Uranium Metal Oxidation, Grinding and Excapsulation in BoroBond™: TRU Waste Management - 11223

Kevin S. Cook*, Larry Addington and Beth Utley

Boron Products, LLC. A Ceradyne Company
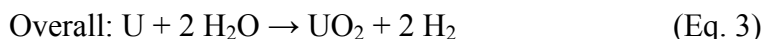
3250 South 614 Road, Quapaw, OK 74363

ABSTRACT

Prior to removal and temporary storage, the Hanford K-East and K-West Basins had been used to store irradiated fuel. In addition to the nonradioactive majority the sludge contains fission and activation products as well as uranium metal up to 6350 μm in diameter. The presence of uranium leads to the production of hydrogen through a hydrolysis reaction. To satisfy WIPP-WAC and RH TRAMPAC regulations hydrogen generation must be significantly slowed and/or eliminated from the final waste forms. The testing performed investigated three different possibilities to aid in the processing of the K Basin sludge streams. Encapsulation of uranium metal in BoroBond™ ($MgKPO_4 \cdot 6H_2O$ matrix) resulted in a twofold decrease in the hydrogen generation rate at 60 °C compared to a uranium metal in water standard. Pressure increase data showed 0.116 torr/h rate for a basic BoroBond™ formulation containing uranium metal compared to 0.240 torr/h for the standard. Ceramic forms containing a stoichiometric excess of water or incrased uranium loading led to increased hydrogen generation. Presence of K Basin physical simulant materials $FeO(OH)$ and $Al(OH)_3$ had no effect on hydrogen generation rates. Pre-oxidation of uranium metal using Fenton's Reagent was highly successful. A ¼" cube uranium coupon was fully oxidized at room temperature in under 4 days using a system of $FeSO_4 \cdot 7H_2O$ (catalyst), HCl, and hydrogen peroxide. This compares to 175 days in 90 °C water. The oxidative corrosion of uranium metal is shown to increase with increases in hydrogen peroxide addition rate and catalyst concentration as well as a decrease in pH. Grinding Densalloy SD170, an irradiated uranium metal surrogate, was also successful with a Hockmeyer HSD Immersion Micromill. All densalloy that was appropriately sized for the Micromill and grinding media was quickly reduced to < 90 μm. This would decrease oxidation time of the largest uranium metal pieces to ~2 days in 90 ° C water. Wear rates of the mill were acceptable.

INTRODUCTION

The Hanford K-East and K-West Basins had been used to store irradiated fuel. Since the closure of the fuel reprocessing facility on the Hanford site, the fuel has remained in K-Basin and with incorporation of debris, silt, sand and other materials has resulted in the formation of sludge at the bottom of the basins. In addition to the nonradioactive majority (sand, silt, dirt), the sludge contains fission and activation products as well as uranium metal [1].

The presence of uranium metal (up to 0.052 g cm^{-3}) leads to the production of hydrogen through a water oxidation pathway according to Eq. 1-3:

$$U + 1.5\ H_2 \rightarrow UH_3 \qquad \text{(Eq. 1)}$$

$$UH_3 + 2\ H_2O \rightarrow UO_2 + 3.5\ H_2 \qquad \text{(Eq. 2)}$$

$$\text{Overall: } U + 2\ H_2O \rightarrow UO_2 + 2\ H_2 \qquad \text{(Eq. 3)}$$

As hydrogen is flammable, its production is a concern during storage, processing, immobilization, shipment and disposal of K Basin Sludge. To satisfy WIPP-WAC and DOT regulations hydrogen generation must be significantly slowed and/or eliminated from the final waste forms. To mitigate hydrogen generation from K Basin sludge, the waste may be encapsulated "as is" in materials (grouts, cements, ceramics, etc.) that prevent the reaction expressed in Eq. 3. The other option is that the K Basin sludge may be oxidized prior to immobilization eliminating the possibility of the hydrogen generation reaction occurring.
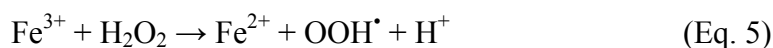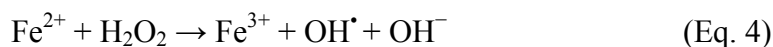
In order to find application for direct immobilization of K Basin sludge, the hydrogen generation must be reduced by at least two orders of magnitude compared to the reaction of uranium metal with anoxic water at 60 °C [2, 3]. Delegard and co-workers have summarized past uranium oxidation by water and investigated hydrogen mitigation in grouts [2, 4, 5]. The four Portland cement and two magnesium ammonium phosphate formulations decreased hydrogen generation by only a factor of two to three compared to the reaction of uranium metal in anoxic water. Though liquid water was not present, the water vapor produced at temperature was sufficient to result in uranium metal corrosion. It must be noted that in all but one sample, the grout was water starved. There was not enough water added to form the necessary $MgNH_4PO_4 \cdot 6H_2O$ matrix for the magnesium phosphate formulations. Furthermore, magnesium potassium ceramic, $MgKPO_4 \cdot 6H_2O$ (BoroBond™) was not investigated.

Alternative methods for dealing with K Basin sludge include pre-oxidation of the uranium metal prior to immobilization of the waste stream. According to Delegard and Schimdt, a ¼" diameter sphere of uranium metal is expected to take 175 days at 90 °C [4]. While this oxidation process is ultimately effective in oxidizing uranium metal for subsequent disposal it would be extremely desirable to determine an oxidation process that:

- Has a reduced reaction time for complete oxidation of uranium metal
- Limits off gassing of flammable gases such as hydrogen
- Uses common reagents in a predictable reaction

A study by Gates-Anderson *et. al.* at Lawrence Livermore National Laboratory investigated several other possible oxidation systems [6]. While some systems were investigated and found to oxidize uranium at a significant rate, many of the systems involve high concentrations of corrosive acids/bases as well as other reagents, resulting in varying degrees of off-gassing. Some reactions are expected to complicate sludge processing through production of byproducts such as chlorine gas, oxychloride and NO_x gases.

