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STABILIZATION OF MERCURY IN HIGH pH TANK SLUDGES

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ABSTRACT

The DOE complex contains many tank sludges contaminated with mercury. The high pH of these tank sludges typically fails to stabilize the mercury, resulting in these radioactive wastes also being characteristically hazardous or mixed waste. The traditional treatment for soluble inorganic mercury species is precipitation as insoluble mercuric sulfide. Sulfide treatment and a commercial mercury-stabilizing product were tested on surrogate sludges at various alkaline pH values. Neither the sulfide nor the commercial product stabilized the mercury sufficiently at the high pH of the tank sludges to pass the Toxicity Characteristic Leach Procedure (TCLP) treatment standards of the Resource Conservation and Recovery Act (RCRA). The commercial product also failed to stabilize the mercury in samples of the actual tank sludges.

Tank sludge samples were sequentially extracted with deionized water, a weak hydrochloric acid solution (pH of 2), a 1 *N* potassium hydroxide solution, a 12 *N* nitric acid solution, and aqua regia. Only insoluble species such as mercuric sulfide typically survive to the aqua regia step. Surprisingly, significant amounts of mercury were extracted from the tank sludge at each step. One possible explanation is a distribution of various mercury compounds, soluble in different extractants. Such a suite of compounds is not expected for these sludges, especially a relatively insoluble specie(s) only extracted by aqua regia. Another possible explanation is that significant amounts, if not most, of the mercury is bound in the undissolved sludge solids and this mercury is released as more of this matrix is dissolved at each step of the sequential extraction.

Only soluble inorganic mercury compounds or elemental mercury were disposed into these tank wastes based on process knowledge, not mercuric sulfide. In addition, soluble sulfides were not disposed into the tanks, although significant amounts of sulfates do exist in the tank waste. Thermodynamic evaluation indicates that mercuric oxide is the equilibrium specie at the tank waste conditions. Mercuric oxide has a small, but significant solubility at the tank pH. The mercuric oxide distributes between mercuric hydroxide in solution and solid mercuric oxide. It is surmised that the undissolved mercuric oxide becomes bound, perhaps co-precipitated, with other different undissolved species. Some clay is known to be in the tank wastes, which may even be resistant to the aqua regia. Perhaps, mercury bound to these clays is not released until extracted by aqua regia.

INTRODUCTION

Mercury is a toxic substance that can accumulate over time to toxic levels in the body. For these reasons, the Resource Conservation and Recovery Act (RCRA) regulates disposition and/or land disposal of mercury. The best demonstrated available technology for RCRA metals is stabilization/solidification (S/S) at a high pH of 10±1. Traditionally, mercury has been one of the more difficult contaminants to stabilize in hazardous or mixed waste. High pH does not directly stabilize either elemental mercury or mercury salts, and high-temperature techniques, such as incineration or vitrification, volatilize the mercury.

Unlike the case for many of the RCRA metals, high pH does not reduce mercury solubility to the characteristic limits for RCRA waste, much less the low levels required for land disposal. Figure 1 illustrates the estimated mercury solubility as a function of pH using the published solubility data for HgO in aqueous solutions of various acids and bases. (1) Distribution into a solid matrix, precipitated or cementitious, lowers the mercury concentration below the level of aqueous solubility illustrated in Figure 1, as it does for other RCRA metals; however, the mercury concentration at equilibrium still approaches the levels in Figure 1, which are well above regulatory limits. Thus, significant amounts of mercury remain soluble in the many tank wastes at high pH within the U.S. Department of Energy (DOE) complex. This paper reports on laboratory studies of mercury stabilization at high pH using a commercially available proprietary reagent (ThioRed®) and sulfide precipitation (the traditional treatment for wastewater contaminated with dissolved mercury).

