

Stabilization of Hanford K-Basin Sludge by Dissolution of Uranium Metal with Carbonate / Peroxide Solution - 11210

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ABSTRACT

The Hanford K Basins were used until the mid 1960s to store, under water, spent nuclear fuel from the site's reactors before it was reprocessed to recover uranium and plutonium. A sludge consisting of cladding corrosion products, uranium, fission products and other debris accumulated on the floor of the K Basins while they were in operation and during the period following cessation of reprocessing when some spent fuel was left in the Basins for an extended period. The spent fuel was recovered, dried and placed in dry storage early in the 2000s and, following that, the sludge was retrieved and placed into temporary containers to await treatment to stabilize and package it for permanent disposal at the Waste Isolation Pilot Plant (WIPP). One of the requirements for the treatment phase is to identify and demonstrate technologies that can be used to chemically treat the K Basin sludge. In particular, there is a requirement to oxidize the uranium metal particles contained in the sludge so that these cannot react with water and generate hydrogen gas during transport to WIPP. EnergySolutions was awarded a contract in mid 2010 by CH2M Hill Plateau Remediation Company to demonstrate a stabilization process based on oxidizing the uranium metal with hydrogen peroxide and subsequently converting the oxidized metal to uranyl carbonate with ammonium bicarbonate. The resulting slurry would then be stabilized in grout for disposal at WIPP. There are several advantages of this process over others that have been proposed. The reaction occurs at ambient temperature and does not require removal of any significant reaction heat. In addition, aside from the generation of oxygen arising from peroxide decomposition, no off-gas, including hydrogen, is generated. One of the main constituents of the K Basin sludge is iron oxide hydroxide, which is known to catalyze peroxide decomposition. Therefore, one of the early challenges was to identify process conditions that would minimize the volume increase arising from continuous addition of fresh peroxide to maintain its concentration. Results from small-scale tests using simulated K-Basin slurry were used to develop a process concept and timeline for treating the actual slurry. The work showed all of the K-Basin sludge could be stabilized in less than 4 years for shipment to WIPP.

INTRODUCTION

In 1996 the K Basins Spent Nuclear Fuel Project attained a CERCLA Record of Decision (ROD) to retrieve the 2,100 metric tons of N Reactor Spent Nuclear Fuel (SNF) from the two aging water-filled K Basins (KE Basin and KW Basin); to clean, repackage and dry it; and to place the dried SNF in sealed containers for interim storage in a new dry storage facility in the Hanford 200 Area. SNF retrieval, removal and drying began in December 2000 and was completed in October 2004.

A significant fraction of the SNF degraded during the lengthy underwater storage period due to damage to the Zircaloy cladding sustained during reactor discharge and the subsequent corrosion of the metallic uranium. The K Basins corrosion products, together with other debris accumulated in the K Basins over the years, that will pass through a screen with a 0.64 cm (1/4-inch) opening is collectively referred to as sludge. The sludge on the KE Basin floor and in its adjacent pits has been transferred to KW Basin and consolidated into large (~12 ft x ~6 ft x ~12 ft) Engineered Containers for underwater storage in the KW Basin. Most of the sludge on the KW Basin floor and in its adjacent pits has also been consolidated into Engineered Containers for underwater storage on the floor of the KW Basin. A small amount of sludge

remains on the floor of the KW Basin and efforts to recover this sludge and place it in an Engineered Container continue.

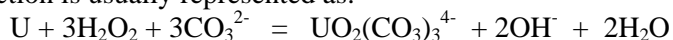
In addition, during cleaning and repackaging operations for SNF that were conducted in KW Basin, material with particle sizes smaller than 600 microns was recovered and temporarily stored in Settler Tanks within KW. Material with larger particle sizes was also recovered. The smaller than 600 microns material has been transferred to an Engineered Container and kept separate from the main Engineered Container sludge.

Once the sludge that remains on the KW Basin floor is recovered and interim stored in an Engineered Container and the Settler Tank sludge is consolidated into another Engineered Container, the K Basin sludge will be transferred into Sludge Transport and Storage Containers (STSCs) and will be shipped to the 200 Area plateau for interim storage.

