

## TREATABILITY STUDY FOR THE STABILIZATION OF CHROMIUM CONTAMINATED WASTE

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### ABSTRACT

A process has been developed which immobilizes chromium in calcined uranyl nitrate mixed waste, resulting in a waste form disposable as radioactive, non hazardous waste.

A prime contractor at the Idaho National Engineering Laboratory generates a radioactive waste contaminated with chromium. During handling, the waste becomes contaminated at a concentration sufficiently high to cause the waste to exceed the EPA's Toxicity Characteristic Leaching Procedure (TCLP) leachable limit for chromium.

A treatability test program was instigated to define the optimum conditions for the chemical reduction pretreatment step necessary for the stabilization of the contaminated waste. Sodium dithionite was determined to be the reducing agent of choice. A dithionite demand experiment was run to determine optimum dithionite dose. This dose, plus 67 percent excess, was added to each sample. Four different stabilization systems, at three different dosage levels, were investigated. The best performing reagent system was chosen for scale-up and more stringent performance testing. In one of the tested reagent systems, Portland cement sodium silicate and dithionite, all of the samples exhibited TCLP extract concentrations for chromium well below the regulatory limit. Portland cement/blast furnace slag blend had one passing sample, and for cement/fly ash and cement alone none of the samples had passing values for leachable chromium. The samples scaled-up passed the performance criteria and the process which is currently undergoing implementation at INEL has successfully converted mixed waste into radioactive waste for disposal.

### INTRODUCTION AND BACKGROUND

A bench-scale treatability study was conducted to develop a stabilization process for a calcined uranyl nitrate waste which had failed the EPA's TCLP test for total leachable chromium. The waste had a leachable chromium concentration in excess of 1000 mg/L making it a characteristically hazardous waste under RCRA. The waste is generated when sheets of depleted uranium are pickled by a nitric acid solution to remove an oxide coating. The uranium oxides are converted to uranyl nitrate in this process. The aqueous uranyl nitrate stream is concentrated in an evaporator and the nitric acid fractionated and recycled. The concentrated uranyl nitrate flows by gravity to the calciner feed tank. The waste uranyl nitrate is further processed in the calciner operated at 800°F. The uranyl nitrate is reconverted to the oxide(s) in this step, and the remaining chemically bound nitric acid and water is recovered and recycled. The calciner will not be operated until a treatment for the calcined nitrate is developed. In the interim, the evaporator-concentrated uranyl nitrate is cycled back to the spent acid tank. It has been postulated that the chromium contamination is from the process stream's contacting stainless steel equipment and that the chromium metal may have been oxidized to hexavalent chromium during the calcination process. The calciner is operated by Babcock and Wilcox, Idaho, Inc.

The objective of the treatability study was to develop a stabilization process for the treatment of this waste to reduce the leachable chromium to below regulatory concern. Additionally, the process was required to be adaptable to in-drum mixing. Another objective was to develop the process so that it could be carried out in the accumulation containers.

### STATEMENT OF THE PROBLEM

A sample of the calcined uranyl nitrate was subjected to the Toxic Characteristic Leaching Procedure-EPA Method 1311. The sample failed the criterion for chromium. The

Babcock and Wilcox analytical laboratory found that the sample leached about 1200 ppm of chromium. Therefore, this material is classified as a "characteristically hazardous waste" under EPA Waste Code D007 and is regulated under RCRA. Since the material is also radioactive, the waste is known as a "mixed" waste, i.e., containing both radioactive and, in this case, a characteristically hazardous constituent. The primary disposal option available to B&W does not accept mixed wastes for disposal.

Some current technical approaches to the solution of mixed waste problems involve treatment of the matrix to separate the radionuclides from the RCRA constituents. Another approach is to alter the matrix to pass the RCRA treatment criteria thereby facilitating reclassification of the waste matrix as low level radioactive waste only. For this specific waste stream, treatment can be accomplished by chemically reducing the hexavalent chromium to trivalent chromium which has limited solubility in aqueous solutions. Once this is done, the waste can be stabilized in a cementitious matrix providing that the pH is controlled to prevent solubilization of the chromium hydroxide which is amphoteric. The technical challenges for the development of the treatment process becomes the selection of a reducing agent which will operate under alkaline conditions and specifically reduce the hexavalent chromium over the hexavalent uranium, preferably in a one-step process that requires no pre-treatment steps. If the selectivity of the reducing agent is non-specific, reagent costs to chemically reduce both the uranium and chromium in the waste, which contains 40 percent uranium (w/w) and 3200 ppm hexavalent chromium, would be extremely high. A literature search showed that sodium dithionite and sodium hypophosphite were potential chemical reducing agents suitable for this process.

