Geochemistry Related to NH₃ Gas Used for Uranium Remediation in the Vadose Zone

DOE-FIU SCIENCE & TECHNOLOGY WORKFORCE DEVELOPMENT PROGRAM

FIU | **Applied Research Center**
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ABSTRACT

Claudia Cardona, a DOE Fellow, completed an eight weeks internship with the Pacific Northwest National Laboratory (PNNL) in Richland, Washington under the mentorship of Dr. Szecsody. Throughout her internship, Mrs. Cardona assisted Dr. Szecsody in his current PNNL NH_3 gas experiments focusing on the sequestration of uranium in the vadoze zone sediments at the Hanford Site 200 Area. These experiments helped to improve her knowledge of the experimental methods and enhance speciation modeling capabilities to apply in the associated research being conducted at the Florida International University's Applied Research Center (FIU-ARC). Mrs. Cardona received guidance on the use of the geochemical modeling software, Geochemical Workbench (GWB), as well as learned additional experimental techniques to continue her studies on uranium remediation in the vadose zone of the Hanford Site Area.

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1. INTRODUCTION

Large volumes of high-level nuclear waste were generated from plutonium production and separation processes at the Hanford Site during World War II as part of the Manhattan project and the Cold War. Four main areas at Hanford Site, 100, 200, 300, and 1100 Areas, are on the National Priority List (NPL) site of the Environmental Protection Agency (EPA). The 200 Area is well known, and is associated with the removal of plutonium from the uranium fuel rods. This plutonium extraction process produced large amounts of radioactive waste containing uranium in the Hanford Site's 200 Area, resulting in contamination of the groundwater and soil. Hanford Site is considered the most contaminated nuclear site in the United States (Wu, 1999) and the most complex environmental cleanup project in the nation (DOE, 2009; Lichtenstein, 2005).

Scientists from the Pacific Northwest National Laboratory (PNNL) Energy and Environment Directorate (EED) have conducted an extensive range of studies regarding the current conditions and potential mitigation of these leakages into the vadose zone which represent a potential source for groundwater contamination and possible risk to receptors that will use this water down-gradient through water uptake from contaminated wells or discharge to surface water.

Innovative in-situ technologies to treat inorganic contaminants in unsaturated sediments are still being developed. The vadose zone contamination of uranium requires in-situ stabilization to convert aqueous U-carbonate mobile phases to lower solubility precipitates that are stable in the natural environment. Injection of reactive gases such as NH₃ gas to create alkaline conditions in the vadose zone is an innovative technology used to decrease uranium mobility by creating stable precipitates in the subsurface contaminated with radionuclides. Previous short-term laboratory evaluation showed a decrease in uranium mobility after ammonia injection in the low water content sediments of Hanford Site (Szecsody et al. 2010a). However, additional studies are needed for a better understanding of the effects of the major pore water constituents on the uranium removal and the formation of precipitates after the injection of NH₃ into the vadose zone of Hanford Site.

The objective of this internship was to improve and develop an understanding of the previous and future research related to the treatment of the deep vadose zone using NH₃ gas by working closely with PNNL scientists. The main focus was on the speciation and prediction of the major uranium species created after injection of the NH₃ gas by using a geochemical equilibrium modeling software, as well as identified additional experimental approaches to support the predictable uranium species.

2. EXECUTIVE SUMMARY

This research work has been supported by the DOE-FIU Science & Technology Workforce Initiative, an innovative program developed by the U.S. Department of Energy's Office of Environmental Management (DOE-EM) and Florida International University's Applied Research Center (FIU-ARC). During the summer of 2015, a DOE Fellow intern, Claudia Cardona, spent eight (8) weeks doing a summer internship at the Pacific Northwest National Laboratory (PNNL) in Richland, Washington under the supervision and guidance of Dr. Jim Szecsody, Senior Scientist with the Environmental Group. The intern's project was conducted between June 15, 2015 and August 7, 2015 with the objective of the assisting with the experimentation related to the use of NH_3 gas for uranium remediation in the vadose zone of the Hanford Site 200 Area and learning additional experimental procedures to be continued at Florida International University's Applied Research Center (FIU-ARC).