The sludge will then be treated to stabilize and package it such that it can be transported to and disposed at the Waste Isolation Pilot Plant (WIPP) or other suitable repository as remote-handled transuranic (RH-TRU) waste. One of the requirements is to identify and demonstrate technologies that can be used to chemically treat the K Basin sludge. In particular, there is a requirement to oxidize the uranium metal particles contained in the sludge so that these cannot react with water during transport and generate hydrogen.

In May 2010 *EnergySolutions*, among others, was awarded a contract to provide Alternatives Analysis Support to the Hanford site contractor responsible for executing the Sludge Treatment Project, CH2M Hill Plateau Remediation Company (CHPRC). For *EnergySolutions*, this support consisted of proof-of-concept testing a technology proposed by *EnergySolutions* to treat the sludge and particularly convert the uranium metal to a form that will not generate flammable gas.

The *EnergySolutions* process uses hydrogen peroxide to oxidize the uranium metal to U(VI), and reacts the U(VI) with carbonate in solution to form uranium carbonate. The concept for this approach has been demonstrated by Soderquist et. al [1] in small-scale experiments of typically one hour duration. The stoichiometry of the reaction is usually represented as:



Peper et al. [2] have observed the reaction proceeding further to produce $[\text{UO}_2(\text{O}_2)_x(\text{CO}_3)_y]^{2-2x-2y}$, where x and y depend on the peroxide and carbonate concentrations. As well as being an oxidizing reagent, the hydrogen peroxide is a good ligand for uranium so some uranium may be present after reaction as a complex with the hydrogen peroxide. A key advantage of this reaction is that no hydrogen is evolved and no uranium hydride is produced (as it is when uranium reacts with water). Earlier work by Watts et al. [3] and Shu-Sung and Gurol [4] showed that ferric oxide hydroxide could promote the decomposition of hydrogen peroxide to oxygen gas. Fenton [5] first observed the reaction of peroxide with soluble ferric ions to form peroxide radicals (Fenton's reagent) and the peroxide radicals can react with additional hydrogen peroxide to produce oxygen gas. Therefore, limiting hydrogen peroxide decomposition was identified early as an overall project objective to minimize the quantity of reagents needed for implementing the process.

Proof-of-concept testing, conducted at Oak Ridge National Laboratory (ORNL) under a Commercial Work for Others Agreement, was performed in two phases. The objective of the first phase was to define the set of conditions that would minimize the decomposition of peroxide in tests using a reaction slurry of ferric oxide hydroxide and uranium. The second phase used simulated K-Basin slurry to demonstrate the technology with a representative feedstock and to further refine the process conditions. The test results were used to develop a concept for a full-scale process.

TEST MATERIALS AND METHODS

All of the reaction tests were conducted in 250-mL polycarbonate flasks inside an environmental shaker, swirling at a rate adequate to maintain good solids suspension. Each flask contained an initial slurry volume of 65 mL. Tests were conducted at ambient room temperature and at 10°C. The tests at room temperature used a Lab-Line Model 3527-5 Environ Shaker (Melrose Park, IL) and the tests at 10°C used a VWR Refrigerated Shaker (West Chester, PA). The headspace of the flasks was vented to Tedlar bags through a tube in the rubber stopper in the top of the flask, for collection of any off-gas that was generated (see Fig. 1).

Reagent grade chemicals were used to prepare the solutions and a sample of ferric oxide hydroxide from Shepherd Chemical Company (Norwood, OH) was supplied by Pacific Northwest National Laboratory (PNNL). Concentrated hydrogen peroxide (50 wt%, Fisher Chemical, lot #104210, stabilized with 0.002% tin) and solid ammonium bicarbonate from J. T. Baker (lot #C11663, reagent grade) was used.



Fig. 1. Photograph of shaker, flasks and Tedlar bags

The simulated K-Basin slurry was prepared at PNNL and shipped to ORNL as a concentrated sludge (47.8% water). The nominal dry composition of the sludge is presented in Table I. The sludge also contains 0.3 g of Nalco Optimer 7194, which was used in the K Basin sludge recovery effort to help flocculate and settle the solids. The Purolite NRW 37 resin is a mixed strong-acid cation and strong-base anion resin composed of polystyrene sulphonic acid and polyvinyl benzyl trimethyl ammonium hydroxide. The simulated sludge was mixed well, and then portions were quickly poured out and weighed to maintain the solids suspended.