Absent from the studies is a powerful oxidation system comprised of a mixture of acid, hydrogen peroxide and $Fe^{II/III}$ catalyst. The mixture is generally known as Fenton's reagent and is used extensively in municipal waste treatement. The Fenton system is based on the catalytic reaction of $Fe^{II/III}$ with hydrogen peroxide (see equations 4 and 5).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^\bullet + OH^- \qquad \text{(Eq. 4)}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + OOH^\bullet + H^+ \qquad \text{(Eq. 5)}$$

In the presence of Fe^{II}, a hydroxyl radical and hydroxyl anion is produced along with Fe^{III}. If the reaction proceeds starting with Fe^{III}, a proton, a peroxide radical and Fe^{II} are produced. The highly reactive radicals are powerful oxidizing agents.

Water oxidation of K-Basin sludge may be accelerated by reducing the size of the uranium metal. A < 90 μm sized uranium metal particle is expected to oxidize in 2-3 days at 90 °C. Measurements show that the irradiated uranium metal has a hardness rating about double that of non-irradiated uranium; 30 ± 8 compared to ~15 on the Rockwell "C" Scale [1]. Furthermore, though the ductility of uranium has a significant decrease after irradiation, the uranium metal in K Basin sludge remains highly resistant to fracture. These unique properties have made past grinding procedures, such as mortar and pestle techniques, unsuccessful in significantly breaking down uranium metal [1].

This paper documents the results of the research projects completed for the K Basin sludge. Research includes:

- encapsulation of uranium metal in BoroBond™
- oxidation of uranium metal in an aqueous Fenton's Reagent system
- attrition milling of uranium surrogate

EXPERIMENTAL

Encapsulation of Uranium Metal in BoroBond™

Preparation of BoroBond™ Samples

An example is provided: MgO (36.921 g) and Fly Ash (272.813 g) were combined in a beaker and thoroughly blended. To a plastic beaker, $KH_2PO_4 \cdot H_2O$ (113.317 g) and water (75.020 g, T = 25.5 °C) were added and the thin white slurry stirred for 10 minutes. The pre-blended dry ingredients were added to the KH_2PO_4 slurry (T = 22.7 °C). The mixture was continually stirred until a thick consistency, that would not allow uranium metal to sink, was achieved (T = 31.7 °C). The BoroBond was cast in three layers into a 300 mL polypropylene mold with lid. At each interface (40 % and 70 % filled), half of the uranium (1.9245 g total) was dispersed. The mold was tightly closed, a Tempilabel attached and placed under a loose paper towel tent for 48 hours. After 48 hours, the Tempilabel was checked (54 °C) and paper towel tent removed.

Alternative procedures did not seem to affect the integrity of the cast. This included casting the material while the viscosity was still low and stirring was continued inside the mold. When the viscosity increased sufficiently, the uranium metal was added piece by piece and pushed into the ceramic form. For sample 1a, the mixture was cast early and the uranium was added before the appropriate viscosity (necessary to suspend the uranium) was achieved. The mixture was vigorously stirred in the mold and when the viscosity was sufficient to suspend uranium the mold was inverted several times. In all procedures, uranium metal was fully surrounded with BoroBond™.

Following a minimum 48 hour cure in the molds, the ceramic forms were removed by cutting away the mold. Any minor amount of salt left behind from the bleed water during the cure was brushed away. In addition to the height, the diameter of the ceramic form was measured at three places (top, middle and bottom) using calipers. The temperature on the Tempilabel was also recorded and ranged from 54 °C to 65 °C, indicating that the exothermic acid-base reaction proceeded as expected. The molds were placed in plastic bags and sealed from the atmosphere until transfer to the pressure vessels.

A water standard containing uranium was prepared by deoxygenating 500 mL of deionized water by bubbling ultra high purity (UHP) helium through the water for 2 hours in an air tight system. Glass beads (2520 beads) were added to a pressure vessel and deoxygenated water (92.8617 g) was added to the vessel. The water just barely covered the upper most glass beads. Uranium metal (1.9805 g) was added to the vessel and the vessel purged according to the procedure below. The composition of the samples are provided in Table I.

Table I. BoroBond™ Sample Compositions

Sample	Description	KH_2PO_4 (g)	Water (g)	MgO (g)	Fly Ash (g)	other (g)	U metal (g)
1a	Baseline 55% bond phase	138.819	91.915	45.319	222.131	0	1.9022
1b	Baseline duplicate	138.835	91.924	45.323	222.117	0	1.9080
2	65% bond phase	163.547	108.235	53.323	173.19	0	1.9010
3	45% bond phase	113.317	75.02	36.921	272.813	0	1.9245
4	55% bond phase 10% excess water	138.804	101.113	45.347	222.149	0	1.8868
5	55% bond phase 9% water shortage	138.81	83.486	45.308	222.148	0	1.8758
6	55% bond phase 17% water shortage	138.822	76.603	45.334	222.138	0	1.9060
7	KH_2PO_4 Pre-stir	138.814	91.949	45.343	222.135	0	1.8890
8	contains FeO(OH) and $Al(OH)_3$	138.822	91.927	45.338	218.099	4.22[a]	1.9067
9	1.8 times uranium loading	138.842	91.904	45.331	222.152	0	3.3580
10	U metal in water	---	92.8617	---	---	---	1.9805
11	No U metal	138.832	91.913	45.319	224	0	0.0000