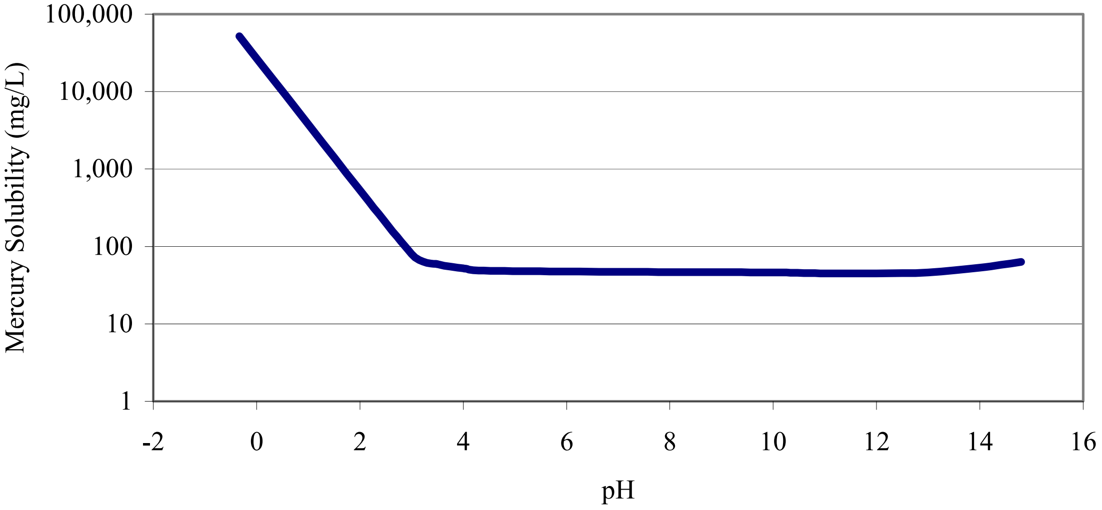

Figure 1. Mercuric oxide solubility as a function of pH (from the data of reference 1)

STABILIZATION STUDIES OF ACTUAL TANK SLUDGE SAMPLES

DOE awarded a contract to treat Melton Valley Storage Tank (MVST) waste for storage and disposal. The vendor's proposed baseline process consists of:

(1) Separating the supernate from the sludge,
(2) Washing the sludge with water and adding this wash water to the supernate,
(3) Adding stabilizing agents to the supernate/wash water and/or the washed sludge, if projected to fail RCRA TCLP criteria, and
(4) Solidifying both the washed sludge and supernate/wash water by vacuum evaporation.

In addition, the vendor's strategy includes gaining regulatory agreement that the sludge will not be considered waste until after the above treatment. In this case, the waste would not be hazardous, if it meets the characteristic limits established by RCRA. Thus, the regulatory drivers assumed for this study were the characteristic limits in the TCLP extract on the dried sludge after the above vendor processing. In other words, if the treatment is successful and regulatory approval is obtained, the waste would never have been considered hazardous waste by regulatory definition.

The 'Optimum' treatment consisted of adding a specified quantity of two stabilizers — ThioRed® and soil polymer — and the 'Alternate' treatment increased the amount of ThioRed® added.

Two surrogate and seven actual tank wastes were processed in the laboratory using the vendor's process. The results of this evaluation were submitted in a letter report at the end of FY01. (2) All of the surrogate work and the initial work with actual tank sludge were based on an existing sludge sample from Tank W23. One surrogate was required to be based on a surrogate previously developed to mimic the weighted average chemical composition of the MVST-BVEST using a simple mix of reagent grade chemicals and water, called the "quick and dirty" surrogate (QnD). The composition of the prior surrogate was adjusted toward the measured composition of the W23 sample. The other surrogate was prepared to be more representative of the W23 sludge sample. This was done by precipitation of a nitrate solution at high pH, separating the solution from the solids, measuring the composition of the wet solids, and adding reagent grade chemicals to closely mimic the measured composition of the W23 sample.