Table I. Simulated K-Basin Sludge Composition

Material	Concentration (weight%)
Ferric oxide hydroxide (FeOOH)	9.86
Aluminum hydroxide (Al(OH) ₃)	3.52
Sand (from Hanford Site)	7.38
Organic ion exchange resin (Purolite NRW 37)	3.46
Zeolite (Mordenite)	3.38
UO ₂ /UO ₃ · 2H ₂ O (50-50 mole% mix in a slurry containing 19.6 g of water)	24.59
Water	47.8

Depleted uranium metal cubes (0.25 in ± 0.01 in) used in the reaction tests were obtained from Manufacturing Sciences Corporation (Oak Ridge, TN). Just prior to use, each cube was placed in a 1 M hydrogen peroxide and ammonium carbonate solution for about 1 minute to remove any surface oxide, then dipped in de-ionized water, and then in ethanol, and dried before weighing and adding to the test flasks.

The uranium cubes were periodically removed from the flasks during the tests, rinsed in water, adhering solids, if present, were wiped off with a paper towel and then the cubes were dipped in ethanol and dried before weighing. The linear metal loss rates (penetration rates) were calculated using the cube weights and a uranium density of 19.1 g/cc to calculate the volume of the cubes at each sampling event, and using the change in size from the previous sampling event to calculate the depth of uranium removed from each surface of the cubes. This procedure assumes that the uranium samples stay cubic, which is supported by visual evidence.

Peroxide concentrations were measured at each sampling event by titrating filtered and weighed test solution samples with potassium permanganate solution, which was standardized by titrating a sodium oxalate primary standard solution. Gas volume in the Tedlar bags was periodically measured using a 1-L gas syringe. Selected gas samples were collected in evacuated stainless steel cylinders for analysis at the Y12 Analytical Laboratory.

RESULTS AND DISCUSSION FROM PHASE I TESTS

Preliminary tests with only hydrogen peroxide, ammonium carbonate or bicarbonate, and iron oxide hydroxide showed significant decomposition of the peroxide. Several potential chemicals that could complex soluble iron or change the surface interaction between peroxide and iron oxide hydroxide were tested in samples of 2 M hydrogen peroxide and 1 M ammonium carbonate solution with 2.8 g ferric oxide hydroxide in a test volume of 65 mL (the ferric oxide hydroxide concentration is representative of that expected in the implemented process), including ethylene diaminetetraacetic acid (EDTA), sodium silicate, and sodium phosphate, but the peroxide decomposition rate was not reduced. Reducing the concentration of ferric oxide hydroxide reduced the decomposition rate but was not pursued given the anticipated difficulty in separating ferric oxide hydroxide from uranium solids at large scale.

Other methods that were tested to reduce the peroxide decomposition rate included lowering the temperature of the slurry and reducing the pH. A mixture of 2 M hydrogen peroxide and 1 M ammonium bicarbonate, with no ferric oxide hydroxide and an initial pH of 8.1, showed a 20% reduction in peroxide concentration after 24 hours at room temperature and no reduction in concentration at 10°C. A mixture of

2 M hydrogen peroxide and 1 M ammonium carbonate, with no ferric oxide hydroxide and an initial pH of 8.9, had no measurable peroxide after 6 hours, so the lower pH caused by using ammonium bicarbonate rather than the carbonate, reduced the decomposition rate of the peroxide. On this basis, ammonium bicarbonate was used for all of the remaining tests.

In order to determine the relative reduction in uranium conversion rate compared to the reduction in peroxide decomposition, tests were run at 10°C and 25°C in solutions of 2 M hydrogen peroxide and 1 M ammonium bicarbonate without ferric oxide hydroxide and with one uranium cube per flask.

At 10°C with no ferric oxide hydroxide, the peroxide did not decompose during the first 8 hours, but the peroxide concentration did drop to zero overnight. At 25°C the peroxide decomposed within 8 hours with no ferric oxide hydroxide present. The uranium dissolution rates were 67.1 mg/hour (0.016 mm/hour) during 8 hours at 25°C and 26.7 mg/hour (0.006 mm/hour) during 24 hours at 10°C. The linear dissolution rates are comparable to that of 0.0076 mm/hour measured by Soderquist et al. [1] in a solution of 2 M hydrogen peroxide and 1 M ammonium carbonate over one hour.