[a]FeO(OH) = 3.11 g and $Al(OH)_3$ = 1.11 g

Transfer to and Purging of Pressure Vessels

One hundred (100) 5 mm diameter glass beads were added to a 472 mL Parr 316 stainless steel pressure vessel fitted with an Omega OM-CP-PR2000 pressure data logger. The BoroBond™ ceramic form was placed in the pressure vessel on top of the glass beads. The glass beads are present to prevent entrapment of gases under the ceramic form which may cause it to change positions during the experiment. The pressure vessel was sealed under air according to the manufacturer instructions. Each vessel was then purged of air using the following steps:

- The vessel was first evacuated for 30 seconds and backfilled with ~3700 torr (gauge) of UHP Helium
- The vessel was evacuated again for 10 seconds and backfilled with ~3700 torr
- Pressure was slowly released through a mineral oil bubbler until a reading of ~300 torr was observed. This backfill and slow bleed down was repeated another 12 times

- The vessel was backfilled to ~3700 torr one final time and the pressure brought down to a ~750 torr starting pressure

The uranium in water standard was purged in a slightly different manner. As there was no worry of changing reaction conditions through removal of limited water from a waste form, instead of slowly releasing the backfill pressure (~3000 torr gauge) the UHP He was removed through brief evacuation. This was repeated 15 times. The final backfill was to ~740 torr instead of 3000 torr and used as the starting pressure.

Data Collection

After all vessels were sealed, the pressure data loggers were programmed using OM-CP Datalogging Software (version 2.02.5) from Omega Engineering. Each data logger was set to record a pressure data point every 30 minutes. Following 10 days of curing, the pressure vessels were placed into a 60 °C re-circulating silicone oil bath (time = 0). The vessels were submerged up to the seal (about 1 inch above the ceramic form). The temperature of the oil was continuously monitored every 30 minutes using an Easylog temperature data logger from Microdaq.

Oxidation of Uranium Metal Using Fenton's Reagent

Procedure

A typical procedure is provided: $FeO(OH)$ (2.36 g), $Al(OH)_3$ (0.84 g), and $FeSO_4 \cdot 7H_2O$ (0.525 g) were weighed out into separate weigh boats and then transferred into a suitably sized round bottomed flask containing two ports. Deionized water (25 mL) was added to the flask and the contents of the flask were stirred with a teflon coated magnetic stir bar. This ensured the dissolution of $FeSO_4 \cdot 7H_2O$ and other solubles. A syringe pump was fitted with a 60 mL disposable plastic syringe. Using the withdrawal feature of the pump, the syringe was charged with the desired reagent, either H_2O_2 or, in one case, deionized water (50 mL). Following the reagent charge, ~ 1 mL of air was brought into the tubing and syringe to avoid loss of reagent while the reaction was occurring in apparatus. The tubing from the syringe was pushed through a rubber septum that was fitted on the side neck of the round bottomed flask. The pH of the solution was checked using pH paper and adjusted with concentrated HCl, as needed to maintain the pH. Excluding Test 3, all of the remaining tests were adjusted to a pH between 1 and 2. Test 3 was at pH of 4 prior to any pH adjustment and was left as is. A ¼" uranium metal cube was weighed and added to the reaction flask. The remaining neck was equipped with a hose adapter to limit material loss due to splashing and to provide a vent in case of off gassing. Vigorous stirring was commenced prior to peroxide addition. The hydrogen peroxide was added at a rate of ~0.012 mL/min and the time the peroxide addition was started was noted. The ambient temperature was monitored every 5 minutes throughout the peroxide addition using an Easylog temperature data logger from Microdaq.

The uranium coupon masses were checked at several points during the reaction. Stirring was stopped, the uranium coupon removed with forceps, cleaned with deionized water, dried and weighed. Any black scale on the uranium coupon was not actively removed beyond losses due to the drying method. The time was noted during the weight measurement. Also, the pH of the solution in the flask was checked and adjusted as needed. The uranium was returned to the flask and stirring resumed. The reagents for each test are provided in Table II.

Table II. Table of Reagents for Uranium Oxidation By Fenton's Reagent

Reagent	Plan	Test 1	Test 2	Test 3	Test 4	Test 5
FeO(OH)	2.36 g	2.3580 g	2.3557 g	2.3591 g	2.3312 g	2.3591 g
Al(OH)$_3$	0.84 g	0.8444 g	0.8528 g	0.8491 g	0.8557 g	0.8431 g
FeSO$_4$•7H$_2$O	0.525 g	0.5215 g	0.5210 g	0.5347 g	0.5231 g	1.4477 g
Initial H$_2$O	25 mL	25 mL	25 mL	25 mL	25 mL	25 mL
Added H$_2$O$_2$	50 mL	50 mL	---	50 mL	2 x 50 mL	50 mL
Added H$_2$O	50 mL	---	50 mL	---	---	---
Starting pH	pH = 1-2	pH = 1-2	pH = 1-2	pH = 4	pH = 1-2	pH = 1-2
U metal	One ¼" cube	4.8058 g	4.7026 g	4.8006 g	4.7041 g	4.7351 g

Size Reduction of Uranium Metal Surrogate

Milling Equipment

The tests were conducted on the Hockmeyer HSD Immersion MicroMill, using standard grade components. The mill consists of a 2" diameter Basket/Mill Body which contained the milling media (1mm diameter spherical chrome steel media) and a Hub/Peg assembly which rotated at 5,000 RPM resulting in a peg tip speed of ~2100 ft/minute. The Basket/Mill Body was constructed with slots in the periphery and the bottom which were 0.27mm wide and ~5mm long. A propeller located immediately below the Basket/Mill Body was driven by a shaft from above and conducted the slurry through the mill. The Basket/Mill Body was constructed of Nitronic SS and the Hub/Peg Assembly was constructed of heat treated 440c SS.

