Heat and Radiation Effects on Iodide Sorption by Surfactant Modified Bentonite (SMB)

Minkyung Kim[a], Sungwook Choung[a], and Wooyong Um[a,b*]
[a]Pohang University of Science and Technology (POSTECH), Pohang, Korea
[b]Pacific Northwest National Laboratory (PNNL), Richland, WA, USA
**Corresponding author: wooyongum@postech.ac.kr*

1. Introduction

Radioactive waste repository is designed using multiple barriers to prevent the release of radionuclides to environments. Bentonite has been used as engineering barrier in many countries. Although the bentonite is an effective sorbent for cationic radionuclides, it is not good for anions such as 129-I and 99-Tc because of negative surface charges over the pH [1][2]. Radioactive iodine exists usually as anions such as iodate (IO_3^-) and iodide (I^-) as stable iodine species in groundwater environments. Therefore, the iodine is one of the most difficult elements for its transport through engineering barrier (i.e., bentonite) to be controlled by sorption processes in the geological repository. We modified the bentonite using a cationic surfactant to enhance iodine sorption capability. The goal of this study is addressed to evaluate the effects of sorption of high heat and radiation on iodide sorption to surfactant modified bentonite (SMB) which can be used as engineering barrier in the repository.

2. Methods

2.1 Materials

The bentonite and hexadecyltrimethylammonium bromide (HDTMA-Br) were obtained from Sigma-Aldrich (St. Louis, MO). Cation exchange capacity (CEC) is calculated for the bentonite by ammonium acetate method [3]. Approximately 1 g bentonite was saturated with 30 mL of 1M ammonium acetate at pH=7. The slurry of bentonite was centrifuged at 2,000 rpm for 30 min, and then supernatant was collected. The procedures of saturation, centrifugation, and collection were repeated three times. After the collection supernatant was filled up to 100 mL using the Milli-Q water. The major cations (K, Na, Ca, Mg) concentrations were analyzed by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). The CEC value of the bentonite was determined by the sum of major cation equivalence concentrations divided by the mass of bentonite.

For iodine sorption experiments, potassium iodide (KI) was used to make iodide stock solution. Stable iodine (^{127}I) species was used as surrogate for radioactive iodine (^{129}I) species in this study. Two concentrations for iodide stock solutions (0.15 mM and 15 mM) were individually prepared.

2.2 Surfactant modified bentonite (SMB) preparation

The SMB was synthesized by cation surfactant (i.e., HDTMA-Br) onto bentonite surface. For the production of 100% (-CEC) SMB, the HDMTA-Br 3.71g was dissolved into 500 ml Milli-Q water and reacted with ~10 g bentonite for 6 hours at 60 °C. The 50% and 200% SMB were synthesized by adjustment of surfactant amount using the same manner.

2.3 Iodine sorption experiments with heat and radiation effects

The sorption experiments were conducted using batch techniques. The sorbed concentrations of iodine were determined by mass balance approach in a batch system, based on the aqueous concentrations measured by ICP-MS. Three different temperatures (25, 60, and 90 °C) were used to observe the heat effects on sorption capability of the SMB. The heat effects were evaluated thermodynamically [4]. The SMB were also irradiated using ^{60}Co gamma source (KAERI, Jeongup) to assess the radiation effects on iodine sorption. The radiation dose rate was 19 kGy/hr for 52.6 hrs and samples were irradiated in air under ambient conditions.

3. Results

3.1 Temperature effect

Figure 1 showed the heat effects on the sorption processes of iodide on the 50, 100, and 200% SMB. The sorption was quite similar for the 100 and 200% SMBs, while 50% SMB exhibited ~3 times lower sorption efficiency compared to 100 and 200% SMBs at 25 and 60 °C (Fig. 1A). Iodide sorption was decreased as increasing temperature. In particular, the iodide sorption were approximately four orders of magnitude lower at 90 °C compared to those measured at 25 and 60 °C (Fig. 1B).

The thermodynamic parameters of ΔG^O, ΔH^O, and ΔS^O at different temperatures are summarized in Table I. The negative value of ΔG^O indicates that the sorption was spontaneous process. As temperature increases, only 200% SMB exhibited decrease of the ΔG^O values with positive ΔS^O. The positive value of ΔS^O suggested that the randomness of iodide at the solid/liquid interface increased, in particular, at high temperature. For 50 and 100% SMBs, the negative value of ΔS^O suggested the increase of iodide freedom. The negative

values of ΔH^O reflected that the sorption was exothermic reaction. It was supported by the decrease of iodide sorption with temperature increase as shown in Figure 1 (B).