Continuous addition of hydrogen peroxide to account for that decomposed was, therefore, considered necessary. One test was conducted with a starting peroxide concentration of 2M, with concentrated (50%) hydrogen peroxide added at a rate of 0.32 mL/hour using a syringe pump. The rate of peroxide addition was calculated to match the average rate of peroxide decomposition in the previous test at 10°C. The tubing for the peroxide addition extended through the rubber stopper to the bottom of the flask. The weight of the uranium cube and the peroxide concentration in this flask were determined after 4 and 24 hours. The peroxide concentration in the test with continuous peroxide addition decreased after 4 hours, but then stabilized to approximately 1.2 M. The uranium dissolution rate in this test was 25.6 mg/hour (0.006 mm/hour), which is consistent with the results obtained by Soderquist et. al [1]. Based on the results from this test, it was decided to conduct the remaining tests using continuous addition of concentration hydrogen peroxide.

Three 7-day uranium conversion tests were conducted using one uranium cube in 65 mL of slurry that initially contained 2 M hydrogen peroxide, 1 M ammonium bicarbonate, and 2.8 g ferric oxide hydroxide at 10°C, with continuous addition of 50% hydrogen peroxide. The addition rate of hydrogen peroxide by the syringe pump, which used three syringes to supply the three flasks, measured 0.33 mL/hour for the first day. After the first day, when the peroxide concentration measured in flask 1 was very low, the setting on the syringe pump was increased and the flow rate averaged 0.48 mL/hour for the remaining six days. Flask 1 was sampled for peroxide concentration, pH, and uranium weight each work day, flask 2 was sampled after 3 and 7 days, and flask 3 was only sampled after 7 days. The results are shown in Table II. Off-gas volume in the Tedlar bags was measured periodically and the gas was vented as needed to prevent any back pressure in the flasks,.

The daily uranium dissolution rate slowly decreased during the test. Potential reasons for the decrease include a reduction in peroxide concentration after the first day, reduction of the free carbonate available to complex the oxidized uranium, and possible changes to the surface of the uranium cubes. The overall dissolution rate was similar for all three flasks, so the disturbance caused by cleaning, drying, and weighing the uranium cubes during the sampling activities was minimal. The pH of the solutions increased very slightly during the tests. It appears that gas leaks prevented most of the gas that was generated from being collected. A total of 1,223 mmoles of hydrogen peroxide was added to each of the flasks, including what was in the original solution. If all of this peroxide was converted to oxygen gas, the total gas volume would be almost 15 L at STP. About 2 g (8.5 mmoles) of uranium was dissolved from each cube, which would require 25 mmoles of hydrogen peroxide, so the peroxide used in oxidizing the uranium is a small fraction of what was added. A small amount of peroxide could also be complexed with the soluble uranium.

Table II. Results of 7-day dissolution tests

Day	pH	Peroxide concentration (M)	Cumulative gas volume (mL)	Uranium dissolution rate (a)	
				(mg/hour)	(mm/hour)
Test 1					
0	8.8	2.13	0		
1	8.9	0.05	700	24.7	0.0058
2	8.9	0.20	1825	15.3	0.0039
3	8.9	0.18	2400	11.7	0.0031
6	8.9	0.25	2400	9.0	0.0026
7	8.9	0.20	2500	5.3	0.0017
			Overall average	12.0	0.0032
Test 2					
0	8.8	2.13	0		
3	8.9	0.05	50	18.7	0.0069
7	8.9	0.13	150	8.1	0.0025
			Overall average	12.7	0.0039
Test 3					
0	8.8	2.13	0		
2	--	--	2600		
3	--	--	4100		
6	--	--	7700		
7	8.9	0.29	9450	12.7	0.0039

- a. The dissolution rate is that calculated for the period since the previous sample and accounts for the reduction in surface area.

RESULTS AND DISCUSSION FROM PHASE II TESTS

Phase II tests were intended to confirm the reaction stoichiometry and kinetics with simulated K-Basin sludge provided by PNNL. For this purpose, 24.8 g of the concentrated simulated slurry obtained from PNNL was diluted with de-ionized water to provide a total starting volume of 65 mL. Of the 24.8 g, 2.8 g were ferric hydroxide oxide, which provides a concentration consistent with that used in Phase I. The concentrated simulated slurry contains 96.4 g of dry solids in a total mass of 222.3 g so that the solids concentration in the starting slurry was 16.5 g/mL. The slurry volume increased during the tests from the continuous addition of 50% hydrogen peroxide solution. A single uranium metal cube was added to each test.