Milling Procedures

For the milling tests, the tungsten alloy Densalloy SD170 was used as a surrogate for irradiated uranium metal due to its high density (16.85 g/cm^3) approaching that of uranium (19.05 g/cm^3) and its similarity in hardness and toughness [1]. The Densalloy surrogate was prepared in three particle size ranges that approximated the particle size of metallic uranium in the KW sludge. The coarse Densalloy fraction was prepared by sawing wafers (~2.4mm thick) from 7.0 mm rod stock and then breaking the wafers across the diameter into two pieces resulting in a typical weight of 0.66g/piece. The medium Densalloy fraction was prepared in similar fashion from the same 7.0mm rod stock using wafers ~1.5mm thick and breaking them into 4 pieces across diametric chords resulting in a typical weight of 0.19g/piece. The fine Densalloy fraction was prepared by sawing the rod stock with a coarse hacksaw blade. The fine fraction median particle size was found to be 581μm by the Hockmeyer HPAS-2000 particle size analysis (area distribution) and the <90μm (USS No. 170) component was found to be 8.4 wt% by sieve testing. The Densalloy preparation method tended to make "flat" particles, the HPAS-2000 area distribution was deemed to best characterize the >90μm particles.

The Immersion Mill was placed in a 6" diameter SS slurry container which held ~1 liter of slurry when filled to the normal level. The slurry container was constructed with a cooling jacket. During milling process, chilled water (~4 ºC) was recirculated in the jacket to control the temperature of the slurry within the range of 18 to 55 ºC. Size reduction was monitored using a USS No. 170 sieve (90μm opening), the HPAS-2000 optical system (for particles 90μm to 2000μm), and calipers for the larger Densalloy pieces. The mill wear was monitored by caliper measurements and by weight change of the components. The <90μm material was not

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monitored. Two tests were conducted in the 2" Micromill. The media and slurry recipes are given in Table III below.

Table III. Milling Test Slurry Recipes

Test	Media Mass (g)	Coarse Densalloy (g)	Medium Densalloy (g)	Fine Densalloy (g)	Other Simulant (g)	Tap Water (g)
1	190.3	3.32	5.19	90.06	500 [a]	748
2	177.0	1.77	3.10	90.07	200 [b]	748

[a] KW Container Sludge Simulant (<100μm); CeO_2 plus hydrated oxides of Al and Fe
[b] Components of Test 1 simulant plus larger mineral components, GraFoil, zeolite and ion exchange resins

RESULTS AND DISCUSSION

Encapsulation of Uranium Metal in BoroBond™

BoroBond™ waste forms were cast without a set retarder and in all cases, 10-45 minutes after addition of MgO and fly ash the mix became viscous enough to suspend the uranium metal. The specimens were hard to the touch within 2 hours. When the molds were removed there was no free water noted in any of the specimens including water rich sample 4. This indicated the BoroBond™ recipes used are flexible enough for waste streams containing variable amounts of water. No observable uranium metal could be found, so the uranium was fully encapsulated in the ceramic matrix. There was no swelling or contraction of the poured ceramic and no cracking was observed.

An example of the pressure data is shown in Figure 1. In all cases,after the vessels were heated to 60 °C, there was an induction period of about 100 h before hydrogen generation began and a pressure rise was observed. This differs significantly from Delegard and co-workers who noticed a short induction period of 10 h for $MgNH_4PO_4 \cdot 6H_2O$ grouts. In that case, the grouts were cast and brought to temperature before the ceramic could cure and the induction period was likely overcome by the exothermic acid-base reaction that forms the matrix. In the present work, the $MgKPO_4 \cdot 6H_2O$ forms were cured at room temperature for 10 days. The matrix had time to properly crystallize and gas generation results are better representative of the performance of the material. Gas chromatographic (GC) analysis of the headspace during the hydrogen generation tests indicated that not all of the air was purged from the vessels. Nitrogen concentrations ranged from 5000 ppm to 11,000 ppm (1.1 %) and the highest starting oxygen concentrations were, therefore, ~2500 ppm. This oxygen may have been released from the waste form following purge of the vessel. Given the forms were then sealed from the atmosphere any remaining oxygen would be quickly scavenged.

Once the pressure began to increase, a steady linear rise is noted. There were undulations noted in the pressure readings throughout the day. This is likely due to temperature variations of the ambient air affecting the pressure readings as the top of the vessel and pressure gauge were not submerged in the oil bath. The ceramic form, however, was situated more than 2 inches below the surface of the oil bath so the form temperature was expected to be the oil bath temperature given the tight fit of the form within the vessel (less than 0.1 inch difference in diameter). In