Without any treatment, both surrogate sludges failed toxicity characteristic TCLP limits for mercury, chromium, and lead. Using the 'Optimum' treatment, both rinsed tank sludge surrogates were stabilized and passed TCLP characteristic limits. The wash/rinse from the simple surrogate of reagent grade chemicals and water passed TCLP after 'Optimum' treatment. However, the wash/rinse from a more representative surrogate gave mixed results; failing TCLP for mercury after both an 'Optimum' and an 'Alternative' treatment in the first triplicate set, but passing after either treatment in a repeat triplicate set. Both surrogates (sludge and wash/rinse) failed to pass Universal Treatment Standard (UTS) limits after both 'Optimum' and 'Alternative' treatments, implying that these treatments will not be satisfactory if the sludge is declared hazardous waste per RCRA. The surrogate results are summarized in Table I.

Table I. RCRA pass/failures of the surrogates after treatment.

	After Washing	**Dried Waste (no additives)**	**Optimum Treatment**	**Alternative Treatment**
QnD Sludge	**Fail**	**Not Tested**	**Pass**	**Pass**
QnD Washwater	**Fail**	**Not Tested**	**Pass**	**Pass**
W23S Sludge	**Fail**	**Fail**	**Pass**	**Pass**
W23S Washwater	**Fail**	**Not Tested**	**1. Fail** **2. Pass**	**1. Fail** **2. Pass**

Sludge samples were taken from six tanks: W24, W25, W26, W27, W28, and W31. These samples were characterized then made available for the treatment studies of this project. Sludge samples from Bethel Valley Evaporator Storage Tank (BVEST) W23 and the MVST tank farm were analyzed and subjected to the 'Optimum' stabilization process. Three sludge samples from MVST that could pass a TCLP test after being washed with water also passed after drying without stabilizer addition. These three washed, dried tank sludge samples could also now meet UTS criteria (the washed sludge had previously failed UTS). MVST samples from W26 and W27 failed TCLP RCRA characteristic and UTS criteria for mercury both before and after treatment. W23 sludge passed both criteria after 'optimum' treatment. All TCLP/stabilization tests on sludges were performed in triplicate to ensure accuracy. Prior to laboratory processing of sludge sample washwater, the Optimum process was modified to eliminate partial evaporation to 50 wt % solids prior to adding the stabilizers, because salt crystals were observed to form during partial evaporation of surrogate sludge washwater and stabilizer addition was desired before precipitating any salts via evaporation. The 'Modified' Optimum Treatment process failed to stabilize mercury in the supernate/rinses from W26, W27, and W28 MVST sludges. A simple drying process (without chemical stabilizer addition) was applied to the rinses from W24 and W25 MVST tank sludges per the vendor's process; both supernates/rinses failed in cadmium, while W25 additionally failed in chromium**.** The proposed treatment does not appear to consistently make the treated tank sludge or its surrogate non-hazardous by RCRA TCLP definition. Table II summarizes these results for the actual tank sludge samples.

Table II. RCRA pass/failures of the actual sludge samples after treatment

MVST Tank	**After Washing**		**After Drying**	
	Sludge	**Washwater**	**Sludge**	**Washwater**
W-23	**Pass**	**Pass**	**Pass**	**Pass**
W-24	**Pass**	**Fail**	**Pass**	**Fail**
W-25	**Fail**	**Fail**	**Pass**	**Fail**
W-26	**Fail**	**Fail**	**Fail**	**Fail**
W-27	**Fail**	**Fail**	**Fail**	**Fail**
W-28	**Pass**	**Fail**	**Pass**	**Fail**
W-31	**Fail**	**Fail**	**Not Tested**	**Not Tested**

The treatment results for the actual MVST sludge samples are summarized below:

1. Sludge samples taken from MVST W24, W25, W28 passed TCLP criteria after washing, but not those from W26, W27, and W31.
2. Sludge samples taken from MVST W26 and W27 failed the TCLP criterion for mercury after 'Optimum' treatment. The average and standard deviation of three TCLP extract mercury concentrations were 0.30 ± 0.20 and 0.52 ± 0.22 mg/L for each tank, respectively.
3. Other critical RCRA metals in the MVST sludge samples were stabilized adequately in the 'Optimum' sludge treatment.
4. Examination of the mercury mass balances from the MVST tanks indicates that the rinsing process removes only a small portion of the sludge mercury (between 5 and 10%) from the sludge samples. Characterization has shown that the samples taken from MVST tanks W26 and W27 contain substantially higher mercury levels than samples taken from other tanks. Subsequently, enough mercury extracts from these samples during TCLP testing to fail and the 'Optimum' treatment process failed to adequately stabilize the mercury enough to prevent TCLP failure.