3. RESEARCH DESCRIPTION

The primary focus of the internship was on the application of the geochemical equilibrium modeling software, Geochemist's Workbench (GWB) version 10.0 (Bethke, University of Illinois).The internship was also devoted to learning and assisting with the uranium sequential extraction and dissolution experiments that are currently being conducted by PNNL's scientists.

The GWB modeling was used to predict the formation of uranium aqueous species and solid phases likely to be saturated in the post-NH$_3$ gas-treated pore water. The GWB thermodynamic databases were reviewed to identify the basic components to set up the composition of the experimental synthetic pore water solutions as well as uranium-bearing minerals. The default thermodynamic database was supplemented to include the latest revised thermodynamic data for aqueous and mineral uranium species (Guillaumont et al., 2003). The modeling was conducted by combining the concentrations of four cations and three anions to reproduce the experimental synthetic pore water solutions. The divalent Ca^{2+} was not considered initially in this modeling. The GWB React Module was used to simulate the NH$_3$ gas reaction in multiple synthetic pore water solutions. The pH was fixed from 8 to 11.02 and then repeated from 8 to 11.87, simulating the pH values reached after the 0.1% and 5% of NH$_3$ gas injection. The concentrations of aqueous ammonia in the solutions at equilibrium for each reaction were set as 0.063 M and 3.1 M, respectively. A dissolved oxygen concentration equivalent to the typical on-site conditions was set as 8.4 ppm at constant temperature of 25°C. The concentration of uranium was kept constant at 2 ppm in all simulations. The aqueous uranium species and mineral uranium species were identified and graphed as a function of the pH.

4. RESULTS AND DISCUSSIONS

4.1 Basic pore water composition and NH₃ reaction:

The React module was used for modeling multiple synthetic pore water solution simulations using 0.1% and 5% concentrations of NH_3. The major pore water components dissolved in the synthetic pore water were represented by K^+, Na^{2+}, Al^{3+}, UO^{2+}, $H_2SiO_4^{2-}$, HCO_3^- and NO_3^{2-}. The simulation considered a small concentration of NH^{4+} as an initial input to initiate the simulation of the NH_3 gas reaction. The basic section included all other component concentrations for the specific pore water solution system, the H^+ activity of 8, and the mass solvent water (1 kg by default). The temperature was set up at 25°C and the density and total dissolved solids (TDS) were kept "auto". Figure 1 shows an example of the basic input in the GWB React Module for pore water components.
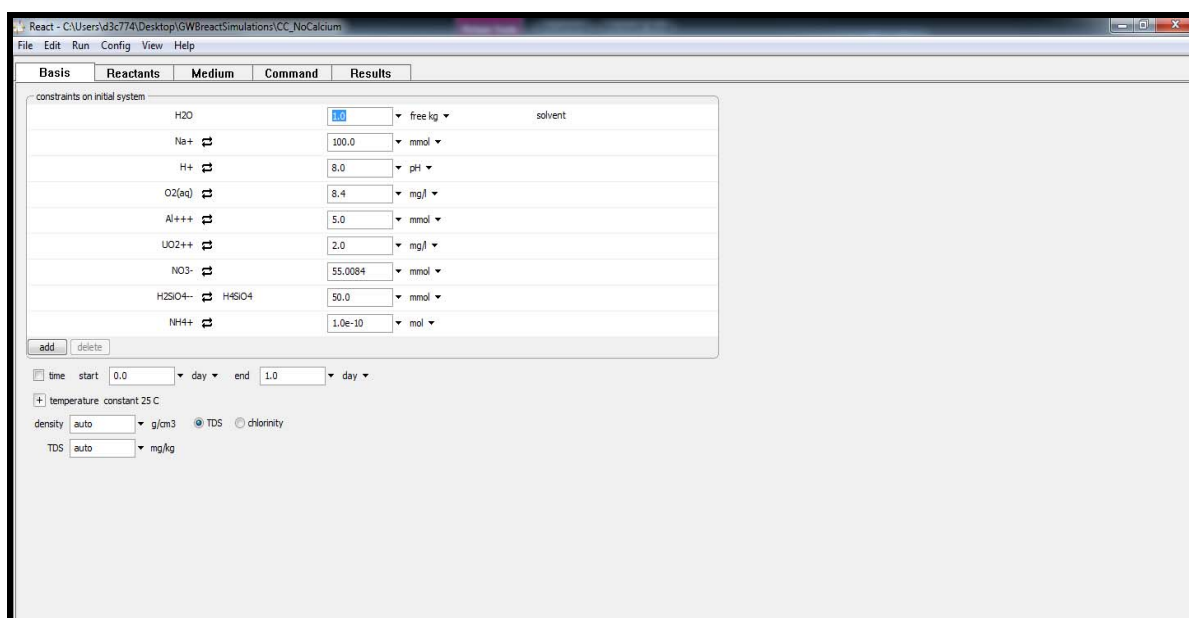

Figure 1. An example of the basic pore water components input in the GWB React Module.