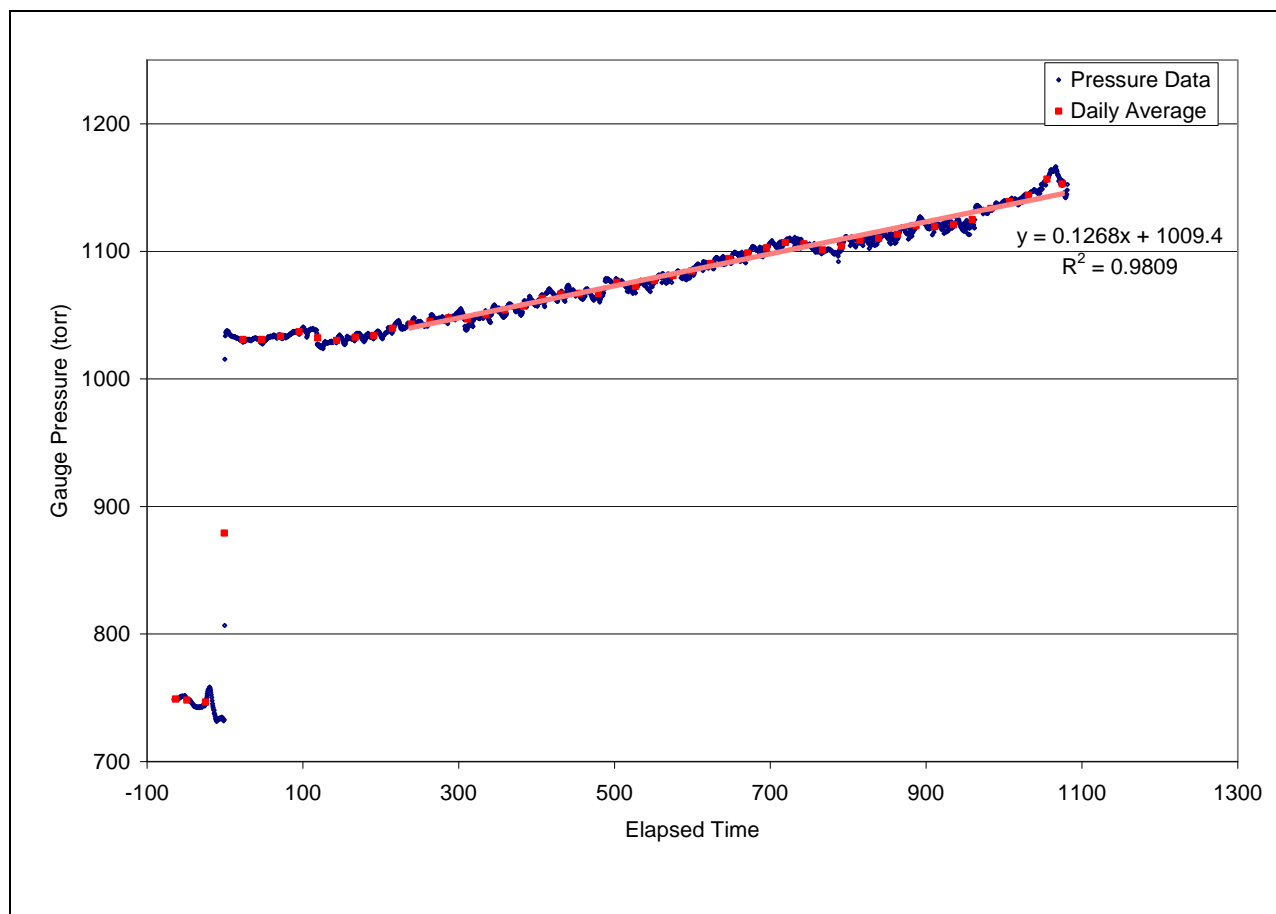order to more easily visualize the trend, the daily averages were calculated and are shown in Figure 1.

Fig. 1. Example Pressure vs Time Data (Sample 1b shown)

Pressure increase data is summarized in Table IV, and pressure increase rates are normalized against a standard containing uranium metal and metal at 60 °C. This standard is used as the baseline comparison for reduction of hydrogen generation owing to the BoroBond™ matrix. Slopes were determined from ~200 hours on in order to ensure that the induction period had passed. Similar to the PNNL work, the BoroBond™ $MgKPO_4 \cdot 6H_2O$ matrix only decrease hydrogen generation rates by a factor of ~2 compared to the water standard [2, 4, 5]. In general, the data follows the expected trends. Sample 2 (with increased bond phase (i.e. $MgKPO_4 \cdot 6H_2O$)) and Sample 4 (with 10% more water than needed to satisfy the bond phase stoichiometry) have higher rates of hydrogen generation. However, the water starved samples 5 and 6 do not show marked decreases in hydrogen generation compared to the baseline samples. As such, the PNNL results may not be affected be the significant shortage of water used in the PNNL studies. Sample 9 shows a pressure increase about double that of the baseline samples 1a and 1b. This was expected due to the fact that Sample 9 has nearly double the uranium metal loading. The presence of K Basin sludge consituents $FeO(OH)$ and $Al(OH)_3$ have little effect on the performance of the BoroBond™ material.

Table IV. Pressure Rise Data for Uranium Encapsulation in BoroBond™

Sample	Description	Slope at ~1100 h (torr/h)	Relative to Sample 10
1a	Baseline 55% bond phase	0.1283	0.53
1b	Baseline duplicate	0.1312	0.55
2	65% bond phase	0.2034	0.85
3	45% bond phase	0.1396	0.58
4	55% bond phase, 10% excess water	0.1856	0.77
5	55% bond phase, 9% water shortage	0.1331	0.55
6	55% bond phase, 17% water shortage	0.1164	0.48
7	KH_2PO_4 Pre-stir[a]	0.1574	0.65
8	contains $FeO(OH)$ and $Al(OH)_3$	0.1273	0.53
9	1.8 times uranium loading	0.2668	1.11
10	U metal in water	0.2404	1.00
11	No U metal	---	---

[a]uranium metal stirred in KH_2PO_4 slurry for 20 hours

Oxidation of Uranium Metal Using Fenton's Reagent

Prior to investigating the Fenton's reagent system in a more rigorous manner, the best acid was chosen based on the results of a quick screen. The uranium mass loss was measured in reactions identical except for the choice in acid used to reduce the pH to between 1 to 2: either HCl, H_3PO_4, H_2SO_4 or HNO_3. The results from the screening tests clearly showed that the use of HCl resulted in the most favorable system.

