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## Chapter 8

# MODELING ACTINIDE SOLUBILITIES IN ALKALINE TO HYPERALKALINE SOLUTIONS: SOLUBILITY OF $\text{Am}(\text{OH})_3(\text{s})$ IN KOH SOLUTIONS

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## ABSTRACT

In this work, a Pitzer model is developed for the  $\text{K}^+(\text{Na}^+) - \text{Am}(\text{OH})_4^- - \text{Cl}^- - \text{OH}^-$  system based on  $\text{Am}(\text{OH})_3(\text{s})$  solubility data in highly alkaline KOH solutions. Under highly alkaline conditions, the solubility reaction of  $\text{Am}(\text{OH})_3(\text{s})$  is expressed as:



Solubilities of  $\text{Am}(\text{OH})_3(\text{s})$  based on the above reaction are modeled as a function of KOH concentrations. The stability constant for  $\text{Am}(\text{OH})_4^-$

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is evaluated using  $\text{Am}(\text{OH})_3(\text{s})$  solubility data in KOH solutions up to  $12 \text{ mol}\cdot\text{kg}^{-1}$  taken from the literature. The Pitzer interaction parameters related to  $\text{Al}(\text{OH})_4^-$  are used as analogs for the interaction parameters involving  $\text{Am}(\text{OH})_4^-$  to obtain the stability constant for  $\text{Am}(\text{OH})_4^-$ . The  $\log_{10} K^0$  for the reaction is  $-11.34 \pm 0.15 (2\sigma)$ .

**Keywords:** nuclear waste management, hydrolysis, Pitzer model, salt formations, high level tank waste, Hanford site, Savannah River site, Thermodynamic modeling

## INTRODUCTION

Knowledge of actinide speciation and solubilities in highly alkaline solutions is important to nuclear waste management. For example, tank wastes such as those at the Savannah River site and the Hanford site, contain solutions with high concentrations of bases (e.g., Delegard, 1987; Karraker, 1995; Rudisill et al., 2004, 2010; King et al., 2010; Rudisill and Thompson, 2011; Delegard and Jones, 2015; King and Hobbs, 2016). Also, solutions in equilibrium with cements in geological repositories would be highly alkaline with concentrations of  $\text{OH}^-$  on the order of hundreds of milli-molars in some repository designs (Vitorge and Tran The, 1991). For instance, in the supercontainer design for the geological disposal of spent nuclear fuel in Belgium, waste is inserted into a canister surrounded by a carbon steel overpack, a buffer and then stainless steel envelope (Cachoir et al., 2016). Ordinary Portland cement based concrete is used as the buffer in the Belgian repository design (Loida et al., 2009; Menecart et al., 2012; Cachoir et al., 2014, 2016). Concrete barriers are also employed in the French repository design (e.g., De Windt et al., 2004; Trotignon et al., 2006). The concrete buffer is expected to produce a high pH environment for the long-term.

Predictions of actinide solubilities in these highly alkaline solutions require a thermodynamic model applicable to high ionic strengths with high base concentrations. Current speciation schemes for actinides do not extend into the highly alkaline region (Silva et al., 1995). If modeling

actinide solubility in the environments mentioned above is required, a parameterized speciation scheme for this region needs to be developed.

The objective of this work is to develop a Pitzer model for the  $\text{K}^+(\text{Na}^+) - \text{Am}(\text{OH})_4^- - \text{Cl}^- - \text{OH}^-$  system based on  $\text{Am}(\text{OH})_3(\text{s})$  solubility data in highly alkaline solutions. The model is applicable to hyperalkaline solutions.

## METHODS

The platform for modeling in this chapter is the computer program EQ3/6 Version 8.0a (Wolery et al., 2010; Xiong, 2011a). The EQ3/6 code has been successfully used as a modeling platform in a number of previous studies including those at ambient temperature (e.g., De Windt et al., 2004; Xiong et al., 2013a, 2013b; Xiong, 2015) and those at elevated temperatures up to 523.15 K (Xiong, 2013a, 2013b, 2014). The database used for the modeling is summarized in Xiong et al., (2010).