The results from tests 1 through 3 are provided in Table III. The slurries were dark brown initially but turned bright red after the first hour of hydrogen peroxide addition. A ~3-cm layer of foam was observed on the surface of the reaction slurry in test 3 and ~0.5-cm layer in test 2. The oxidation, by hydrogen peroxide, of the organic ion-exchange resin in the simulated sludge may be the cause of the foam. Oxidation of organic ion exchange resin gives rise to long-chain sulfonates, which are surface active and which may stabilize the foam. The reason for the foam only significantly occurring in test 3 is unknown.

Table III. Results from Tests 1 through 3 of Phase II

Day	pH	[H ₂ O ₂] (M)	Cumulative gas volume (mL)	Uranium dissolution rate (a)	
				(mg/hour)	(mm/hour)
Test 1 (0.5 mL/hour H ₂ O ₂ addition, 2M CO ₃ , 10°C) at end of day...					
1	8.4	0.05	750	4.3	0.0009
1+3.5 hours (b)	9.2		3875	50.1	0.0110
2	9.2	0.16	5075	7.1	0.0015
5	9.1	0.19	5075	4.9	0.0011
6	9.1	0.23	5125	8.0	0.0017
7	9.1	0.20	5125	7.1	0.0018
8	9.1	0.11	5175	5.8	0.0013
			Overall average	6.1	0.0013 (c)
Test 2 (0.5 mL/hour H ₂ O ₂ addition, 4M CO ₃ , 10°C) at end of day ...					
1	8.05	0.00 (d)	200	0.0	0.0
1+3.5 hours (b)	9.3		5300	27.4	0.0060
2	9.2	0.05	6500	9.9	0.0021
5	9.2	0.09	6500	11.6	0.0025
6	9.2	0.10	6800	9.6	0.0021
7	9.2	0.10	6800	7.9	0.0017
8	9.2	0.09	6850	6.3	0.0014
			Overall average	9.8	0.0021 (c)
Test 3 (0.5 mL/hour H ₂ O ₂ addition, 4M CO ₃ , 10°C) at end of day...					
1+3.5 hours (b)		0	5400	8.1	0.0018 (e)
8	9.1	0.07	5700		0.0016

- Rate over the period between sampling events.
- Rate of peroxide addition inadvertently set to 0.5 mL/minute upon restarting after Day 1 sample event. Reset to 0.5 mL/hour after noticing mistake, stopping tests and sampling 3.5 hours later.
- Average over the period from Day 1+3.5 hours to completion.
- Peroxide addition line was ruptured and leaking during Day 1.
- Average for 27.5 hours, since measurement was not made after 24 hours.

These results showed that the bicarbonate concentration has a significant effect on the dissolution rate since doubling the initial bicarbonate concentration led to an approximately 50% increase in the overall dissolution rate.

Samples of the off-gas were collected when sampling the reaction slurry, and analyzed. As shown in Table IV, very little hydrogen or ammonia was detected in the off-gas samples. The relatively high concentration of oxygen arises from the decomposition of hydrogen peroxide. Oxidation of the ion exchange resin appears to be confirmed by the relatively high concentration of carbon dioxide.

Table IV. Results from analysis of gas samples taken from tests 1 through 3 of Phase II

Analyte	Concentration (volume %)		
	Test 1, Day 1	Test 2, Day 2	Test 3, Day 5
Ammonia	<0.1	<0.1	<0.1
Argon	0.11	0.38	0.19
Carbon dioxide	11.20	0.35	0.55
Carbon monoxide	0.01	0.003	<0.01
Hydrogen	0.004	0.0007	<0.01
Nitrogen	9.50	29.78	14.13
Oxygen	79.03	69.30	85.12
Total	99.85	99.81	99.99

Given the observed effect of bicarbonate concentration on the uranium dissolution rate, dry ammonium bicarbonate was added at each sampling event of further tests 4 through 6 to account for the dilution arising from continuously adding concentrated hydrogen peroxide. In these tests from the third to the tenth day, test 6 had ~1 cm of foam on top of the slurry, test 5 had ~0.5 cm of foam, and test 4 produced only a few bubbles. All of the slurries foamed temporarily when the solid ammonium bicarbonate was added to the flasks, which may indicate the conversion of some of the bicarbonate to carbon dioxide gas. The results from tests 4 through 6 are provided in Table V.

