

**OVERVIEW OF TECHNOLOGIES AND INNOVATIONS BEING DEVELOPED FOR
FLUOR HANFORD PROJECTS AT THE
HANFORD SITE**

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ABSTRACT

Fluor Hanford is responsible for cleanup of legacy wastes, old production facilities, and environmental contamination that remain at the Hanford site. New technologies and technical information are being introduced to improve cost efficiency and assure safety. This paper presents recent advances in four of Fluor's projects. Supporting the Plutonium Finishing Plant Closure Project, laboratory evaluations and thermal analyses were conducted to quantify the potential for self-heating reactions that can develop in materials used to remove plutonium from contaminated equipment. Four commercial products were tested, and safe limits for packaging these wastes have been developed. The Groundwater Remediation Project is testing two technologies that show promise of preventing groundwater contaminants from reaching the Columbia River by innovative *in situ* methods. Laboratory tests are showing that the mineral apatite can sequester Sr-90, and current work to control *in situ* placement of the barrier is supporting a field deployment in late FY 06. In another location, a new approach using zero valent iron is being tested to "mend" areas breached in the *in situ* redox manipulation barrier, which was installed to convert soluble chromium from the +6 to the less mobile +3 state. The Waste Stabilization and Disposition Project has successfully operated a process to grout sludge from spent fuel storage basins. An in-line sensor and a nomogram that correlates readings from the sensor to surface dose rate for drums of grouted sludge, provide the operators with a simple and effective method to assure all waste drums meet WIPP contact-handled dose rate limits. The K Basins Closure Project will be transferring sludge containing fuel fragments using hoses and several pump booster stations. Selection of equipment fabrication materials required testing with a simulant, which in turn required laboratory evaluations of irradiated fuel hardness so that an appropriate non-radioactive material could be selected. A tungsten alloy was selected and used for testing system components.

INTRODUCTION

Fluor Hanford is addressing a broad range of technical challenges in their pursuit of aggressive DOE cleanup goals at the Hanford site. This paper highlights several examples of recent innovations being applied to reduce cost and risks, and to assure operations remain within safe boundaries. Many of these technologies have been developed and deployed with the support of the Pacific Northwest National Laboratory (PNNL). Recognizing that technology advancements are critical to success, Fluor Hanford and PNNL have developed a long-standing partnership to apply the resources of the Laboratory to Hanford projects.

PFM CLOSURE PROJECT: SAFE DISPOSAL OF WASTE FROM PLUTONIUM DECONTAMINATION

Fluor Hanford (Fluor) is in the early stages of decommissioning the Plutonium Finishing Plant (PFP) at the Department of Energy's (DOE) Hanford site located in Southeastern Washington State. Beginning in 1949, the PFP processed plutonium solutions from Hanford's nuclear fuel reprocessing facilities and plutonium scrap from Hanford and other DOE sites to produce metal and oxide products for the nation's defense mission. Most of these chemical operations were conducted in gloveboxes fabricated of stainless steel, glass, and plastic, which must now be decontaminated of plutonium and the accompanying americium before disposal as non-transuranic (non-TRU) waste. The PFP has over 200 of these contaminated gloveboxes.

In support of the PFP decontamination effort, a team of PNNL and Fluor Hanford scientists studied the thermal stability of potential wastes and treated wastes arising from proposed decontamination processes to address safety concerns. The candidate decontamination agents were 1) aqueous ceric (Ce^{4+}) nitrate/nitric acid, 2) a proprietary set of commercial aqueous solutions marketed by EAI RadPro[®] containing acids, degreasers, and sequestering agents, and 3) commercial inorganic-based gels (Glygel[®] and Aspigel[®]) using ceric ammonium nitrate/nitric acid as the active agent. Wastes from the decontamination procedures include the decontamination chemicals, rags, and vacuum cleaner filters (which are used to remove dried gels).

The safety of the anticipated PFP decontamination wastes was a concern because the chemicals are generally strong oxidants, very chemically reactive, and in combination with cloth or other cellulose materials in certain conditions, could develop a self-heating reaction, including the possibility of a fire or rapid propagating reaction.

The safety concern arose because of a fire at Rocky Flats in 2003 [1] that occurred in a glove box treated with ceric nitrate/nitric acid using the same process proposed by Fluor. The accident reviewers could not identify the cause of the event because it was obscured by the copious quantities of chemicals and water used to extinguish the fire and hence the cause of the fire was inconclusive. However, the reviewers noted that cloths were found in the glove box, suggesting that the combination of cloths and the ceric nitrate may have contributed to the fire. With that uncertainty, Fluor began an investigation into the potential for self-heating reactions when using and disposing of the chemicals and materials in the decontamination process.

Analytical Methods and Materials Used for Testing

To assess the thermal stability of potential wastes arising from PFP decontamination wastes, we used the strategy recommended by the Center for Chemical Process Safety (CCPS) [2] of the American Institute of Chemical Engineers to evaluate surrogate first generation and treated wastes characteristic of each process. We used the laboratory thermoanalytical methods differential thermal analysis (DTA), thermogravimetric analysis (TGA), accelerating rate calorimetry (ARC), and for ceric nitrate/nitric acid cotton cloth wastes thermal modeling of 210-L (55-gallon) drum waste packages.