The NH₃ gas reaction was simulated in the reactants section sliding pH to 11.02 and then to 11.87; the NH₃ aqueous total mass to react was set up to 0.063 and 3.1M, respectively. Figure 2. 5% of NH₃ gas reaction in the GWB React Module

shows the input to represent the 5% of NH_3 gas reaction.

Figure 2. 5% of NH₃ gas reaction in the GWB React Module

4.2 5% of NH₃ gas partitioning into the pore water solution:

The partitioning of 0.1% and 5% of NH₃ gas into the pore water solutions and the resulting pH were modeled to observe the mass of NH₃ in the pore water subsequent to the partitioning. The simulation was started by adding 1×10^{-10} mol/L of NH_4^+ to the solution at pH 8 until the pH reached 11.0 (0.063 mol/L(aq)) for 0.1% NH₃ and 11.87 (3.1 mol/L NH₃ (aq)) for 5% NH₃. Figure 3 shows the 5% of NH₃ gas partitioning between an initial pH of 8 (natural conditions) and the resulting pH of 11.87.
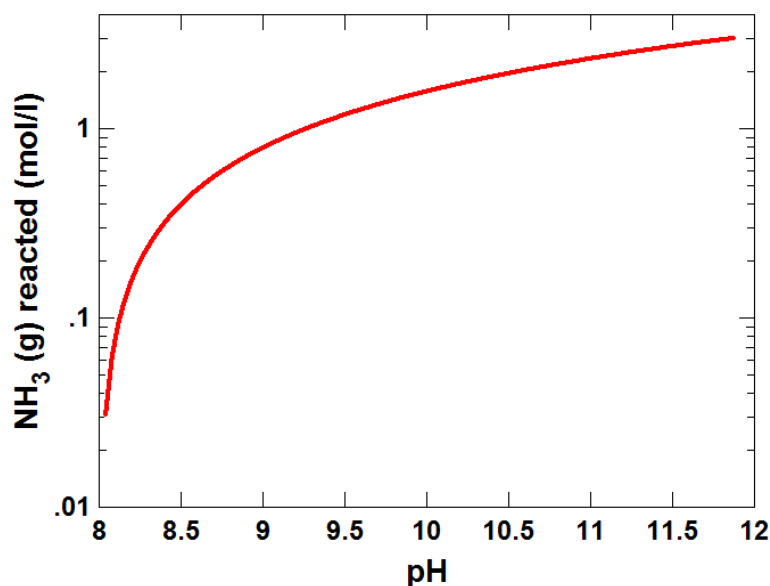

Figure 3. 5% of the NH₃ gas partitioning into water and the resulting pH.

4.3 Predicted aqueous species and uranium-bearing minerals

The initial modeling simulations were free of bicarbonate ions and contained varied silica concentrations in the synthetic pore water compositions to be able to observe the effect of the bicarbonate ions and silica concentration on the formation of the aqueous species and uranium mineral phases after treatment with NH₃ gas. The bicarbonate concentrations were bicarbonate-free, 2.9 mM and 50 mM respectively. The silica concentrations were 5 mM, 50 mM and 100 mM respectively. All the simulations were conducted for 0.1% and 5% of injected NH₃ gas. Figure 4 shows the activity of uranium species obtained from a pore water solution free of bicarbonate ions and 50 mM of Si after reacting with 5% of NH₃ gas. The modeling prediction showed that in the absence of carbonate in solution, the major U(VI) species appear as uranyl-hydroxide $UO_2(OH)_3^-$ and $UO_2(OH)_4^{-2}$. The formation of the highly soluble $UO_2(CO_3)_3^{4-}$ and $UO_2(CO_3)_2^{2}$ resulted from increasing the bicarbonate concentrations.