5. The rinse cadmium concentration for the MVST W24 sludge sample exceeded the RCRA limit for wastewater. The sample was subjected to evaporation without stabilizer addition per the process. This test indicates that the trigger of when to add stabilizer failed to anticipate that evaporation alone was not sufficient to treat the sample from Tank W24 because enough cadmium washed out of the sludge to require stabilization.
6. Rinses from the MVST W25 sample failed for both cadmium and chromium. The sample was subjected to evaporation without stabilizer addition. This test also indicates that evaporation alone is not sufficient to treat waste samples, this time from Tank W25.
7. Rinses from MVST W26, W27, and W28 sludge samples exceeded the RCRA mercury concentration limit for wastewater. All three samples were subjected to the full 'Modified Optimum' process, with stabilizer addition.
8. Mercury was partially stabilized and chromium was not stabilized for treated rinse water.
9. The mix of rinse water and supernate is expected to have a higher toxicity than the rinse water alone and, hence, is expected to exacerbate the problems experienced in treating these rinse water samples to meet RCRA criteria.
10. Durability tests with stabilized surrogate sludge samples, using freeze-thaw thermal cycling and long-term storage under ambient East Tennessee conditions, have indicated that the final waste form does not accumulate any substantial free water and continued to pass TCLP testing after a period of at least 9 months.

In conclusion:

1. The proposed 'Optimum' process fails to provide a robust method for removing the RCRA hazardous characteristic from the range of sludge composition that can be expected.
2. The proposed 'Modified Optimum' process fails to provide a robust method for removing the RCRA hazardous characteristic from the range of MVST sludge-rinse compositions that can be expected.
3. Mixing these tank sludges to the extent possible will help achieve a more uniform feed, but only evens out composition and does not guarantee that the treated waste will meet RCRA criteria based on the observed performance of the stabilizing agent with samples of this sludge
4. Surrogate work indicates that the 'Alternative' process will afford no substantial improvement. No actual tests, however, using the 'Alternative' process were performed on tank samples or tank sludge rinses in this study.

Based on limited surrogate testing, the stabilized sludge will apparently remain stabilized, if not characteristically hazardous after treatment; and not begin hygroscopically accumulating free water on the dried salts during storage at Oak Ridge after treatment and prior to disposal, even if stored in vented TRU containers.

EFFECTIVENESS OF THIORED® AND SULFIDE STABILIZATION AT HIGH pH

In lieu of the failure of ThioRed® to adequately stabilize mercury in the tank sludge samples, the ability of ThioRed® and Na_2S to stabilize a solution of mercuric chloride was studied. According to the ThioRed® vendor, the amount added must be closely matched with the mercury concentration with <10% excess used. This is likely related to mercury solubility passing through a minimum with increasing sulfide concentration, similar to that observed for metal solubility with pH. Just as in the complex metal oxyanions formed at high pH, excess sulfide anions lead to the formation of complex mercury-sulfide anions and increasing mercury solubility with increasing sulfide concentration.

Figure 2 illustrates the effect on the dissolved mercury concentration of adding ThioRed® or sulfide to a solution of mercuric chloride, with no attempt to control solution pH. The fourth point at about 10 % (vol/vol x 100, stabilizer/treated mercury solution) represents the recommended treatment level and is at the minimum mercury concentration for the sulfide addition. The mercury concentration increases then decreases with ThioRed® addition, but recovered at much higher levels. Obviously, matching the additive to the actual mercury concentration is desired both for effective stabilization and economy. Performance of the sulfide was much more variable, but appears much worse than the ThioRed®, decreasing to a minimum mercury concentration of about 5 ppm, and then increasing. Meanwhile the mercury concentration increased to about 55 ppm for a ThioRed® addition at twice the maximum recommended, but decreased back to values approaching 2 ppm with further additions.

