



Investigation of Effects of pH and Temperature on the Carbonate Promoted Dissolution of Meta-autunite

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Abstract

The polyphosphate injection technology is being evaluated as a remediation strategy at the DOE Hanford Site. Release of uranium from autunite, an artificial mineral created as a result of polyphosphate injection in the subsurface, merely takes place during slow dissolution of the mineral structure. Stability information of the uranyl-phosphate phases is limited to conditions involving pH, temperature, and a few aqueous organic materials. Carbonate ion, which creates very strong complexes with uranium, is the predominant ion in the groundwater composition. The objective of this research is to examine the discrete effects of the carbonate complexation, pH and temperature on the dissolution of autunite.

Introduction

This research is funded by the U.S. Department of Energy (DOE) to support Hanford Site's environmental cleanup in the areas of soil and groundwater and D&D by providing technical solutions and needed knowledge through experimental studies.

Hanford Site was the first nuclear production facility and occupies over 586 Sq. miles adjacent to Columbian River. Hanford Site was established in 1943 and operated for over 40 years supporting the Nation's defense authority by producing nuclear weapons. In 1989 DOE and EPA started the world's largest cleanup initiative after shutting down all the reactors at Hanford Site. One of the greatest concerns at the Hanford site is uranium, which is widely spread in the 300 Area located alongside the Columbian River.

Polyphosphate Technology

Injection of a sodium triphosphate amendment into the uranium contaminated groundwater and soil has been an effective remediation technology. Polyphosphate amendment forms insoluble uranyl phosphate minerals making uranium immobile.

Name	Composition
autunite	$\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10\text{H}_2\text{O}$
meta-autunite	$\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot (2-6)\text{H}_2\text{O}$
uranyl orthophosphate	$(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$
chernikovite	$(\text{H}_3\text{O})_2(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$
sodium meta-autunite	$\text{Na}_2(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$
meta-ankoleite	$(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$
phosphuranylite	$\text{Ca}(\text{UO}_2)_3(\text{PO}_4)_2(\text{OH})_2 \cdot 6\text{H}_2\text{O}$
uranyl hydrogen phosphate	$\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$
saleeite	$\text{Mg}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10\text{H}_2\text{O}$

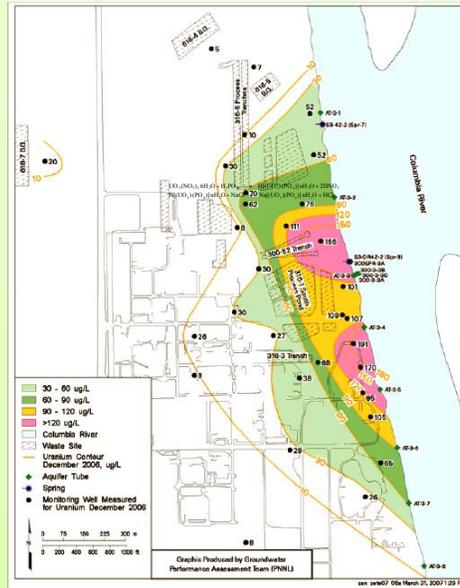
Release of uranium from autunite takes place during slow dissolution of the mineral structure. It is believed that the dissolution of autunite depends strongly on pH and temperature.

Acknowledgements:

Dr. Leonel Lagos, Dr. Yelena Katsenovich, Dr. Dawn Wellman.

Objectives

- Conduct dissolution experiments in a Single-Pass Flow-Through (SPFT) apparatus using carbonate as a buffer solution.
- Quantify the effect of carbonate complexation with autunite minerals and investigate factors such as temperature and pH on the dissolution kinetics.



Benefits

- Quantify kinetic rate law of autunite dissolution in the presence of a carbonate ligand under strictly controlled dilute solution conditions.
- Develop an effective solution for immobilization of uranium and predicting its fate and transport in the subsurface.

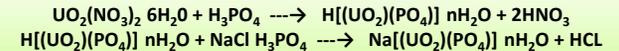


Experimental Approach

Conduct experiments using SPFT cells, under controlled pH and temperature at constant solution flow through a reactor cell filled with the autunite mineral.

Synthesize autunite by indirect precipitation method:

- Mix 110 mM uranyl nitrate and 1.1M phosphoric acid.
- Stir the solution for 30 min followed by curing for 24 hrs.
- Collect the precipitate using vacuum filtration using a 45µm disposable filter.
- Immerse the precipitate in 200mL aliquots of 2M NaCl solution for 2 days.
- Filter the crystals, wash with DI water, wash in isopropyl alcohol.
- Dry crystals at room temperature until a constant weight is achieved.



Results

	pH	6	7	8	9	10	11
Volume of solutions in ml	0.5 mM KHCO ₃	9.958	9.970	10.000	9.980	9.940	9.800
	0.1 M HCl	0.042	0.030	0.000	0.000	0.000	0.000
	0.1 M KOH	0.000	0.000	0.000	0.020	0.060	0.200
	1.0 mM KHCO ₃	9.908	9.950	10.000	9.950	9.920	9.750
	0.1 M HCl	0.098	0.050	0.000	0.000	0.000	0.000
	0.1 M KOH	0.000	0.000	0.000	0.050	0.080	0.250
	2.0 mM KHCO ₃	9.808	9.840	9.900	9.980	9.890	9.650
	0.1 M HCl	0.192	0.160	0.100	0.000	0.000	0.000
	0.1 M KOH	0.000	0.000	0.000	0.020	0.110	0.350
	3.0 mM KHCO ₃	9.715	9.750	9.850	9.980	9.850	9.550
	0.1 M HCl	0.285	0.250	0.150	0.000	0.000	0.000
	0.1 M KOH	0.000	0.000	0.000	0.020	0.150	0.450

Future Work

- Synthesize autunite by indirect precipitation.
- Conduct batch dissolution experiments to quantify kinetics of autunite dissolution in the presence of a carbonate ligand.