Simultaneous DTA/TGA measures heat flow and mass change of 2 to 100 mg-sized samples at operator-controlled thermal conditions. The sample can either be heated or cooled at a known and controlled rate or can be controlled isothermally. DTA is used to determine whether a reaction is exothermic (heat-producing) or endothermic (requires heat to proceed). TGA is used to determine whether a reaction causes the material to gain, lose, or not change mass.

ARC measures exothermic heat flow at adiabatic conditions for 1 to 10-g samples. All heat produced by an exothermic reaction is kept in the sample and the reaction's products. ARC provides a more sensitive measure of heat flow compared to DTA. In an ARC experiment, the sample is heated to an operator-

selected temperature and the sample's temperature monitored to determine if an exothermic reaction occurs. If the instrument observes a reaction that heats the sample and its container at a heating rate $>0.01^{\circ}\text{C}/\text{min}$, the instrument maintains the instrument's temperature at the sample/container's temperature until an operator-selected maximum temperature or the heating rate is less than $0.01^{\circ}\text{C}/\text{min}$.

We assessed the thermal reactivity hazard using the CCPS recommended criteria:

- For DTA and TGA for exothermic reactions, thermal reactivity is of potential concern if the DTA-measured onset temperature is within 100°C of the maximum process operating temperature, where onset temperature is the temperature where the reaction is first detected.
- For the ARC, thermal reactivity is of potential concern if the maximum operating temperature is within 50°C of the ARC-measured onset temperature.

Each surrogate waste was prepared following the planned process. We prepared the surrogate ceric nitrate-nitric acid-cloth waste by saturating the cloth with ceric nitrate-nitric acid and reducing and neutralizing with ferrous sulfate and sodium hydroxide or sodium carbonate. The cloths used for the ceric nitrate-nitric acid studies were 86% cotton-14% polyester, 20% polyamide-80% polyester, and 50% polyamide-50% polyester. We prepared the various RadPro surrogate wastes by saturating the cloths with the decontamination solution and/or the rinsate solution and neutralizing with sodium hydroxide or sodium carbonate. The cloths used were the same cloths as used for the ceric nitrate-nitric acid. The two ceric ammonium nitrate inorganic gels were prepared by spraying or painting them onto a stainless steel surface, allowing them to dry as prescribed by the manufacturer, and recovering them with a commercially available hand-held vacuum cleaner.

Waste Package and Storage Conditions

The waste produced by the decontamination process will be removed from the glovebox in polyvinyl chloride bags and packaged in 210 L (55 gal) waste drums lined with 90-mil polyethylene. Wet and wrung-out rags are acceptable for disposal to the waste package. The drum or storage boxes can contain multiple bags of sealed out waste. The maximum practical loading (from PFP experience) is 30 kg (66 pounds) of rags, although a more typical loading would be about 15 kg (33 pounds) of rags per drum. Each seal out bag contains air space, and air spaces are left between the individual seal out bag packages and between the drum or storage box sides. These air gaps act as insulation and limit the heat rejection capabilities of the drum or storage boxes. These drums will later be stored in a building without temperature control in an environment where outside ambient temperatures can reach 45°C (113°F).

Results and Discussion

Our thermoanalytical studies indicate that through the use of a combination of strategies, the hazard during storage for each of the three waste types could be partially or fully mitigated to acceptable levels. The strategies include neutralization with sodium hydroxide or sodium carbonate, use of synthetic polyamide-polyester cloths as wipes, elimination of an added surfactant from the inorganic gel technology, control of environmental conditions, and separation of gels from the vacuum cleaner filters.

Our studies found that substituting polyamide/polyester materials for cotton improves the thermal stability of decontamination cloth wastes for the neutralized ceric nitrate-nitric acid system. The ARC-observed onset temperature improved to $>170^{\circ}\text{C}$ for the synthetic cloth from 30°C for the cotton cloth. The 125°C difference between 170°C and the maximum recorded Hanford temperature 45°C is much greater than the CCPS-recommended 50°C safety margin (CCPS 1995). Consistent with thermoanalytical results, thermal modeling indicates that drums filled or half-filled with stabilized ceric nitrate nominal cotton cloth waste would self-heat to unacceptably high center-line temperatures.

In accordance with the RadPro manufacturer's guidance, neutralizing RadPro cloth wastes with sodium hydroxide or sodium carbonate raised the ARC-observed onset temperature for the nominal worst case waste (67% decontamination solution/33% rinsate solution) from 65°C to >95°C. The ARC-observed onset temperature of 95°C is at the CCPS-recommended safety margin of 50°C.

As shown in Figure 1, our thermoanalytical studies of the ceric ammonium nitrate inorganic gels indicate that using the surfactant-free inorganic gel Aspigel and neutralizing its dried waste product yields a waste that has an ARC-observed onset temperature of 130°C which is again greater than the 50°C safety margin from Hanford's maximum temperature of 45°C.