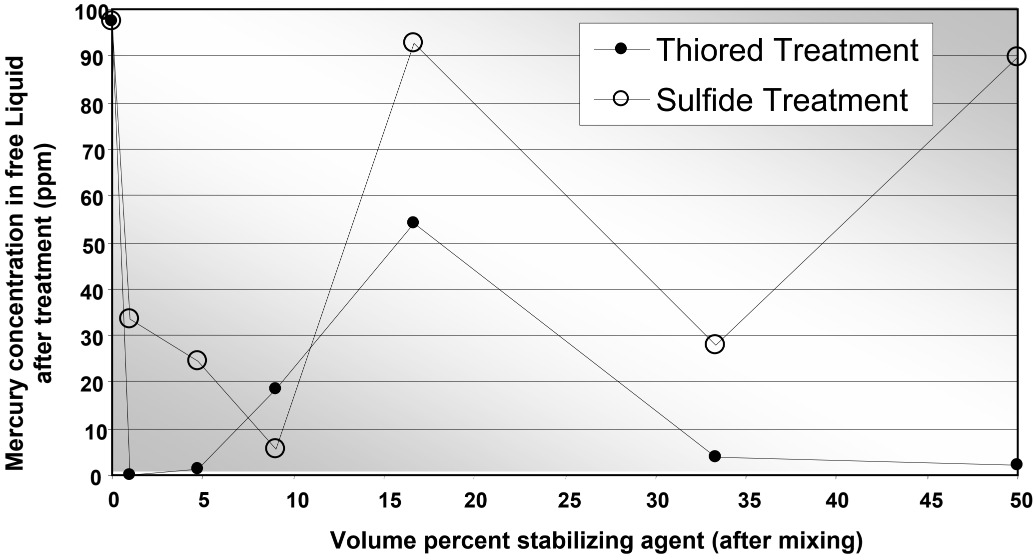

Figure 2. Mercury stabilization with the addition of ThioRed® and sulfide

The pH of these solutions was monitored, but no attempt was made at control. The ThioRed® solution is at a high pH, so the pH increases with addition. The sulfide addition starts at a much lower pH, and is slightly acidic until the third addition. After the third addition, the pH became increasingly basic, approaching the high pH for the ThioRed®. This is also the point at which stabilization appears highly erratic for this data. Perhaps these results are indicative of the problems experienced in stabilizing the high pH sludge samples, but the data are not conclusive at this point and the ThioRed® data is not as erratic as the sulfide data. It is possible that excess sulfide leads to some mercury reduction and confusion in the mercury data, but no definitive data supports this speculation.

Next the pH of a mercuric chloride solution was adjusted and the mercury stabilized was measured with and without the addition of ThioRed® or sulfide. Figure 3 illustrates the mercury stabilized with pH, with and without these stabilizers. As expected, high pH was not effective at stabilizing the mercury, but the stabilizers were surprisingly ineffective for the mercury solution adjusted to high pH. These results are in agreement with the results obtained for the actual sludge samples.