In the modeling, experimental data selected are used to generate EQ3/6 input files in the first step. In the second step, the values of the targeted parameter (e.g.,  $\log K_1^0$ ) are changed until the squared difference between experimental values (e.g.,  $m_{\Sigma\text{Am}}$ ) and model-produced values predicted by the computer code is minimized. In the third step, the final selected value for the targeted parameter is verified to see how it reproduces experimental data.

## MODELING RESULTS AND POTENTIAL APPLICATIONS

### Modeling Results

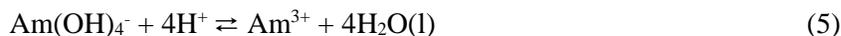
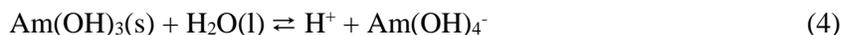
It has been observed that  $\text{Am}(\text{OH})_4^-$  is the dominant species in highly alkaline solutions (Vitorge and Tran The, 1991). Under highly alkaline conditions, the solubility reaction for  $\text{Am}(\text{OH})_3(\text{s})$  is expressed as,



Vitorge and Tran The (1991) conducted solubility experiments at 25°C on  $\text{Am(OH)}_3(\text{s})$  in KOH solutions up to  $10 \text{ mol}\cdot\text{dm}^{-3}$ . Here, the solubility data from Vitorge and Tran The (1991) are modeled to obtain an equilibrium constant for Reaction (1). In the modeling, the experimental data of Vitorge and Tran The (1991) on a molar scale are converted to those on a molal scale, based on the density equation from Söhnel and Novotný (1985).

A Pitzer model is adopted for the modeling and the Pitzer interaction parameters related to  $\text{Al(OH)}_4^-$  (Wesolowski, 1992; Xiong, 2014) are used as analogs for the interaction parameters involving  $\text{Am(OH)}_4^-$  to obtain the stability constant for  $\text{Am(OH)}_4^-$  (see Table 1). These Pitzer parameters have been tested in a high ionic strength range up to  $12 \text{ mol}\cdot\text{kg}^{-1}$  (Wesolowski, 1992; Xiong, 2013b, 2014).

Based on the modeling performed in this work, the equilibrium constant for Reaction (1) is  $-11.34 \pm 0.15$  ( $2\sigma$ ) in logarithmic units (Table 2). To facilitate its use in various databases, the equilibrium constant for Reaction (1) is converted to other equilibrium constants expressed in Reactions (4) and (5), in accordance with the basis reactions in Reactions (2) and (3) from the DATA0.FM1 (Xiong, 2011b),



The equilibrium constants for the above reactions are also listed in Table 2.

**Table 1. The Pitzer interaction parameters at 25°C and 1 bar for the  $K^+—Am(OH)_4^-—Cl^-—OH^-$  system**

Pitzer binary interaction parameters					
Species, <i>i</i>	Species, <i>j</i>	$\beta^{(0)}$	$\beta^{(1)}$	$C^\phi$	Reference
$K^+$	$Am(OH)_4^-$	0.051	0.25	-0.00090	This work <sup>A</sup>
Pitzer mixing interaction parameters (theta and psi parameters)					
Species, <i>i</i>	Species, <i>j</i>	Species, <i>k</i>	$\theta_{ij}$	$\Psi_{ijk}$	Reference
$OH^-$	$Am(OH)_4^-$	$K^+$	0.014	-0.0048	This work <sup>B</sup>
$Cl^-$	$Am(OH)_4^-$	$K^+(Na^+)$		-0.004857	This work <sup>C</sup>

<sup>A</sup> Using the parameters for  $Na^+—Al(OH)_4^-$  from Wesolowski (1992) as analogs.

<sup>B</sup> Using the parameters for  $OH^-—Al(OH)_4^-$  and  $OH^-—Al(OH)_4^-—Na^+$  from Wesolowski (1992) as analogs.

<sup>C</sup> Using the parameter for  $OH^-—Al(OH)_4^-—Na^+$  from Xiong (2014) as an analog.