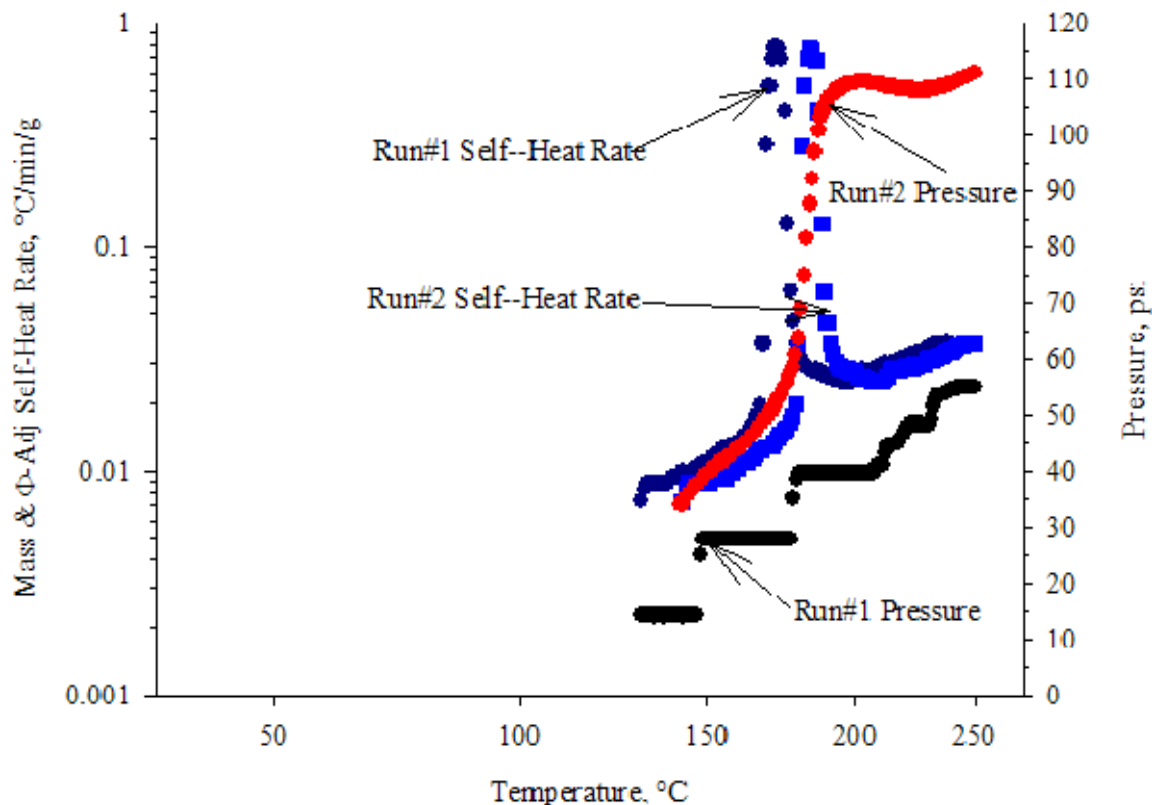


Fig. 1. Arrhenius Plot of ARC-Measured Thermal Sensitivity of Sodium Carbonate-Neutralized Aspigel Recovered from DataVac3 Vacuum Cleaner Filter

GROUNDWATER REMEDIATION PROJECT

Remediation of an Innovative Permeable Reactive Barrier

During operation of two reactors in Hanford's 100-D Area from 1944 to 1967, large volumes of water were pumped from the Columbia River to cool the reactors. Sodium dichromate, which was added to the cooling water to inhibit corrosion of the reactor piping, leaked (or was spilled) into the soil and contaminated the groundwater. In 1995 hexavalent chromium (Cr(VI)) was discovered in the western portion of the 100-D Area near the aquifer/Columbia River interface. This was a great concern because Cr(VI) is known to adversely affect the development of salmon fry, an important cultural and economic resource in the Columbia River. Subsequent installation of groundwater monitoring wells identified a Cr(VI) plume approximately 1000m long and 800m wide.

Beginning in the late 1990s, a permeable reactive barrier, called the In Situ Redox Manipulation (ISRM) barrier, was installed to remediate a chromium groundwater plume in Hanford's 100-D Area. Using a network of 65 wells to access the groundwater, this technology creates a reducing zone in the aquifer by injecting sodium dithionite. This chemical reduces the valence state of material in the aquifer, principally changing ferric iron to ferrous iron, to create a persistent zone of reduction. Hexavalent chromium passing through this zone by natural groundwater flow is reduced to the less toxic and less mobile trivalent chromium (Cr(III)).

Laboratory experiments performed before installation of the ISRM barrier indicated that it would be effective for approximately 20 years, but localized signs of failure were discovered after only 18 months. Some of these wells were reinjected with sodium dithionite in 2002 to maintain the effectiveness of the barrier, but several of these began to show signs of failure again in less than two years. Approximately 20 wells within the barrier have begun to fail only a few years after installation.

The most likely cause of barrier failure is thought to be physical and/or chemical heterogeneity within the aquifer. Preferential pathways within the aquifer have recently been identified through hydraulic conductivity measurements using the Electronic Borehole Flowmeter (EBF). Groundwater flowing through these pathways likely flushes large quantities of naturally oxic water rapidly through the treatment zone, diminishing its reductive capacity and thus barrier longevity. These preferential pathways may also be deficient in reactive iron, further limiting the reductive capacity of the barrier. Another failure mechanism could be the presence of other oxidants, such as nitrate, which were not accounted for in the earliest predictions of barrier longevity.