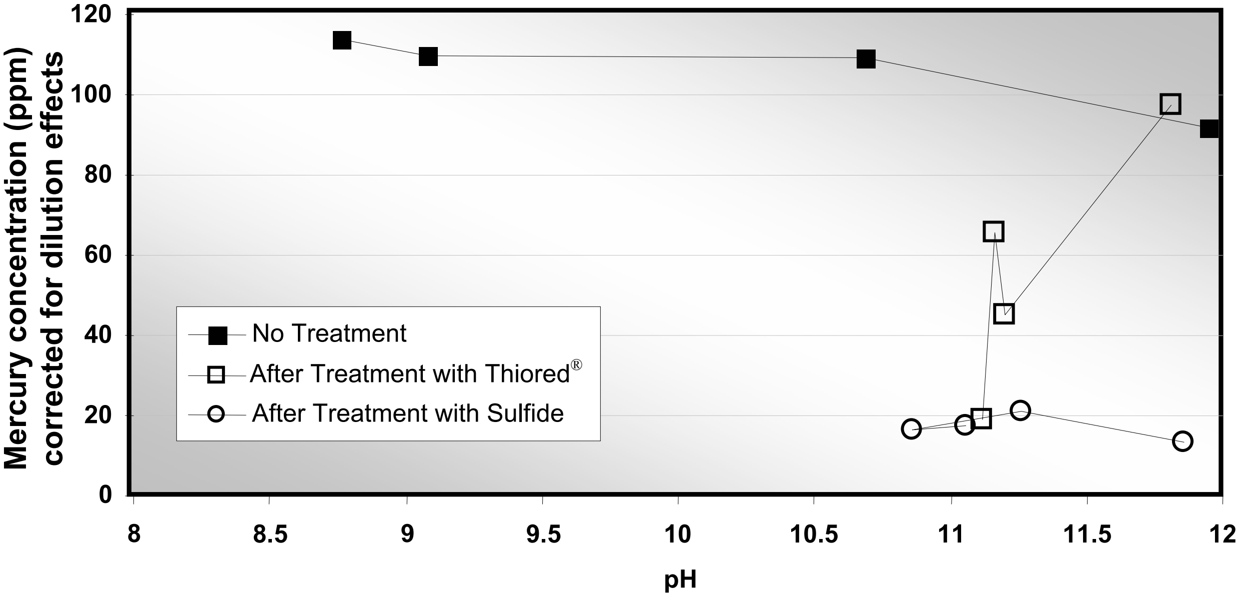

Figure 3. Effect of pH on mercury stabilization with and without stabilizing agents

STUDIES OF MERCURY SPECIATION IN THE TANK SLUDGE

Thermodynamics predicts that the equilibrium species of mercury, chromium, and cadmium are dissolved hydroxides and precipitated hydrated oxides for the MVST tank chemistry. It is not known if these RCRA metals are in equilibrium in the tank waste or if the waste chemistry has been completely characterized. Even the relatively insoluble sulfides would convert into soluble sulfate under oxidizing conditions and result in the same solubility as the nitrate or oxide at equilibrium.

The actual sludge samples were subjected to a sequential extraction procedure previously developed for mercury in mine tailings. (3) This procedure uses extract solutions in the following sequence: deionized water (DI), hydrochloric acid at a pH of 2 (HCl pH = 2), 1 *N* KOH, 12 *N* HNO_3, and aqua regia. The technique was originally benchmarked using pure mercury species in kaolin, with the general results reported in Table III. (3) Table IV lists the sequential extraction results for two actual sludge samples and benchmarking results for pure compounds from a matrix that simulates tank sludge.

Table III. Sequential extraction benchmark summary for kaolin matrix (Ref. 3)

Extractant	**Description**	**Typical Compounds**
DI water	water soluble	$HgCl_2$, $HgSO_4$
pH 2 HCl/HOAc	"stomach acid"	HgO
1*N* KOH	organo complexed	Hg-humics, Hg_2Cl_2
12*N* HNO3	strong complexed	mineral lattice, Hg_2Cl_2, Hg^o
aqua regia	cinnabar	HgS, m-HgS, HgSe, HgAu

Table IV. Results for the sequential extraction procedure

Contaminant	**Contaminant Extracted (wt %)**				
	Deionized Water	**HCl pH=2**	**1*N* KOH**	**12*N* HNO_3**	**Aqua Regia**
Benchmark Results (Surrogate Matrix)					
Sodium dichromate, cadmium nitrate, and mercuric nitrate					
Hg	1.2	74.0	0.3	0.1	
Cd	55.9	35.8	0.3	2.3	
Cr	69.4	15.7	5.9	0.0	
Elemental mercury, chromium trioxide, and cadmium oxide					
Hg	6.6	1.4	0.6	0.0	
Cd	0.9	64.0	0.3	0.1	
Cr	50.5	30.0	0.3	2.1	
Mercuric sulfide and cadmium sulfide					
Hg	0.0	0.0	0.0	0.1	73.6
Cd	0.0	0.5	0.2	86.0	0.1
Actual Sludge Samples					
W25					
Hg	2.1	0.7	2.7	31.2	63.3
Cd	9.4	75.4	0.4	14.2	0.5
Cr	24.4	1.0	2.0	68.6	4.0
W27					
Hg	6.9	0.9	3.5	37.8	51.0
Cd	4.4	6.4	4.8	80.0	4.6
Cr	12.9	0.9	5.8	77.8	2.7