Figure 4. Uranium aqueous species activity as a function of pH for concentrations of 50 mM of Si and free of HCO₃⁻.

Figure 5 shows the concentration activity of the uranium species for synthetic pore water containing 50 mM of bicarbonate and 50 mM of silica. The major uranyl carbonate species formed at these bicarbonate and silica concentrations are highly soluble $UO_2(CO_3)_3^{4-}$ and $UO_2(CO_3)_2^{2}$. However, the concentration of uranyl carbonate species is predicted to slightly decrease under alkaline conditions, between pH 11 and 11.5.
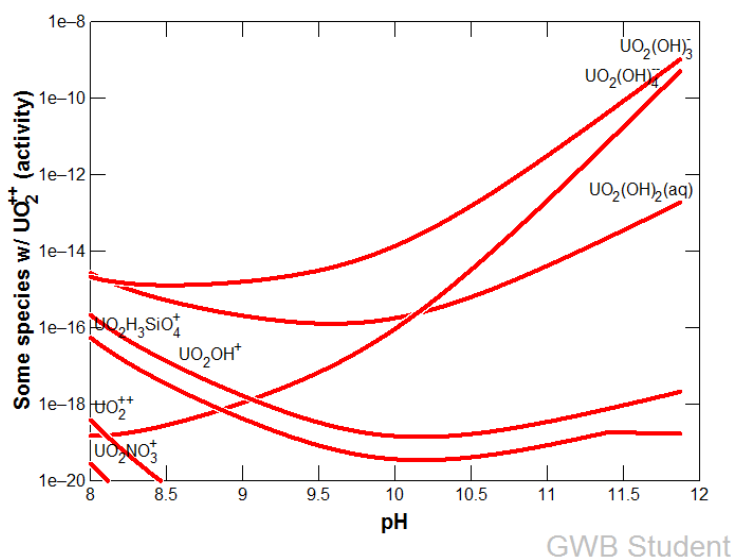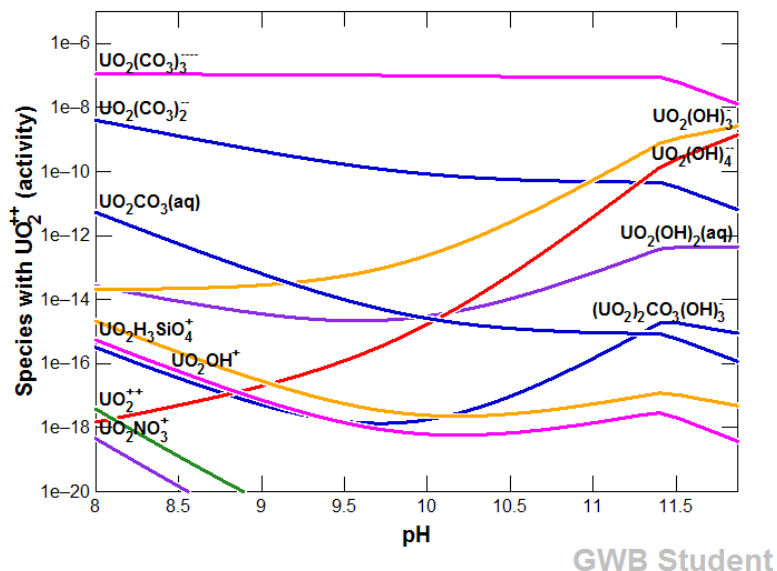
Figure 5. Uranium aqueous species activity as a function of pH for concentrations of 50 mM of Si and 50 mM of HCO₃⁻.