One method that could be used to mend the ISRM barrier is to supplement the reduction capacity by injecting iron into the formation. This could involve injection of micron-sized particles of zero-valent iron (Fe^0) into the most permeable zones of the ISRM barrier, together with a shear-thinning fluid containing polymer. Polymers are advantageous because they create a viscosity that is high enough to keep the Fe^0 in suspension for extended time periods to improve colloid movement into the porous media, and they do not cause a permanent detrimental decrease in hydraulic conductivity.

To evaluate this technology at an intermediate scale, sediments from the 100-D Area aquifer were packed in a wedge-shaped flow cell 1.35 m long and 0.2 m deep, with a total volume of 59 L. Two experiments were conducted: one with a horizontal high-permeability zone sandwiched between two low-permeability zones, and the other with a high-permeability channel surrounded by low-permeability materials. The injection flow rate, polymer type, polymer concentration, and injected pore volumes were determined based on preliminary short- and long-column experiments. Thirty pore volumes of the iron/polymer solution were injected into each flow cell using moderate flow rates. Although the aqueous pressure increased by up to 25 KPa (~3.5 PSI) during infiltration, there was no detrimental effect to the hydraulic conductivity observed. After injection, the flow cells were sampled at five levels: 2.5 cm, 7.5 cm, 10 cm, 12.5 cm, and 17.5 cm from the bottom. A total of 64 samples were taken at each level.

Sampling results show that iron concentration enhancements of at least 0.6% (weight/weight) can be obtained under these laboratory conditions (Figure 2). Calculations show that a 1 m zone amended with 0.6% w/w iron as Fe^0 subject to a pore water velocity of 1 m/day will have longevity of 7.2 years. The calculations are based on moving groundwater with a composition of major oxidizing species similar to that at 100-D: 8 mg/L dissolved oxygen, 60 mg/L nitrate, and 2 mg/L chromate.

More testing of this technology needs to be done, but if results continue to be encouraging this technology may be used to mend the ISRM barrier and perhaps be used on its own to install permeable reactive barriers in suitable aquifers without the need for surface disruption caused by trenching.

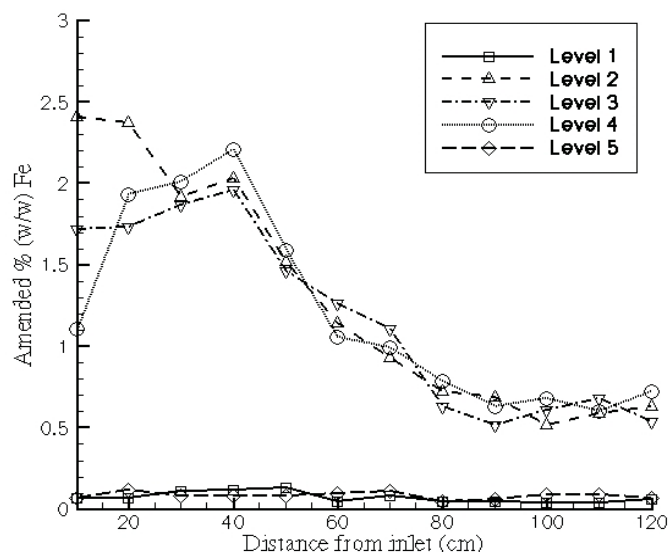


Fig. 2. Amended % (w/w) Fe⁰ at all five levels as a function of distance from injection location. Levels 1 and 5 were low-permeability zones, Levels 2 through 5 were high-permeability zones.

Sr-90 Sequestration by Apatite at the Hanford 100N Area

A novel remediation technology is being developed to sequester Sr-90 in soils and groundwater at the Hanford 100-N Area. Using an aqueous apatite mixture, Sr-90 sequestration occurs by the following steps:

- 1) injection of Ca-PO₄-citrate solution (with a Ca-citrate solution complex)
- 2) in situ biodegradation of citrate resulting in apatite [Ca₆(PO₄)₁₀(OH)₂] precipitation (amorphous, then crystalline)
- 3) adsorption of Sr-90 to the apatite surface
- 4) apatite recrystallization with Sr-90 substitution for Ca (permanent)
- 5) radioactive decay of Sr-90 to Y-90 to Zr-90

During earlier development of this technology, previous studies [3] demonstrated that citrate biodegradation/apatite precipitation occurs in several sediments, and that U, Tc, Sr, and Pb were sequestered. The purpose of this study was to determine if this technology could effectively reduce the mobility of the Sr-90 to protect the Columbia River from contamination. The study has been designed to address the principle questions influencing overall effectiveness:

- will sufficient apatite precipitate in 100-N Area sediments to create an effective treatment zone
- will the Sr-90 removal rate be rapid enough in this zone to allow capture (ion exchange) of the Sr-90 before the contaminants pass through the zone
- can the chemicals be emplaced in the treatment zone without unacceptably mobilizing the Sr-90

Laboratory-scale studies have characterized the sequential processes of this technology in 100-N Area sediments:

1. amorphous and crystalline apatite precipitation occurs
2. aerobic and anaerobic citrate biodegradation pathways and rates are quantified
3. Sr-90 uptake in apatite-laden 100N sediment occurs
4. Sr-90 is initially held by ion exchange, but then over 6-20 weeks more permanently held (presumed incorporated into apatite)
5. similar sequential processes occur during reactive transport.