A layer of adhering ferric oxide hydroxide on the cubes in tests 5 and 6 was observed but this was absent from the cube in test 4 (Fig. 2). The adhering layers may be shielding the uranium metal from the reagents leading to the lower reaction rates observed for tests 5 and 6. However, previous work by Peper et al. [2] has shown the dissolution rate of uranium dioxide in a solution of hydrogen peroxide and ammonium carbonate decreases with increasing concentration of the latter. These authors speculate that this is due to either the higher ionic strength of the solution or due to a greater peroxide decomposition rate caused by the higher concentration of ammonium carbonate. The latter would be consistent with the lower concentration of peroxide measured in the samples from tests 5 and 6.

The results of these tests with fully simulated sludge also show that any relative increase in uranium conversion rate arising from the reduced peroxide decomposition rate achieved by reducing the temperature is outweighed by its reduction arising from the lower temperature. This is apparently in contrast to the result from the Phase I tests that used only ferric oxide hydroxide as sludge.

Table V. Results from tests 4 through 6 of Phase II

Day	pH	[H ₂ O ₂] (M)	Gas volume (mL)	Uranium dissolution rate (a)	
				(mg/hour)	(mm/hour)
Test 4 (7.4 mL/hour first hour then 0.5 mL/hour H ₂ O ₂ addition, 2M HCO ₃ with periodic addition, 25°C) at end of day...					
0	7.6	0	0		
1 hour		0.09	1100		
1	8.7	0.12	400	16.2	0.0037
2	8.6	0.13	750	22.8	0.0056
3	8.6	0.21	950	22.1	0.0059
6	8.8	0.15	200	16.5	0.0054
7	8.6	0.08	700	14.1	0.0056
8	8.6	0.11	750	11.6	0.0052
9	8.7	0.11	700	8.9	0.0044
10	8.7	0.10	600	8.9	0.0052
			Average dissolution	15.4	0.0052
Test 5 (7.4 mL/hour first hour then 0.5 mL/hour H ₂ O ₂ addition, 4M HCO ₃ with periodic addition, 25°C) at end of day...					
0	7.6				
1 hour		0.02	1450		
1	8.6	0.02	150	12.2	0.0027
2	8.6	<0.01	700	16.2	0.0038
3	8.7	<0.01	700	13.0	0.0033
6	8.8	0.03	700	4.9	0.0013
7	8.6	<0.01	500	0.5	0.0001
8	8.6	<0.01	600	0.1	<0.0001
9	8.7	0.01	50	2.1	0.0006
10	8.7	<0.01	300	1.4	0.0004
			Overall average	6.0	0.0015
Test 6 (7.4 mL/hour first hour then 0.5 mL/hour H ₂ O ₂ addition, 4M HCO ₃ with periodic addition, 10°C) at end of day...					
0	7.7				
1 hour		0.05	1750		
1	8.5	0.03	1100	5.4	0.0012
2	8.5	<0.01	2000	7.0	0.0016
3	8.6	0.03	1100	0.8	0.0002
6	8.7	<0.01	1300	2.1	0.0002
7	8.6	<0.01	100	2.1	0.0002
8	8.6	<0.01	800	0.1	<0.0001
9	8.6	<0.01	1100	0	0
10	8.7	<0.01	1000	0	0
			Overall average	1.5	0.0003

- a. Rate over the period between sampling events.

The product solutions' yellow color (Fig. 2) indicates the presence of the uranyl tricarbonate ion, $\text{UO}_2(\text{CO}_3)_3^{4-}$ and the deeper color of test 4 is indicative of the higher uranium concentration. Fig. 2 also illustrates the uranium cubes and the significantly smaller size of the cube from test 4. Fig. 3 shows the pitted and rough surface of the uranium cube from test 4 in a photomicrograph. Foaming was again observed, mainly in test 6 with smaller amounts in test 5.