The concentration of the aqueous uranium species and saturated uranium-bearing mineral phases were plotted as a function of pH for the 100 mM of HCO_3^-, 50 mM and 100 mM of Si, and 5% of NH_3 (3.1 M of NH_3(aq)) gas reaction. The major aqueous species predicted were $UO_2(CO_3)_3^{4-}$ and $UO_2(CO_3)_2^{2-}$. In all simulated component concentrations, modeling suggested the formation of the following uranium mineral phases: uranyl carbonate, Rutherfordine ($UO_2(CO_3)$), uranyl-silicates, Boltwoodite and Na-boltwoodite $(K,Na)(UO_2)(SiO_3OH)4(H_2O)_{1.5}$, Schoepite, $(UO_2)_8O_2(OH)_{12}\cdot12H_2O$ as uranyl-hydroxides, and Gummite, which is a mixture of Boltwoodite $K(UO_2)(SiO_3OH)4(H_2O)_{1.5}$, Clarkeite $Na(UO_2)O(OH)\cdot H_2O$, Soddyite, $(UO_2)_2SiO_4\cdot2H_2O$, and Uraninite, UO_2. Additional uranyl carbonates species are formed due to the addition of carbonates to the system (100 mM), which results in orders of magnitude increases in uranium solubility compared to the carbonate-free system shown in Figure 4. Since Ca^{2+} was not included in these initial simulations, there were no observed complexes that included Ca, such as Uranophane, which is included in the default thermodynamic database. Figure shows the diagrams for 100 mM of HCO_3^-, 50 mM and 100 mM of Si, and 5% of NH_3 gas. The concentration of aqueous uranium species and the saturation indexes of uranium-bearing minerals showed a similar trend for both Si concentrations tested.
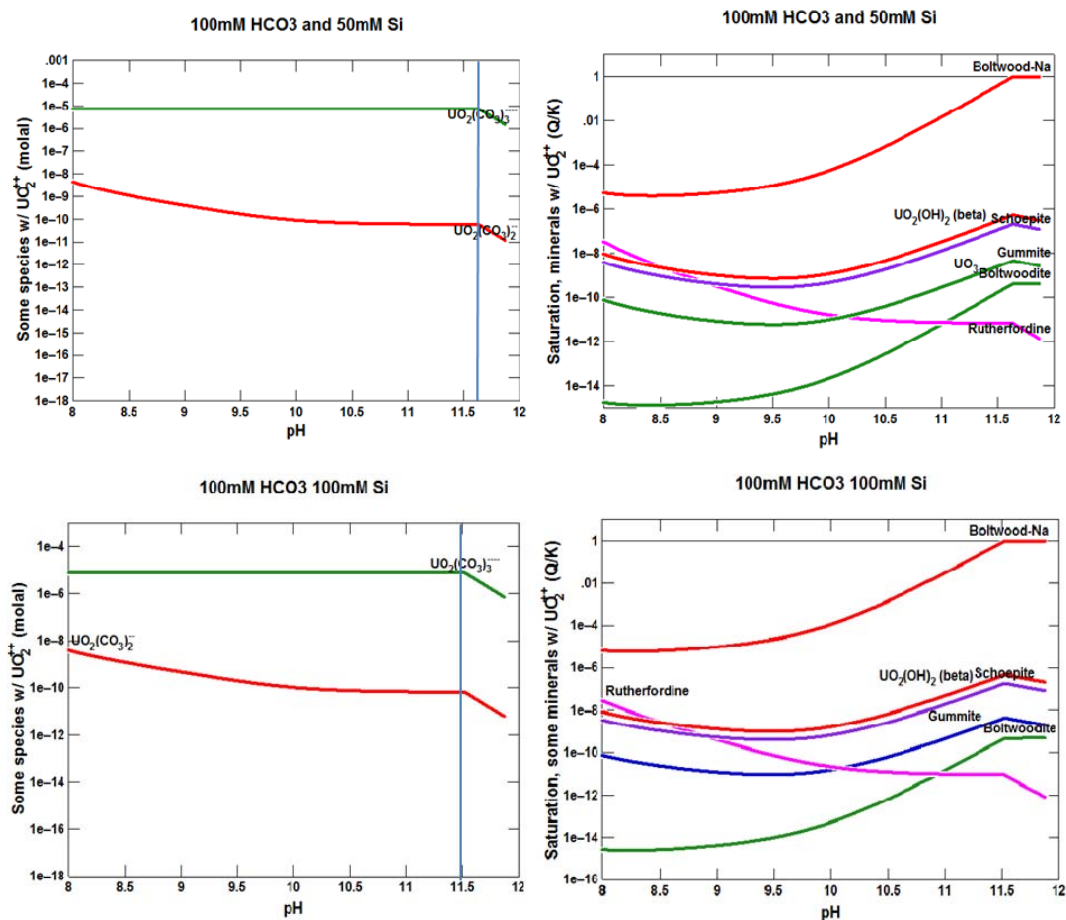
Figure 6. Diagrams showing concentrations of uranium aqueous species and saturated uranium-bearing mineral phases plotted as a function of pH for 100 mM HCO₃⁻ and 50 mM and 100 mM of Si. The reaction simulations were done for 5% of NH₃.