Apatite precipitation in batch and 1-D column systems occurred within 75-100 h in aerobic systems (citrate biodegradation to CO₂; Fig. 1a). In anaerobic systems (citrate biodegradation to formate and acetate (Fig. 1b, 1c), the apatite precipitated within 100-200 h. In the 100N aquifer, most of the citrate biodegradation will occur anaerobically, given the relative concentrations of citrate to oxygen. Initial precipitate within 100 h is amorphous, but then crystallizes within 2 - 4 weeks to apatite. Batch experiments varying mixing, trace nutrient addition, and nitrate addition showed similar results.

Testing showed that apatite precipitate was formed in 100-N area columns. Without apatite, sequential extractions showed 90% of the Sr-90 could be removed from the sediment by ion exchange. Long-term experiments showed that by 6 weeks, only 45% of the Sr-90 could be removed by ion exchange, and this slowly decreased to 32% by 24 weeks. This may be caused by the slow Sr-90 incorporation into apatite.

To minimize Sr-90 mobilization (by ion exchange) during barrier emplacement, a sequence of injections from low to high concentration Ca-citrate/phosphate is needed. Sr-90 mobilization is minimal with the low concentration injection, and the apatite formed in the injection zone (after 4 weeks) immobilizes most of the Sr-90. Then a high concentration injection can be injected with minimal Sr-90 desorption. This higher concentration injection is needed to create sufficient treatment capacity to capture the Sr-90 plume as it migrates through this zone. This sequential injection scheme was successful at the laboratory scale.

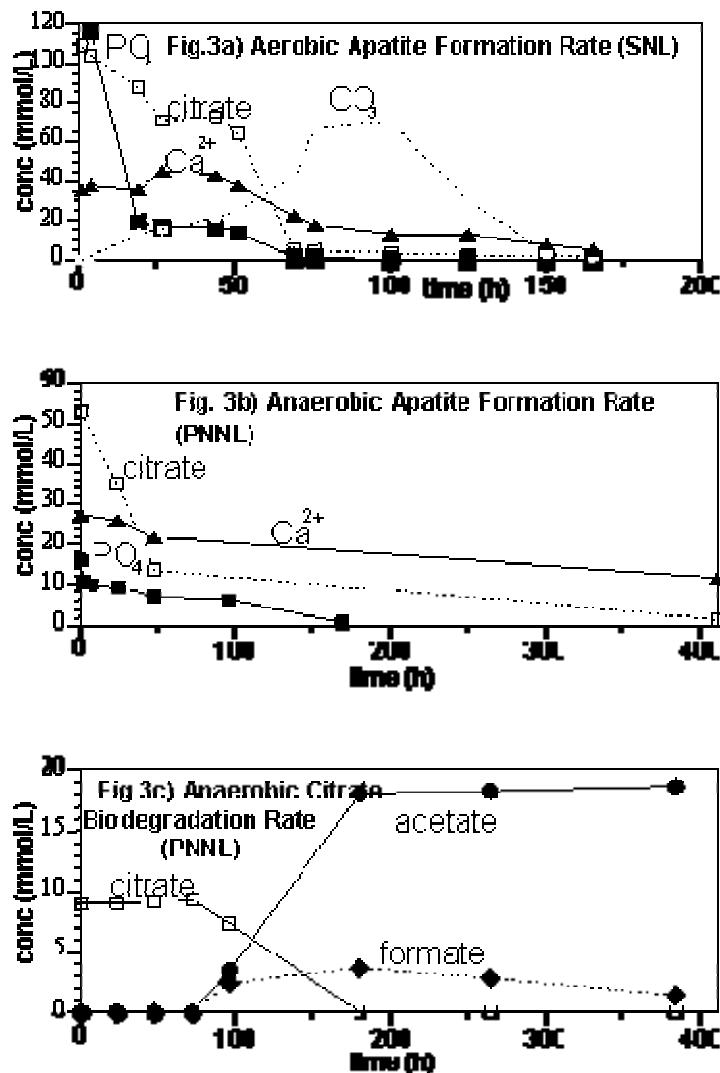


Fig. 3. Batch and 1-D column experimental results a) apatite precipitation rate in aerobic system (SNL exp.), b) apatite precipitation rate in anaerobic system (PNNL exp.), c) citrate biodegradation rate in anaerobic system (PNNL exp.).

Using these results, Fluor and PNNL are designing a system to install a barrier using well injection and near-surface infiltration to place the apatite in the upper aquifer and lower vadose zone near the Columbia River. Current plans are to have a functioning barrier deployed by the end of FY 06. Given the stability of apatite in the conditions at 100-N, the barrier is predicted to be effective over the 300 year period needed for natural decay.