## BENCH-SCALE PROCEDURES

### Homogenization

The sample, as received, was screened to remove particles greater than 3/8 inch. To incorporate greater than 3/8 inch material into the process would require the use of larger molds in the compressive strength tests (c.f., ASTM D-2166). In addition, Modified TCLP (MTCLP) testing showed that the oversized material exhibited higher leachable chromium than the rest of the matrix. Minus 3/8 inch material was thoroughly mixed and blended in a jar mill for one hour. Homogenization was performed to minimize sampling errors. The jar was placed on end and five (5) aliquots were removed, one from each quadrant and one from the center. These samples were subjected to the IT MTCLP, a screening tool developed to facilitate stabilization reagent performance comparisons. After the MTCLP extraction, the extracts were syringe-filtered through 0.6-0.8 micron filters then analyzed for chromium by inductively coupled plasma (ICP). The MTCLP mimics the full-scale TCLP without the generation of large quantities of wastes. It uses the same 20:1 extractant-to-sample ratio as the full-scale test and the same extraction time and 0.6 to 0.8 micron filter porosity. The data was reduced, then compared for the percent relative standard deviation (RSD) of the measurements. Since the RSD was less than plus or minus 20 percent, the sample was considered homogeneous based on previous laboratory experience and it was aliquotted for characterization testing.

### Characterization Testing

Initial characterization testing of the homogenized and screened sample included submission of 400 grams of sample to the IT Laboratory for the following analyses:

- TCLP extraction and analysis for RCRA Metals
- Uranium by gamma spectroscopy
- Thorium by gamma spectroscopy
- Total nitrate

An additional sample was analyzed by IT for:

- Total RCRA metals by ICP
- Total uranium, iron and thorium by ICP
- Gross alpha/beta
- Hexavalent chromium by HACH test

### Reagent Preparation

For the samples requiring blended stabilization reagents, the blends of the selected stabilization materials were prepared in the laboratory by mixing the required amounts of the separate reagents until visually homogeneous. All blends were mixed for at least 10 minutes in a laboratory jar mill. The moisture content of the dry reagents was determined by oven drying.

For the experiments with only one reagent, the reagents were used as-is directly from the manufacturer. Sodium silicate was added with the water in the cement/silicate samples.

### Stabilization Testing - Mixing and Blending

It was determined that, because of the high bulk density of the waste, it would require over 100 grams of waste to fill the molds. Therefore, 150 grams of waste were blended with the required amount of stabilization reagent according to the test matrix, which provided for testing four stabilization systems in quadruplicate at three different doses. The stabilization reagents tested were Portland cement/dithionite; 80 parts Portland cement blended with 20 parts blast furnace slag plus

dithionite; 80 parts Portland cement blended with 20 parts fly ash plus dithionite; and Portland cement/sodium silicate (5 percent of cement dose) plus dithionite. The samples were packed into 1.75-inch by 3-inch cylindrical molds, capped securely and allowed to cure for three days.

In addition to the samples in the matrix, each sample point was mixed with three different amounts of water. Because of the unknown high water solubility of the waste, the amount of water originally estimated was found to be much too high. The product from the original work plan water dosages was judged to be unacceptable. The mixes were too fluid. Thereafter, the following method was used to determine the water content to be tested. Water was added to the sample/reagent blend until a mixture with the viscosity of a thin paste was obtained. This amount of water was measured. Two more samples were prepared, one with a water dose of approximately one percent higher of the total mix weight and one with approximately one percent lower water content. Sodium silicate was added after the water charge for these screening samples.

Additionally, seven method duplicates were prepared and one sample with cement only, without the reducing agent. The reducing agent concentration to be added to the mix was determined by titrating a sample with dithionite solution until all of the hexavalent chromium was reduced to trivalent chromium. Excess reducing agent was added to assure that the process could handle potential chromium hot-spots and concentration variations. Sodium hypophosphate was dropped from the program for safety and economic reasons.

### Stabilization Testing - Compressive Strength Development

The samples were blended together and mixed in the laboratory mixer until visually homogeneous, then for two additional minutes. The bulk of the sample was packed into the molds and immediately capped to allow curing under ambient conditions (approximately 72°F). Approximately 50 grams of mixture were transferred to a polypropylene specimen cup with a tight fitting cap for penetration resistance strength development measurements. These measurements were taken on days one, two, and three after preparation. Additionally, on the fourth day, the cured waste blends were removed from the cylindrical molds. Their unconfined compressive strengths (UCS) were tested using a Brainard-Kilman load frame configured for unconfined compressive strength.