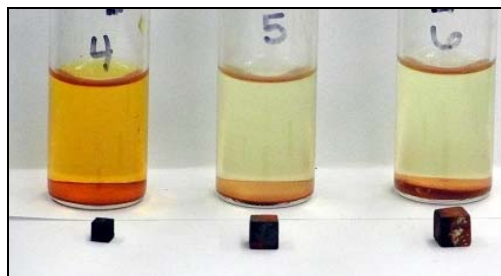


Fig. 2. Reaction product solutions and uranium cubes from tests (left to right) 4, 5 and 6

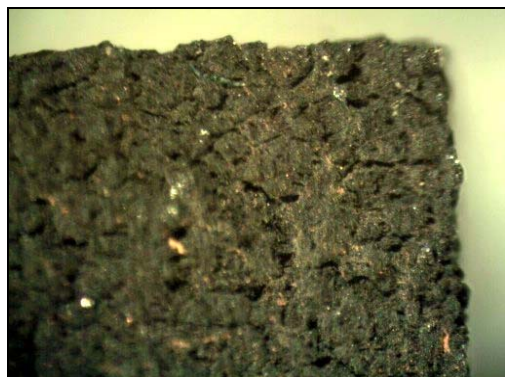


Fig. 3. Photomicrograph of uranium cube from test 4 at 40X magnification

PROCESS CONCEPT DESCRIPTION

The results of the tests described above were used to develop a preliminary plant concept for treating three K Basin sludge types for the purpose of engineering evaluation. For KE and KW Basin sludge, the linear rate calculated from Phase II / test 4 was used to project a time of 25 days to complete conversion of the uranium metal in a single STSC assuming a shrinking core model. In addition, we assumed the ¼-inch uranium cube used in the tests was representative of the particles in the KE and KW Basin sludge. The latter is a conservative assumption because the sludge had been pumped through a screen with ¼-inch openings so that the uranium particles are no larger than ¼-inch. In contrast, the Settler sludge contains particles no larger than 600 microns. In this case, we calculated the time to complete conversion of the uranium in a single STSC as 1.9 days though 4 days was assumed for conservatism.

The rate of decomposition of hydrogen peroxide in this system means that it must be continuously added to maintain its concentration. Ammonium bicarbonate is also continuously added to maintain its concentration at approximately 1M. The volume added to the sludge from the continuous addition of concentrated hydrogen peroxide and ammonium bicarbonate requires that the reaction mixture must be periodically volume-reduced by evaporation. We envision the condensate arising from this operation is transported to Hanford's Effluent Treatment Facility for treatment and disposal.

The preliminary plant concept includes a single jacketed process vessel in which the reaction and volume-reduction operations are sequentially conducted. Steam is used to heat the contents for evaporation and chilled water to subsequently cool them ready for further reaction or stabilization. Taking account of the volume reduction operations, the total treatment time for each KW and KE Basin sludge batch is 50 days and that for each Settler sludge batch is 14.5 days.

Stabilization of the treated sludge in a grout matrix is envisioned in a fully automated skid-mounted unit, EnergySolutions' MOBILE Solidification System (MOSS) illustrated in Fig. 4. The MOSS is a conversion of EnergySolutions' MOSS 200 system that is operated in Europe. It is anticipated that this unit can process five to eight 55-gallon drums per 8-hour shift, as described by Gesser et al [6].