WASTE STABILIZATION AND DISPOSITION PROJECT: CONTROL OF SURFACE DOSE RATE IN GROUTED TRU SLUDGE DRUMS

In 2004 a determination was made that the spent nuclear fuel sludge in the K-East Basin north loadout pit (KE NLOP) would be grouted in 55 gallon drums as contact-handled transuranic (CH-TRU) waste for shipment to the Waste Isolation Pilot Plant in New Mexico for permanent disposal. The KE NLOP

sludge is variable mixture composed primarily of spent nuclear fuel corrosion products, water, and sand from filters used for maintaining the water quality in the K-East fuel storage basin.

At the request of Fluor Hanford (FH), PNNL developed an approach for metering an appropriate volume of sludge into each drum that would maximize the amount of sludge in each drum (thus minimizing the number of drums) while not exceeding the 200 mRem/h surface dose limit for CH-TRU. The essential elements of this approach included use of a gamma detector mounted on a recirculation line to measure the dose rate of the sludge, and a nomogram that specifies the amount of sludge to add to each drum as a function of the gamma detector reading.

The KE NLOP sludge is processed in ~1000 liter batches. Each batch is transferred into a buffer tank where it is agitated to prevent settling. The buffer tank has a 1 in. recirculation line. Material from this line is diverted using a valve to transfer sludge to the drums for grouting. Additional water (if necessary for grouting) and grout formers (Portland cement and bentonite clay) are added to the drum and mixed to produce the grouted sludge.

There were a number of reasons for using the gamma detector/nomogram approach instead of sampling and analyzing the sludge. By mounting a gamma detector on the recirculation line, the dose rate of the sludge to be transferred to the next drum can be measured in real-time. Based on this measurement the operators determine the amount of sludge to transfer to that drum to meet a pre-determined target value for surface dose rate (160 mRem/h was selected by FH). Obtaining representative samples from the buffer tank for radiochemical analysis would have been difficult due both to spatial concentration gradients within the buffer tank, and the difficulty associated with obtaining a small but representative sample of the sludge at any particular location in the buffer tank. Also, use of the gamma detector and nomogram eliminates the cost of taking and analyzing samples, the delay in processing while the samples are being analyzed, and the secondary waste generated by sampling and analysis. This approach is also consistent with As Low As Reasonably Achievable (ALARA) principles because personnel doses associated with sampling and analysis are eliminated.

The nomogram was developed using the Monte Carlo N-Particle eXtended (MCNPX) radiation transport code. MCNPX was used to model the dose rate to be seen by the gamma detector, and also the surface dose rate of the drums containing the grouted sludge. The source term for this modeling was the isotopic concentration of the KE NLOP sludge based on analyses of core samples of this sludge reported by Mellinger [4]. "Nominal" isotopic concentrations are shown in Table I.

Table I. Nominal Isotopic Concentrations of KE NLOP Sludge

Nuclide	Activity, $\mu\text{Ci/ml}$
^{241}Am	2.06
^{60}Co	8.37E-2
^{137}Cs	8.52
^{154}Eu	1.58E-1
^{155}Eu	4.03E-2

Modeling of the dose rate to be seen by the detector was based on the geometry and materials of construction of the sludge processing equipment (buffer tank, recirculation line, pumps, valves, shielding, etc.). The surface dose rate of the drums was modeled based on the drum dimensions, and grout density and drum fill height information provided by FH.

In modeling the dose rate to be seen by the detector, a linear relationship between the concentration of the settled sludge and the predicted dose rate of the detector was found. This relationship is shown in Figure 5. Because the recirculation line and detector are located above the buffer tank, and the volume of sludge in the tank changes as material is transferred to drums for grouting, the contribution of the dose rate from the buffer tank to the detector will change as well. To ensure the accuracy of the model, the influence of the buffer tank on the detector needs to be negligible. Modeling of the piping system and buffer tank showed that the shielding located between the detector and the buffer tank effectively eliminates the influence of the buffer tank on the detector.

Based on the modeling, the AMP-50 detector initially selected for measuring the dose rate of the sludge in the recirculation line was confirmed to be well suited to this application. The detector should see dose rates in the range of 1 mRem/h to 100 mRem/h, which is well within the 10 μ Rem/h to 4 Rem/h range of the AMP-50 detector.

The effect on the dose rate produced by variations in the isotope activity was also investigated. To determine the sensitivity of the measurements to the isotopic mix in the sludge, the dose rate was calculated with twice the activity of Co-60, Eu-154, and Eu-155 and the given activity of Cs-137 and Am-241. This only affected the dose rate by approximately 10%. It was concluded from this that variations in isotopic mix should have a negligible impact on the dose rate seen by the detector.

In modeling the relationship between the dose rate at the surface of the drum and the concentration of the settled sludge in the drum, the dose rate was modeled at two inches from the surface of the drum, which is the effective measurement point when using the standard survey instrument. Although only one mixture (the nominal concentration) was modeled, it is expected that the relationship between the concentration of the settled sludge and the predicted drum surface dose rate to be linear because it is assumed to be uniformly mixed, so the relationship between predicted surface dose rate and settled sludge concentration can be extrapolated from this calculation. This extrapolation is also shown in Figure 5.

