R^2$ values were observed for both models under the conditions investigated. Note that Langmuir and Freundlich describe sorption in a mono- and multi-layer domains, respectively (see additional discussion in Section S.4.2 of SI).

In terms of chi-squared ($\chi^2$) test, the Langmuir model $\chi^2$ value (8.666) at L: S=200 was found lower than the $\chi^2$ critical value at a significance level of 0.05 and 5 degrees of freedom (11.071); while the Freundlich model $\chi^2$ value was higher (14.797), indicating an acceptable and better fit of Langmuir model at L:S = 200. But for higher L:S ratios (i.e., 500 and 1000), both models had higher $\chi^2$ values (15.751-67.062) than the tabulated value (11.071). These high $\chi^2$ values indicate that, despite high $R^2$ values, the models did not robustly describe HS$^-$ sorption onto bentonite, particularly at high L:S values. The L:S dependency in Figure 5, which has been observed by other researchers (e.g., (C. B. Gupt et al., 2019)), ultimately invalidates the strict application of either model to predict sorption. Moreover, both models were developed assuming a reversible adsorption process (Nguyen et al., 2017; González-lópez et al., 2022), whereas HS$^-$ sorption could be better described as an irreversible surface precipitation process (Sections 4.6 and 4.7 provide additional analyses to support this hypothesis). Therefore, the sorption results from Figure 5 might not be appropriate to use directly in predictive models – but may instead provide insight into the sorption mechanisms.
Figure 5. Isotherm models for HS⁻ sorption on bentonite (a) Langmuir and (b) Freundlich (experimental conditions: pH = 9.5, temperature = 22±2°C, contact time = 28-30 hours). Points represent experimental data and dotted lines represent non-linear fit of models to the experimental data.

4.5 Thermodynamic study

As discussed earlier in Section 4.1, the increase in HS⁻ sorption onto bentonite with increasing temperature indicates that sorption was endothermic (Figure 2). To further explore this result, thermodynamic parameters for HS⁻ sorption onto bentonite were quantified. In this study, the thermodynamic equilibrium constants \( K_o \) at different temperatures (10 to 40°C) were determined from the intercepts of the plots of \( \ln(q/e/C_e) \) versus \( C_e \) (Figure S.6(a), SI) (Khan and R.P.Singh, 1987; Demirbas et al., 2006). The \( K_o \) values obtained were used to plot \( \ln K_o \) vs \( 1/T \) (Figure S.6(b), SI), which was used to approximate \( \Delta H^0 \), \( \Delta S^0 \) and \( \Delta G^0 \) following Eq. (S14) and (S15), SI. Negative values of \( \Delta G^0 \) (Table 3) indicate that HS⁻ sorption onto bentonite was spontaneous, and
the degree of spontaneity increased with increasing temperature (Boparai et al., 2011). In addition, the positive enthalpy change, $\Delta H^0 (2.6 \text{ kJ mol}^{-1}$, Table 3) indicates that the sorption of HS$^-$ on bentonite was endothermic, which agrees with the increased sorption observed with increasing temperature (see Figure 2). Moreover, the positive values of the entropy $\Delta S^0$ (Table 3) indicates an increase in the system disorder, which may suggest the affinity of bentonite towards HS$^-$ and some structure changes associated with the sorption (Zhao et al., 2008; Yang et al., 2009; Boparai et al., 2011).

**Table 3.** Thermodynamic parameters of HS$^-$ sorption onto bentonite

<table>
<thead>
<tr>
<th>Thermodynamic parameters</th>
<th>Temperature (°C)</th>
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<tr>
<td></td>
<td>10</td>
</tr>
<tr>
<td>$\Delta G^0$ (kJ mol$^{-1}$)</td>
<td>-4.38</td>
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<tr>
<td>$\Delta H^0$ (kJ mol$^{-1}$)</td>
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<tr>
<td>$\Delta S^0$ (J mol$^{-1}$)</td>
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4.6 Desorption test

No desorbed HS$^-$ was detected in the aqueous phase at any of the applied test conditions (as described in Section 2.3). In other words, HS$^-$ sorption onto bentonite was irreversible under the conditions investigated. This finding further supports the hypothesis that HS$^-$ was sorbed onto bentonite via chemical processes, which would likely be irreversible.