Following acid selection, the influence of Fe^{II} concentration, rate of peroxide addition, and pH were explored. All experiments were run simultaneously to negate temperature effects that may be caused by the fluctuation of the ambient air temperature. While gaseous by products were not monitored, no significant off-gassing was observed and at the addition rates used there were no thermal excursions. The mass loss of the uranium coupons is shown in Figure 2. The data clearly shows that Fenton's Reagent is extremely effective in oxidizing uranium metal even at room temperature.

For all systems at a pH of 1 to 2, there was a rapid mass loss of the uranium coupon during the peroxide addition, except in the case where water was added in place of uranium (Test 2). This experiment showed a minor decrease in the uranium mass and it is likely due to the corrosion of the uranium coupon from the acid. The baseline test (Test 1) shows a leveling off of the oxidation rate soon after peroxide addition was completed. This mirrored Test 2 and demonstrated that the oxidation system was dependent on the presence of hydrogen peroxide. Furthermore, the addition rate of peroxide has not resulted in a large buildup of hydrogen peroxide in the solution.

The oxidation rate of uranium metal was further influenced by Fe^{II} concentration. At ~90 h, the uranium coupon was fully oxidized in Test 5 which contained three times the catalyst concentration as Test 1. This compares to ~32 % of the coupon remaining for the baseline test (Test 1). Similarly, doubling the hydrogen peroxide addition rate resulted in full oxidation of the uranium coupon before peroxide addition was complete (Test 4). Note that in addition to

doubling the addition rate, a total 100 mL of hydrogen peroxide was added in Test 4 while 50 mL was added in Test 1.
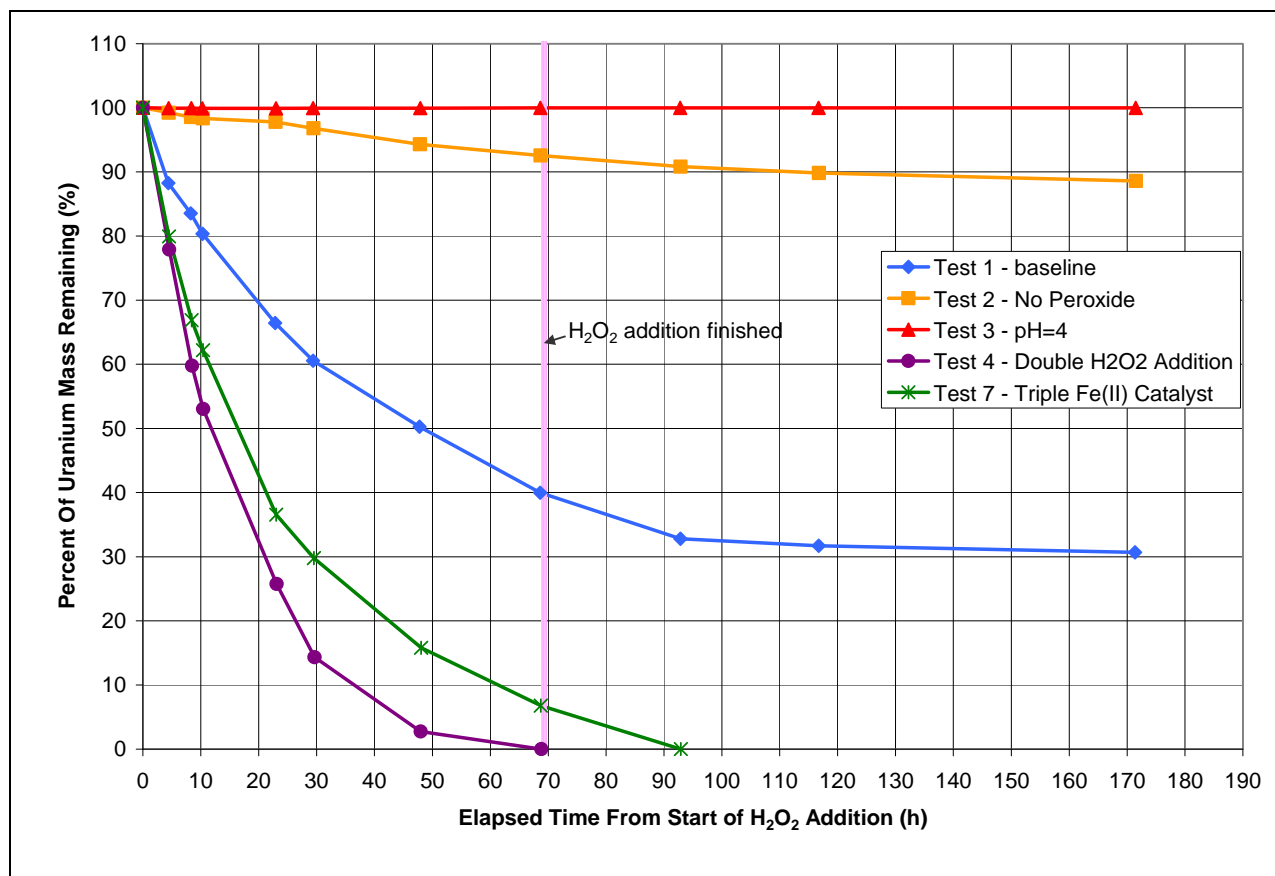

Fig. 2. Percentage of Uranium Mass Loss vs Time

The effect of reducing the pH from ~4 down to ~1 is startling. Test 3 showed no uranium mass loss. Visually, the uranium coupon remained somewhat shiny with an orange patina in some areas. The coupons for the other tests were covered in coatings of loose, black UO_2. This patina was likely caused by the K Basin simulant material, FeO(OH), present in the reaction solutions. While the decrease in oxidation rate at higher pH is significant, it is not known at this time whether this decrease is due to the pH or the lack of chloride ion. No acid was required to reach a pH of 4 so no HCl was added. Exploration of this potential chloride factor is ongoing.