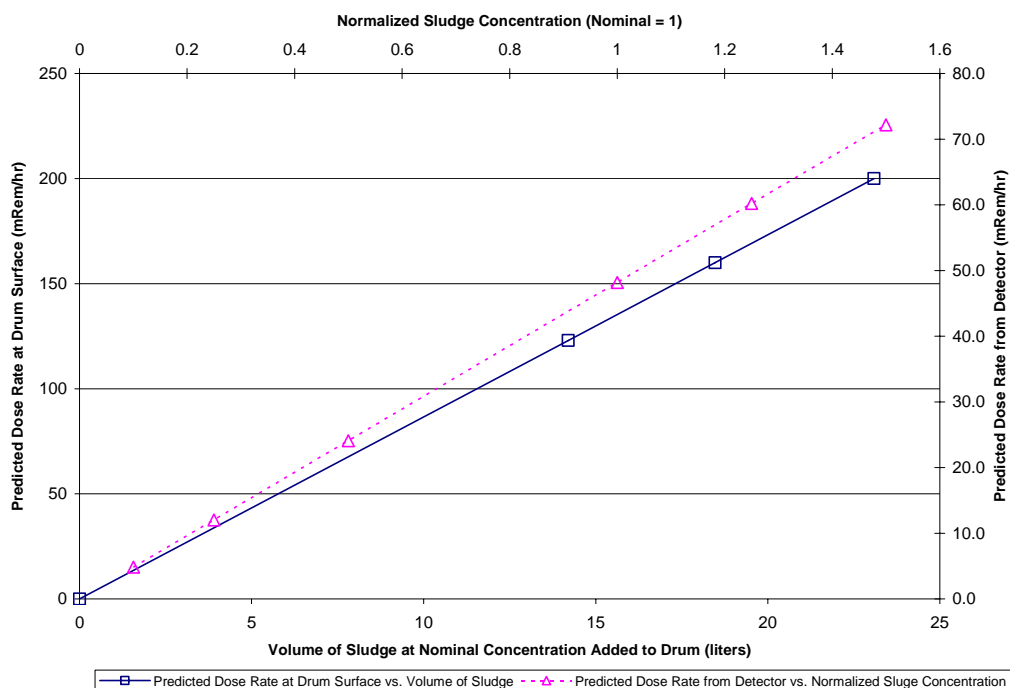


Fig. 5. Detector Reading as a Function of Sludge Concentration; Drum Surface Dose Rate as a Function of Volume of Sludge Added to Drum

Using the data that was used to prepare Figure 5, the following steps were used to construct the nomogram. As noted above, FH selected a surface dose rate of 160 mRem/h for their target value. Based on the MCNPX modeling, drums with this surface dose rate would contain 18.5 liters of sludge at the nominal concentration. At the nominal concentration, the detector will read 48.2 mRem/h. As found by the MCNPX modeling, the detector reading will increase and decrease linearly with increases and decreases in sludge concentration. At a constant drum surface dose rate, the volume of sludge added to each drum will vary inversely with the sludge concentration. This is shown in Table II.

Table II. Nomogram Basis

Normalized Sludge Concentration (Nominal =1)	Detector Reading (mRem/h)	Volume of Sludge/Water Mixture in Buffer Tank to Transfer to Drum for Surface Dose Rate of 160 mRem/h (Liters)
0.1	4.8	184.7
0.25	12.0	73.9
0.5	24.1	36.9
1	48.2	18.5
1.25	60.2	14.8
1.5	72.2	12.3

A linear regression of the values in Table II was performed to develop an equation that relates the detector reading and volume of sludge to be transferred to a drum. This equation was used to prepare a table that identifies the amount of sludge to transfer to a drum in order to produce a drum with a surface dose rate of 160 mRem/h; values are provided for all detector reading between 0 and 99 mRem/h in one mRem/h increments. At detector readings lower than 10 mRem/hr the volume of the sludge transferred to the

drum, rather than the surface dose rate of the drums, limits the amount of sludge transferred to each drum; this is reflected in the table. This table is used by the operators during processing to determine how much sludge to add to each drum based on the detector reading.

Processing of the KE NLOP sludge was initiated in late October 2005. While it was expected that the models used to develop the nomogram would predict the relationship between detector reading and surface dose rate of the drums fairly accurately, it was also anticipated that the nomogram might need to be adjusted based on the results from initial production. During initial production the dose rate measured for the drums was approximately 120 mRem/h to 140 mRem/h, compared to a predicted/target value of 160 mRem/h. As a consequence, a revised nomogram was prepared that increased the amount of sludge added to each drum for each detector reading by 11%. It is expected that use of this nomogram will result in production of grouted drums with surface dose rates that are closer to the target value of 160 mRem/h. During remaining production, the relationship between predicted and actual surface dose rates of the drums will continue to be monitored.