### Stabilization Testing - MTCLP

After three days curing, each sample that had undergone UCS testing was crushed and sieved for MTCLP testing. The extracts from the MTCLP tests were syringe-filtered through the 0.6 to 0.8 micron filter, then analyzed for leachable chromium content by ICP. It should be noted that for most mixes, significant uranium concentration in the leached extracts presented serious background interference problems with the ICP analysis. Inter-element correction was required for the chromium analysis. The sample mix exhibiting the best performance, based both on minimum chromium leached and maximum compressive strength development, was chosen for scale-up.

## DESIGN MIX SCALE-UP

### Design Mix

The mix that best satisfied the stated performance goals, i.e. had the lowest chromium concentration in the MTCLP extract, was chosen as the design mix. The dry blend for this

mix contained 150 parts of sample plus 30 parts of Portland cement and 10 parts of sodium dithionite. Thirty parts of water and 1.8 parts of PQ Type N<sup>®</sup> sodium silicate solution were then added and mixed into the dry blend. PQ sodium silicate was obtained from the PQ Corporation, Valley Forge, Pennsylvania. Type "N" sodium silicate solution contains 40 percent solids with a SiO<sub>2</sub>/Na<sub>2</sub>O ratio of 3.22.

**Scale-up**

The design mix was prepared by weighing the remainder of the "as received" sample into the bowl of a 4 liter laboratory Hobart planetary mixer. This did not include the 200 grams (approximately 1.6 percent of total feed) of greater than 3/8 inch material. The 200 grams was kept aside because it leached more chromium than the bulk of the sample. This resulted in 900 grams feed to the design mix. The sample was then blended with the calculated amounts of dry reagent, water and reducing agent. The blend was mixed until visually homogeneous, plus an additional five minutes in the Hobart mixer. The samples were then packed into 2-inch by 4-inch long capped cylindrical molds for curing for three days prior to UCS testing.

**RESULTS AND DISCUSSION**

**Homogeneity**

The sample was considered homogeneous after mixing. The RSD for the chromium analysis was plus or minus 6.97 percent.

**Characterization**

The results of the raw material characterization analyses are presented in Table I.

**MTCLP**

An assessment of the MTCLP data shows that for all the mixes tested, 11 passed the TC regulatory criteria. Of these 11 mixes, 10 contained cement/silicate as the binder. This assessment can be found in Table II. Some mixes were better performers than others. With the exception of the cement/silicate mixes, all mixes with higher doses of cement did not perform as well as those with more moderate doses, most likely caused by the higher pHs of the higher cement concentration and the amphoteric nature of chromium hydroxide. The pH of a raw cement slurry can be as high as 12.0. The

TABLE I  
Raw Waste Characterization Analytical Data

shear strength	.....	N/A <sup>a</sup> (not analyzed)
pH	.....	11.6 s.u. (1:1 with D.I. H <sub>2</sub> O)
bulk density	.....	1.8 g/ml
total uranium	.....	40.5% (ICP)
total thorium	.....	<2.0 mg/kg (ICP)
hexavalent chromium	.....	3,170 mg/kg
nitrate/nitrite	.....	non-detectable
total uranium	.....	42.0% (gamma spec)
total thorium	.....	1.69E-05 mg/kg (gamma spec)
paint filter	.....	pass
gross alpha	.....	2.64E-01 μCi/g
gross beta	.....	2.12E-01 μCi/g

a = could not be determined; sample was non-cohesive

Metal	Total RCRA Metals (mg/kg)	TCLP Extract Metals (mg/L)	Regulatory Limit
Ag	< 15 <sup>a</sup>	3.470	5.0
As	< 250 <sup>a</sup>	1.674	5.0
Ba	94	0.105	100.0
Cd	6.8	0.003	1.0
Cr	10,290	406 400 dup	5.0
Pb	< 155 <sup>a</sup>	1.103	5.0
Se	< 3.4 <sup>a</sup>	0.020	1.0
Hg	N/A	0.001	0.2

<sup>a</sup>< indicates parameter at a concentration less than the detection limit.

TABLE II  
Mixed Blends that Passed TCLP Sample Weight-150 Grams

Reagent	Dose (grams)	Water (grams)	Extract pH	MTCLP Cr (ppm)
PC/BFS	22.55	23.0	9.16	4.53
PC/PQ	22.5/1.35	20.6	9.04	4.85
PC/PQ	22.5/1.35	22.8	9.08	1.74
PC/PQ	22.5/1.35	26.0	9.13	1.57
PC/PQ	30/1.80	26.0	9.09	1.65
PC/PQ	30/1.80	28.0	10.05	0.85
PC/PQ	30/1.80	30.0	9.92	0.60
PC/PQ	45/2.70	31.2	11.05	1.30
PC/PQ	45/2.70	34.0	11.19	1.45
PC/PQ	45/2.70	36.6	10.59	0.73
PC/PQ	45/2.70	36.6	11.09	1.48