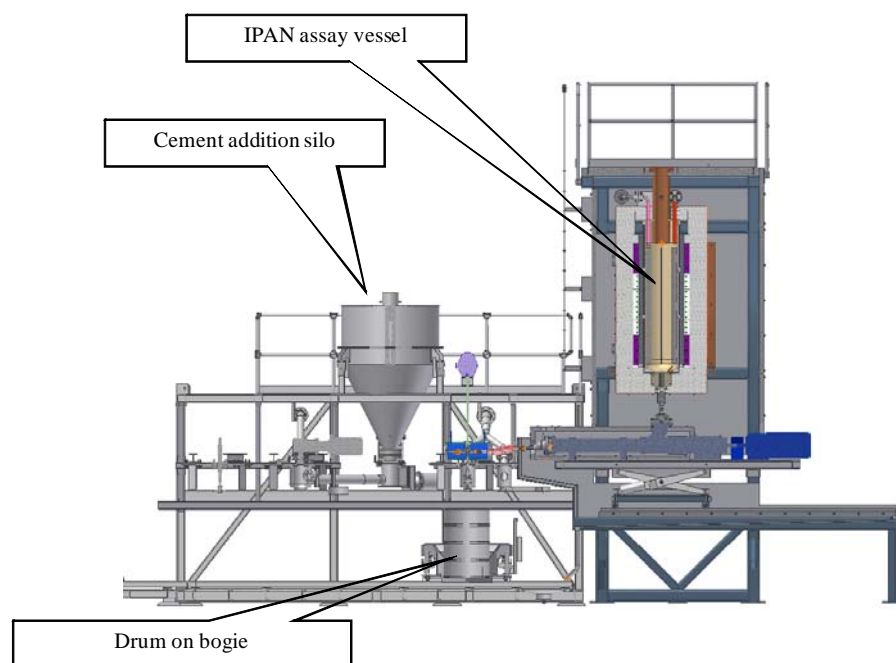


Fig. 4. Major Elements of the MOSS

For K Basin sludge treatment, MOSS will be supplied with waste which has been assayed through the Imaging Passive Active Neutron (IPAN) system to determine the appropriate amount of waste to dose into the drum. No tank sampling is conducted in the MOSS and instead the IPAN system measures the plutonium-239 fissile gram equivalents (FGE) and cesium activity of waste including total measurement uncertainty. This information is then used to determine the volume of sludge to dose into each 55-gallon drum. Additionally, the information could be used as the waste characterization data for WIPP if the IPAN approach becomes acceptable. The IPAN information would replace that obtained from using a dose to curie based characterization approach currently accepted at WIPP.

The time required to complete stabilization and packaging of KW and KE Basin sludge is expected to be generally within the window required for treatment of 50 days. This is not true of Settler sludge, which requires 28 days to stabilize and package assuming 40 FGE/drum limit. Therefore, the total time required to process the contents of all 24 batches of sludge (11 KE, 5 KW and 8 Settler) is estimated at three years and seven months assuming 70% total operating efficiency and a single process line. A summary of the projected process operations is presented in Table VI assuming a 40 FGE/drum limit.

Table VI. Summary of projected process operations

Parameter	Sludge type		
	KE	KW	Settler
Number of batches (STSCs)	11	5	8
Number of days to complete conversion	50	50	14.5
Equivalent volume of settled sludge (20 vol% solids) per drum (L)	71.2	33.3	8.2
Total number of drums	323	199	991
Number of days to complete drumming per batch	4	6	18

CONCLUSIONS

The potential feasibility of treating the K Basin sludge by carbonate conversion and subsequently assaying, stabilizing and drumming it using proven *EnergySolutions'* equipment was demonstrated. Important elements of the proposed preliminary plant concept include:

- A process vessel in which the sludge is reacted with peroxide and bicarbonate to form uranyl carbonate. Volume reduction by evaporation of excess water is also undertaken in this vessel to optimize the water content of the sludge product for subsequent assay and stabilization.
 - The reagents selected for reaction are 50% hydrogen peroxide and 12M ammonium bicarbonate. Steam, process water and chilled process water are the major utilities required.
- *EnergySolutions'* Imaging Passive Active Neutron (IPAN) system is proposed to measure the plutonium-239 fissile gram equivalent (FGE) and cesium activity of sludge, including TMU, prior to dosing into 55-gallon drums.
- *EnergySolutions'* MOBILE Solidification System (MOSS) is a conversion of *EnergySolutions'* MOSS 200 system that is operated in Europe and is used to stabilize the sludge in grout in 55-gallon drums.

On the basis of the plant concept described in this report, the KE and KW Container and Settler sludge contained in 24 STSCs could possibly be treated, stabilized and drummed in approximately 4 years given certain operating assumptions.

The tests described conducted for this project demonstrated complex inter-relationships between peroxide and bicarbonate concentrations, temperature and pH. Maintaining the peroxide and bicarbonate concentrations was found key to maintaining the uranium metal conversion rate. Off-gas samples taken from the tests were analyzed and found enriched in oxygen, from decomposition of the hydrogen peroxide. Neither hydrogen nor ammonia gas could typically be detected.

While the tests conducted to date have identified a candidate set of reaction conditions, this set may not be optimal and further tests to refine and optimize the process are recommended. Nonetheless, the conditions identified in the tests described in this paper giving rise to the highest uranium metal conversion rate were adopted for the engineering evaluation.

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