4.7 Surface analysis

Figure 6 presents a comparison of SEM images from a test sample (L:S = 1000, initial HS$^-$ concentration = 6 mg L$^{-1}$) and blank sample (only bentonite at L: S = 1000, no HS$^-$). As shown in
Figure 6(a) and 6(b), some distinct crystal structures oriented together were identified in both the blank and test samples. These structures were found in different shades (relatively brighter) than the bulk area of the bentonite, indicating the presence of different atoms with higher atomic mass and different chemical composition. The EDS point analysis results indicate these structures contained iron (Fe) and sulfur (S) with atomic% ratio nearly 1:2 (EDS point analysis results shown in Figure S.7(a) and S.7(b), SI). This ratio indicates the presence of pyrite (FeS2) (Rickard and Luther, 2007; Wen et al., 2017) in both the test and blank sample, which was expected as MX-80 bentonite often contains ~0.6 w% of pyrite (Dixon et al. (2018) and Dixon (2019)). In addition, Figure 6(c) shows that relatively irregular shaped particles without sharp crystal edges were identified at some locations in the test sample. The atomic% ratio of Fe and S from EDS analyses at these locations were found to be very close to 1:1 (EDS point analysis results shown in Figure S.7(c), SI). This observation indicates the presence of a newly formed FeS compound, likely amorphous FeS/mackinawite (Szczepanik and Sawlowicz, 2010; Marić et al., 2019; Lemire et al., 2020; Behazin et al., 2021; Bolney et al., 2021). The co-existence of Fe and S in the test sample (as shown in Figure 6(c)) was also reflected in EDS mapping (i.e., spatial distribution of Fe and S over the image area shown in Figure S.8, SI). However, no such FeS compounds (i.e., with Fe:S = 1:1) were identified in the blank sample. Altogether, this preliminary analysis shows, while Fe and S are present together in the initial sample as pyrite, it appears that new iron-sulfide minerals (possibly, amorphous FeS/mackinawite) were formed from HS− sorption experiments, which aligns with previous studies (Wersin et al., 2014; Pedersen et al., 2017; Maanoja et al., 2020; Miettinen et al., 2022).
As reported in literature, in aqueous solutions at ambient temperature sulfide reacts rapidly with Fe(II) and first forms iron (II) mono-sulfide known as mackinawite (FeS), which is subsequently transformed to more insoluble compounds such as greigite (Fe₃S₄) and pyrite (FeS₂) depending on geochemical conditions such as pH and polysulfide concentration (Rickard and Luther, 2007; Cloet et al., 2017). According to Szczepanik and Sawlowicz, (2010), pyrite is the most stable iron sulfide formation that are generally found in well-defined crystal shapes; conversely, greigite and mackinawite have less regular shapes and typically form smaller crystals than pyrite. Another study reported that at reducing conditions and low temperatures (i.e., below 100°C), the rate of pyrite formation from mackinawite is insignificant (Benning et al., 2000). As such, pyrite was probably not formed in the sorption experiments (i.e., conducted under anaerobic condition and room temperature). Instead, the newly formed Fe and S structures observed in the test samples (Figure 6(c)) suggest that HS⁻ sorption on bentonite might have been governed by chemical interactions with the Fe present in bentonite, and subsequent formation of an FeS compounds, e.g., amorphous FeS/mackinawite. Additional investigation might be necessary to better understand the fate of HS⁻ in these sorption experiments (e.g., whether HS⁻ reacted only with Fe or also with other elements/functional groups on the bentonite surfaces) to help guide the development of a thermodynamic-based sorption model. Altogether, these surface analyses further support that HS⁻ sorption onto bentonite was driven via chemical reactions, particularly with Fe.
Figure 6. SEM (back-scattered) images of blank (only bentonite with L: S = 1000, no HS⁻) and test sample (with L:S = 1000, initial HS⁻ concentration = 6 mg L⁻¹) (a) pyrite identified in the blank sample; (b) pyrite identified in the test sample and (c) FeS identified in the test sample. The circles denote the EDS point analyses locations, and the Fe:S atomic% ratios are also listed from these EDS analyses.

