Dissolution of Uranium Metal from Hanford K Basin Sludge Simulant, Without Producing Hydrogen

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Background

- About 2100 metric tons of Spent Nuclear Fuel has been retrieved from the two K Basins at Hanford
- The sludge contains metallic uranium, ≤ ¼ in.
- The uranium must be stabilized before solidifying the sludge for disposal as TRU waste

Objectives

- Determine the rate of uranium metal oxidation/solubilization, using hydrogen peroxide and ammonium bicarbonate
- Determine the quantity and composition of off gas produced
- Determine the effect of peroxide and carbonate concentrations, pH, and temperature on the metallic uranium removal rate

Experimental Methods

- Conduct tests in polycarbonate flasks inside environmental shaker
- Connect flasks to Tedlar bags to collect off-gas and measure volume
- Analyze selected gas samples for ammonia, carbon dioxide, hydrogen, etc.
- Use ¼" depleted uranium metal cubes, and periodically clean, dry, and weigh uranium cubes to determine loss rate
- Add FeOOH or sludge simulant
- Continuously add 50% H_2O_2 for selected tests, using a syringe pump
- Peroxide determination by potassium permanganate titration

Composition of K Basin sludge simulant (prepared at PNNL)

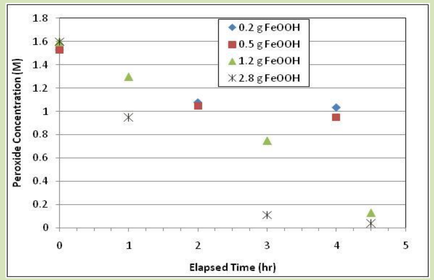
Component	Weight (g)	Weight %
Ferric oxide hydroxide (FeOOH)	21.915	9.86%
Aluminum hydroxide ($Al(OH)_3$)	7.819	3.52%
Sand (from Hanford Site)	16.402	7.38%
Organic ion exchange resin (Purolite NRW 37)	7.702	3.46%
Zeolite (Mordenite)	7.505	3.38%
$UO_2/UO_3 \cdot 2H_2O$ (50-50 mole% mix)	54.657	24.59%
Sub-total of dry ingredients	**116.00**	**52.18%**
Water - By difference from total simulant weight	106.30	47.82%
Total	**222.30**	**100%**

Tests flasks in shaker, connected to Tedlar bags

Test slurry before adding peroxide

Preliminary Work: Decomposition of H_2O_2 by FeOOH and Carbonate

Preliminary experiments showed that iron oxide causes rapid peroxide decomposition. Also shown by R. J. Watts, et.al., *Journal of Hazardous Materials* B69, 229–243, 1999, for soil.

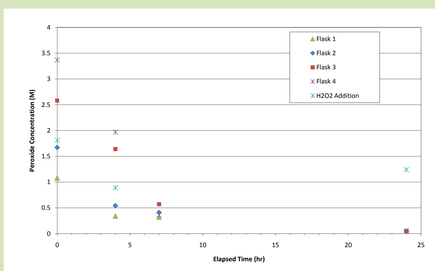


Later work showed that carbonate or bicarbonate promotes peroxide decomposition. Also shown by S. M. Peper, et.al., *Ind. Eng. Chem Res.*, **43**, 8188-8193, 2004.

24hr Uranium Dissolution Testing

Uranium dissolution rates at various initial peroxide concentrations
Each flask contains 2.8 g FeOOH/65 mL solution, 1 *M* NH_4HCO_3, and one ¼-in. uranium cube, temperature = 10ºC, 50% H_2O_2 added at 0.3 mL/hr

Initial $[H_2O_2]$ (M)	Metallic Uranium Removal Rate (mg/hr)	(mm/hr)
1.08	15.0	0.0034
1.67	24.3	0.0056
2.58	29.2	0.0068
3.37	32.4	0.0076
1.81 + 50% H_2O_2	25.6	0.0060



Peroxide concentration during 24hr testing

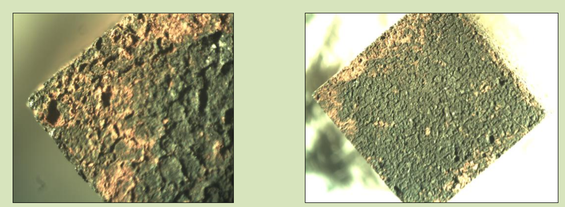
Conclusions

- There is complicated relationship between pH, bicarbonate concentration, hydrogen peroxide concentration, and uranium dissolution rate
  - A concentration of 2 *M* NH_4HCO_3 at 25ºC showed the best uranium removal rate
  - 4 *M* NH_4HCO_3 reduced the peroxide concentration in the slurry and also reduced the uranium removal rate
  - 1 *M* NH_4HCO_3 showed a higher peroxide concentration in the slurry but a lower uranium removal rate
  - Reducing the pH to 7.0 did not increase the peroxide concentration or the uranium removal rate
  - Reducing the temperature to 10ºC increased the peroxide concentration with FeOOH, but not with simulant sludge; the uranium removal rate was lower
- A large amount of oxygen gas is produced from decomposition of the peroxide
- Using hydrogen peroxide and ammonia bicarbonate to oxidize the metallic uranium is a viable method to treat the uranium in the K Basin sludge
- The process has not been optimized

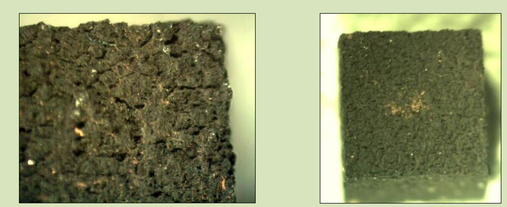
Experimental results

Summary of 7-10 day uranium dissolution tests. 50% H_2O_2 was added at 0.5 mL/hr for all tests.

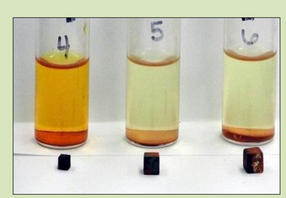
Test #	pH	Temp (ºC)	$[NH_4HCO_3]$ (M)	Solids	Off-Gas (L)	$[H_2O_2]$ (*M*)	U penetration (mm/hr)
1	8.8-8.9	10	1→0.5	FeOOH	2.5	0.18-2.1	00032
2	8.4-9.2	10	2→1	Simulant	4.4	0.05-0.23	0.0015
3	8.0-9.3	10	4→2	Simulant	6.8	0.05-0.1	0.0025
4	7.6-8.8	25	2	Simulant	6.2	0.08-0.21	0.0052
5	7.6-8.8	25	4	Simulant	5.2	0.01-0.03	0.0015
6	7.7-8.7	10	4	Simulant	10.2	0.01-0.05	0.0003
7	7.0-8.3	25	2	Simulant	2.4	0.03-0.11	0.0032
8	7.0-8.5	25	2	Simulant	4.6	0.02-0.16	0.0027



Photomicrographs of uranium cube from test 1.
Photo on left is about 40X and photo on right is about 10X.



Photomicrographs of uranium cube from test 4.
Photo on left is about 40X and photo on right is about 10X.



Uranium cubes and slurries at end of tests, test 4 on left, 5 in center, and 6 on right

Typical off-gas composition

Analyte	Concentration (%)
Ammonia	<0.01
Argon	0.3
Carbon dioxide	3.7
Carbon monoxide	<0.01
Hydrogen	<0.01
Nitrogen	26
Oxygen	70

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