K BASIN CLOSURE PROJECT: SELECTION OF SURROGATE MATERIALS FOR EROSION TESTING OF SPENT FUEL SLUDGE TRANSPORT

A system is being design to transfer K East (KE) Basin sludge from containers in the KE Basin to containers in the K West (KW) Basin. The sludge transfer system, referred to as the hose-in-hose system, is expected to include approximately 2500 ft of 1.25 in. hose with four booster pump stations located approximately every 500 ft. The sludge includes metallic uranium fuel fragments which are hard and will affect the service life of the pumps and associated hoses and fittings. Testing is being conducted to determine the durability and performance of pumps and other sludge-handling hardware being considered for the final design. Because the actual K Basin sludge is highly radioactive, testing is being conducted with non-radioactive simulants.

Understanding the characteristics and behavior of the sludge constituents is important for selecting appropriate surrogate materials for use in testing pumps and associated equipment that will be used for transferring and handling the sludge as a slurry for treatment and disposal. The inorganic components of the sludge include irradiated uranium metal and its radioactive corrosion products, such as uranium dioxide (UO₂), as well as non-radioactive materials. The mechanical properties of the irradiated uranium and its oxides are especially important, because they are very high density, hard materials with potentially jagged, sharp particle geometry that could be a challenge to slurry handling equipment.

In slurry pumping, the solid sludge particles will be lifted and transported by high-velocity water. The high velocities, which are required to keep the dense uranium particles suspended, can cause significant wear on the slurry transfer equipment. Consequently, testing is being conducted to characterize and evaluate the performance of candidate pumps and handling equipment. These tests require the identification/specification of non-radioactive surrogates for the radioactive components of the sludge. The surrogates must have mechanical properties (principally particle size distribution, shape, density, and mechanical hardness) similar to the irradiated uranium metal and uranium dioxide (and other sludge components). The impact strength of the simulant (“toughness to impact fracturing”) also is important with respect to its impingement on the pump’s internal parts. This is particularly true in some engineering tests when a small quantity of simulant is recycled hundreds of times in a closed loop to represent the transfer of a large volume of sludge.

A literature review showed that uranium metal hardness increases steeply with radiation exposure to 1260 MWd/t, but information was lacking on the hardness of uranium metal at the higher exposures received by the N Reactor fuel stored in the K Basins (typically up to 3000 MWd/t). The strong correlation of

hardness to exposure levels indicated a need for data defining the hardness in the range of the N Reactor fuel. This study included hardness measurements of irradiated uranium metal, using N Reactor fuel sample coupons from three different fuel elements. Samples were taken from the broadest available range of locations within the fuel elements—along the axial length of the elements near the end and the middle, and from faces directly under cladding and within the “meat” of the fuel on cut faces.

The hardness of the fuel coupons was measured with a commercial penetrometer device (Ames Model 1 Portable Hardness Tester) modified for hot cell application. The coupon hardness values averaged 30 ± 8 Rockwell C units, which were surprisingly close to the value reported in the technical literature for the lower-exposure uranium. Hardness values were greater underneath the cladding, but were not measurably different when obtained over the fuel length. The hardness values were significantly lower than that of the tungsten carbide (i.e., Rockwell C of 69 to 74) used to represent irradiated uranium metal in previous K Basin sludge simulants.

The density and hardness of the two primary uranium corrosion products, uranium dioxide and schoepite, also were reported in the technical literature. The hardness of UO_2 is equal to or greater than that of any non-uranium phase, and its density is higher. While UO_2 particles are expected to be micron-scale, some accreted uranium-rich particles have been observed in sludge. Therefore, the mechanical aggressiveness of UO_2 is also likely to be greater than that of any non-uranium sludge phase. Schoepite hardness and density are matched well by non-uranium sludge phases and contribute no added mechanical aggressiveness to the sludge.

The mechanical/physical properties of uranium metal and uranium dioxide were compared with their candidate surrogates. Surrogates having properties closest to those of irradiated uranium metal from N Reactor fuel appear to be alloys of tungsten. Based on hardness and impact strength and a review of the available materials, the tungsten material recommended for use as irradiated uranium metal surrogate is Densalloy SD170 or equivalent. The surrogate for uranium dioxide, present both as particles and agglomerates in actual K Basin sludge, likely requires two materials in order to cover the range of particle sizes. Commercially available materials— CeO_2 , to represent the smaller particles, and steel grit, for the agglomerates were identified for the UO_2 surrogates.

REFERENCES

1. Beyler C. 2004. *Analysis of the Cause of the Fire in Glovebox 8, Room 2325, Building 371 at RFETS on 6 May 2003*. Hughes Associates, Inc. Baltimore, MD.
2. Center for Chemical Process Safety (CCPS). 1995. *Guidelines for Chemical Reactivity Evaluation and Application to Process Design*. American Institute of Chemical Engineers, New York, NY.
3. Moore, RC; C Sanchez, K Holt, p Zhang, H Xu and GR Choppin (2004) “Formation of Hydroxyapatite in Soils Using Calcium Citrate and Sodium Phosphate for Control of Strontium Migration”; *Radiochem Acta* **92**, 719-723.
4. Mellinger, GB, CH Delegard, AJ Schmidt, GJ Sevigny. 2004. Evaluation and Recommendation of Waste Form and Packaging for Disposition of the K East Basin North Loadout Pit Sludge. PNNL-14741. Pacific Northwest National Laboratory, Richland, Washington.