4.8 Consequences to the DGR

The above observations indicate that HS⁻ sorbs/retains onto bentonite via very rapid and irreversible chemical reactions (likely with Fe), which will prevent it from reaching the surface of the UFC and causing corrosion. While this study does not attempt to quantify the amount of available iron (Fe²⁺ or Fe³⁺) in the octahedral sites in the alumina lattice of bentonite capable of immobilizing HS⁻, preliminary estimates can be performed to quantify the implications of these reactions on HS⁻ induced Cu corrosion in a DGR. From the literature, bentonite may have 0.8-3.0 wt.% of iron (Torstenfelt et al., 1983; Karnland et al., 2006; Dixon, 2019). Thus, as per the stoichiometry of Eq. (2) (Pedersen et al., 2017) and Eq. (6) (Rickard, 1995; Behazin et al., 2021),
the total iron in 1 kg of bentonite may immobilize as much as 0.143-0.537 mole of HS\(^-\). This immobilization can therefore offset 0.286-1.074 mole of Cu corrosion, as per Eq. (1), i.e., 2.03-7.62 µm m\(^2\) of corrosion depth (a summary of the calculation is provided in Section S.10 of SI).

\[ \text{HS}^- + \text{Fe}^{2+} \rightarrow \text{FeS}_m + \text{H}^+ \] (6)

where, FeS\(_m\) indicates the mackinawite phase of iron (II) monosulfide (Rickard and Luther, 2007).

This preliminary estimation indicates the theoretical maximum possible Cu corrosion reduction per 1 kg of bentonite. As shown in Sections 4.1 and 4.3, the sorption capacity will depend on various geochemical conditions (e.g., temperature, HS\(^-\) concentration). Moreover, additional research is required to identify whether HS\(^-\) reacts only with Fe or with other elements in bentonite and whether all Fe in the bentonite is available for reaction with HS\(^-\). In addition, various geochemical conditions in DGR may also impact HS\(^-\) sorption, such as groundwater composition. Therefore, future work will use the current study findings to develop a thermodynamic sorption model to estimate HS\(^-\) sorption under various geochemical conditions (including pH and ionic strength) expected in the DGR. The findings of the sorption model will be integrated into a future reactive-transport modelling work to better forecast HS\(^-\) induced corrosion in a DGR.

5 Conclusions

This research conducted a series of laboratory batch experiments to understand the sensitivity of key parameters (i.e., contact time, temperature, liquid to solid ratio (L:S), initial HS\(^-\) concentration)
on HS\textsuperscript{−} sorption onto bentonite. It was found that HS\textsuperscript{−} sorption on bentonite increased with increasing contact time and occurred faster with increasing temperatures, where equilibrium was reached after 16 hours (at 40°C), 24 hours (at 22 and 30°C) and at 96 hours (at 10°C). In addition, the sorption capacity increased (by about 3%) with increasing temperature. Among the kinetic models studied, the pseudo-second-order model showed the best agreement with the experimental results, which implies that the rate of sorption might have been limited by chemical processes. The Freundlich isotherm constant $n > 1$ reflected that the sorption process was favorable, and bentonite has a high sorption affinity towards HS\textsuperscript{−}. Under the experimental conditions investigated, both the Langmuir and Freundlich isotherm models fitted the data with high $R^2 (> 0.9)$ values. However, high $\chi^2$ values indicated that these models might not reliably describe HS\textsuperscript{−} sorption onto bentonite – particularly at high liquid to solid ratios. Thermodynamic analysis results showed that the sorption process was endothermic and spontaneous in nature. The desorption test results indicated that HS\textsuperscript{−} was irreversibly sorbed on bentonite under the applied test conditions, which further supports the sorption was a chemisorption process. The FESEM/EDS analysis suggests that HS\textsuperscript{−} sorption on bentonite might have been governed by the chemical interactions with the Fe present in bentonite, and subsequent precipitation of FeS minerals. However, further analyses might be necessary to explore possible products produced during HS\textsuperscript{−} sorption onto bentonite to better understand the fate of HS\textsuperscript{−} in the sorption experiments.