PC = Portland Cement Type I  
BFS = Blast Furnace Slag  
PQ = Type "N" Sodium Silicate

silicate dosed samples did not show as great a dependence of the leachable chromium concentration on the pH as the rest of the mixes. This is indicative of the formation of a chromium species other than the hydroxide in the silicate system because the solubility of the chromium compound versus pH is different than systems without the silicate. The cement/silicate reagent performed better than any of the others. The sodium dithionite gave excellent hexavalent chromium reduction under the alkaline conditions of the test. Time constraints and limited sample precluded optimization of the sodium dithionite dose. It has been postulated that the hexavalent uranium in the uranyl ion is extensively hydrated and therefore does not respond kinetically to chemical reduction as readily as does hexavalent chromium. This fortuitous result is very beneficial to the process since, as mentioned earlier, if it were necessary to reduce all of the uranium this would consume vast amounts of reducing agent. This would result in a very expensive process. The sample dosed with cement only and no dithionite failed the MTCLP for leachable chromium.

#### Design Mix TCLP

A sample prepared to design mix specifications was cured three days and submitted to the IT laboratory for TCLP extraction and chromium analysis. The results showed that the sample passed, exhibiting a TCLP extract chromium concentration of 0.890 ppm.

#### Compressive Strength Development

The design mix exhibited an average unconfined compressive strength of 158 psi after 3 days curing. The screening mix did not develop as high a strength as some of the other

screening mixes using the reagents that failed MTCLP but it was considered more than adequate. The data ranged from a low of 27.2 psi for Portland cement and dithionite to a high of 673 psi for cement/blast furnace blend.

It should be noted that, given the nature of cement/silicate systems, the compressive strength will increase with increasing cure time. The short cure time given in this project was chosen in the interest of saving time.

#### Waste Handling

All failing samples plus the 200 grams of greater than 3/8 inch material were combined into one batch, ground to less than 3/8 inch then stabilized with the design process. This material passed the MTCLP for chromium and was returned to the client for disposal.

### CONCLUSIONS AND RECOMMENDATIONS

#### Optimum Design Mix

Using the following process, calcined uranyl nitrate can be treated and stabilized to pass TCLP leachate criteria, and subsequently disposed of in a radioactive waste disposal facility: Portland cement/sodium silicate at a dose rate of 20 pounds of cement, 10 pounds of sodium dithionite, and 21.2 pounds of a 6 percent w/w aqueous solution of PQ Type "N" sodium silicate solution is mixed with 100 pounds of waste. The cement used was Type 1 Portland cement obtained from the Dundee Cement Company. This is the recommended type of cement. However, if a different source of cement is used, IT recommends that its performance be confirmed by a small laboratory batch. The dry stabilization reagents were blended first, then the water/sodium silicate solution was added.

**Reducing Agent**

The only reducing agent examined was sodium dithionite, also called sodium sulfoxylate (sometimes misnamed sodium hydrosulfite). The choice of this reagent was based on IT's prior knowledge and experience. It is a powerful reducing agent under alkaline conditions but not strong enough to reduce the hexavalent uranium under the conditions of the test. It may be that under aqueous alkaline conditions the uranium is precipitated so that not enough uranium ions are available to interact effectively with the reducing agent.

The dose was not optimized but was determined by a simple titration of a sample with dithionite solution. It may be cost effective to optimize the reducing agent dose as soon as more sample is available. This can easily be done in the laboratory. Sodium dithionite is available from the Hoechst Celanese Corp. in Kalama, Washington as a solution and from their plant in Bucks, Alabama as a powder.

The Portland cement/dithionite samples without the sodium silicate failed the TCLP criteria while those with the sodium silicate passed.

The laboratory mixer performed adequately. Insufficient sample remained after the screening tests to provide an adequate charge for the 5 gallon change-can mixer. IT recommended a mixer that is specially designed for five gallon pails. IT also recommends that the mixing be done within the existing five gallon containers and that it be done *immediately after* the addition of the water. No exact set time was evidenced during the penetrometer testing. If there is one, it occurs sometime between mixing and 24 hours later. After 24 hours cure the performance sample registered greater than 4.5 t/ft<sup>2</sup> penetrometer compressive strength in nearly all cases.

**Performance TCLP**

A sample prepared to design mix specifications was cured three days then submitted to the IT St. Louis laboratory for TCLP extraction and chromium extract analysis. The results showed that the sample's TCLP extract chromium concentration was well below the TCLP limit for chromium of 5.0 ppm. The sample showed 0.89 ppm leachable chromium. Patent disclosure documents submitted earlier for this process are currently under review by DOE.