

THORIUM OXIDE DISSOLUTION KINETICS FOR HYDROXIDE AND CARBONATE COMPLEXATION

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INTRODUCTION: The purpose of this project was to determine the kinetics and thermodynamics of thorium oxide dissolution in the environment. Solubility is important because it establishes an upper concentration limit on the concentration of a dissolved radionuclide in solution [1].

While understanding the behavior of thorium fuels in the proposed repository at Yucca Mountain is most applicable, a more rigorous study of thorium solubility over a wide pH range was performed so that the data could also be used to model the behavior of thorium fuels in any environmental system. To achieve this, the kinetics and thermodynamics of thorium oxide dissolution under both pure argon and argon with P_{CO_2} of 0.1 were studied under the full pH range available in each atmosphere. In addition, thorium oxide powder remnants were studied after each experiment to examine structural changes that may affect kinetics.

PROCESS: The kinetics and thermodynamics of thorium oxide dissolution were studied under two atmospheres. A pure argon atmosphere was used to examine the formation of the hydroxide species, and a mixture of 90% argon and 10% CO_2 was used as the cover gas when studying carbonate complexation. Thorium oxide powder was placed in a pH adjusted solution of 0.1 M ionic strength and allowed to dissolve over a period of one month. For the experiments under argon, the pH ranged from 2 through 12 in steps of 0.5. Under the argon/ CO_2 mixture, the pH range was limited to 2 through 6.5 due to strong carbonate buffering. Steps were also of 0.5 pH.

Filtered samples were taken every three days for the kinetics data. In addition, with every third sample, an unfiltered sample was also taken in order to determine if any colloids greater than the filter size of 0.2 μm were forming. Colloids are small particles composed of either single large molecules or clusters of smaller molecules which range in size from 0.001 to 1 μm . Since the presence of colloids could affect reaction kinetics, it is important to determine if any are being formed. In addition, mobile colloids in significant concentrations can increase migration of radionuclides through groundwater [2]. Samples of sufficient concentration were analyzed using a Spectroflame ICP-AES. Lower concentration samples were either analyzed using an ICP-MS or by neutron activation analysis.

BACKGROUND: The thorium aqueous phase consists of three parts: the free thorium (Th^{4+}), thorium hydroxide species, and thorium carbonate species, as expressed by

$$[Th]_{aq} = [Th^{4+}] + \sum_{x=1}^4 [Th(OH)_x^{4-x}] + \sum_{y=1}^4 [Th(CO_3)_y^{4-2y}]$$

Due to buffering by the carbonate system, the maximum attainable stable pH of a system under CO_2 is limited. This limit is dependant on the partial pressure of the CO_2 cover gas. The carbonate concentration of a system under high CO_2 partial pressure and



IL0206941

low pH can be extrapolated to a corresponding system under lower CO₂ partial pressure and a higher pH using the following equation [3]:

$$\log[\text{CO}_3^{2-}] = -17.55 \pm 0.09 + 2\text{pH} + \log p\text{CO}_2$$

With this information, the stability constants can be calculated and the total thorium concentration under those conditions can be determined from the equation:

$$[\text{Th}]_{\text{aq}} = [\text{Th}^{4+}] + \sum_{x=1}^4 \beta_{\text{Th}(\text{OH})_x} [\text{Th}^{4+}] [\text{OH}^-]^x + \sum_{y=1}^4 \beta_{\text{Th}(\text{CO}_3)_y} [\text{Th}^{4+}] [\text{CO}_3^{2-}]^y$$

Figure 1 shows an initial estimate of the solubility of thorium over a range of pH (3 through 10). Higher solubility at low and high pH is expected, with a minimum in between. The pH range of Yucca Mountain (6.7 to 9.3) is expected to lie in the minima. Data for this graph is from a combination of values from the literature and estimates [4].

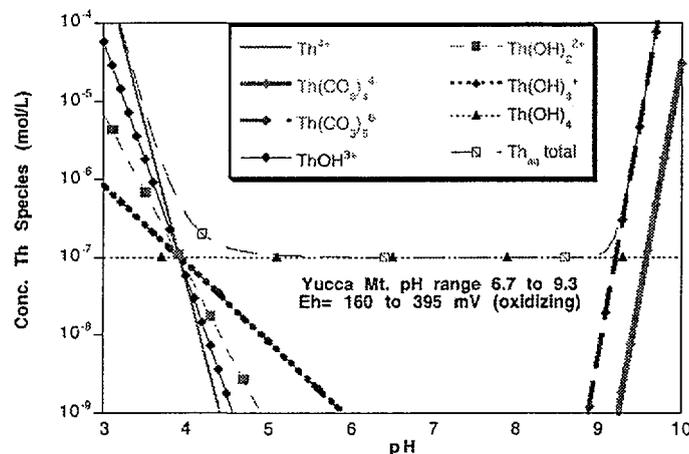


Figure 1. Thorium solubility estimate.

CONCLUSION: The kinetics of crystalline thorium oxide dissolution were studied under argon and argon/10% CO₂ over a broad pH range in 0.1 M ionic strength NaClO₄ solution. Under pure argon, $k = 0.0107 \pm 0.00123 \text{ h}^{-1}$ for pH 2-3. Under 10% CO₂, $k = 0.00511 \pm 0.000863 \text{ h}^{-1}$. No kinetics results could be discerned from the data at higher pH. Under argon, solubility at pH greater than 3 was at nm/L levels, three orders of magnitude lower than at pH 3 and below. Under 10% CO₂, solubilities decreased from 10 $\mu\text{mol/L}$ at pH 2.06 to 80 nm/L at pH 3. Log k_{sp} was calculated to be -51.2 ± 1.5 under 100% argon, and -50.2 ± 2.2 under 10% CO₂.

XRD and BET analysis of ThO₂ remnants from each experiment showed that other than a small surface area increase of 15–30%, the ThO₂ was otherwise identical to the untreated standards.

References

- [1] C. Sherman, *Np(V) Sorption on Goethite, Montmorillonite, and Tuff*, SM Thesis, MIT, 2001.
- [2] R. C. Eckhardt, *Summary and Synthesis Report on Radionuclide Retardation for the Yucca Amount Site Characterization Project*, Yucca Mountain Site Characterization Program Milestone 3784M, October 1997.
- [3] K. Czerwinski, *Nuclear Waste Management lecture notes*, lecture 4.
- [4] K. Czerwinski, *Waste Management Issues*, MIT, February 1999.