Altogether, the sorption dynamics, equilibrium behaviour, and surface analyses indicate that HS\textsuperscript{−} sorption onto bentonite was driven by chemical reactions, likely with Fe in the bentonite, which
aligns with other studies. These findings will be useful to validate a thermodynamic-based sorption model, which will help better understand the underlying mechanisms governing HS\(^{-}\) interactions with bentonite. Ultimately, this work is in support of a broader modelling effort to simulate reactive transport of HS\(^{-}\) in bentonite over a wide range of physical and geochemical conditions anticipated in a DGR.

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7 Authorship contribution

Sifat Azad Papry: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Visualization, Writing- original draft; Tarek L. Rashwan: Conceptualization, Investigation, Methodology, Visualization, Writing – review & editing; Pulin Mondal: Conceptualization, Methodology, Supervision, Writing - review & editing; Mehran Behazin: Project administration, Resources, Supervision, Writing - review & editing. Peter G. Keech: Project administration, Resources, Supervision, Writing - review & editing. Magdalena M. Krol:
References


Benning, L.G., Wilkin, R.T., Barnes, H.L., 2000. Reaction pathways in the Fe-S system below

Bolney, R., Grosch, M., Winkler, M., van Slageren, J., Weigand, W., Robl, C., 2021. Mackinawite
formation from elemental iron and sulfur. RSC Adv. 11, 32464–32475.
https://doi.org/10.1039/d1ra03705f

Boparai, H.K., Joseph, M., Carroll, D.M.O., 2011. Kinetics and thermodynamics of cadmium ion
https://doi.org/10.1016/j.jhazmat.2010.11.029

Briggs, S., McKelvie, J., Sleep, B., Krol, M., 2017. Multi-dimensional transport modelling of
corrosive agents through a bentonite buffer in a Canadian deep geological repository. Sci.

https://doi.org/10.1016/j.clay.2020.105630

Can, M., 2015. Studies of the Kinetics for Rhodium Adsorption onto Gallic Acid Derived Polymer:
https://doi.org/10.12693/APhysPolA.127.1308

Chen, J., Behazin, M., Binns, J., Birch, K., Blyth, A., Briggs, S., Cheema, G., Crowe, R., Doyle,
D., Garisto, F., Giallonardo, J., Gobien, M., Guo, R., Hirschorn, S., Hobbs, M., Ion, M., Jacyk,
J., Keech, P., Kremer, E., Lawrence, C., Leung, H., Liberda, K., Mckelvie, J., Medri, C.,
Mielcarek, M., Parmenter, A., Castejon, M.S., Stahmer, U., Sykes, E., Sykes, M., Yang, T.,


Ho, Y.S., Mckay, G., 1998. A COMPARISON OF CHEMISORPTION KINETIC MODELS APPLIED TO POLLUTANT REMOVAL ON VARIOUS SORBENTS 76.


Highlights

- HS⁻ sorption onto bentonite was fast and increased with increasing temperature
- The pseudo second order model best described HS⁻ sorption kinetics
- HS⁻ sorbed irreversibly on bentonite under the conditions investigated
- SEM/EDS results show that HS⁻ likely reacted with Fe in bentonite and formed FeS
Declaration of interests

☐ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☒ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Magdalena Krol reports financial support was provided by Natural Sciences and Engineering Research Council of Canada. Magdalena Krol reports financial support was provided by Ontario Ministry of Research and Innovation. Magdalena Krol reports financial support was provided by Nuclear Waste Management Organization of Canada. The authors declare the following interests/personal relationships which may be considered as potential competing interests: Peter G. Keech and Mehran Behazin are employed by NWMO, an organization seeking a solution to nuclear waste disposal for Canada. While geological disposal is not a certainty in the company mandate, it is the primary topic of research for Canada as well as nearly all other countries with nuclear energy programs.