**Table 2. Equilibrium constants at infinite dilution and at 25°C and 1 bar for the  $K^+—Am(OH)_4^-—Cl^-—OH^-$  system**

Reaction	$\log_{10} K^0$	Reference
$Am(OH)_3(s) + 3H^+ \rightleftharpoons Am^{3+} + 3H_2O(l)$	14.4900	DATA0.FM1 (Xiong, 2011b)
$H_2O(l) \rightleftharpoons H^+ + OH^-$	-13.9967	DATA0.FM1 (Xiong, 2011b)
$Am(OH)_3(s) + OH^- \rightleftharpoons Am(OH)_4^-$	$-11.34 \pm 0.15 (2\sigma)$	This work
$Am(OH)_3(s) + H_2O(l) \rightleftharpoons H^+ + Am(OH)_4^-$	$-25.34 \pm 0.15 (2\sigma)$	This work
$Am(OH)_4^- + 4H^+ \rightleftharpoons Am^{3+} + 4H_2O(l)$	$39.83 \pm 0.15 (2\sigma)$	This work

Shown in Figure 1 is the comparison of solubilities of  $Am(OH)_3(s)$  predicted by the model developed in this study with the experimental data, as a function of ionic strength. The experimental data are from Vitorge and Tran The (1991). There are five sets of experimental data in Vitorge and Tran The (1991). The first two sets of experimental data are in KOH solutions and lime water without the redox adjustment at 70 and 105 days, respectively (Figure 1). The third set is in KOH solutions and lime water with initial oxidation and subsequent reduction. The last two sets of experimental data are in KOH solutions and cement water with the fourth

being started with initial oxidation and subsequent reduction, and with the fifth being without a redox change. The results from the first two sets of experiments with KOH solutions and lime water [i.e., saturated with  $\text{Ca}(\text{OH})_2(\text{s})$ ] are used in the model development, and therefore they are model-dependent. The rest of sets are not used in the model development. They are model-independent. All of the experiments of Vitorage and Tran The (1991) approached the equilibrium from the direction of supersaturation. Figure 1 demonstrates that the model developed in this study can reproduce the model-dependent experimental data with good agreement. It is also in good agreement with the model-independent experimental data.

There was a wide range of estimated values for  $\text{Am}(\text{OH})_4^-$  in the literature. Regarding Reaction (5), Allard et al., (1978) estimated a value of 31 in logarithmic units. Baes and Mesmer (1976) estimated a value of 37.1 in logarithmic units for  $\text{Nd}(\text{OH})_4^-$ . In comparison with the value of  $39.83 \pm 0.15$  ( $2\sigma$ ) for  $\text{Am}(\text{OH})_4^-$  in logarithmic units obtained in this study (Table 2), the estimated value provided by Baes and Mesmer (1976) is closer to the current value based on experimental data.

## Potential Applications

Potential, immediate applications of the results obtained in this study would be to model the solubilities of actinides in the +III oxidation state [i.e.,  $\text{An}(\text{III})$ ] in a high level tank waste. Potential candidates would be the high level tank waste at the Hanford and Savannah River sites. As indicated by Table 3, the high-level tank waste at the Hanford site has a high NaOH concentration at  $4 \text{ mol}\cdot\text{dm}^{-3}$ . In addition, the liquid waste has relatively high concentrations of EDTA and citrate. As EDTA and citrate form strong complexes with actinides in the +III oxidation state, the formation constants of EDTA and citrate with  $\text{An}(\text{III})$  applicable to high ionic strength solutions from Thakur et al., (2012, 2014) need to be used in such a modeling.