5. CONTINUOUS FLOW REACTOR (CFR) EXPERIMENTS

5.1 Dissolution Experiments

In addition to the GWB modeling, incorporation of procedures for the Continuous Flow Reactor (CFR) experiments were discussed which will extend the FIU-ARC experimental work plans to measure uranium precipitate dissolution that could occur in the vadose zone after treatment with NH_3. Similar dissolution experiments have been conducted by PNNL scientists. The procedures, equipment, and techniques to implement this experiment were reviewed under the mentorship of Dr. Szecsody during the internship. The dissolution experiments will consist of continuous injection of the Hanford Site synthetic groundwater through the precipitate samples using a single pass flow through apparatus. The set up will include a peristaltic pump for controlling water flow rate and pressure. Effluent solutions from each precipitate sample will be collected continuously and aliquots of the fluid samples will be retained for both pH measurements and chemical analysis of the major constituent by an Inducted Coupled Plasma (ICP-OES) and Kinetic Phosphoresces analyzer (KPA). The mass of uranium will be calculated and correlated with the major constituents (Si, Ca, Al, and bicarbonate concentrations) each time that samples are collected. After completing the CFR experiment, precipitate samples will be analyzed using the X-Ray Diffraction (XRD) and Scanned Electron Microscope (SEM) to determinate morphological and mineralogical changes in the precipitate samples. The CFR experiment will be conducted at a range of temperatures, between 5ºC and 50ºC.

5.2 Sequential Liquid Extraction and Leaching Experiments

The sequential liquid extraction experiments have been conducted by PNNL scientists to define the potential of uranium (U) and technetium (Tc) leaching from mineral phases. A series of six sequential liquid extractions were used to measure U and Tc in aqueous and surface phases. "The first two extractions helped to identify the aqueous and absorbed uranium, respectively. The remaining four extractions determined progressively harder-to-extract uranium phases or phases coated with non-uranium minerals." Table 1 and

Table 2 provide information on the sequences to identify U and Tc phases.

Table 1. U Sequential Extraction Experiment

Solution	Time (h)	Target Compounds
Synthetic groundwater	1	Aqueous U phases
0.0144 M $NaHCO_3$ + 0.028 M Na_2CO_3	1	Adsorbed U phases
1 M Sodium-Acetate	1	Dissolved some U-Carbonates
Acetic Acid	120	Most U-Carbonates and hydrated boltwoodite
8 M Nitric Acid	2	Dissolved harder U phases
0.0144 M $NaHCO_3$ + 0.028 M Na_2CO_3	1000	Carbonate Solution

Table 2. Tc Sequential Extraction Experiment

Solution	Time (h)	Target Compounds
Hanford Groundwater	1	Aqueous pertechnetate
0.5 M Mg $(NO_3)_2CO_3$	1	Adsorbed pertechnetate
1 M Sodium-Acetate	1	Dissolved some U-Carbonates
Acetic Acid	120	Most Tc Carbonates
0.1 M Ammonium oxalate + 0.1 M oxalic acid	1	Dissolved oxides
8 M nitric acid	2	Dissolve hard-to-extract phases

6. CONCLUSIONS

The geochemical equilibrium modeling and assisting with the experiments conducted by the Pacific Northwest National Laboratory (PNNL) scientists helped me to learn experimental procedures that can be applied in the research being conducted by FIU-ARC. The geochemical equilibrium modeling software, Geochemical Workbench, was studied and applied to current research being conducted by FIU-ARC. The results obtained correlated with previous experimental results. However, more simulations need to be performed using an enhanced thermodynamic database. The speciation modeling results need to be compared with batch experimental and XRD results. The dissolution experiments will be set up and conducted in the ARC laboratories during FIU Year 6. The opportunity to assist Dr. Szecsody has enhanced my knowledge and experience and increased my confidence to conduct ongoing FIU-ARC studies and be able to finalize my PhD research.

7. REFERENCES

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