Size Reduction of Uranium Metal Surrogate

Milling Tests 1 and 2 both show the Micromill with 1mm diameter media to be highly effective in reducing the particle size of the fine fraction of Densalloy – which was initially 581μm median particle size with only 7.6 wt% <90μm (Figure 3 and Table V). The median particle size of the fine fraction of Densalloy was slightly greater than ½ of the media diameter. The fine fraction of the Densalloy has been ground to the <90μm objective in less than 4 hours.
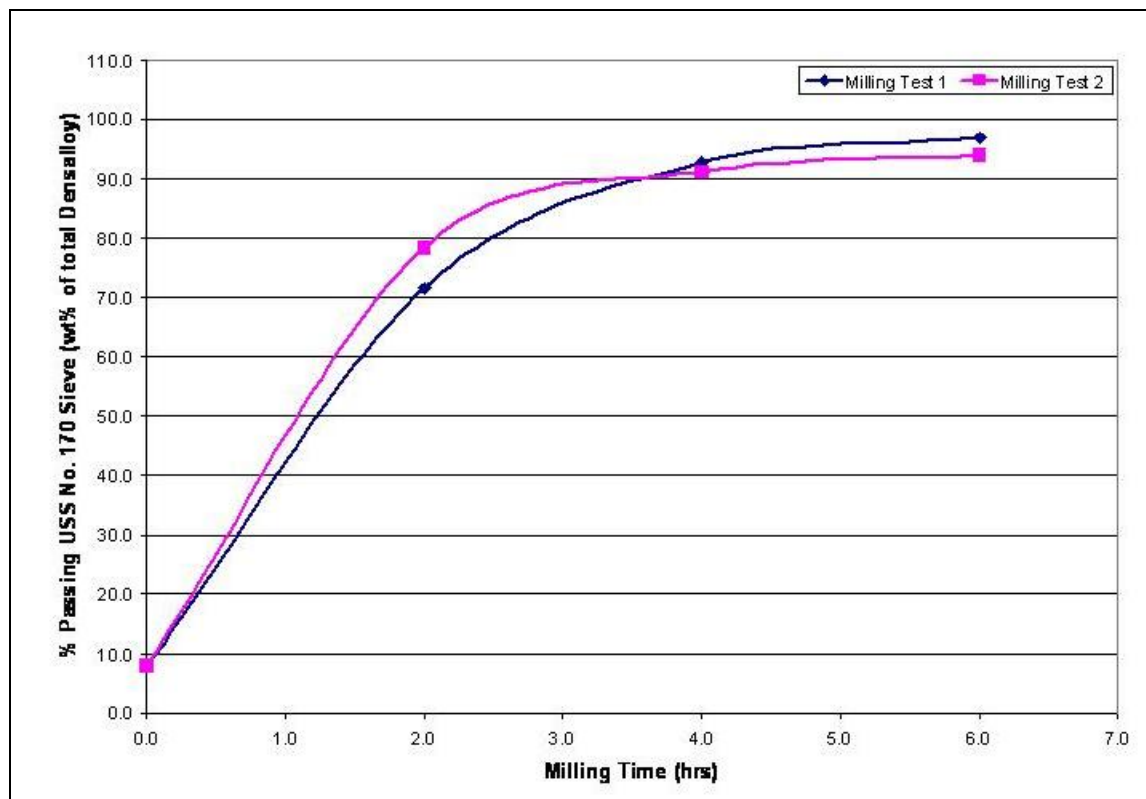
Fig. 3. Percent Densalloy <90 μm During Milling

Table V. Densalloy SD170 Milling Results

Test	Milling Time (h)	Fine Densalloy (g)	Medium Densalloy (g)	Coarse Densalloy (g)	Total Densalloy (g)	Mass of Densalloy > 90 μm (g)	Densalloy < 90 μm	
							(g)	(wt %)
1	0.0	90.06	5.19	3.32	98.57	91.04	7.53	7.6
	2.0	---	2.17	2.74	98.57	23.00	70.66	71.7
	4.0	---	0.70	2.09	98.57	4.40	91.38	92.7
	6.0	---	0.16	1.77	98.57	1.10	95.54	96.9
2	0.0	90.07	3.10	1.77	94.94	87.41	7.53	7.9
	2.0	---	2.67	1.66	94.94	16.15	74.46	78.4
	4.0	---	1.72	1.57	94.94	5.08	86.57	91.2
	6.0	---	1.54	1.49	94.94	2.80	89.11	93.9

The medium fraction of Densalloy was also substantially ground as witnessed by the particle count reduction for the medium fraction. The coarse fraction of Densalloy continued to wear as evidenced by rounded edges, however, these pieces were milled at a slower rate. The clearances within the Micromill limit the media size to no more than 1.2mm. Tracking the large Densalloy pieces through milling allowed observation that milling efficiency is strongly effected by the ratio of input particle size to media size and that efficiency was much better for the fine (581μm median particle size) fraction of the Densalloy. The Micromill constraint with regard to media size limits the capability of the mill to attack the coarse size fraction of Densalloy particles. In

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spite of this limitation, the proportion of <90µm Densalloy particles increased to 96.9 and 93.9 wt% respectively for Test No. 1 and No. 2 at the end of 6 hrs cumulative milling. The mill effectively grinds Densalloy and proper attention to media size should extend this behavior to larger Densalloy particles.