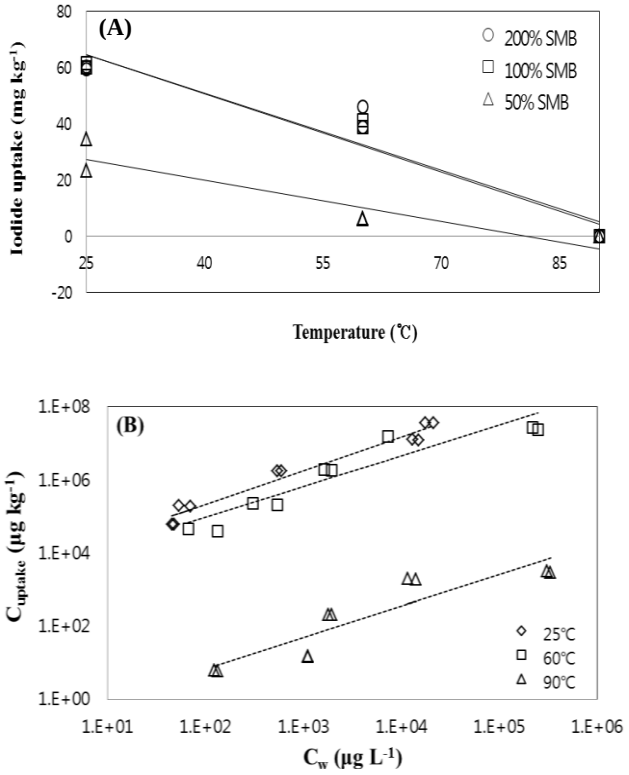

Fig. 1. (A) Sobed concentrations of iodide by 50, 100 and 200% SMBs at different temperatures of 25, 60, and 90 °C. (B) Iodide sorption isotherms on 200% SMB at different temperatures. The dashed lines indicate Freundlich isotherm fits for each condition.

Table I: Thermodynamic parameters of the iodide adsorption onto SMBs at different temperatures.

	T (°C)	G (kJ mol^{-1})	S (J mol^{-1} k^{-1})	H (kJ mol^{-1})
200% SMB	25	-17743	12.45	-14.032
	60	-18178		
	90	-18552		
100% SMB	25	-18380	-27.53	-26.584
	60	-17417		
	90	-16591		
50% SMB	25	-10152	-28.71	-18.707
	60	-9147		
	90	-8285		

3.2. Radiation effect

Radiation effect on the iodide sorption capability by the SMBs was evaluated through comparison between the SMBs before, and after 10^6 Gy-irradiation. However, the irradiation rarely influenced the sorption of iodide by SMB (Fig. 2).

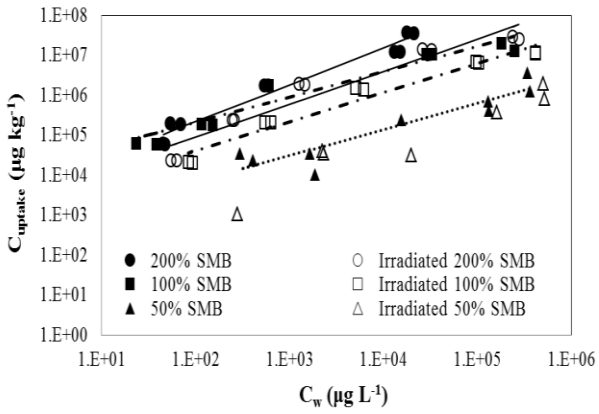

Fig. 2. Iodide sorption isotherms for SMBs and irradiated SMBs at 25 °C.

4. Conclusion

The iodide sorption on the SMBs was significantly affected by temperature conditions rather than radiation. As temperature increases, the iodide sorption decreases. Considering the similar sorption abilities between 100 and 200% SMBs, the 100% SMB is economical sorbent to apply for engineering barrier in a geological repository.

5. Acknowledgement

This research project was supported by World Class University (WCU) Program (grant no. R31-30005) and Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science, and Technology (grant no. NRF-2012R1A1A2044287).

REFERENCES

[1] Riebe, B., Dultz, S., and Bunnenberg, C., Temperature effects on iodine adsorption on organo-clay minerals: I. Influence of pretreatment and adsorption temperature, Applied Clay Science, Vol. 28, No. 1–4, pp. 9-16, 2005.
[2] Yoon, J.-H., Ha, J.-Y., Hwang, J.-Y., Hwang, B.-H., and Gordon E. Brown, Jr., Study of Iodide Adsorption on Organobentonite using X-ray Absorption Spectroscopy, Vol. 22, No. 1, pp. 23-34, 2009.
[3] Inglethorpe, S., Morgan, D., Highley, D. and Bloodworth, A., 1993, "Industrial minerals laboratory manual: Bentonite" British Geological Survey Technical Report
[4] Donat, R., Akdogan, A., Erdem, E., and Cetisli, H., Thermodynamics of Pb^{2+} and Ni^{2+} adsorption onto natural bentonite from aqueous solutions, Journal of Colloid and Interface Science, Vol. 286, No. 1, pp. 43-52, 2005.