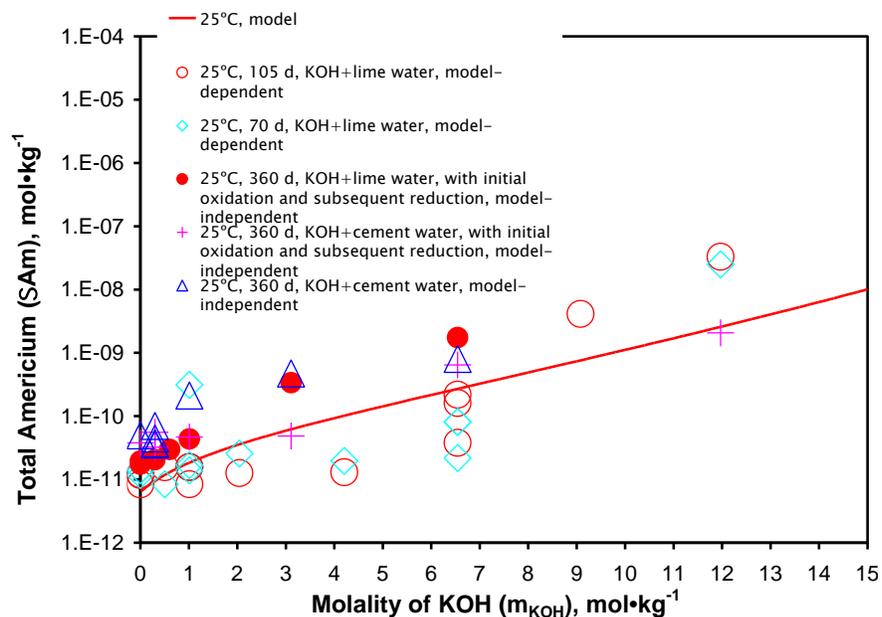


Figure 1. A plot showing the comparison of solubilities of Am(OH)<sub>3</sub>(s) predicted by the model developed in this study with the experimental data, as a function of ionic strength. The experimental data are from Vitorge and Tran The (1991).

**Table 3. Typical compositions of high-level tank waste at the Hanford site\***

Component	Concentration, mol·dm <sup>-3</sup>
NaOH	4
NaNO <sub>3</sub>	2
NaNO <sub>2</sub>	2
NaAl(OH) <sub>4</sub>	0.5
Na <sub>2</sub> CO <sub>3</sub>	0.05
Na <sub>2</sub> SO <sub>4</sub>	0.01
Na <sub>3</sub> PO <sub>3</sub>	0.01
NaF	0.01
Na <sub>4</sub> EDTA	0.05
Na <sub>3</sub> Citrate	0.03
NaGlycolite	0.1

\* From Delegard (1985).

**Table 4. Typical compositions of high-level tank waste at the Savannah River site\***

Component**	Concentration, mol·dm <sup>-3</sup>
OH <sup>-</sup>	0.0001 to 15
NO <sub>3</sub> <sup>-</sup>	0.1 to 6
NO <sub>2</sub> <sup>-</sup>	0.1 to 6
Al(OH) <sub>4</sub> <sup>-</sup>	0.001 to 1
CO <sub>3</sub> <sup>2-</sup>	0.001 to 1
SO <sub>4</sub> <sup>2-</sup>	0.001 to 0.5

\* From Rudisill et al., (2004).

\*\* The cation is predominantly Na<sup>+</sup>.

Similarly, the high-level tank waste at the Savannah River site also has high NaOH concentrations up to 15 mol·dm<sup>-3</sup> (Table 4). It also has high concentrations of NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, and Al(OH)<sub>4</sub><sup>-</sup>. It also contains relatively high concentrations of CO<sub>3</sub><sup>2-</sup> and SO<sub>4</sub><sup>2-</sup>. However, the high-level tank waste at the Savannah River site is different from the high-level tank waste at the Hanford site in that it is poor in organic ligands (cf. Tables 3 and 4).

## CONCLUSION

In this study, we have developed a Pitzer model for the K<sup>+</sup>(Na<sup>+</sup>)—Am(OH)<sub>4</sub><sup>-</sup>—Cl<sup>-</sup>—OH<sup>-</sup> system based on Am(OH)<sub>3</sub>(s) solubility data in highly alkaline solutions. This model is expected to find immediate applications in modeling the solubility of An(III) in high level tank waste. It is anticipated that the model will also be applicable to the modeling of the solubility of An(III) in geological repositories in various geological media including salt formations, where cement is used as one of multiple buffers.

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