Simulant used in Test 2 contained quartz-like particles up to ¼" in size. While these were very hard, they were also brittle and were reduced to < 90 µm by the 4 hour interval. As Test 2 progressed, the material retained on the USS No. 170 sieve was found to have a significant population of particles that were highly flattened (or peened) in addition to the more round-edged particles of Densalloy generated in both tests (Figure 4). The likely identity of the peened metal particles in Test 2 is metallic iron that was a constituent of the simulant. The effectiveness of the Micromill in grinding Densalloy in Test 2 may be somewhat understated by the mass-based data in Table V and Figure 3 due to the presence of non-Densalloy particles in the material retained on the sieve. Milling rate did not appear to be sensitive to slurry concentration, so this parameter may be tailored specifically for ease of operation.

Fig. 4. Starting Coarse, Medium and Fine Densalloy (left). Rounded Densalloy Following Milling (right).

The wear of mill components was tracked by dimensional measurements, mass changes, and direct observation (Table VI). None of the components failed, excepting the first Hub/Peg assembly which failed within the first 15 minutes of operation. This failure was determine to be caused by improper weld attachment of the pegs to the hub. A correctly built Hub/Peg assembly was installed at the end of 30 minutes grinding and it remained in effective service, with normal wear, through the duration of milling (12 hrs total). Wear of the milling media was expected. While the mill was able to grind the hard, quartz-like particles of the simulant (Test 2), the wear rate on the media was increased for Test 2.

Due to the majority of the mass being in the hub and the wear being concentrated on the pegs, weight change was not the most sensitive method of monitoring wear of the Hub/Peg Assembly. Peg diameter was 0.187" for the new assembly and had worn to ~0.170" after 12 hours cumulative milling. The assembly is designed with a greater peg extension on the bottom row relative to the top row. For a new Hub/Peg assembly the tip-to-tip measurement for the top row was 1.633" and for the bottom row was 1.751". At the conclusion of grinding (12 hours cumulative) the Hub/Peg Assembly tip-to-tip measurements were 1.596" for the top row and 1.685" for the bottom row, reflecting a wear of ~0.018" at each tip for the top row and ~0.033" at each tip for the bottom row.

Table VI. Mill Wear Rates

Test	Cumulative Milling Time (h)	Media Mass (g)	Hub/ Peg Mass (g)	Peg Dia. (in)	Basket/ Body Mass (g)	Rulon Bushing Mass (g)	Prop Mass (g)	Media Wear Rate (wt%/h)	Hub/ Peg Wear Rate (wt%/h)
	0.0	190.31	68.40	0.187	198.45	4.06	21.78	---	---
1	2.0	183.98	68.21	0.186	200.39	4.02	---	1.66	0.14
	4.0	179.78	67.64	0.186	198.26	4.04	---	1.14	0.42
	6.0	177.04	67.33	0.186	198.03	4.00	21.77	0.76	0.23
2	8.0	152.72[a]	66.81	0.177	198.35	3.90	21.75	6.87	0.39
	10.0	160.42	66.53	0.170	197.67	3.80[b]	---	7.85	0.21
	12.0	150.0	66.30	0.175	198.03	4.02	21.76	3.25	0.17

[a]Replenish Media to 190.3 g and recharge simulant (200 g)
[b]Replace Rulon Bushing. New bushing mass = 4.06 g

The Basket/Mill Body mass change was ~1% over the 12 hours cumulative milling. The sensitivity of Basket/Mill Body mass as means of monitoring wear was limited due to the large mass of the Basket/Mill Body and the lodging of particles in the basket openings. The blocking of openings reached a relatively steady state and did no appear to decrease milling efficiency. The ability of the Basket to "pass" particles is enhanced by the opening being formed with a draft that results in a wider opening on the outside diameter of the Basket. Most of the lodged particles were Densalloy. Some deformation of the Basket/Mill Body interior surface was observed but this did not decrease milling efficiency.

CONCLUSIONS

The testing performed investigated different possibilities for the processing of K Basin sludge in order to eliminate or mitigate hydrogen generation resulting from the reaction of uranium metal with water. Direct encapsulation of uranium metal into the BoroBond™ $MgKPO_4 \cdot 6H_2O$ matrix resulted in a twofold decrease in the hydrogen generation rate. This agrees with previous findings from PNNL. As tested in the most basic formulation, BoroBond™ does not show the necessary hydrogen inhibition to be used for direct immobilization of this waste stream. Current work is aimed at developing new formulations that can be successful in this application. Pre-oxidation of uranium metal using Fenton's Reagent was successful. A ¼" cube uranium coupon was fully oxidized at room temperature in under 4 days, compared to an expected 60 days in 90 °C water. The experiments have shown that the corrosion rates can be easily controlled through hydrogen peroxide addition rate and that it can be further tailored through changes to catalyst concentrations and pH. Furthermore, the system consists of simple to use and add reagents that do not appear to lead to harmful by product formation. Grinding Densalloy SD170, the recommended irradiated uranium metal surrogate, was also successful with a Hockmeyer HSD Immersion Micromill. All densalloy that was appropriately sized for the Micromill and grinding media was quickly reduced to < 90 μm, which will decrease oxidation time of the largest uranium metal pieces in 90 ° C water from 60 days to ~2 days. Wear rates of the mill were acceptable and can be decreased if constructed with wear resistant materials rather than the standard materials used.

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