Prior benchmarking of the sequential extraction indicates about 25 and 75 wt % of mercuric oxide extracts into the water wash and hydrochloric acid (pH = 2), respectively. (3) However, relatively little mercury was extracted by these two extractants for either the W25 or W27 samples, implying the bulk of the mercury in these two samples was not the oxide. For the sludge samples, 28-48 and 44-63 wt % were extracted by the 12 *N* nitric acid and aqua regia, respectively. Survival of this much mercury for the aqua regia extraction was unexpected. Only mercuric sulfide and some mercury-metal amalgams survived for aqua regia extraction in prior testing. In the current benchmarking, the mercuric nitrate and mercuric sulfide extracted into the pH 2 hydrochloric acid and aqua regia, respectively. This implies the mercury is present as mercuric sulfide, which was unexpected.

Mercuric sulfide would not be expected to thermally desorb from the sample at 260ºC as was previously observed for these samples. Table V lists the thermal properties reported in the literature for pure mercury and mercury compounds. (4) Based on Table V, the mercury species expected in this sludge from thermodynamic evaluation, HgO, would not decompose or vaporize (i.e., desorb) at temperatures as low as 260ºC. Several species would desorb ≤260ºC, but Hg^o and $Hg(NO_3)_2$ appear the most likely species based on the background sludge matrix and process history. For the current studies, 2-45, 80-93, and 99 wt % desorbed from the sludge samples at 105, 200, and 300ºC, respectively, confirming the earlier result (see Table VI). Less than 10 and 50 wt % of mercuric oxide and mercuric nitrate desorbed during benchmark testing over this same temperature range (see Table VI).

Desorption of elemental mercury gave results similar to those for the sludge samples; implying elemental mercury was present in the tank waste. During the current benchmark testing, only 6-16 wt % of elemental mercury extracted during sequential extraction and most in the first step with just water. Prior testing indicated that elemental mercury should mainly extract in the strong nitric acid step. The sludge simulant may have made the elemental mercury slightly more soluble than the kaolin used in the prior testing, but the low recovery of the mercury added indicates a problem with the technique for this benchmark. Possibly the mercury vaporized during the subsequent separation and handling steps, but only further refinement for this benchmark can resolve this discrepancy. None of these results are definitive for speciation. The best interpretation may be that the sludge mercury is mainly elemental. Significant amounts may be bound in a matrix that allows it to survive extraction by strong nitric acid, but not aqua regia, presumably because of matrix destruction.

The sequential extraction of cadmium and chromium was different between the W25 and W27 samples. The cadmium mainly extracted into the dilute hydrochloric acid for W25 (about 75 wt %) and into the strong nitric acid for W27 (about 80 wt %). This implies different cadmium species for these two sludge samples. Cadmium nitrate extracted about equally into water and dilute hydrochloric acid; cadmium oxide extracted into dilute hydrochloric acid; and cadmium sulfide extracted into strong nitric acid. This implies the W25 contains cadmium oxide and W27 contains cadmium sulfide. Since cadmium oxide is the expected species for the observed tank chemistry, the cadmium may be bound in the W27 sludge and required the stronger acid for extraction.

The chromium mainly extracted into the dilute hydrochloric acid for W25 (about 75 wt %) and the strong nitric acid for W27, similar to the cadmium. The sodium dichromate extracted in the water and chromium trioxide extracted into both the water and dilute hydrochloric acid. Chromium (III) is notably more insoluble than chromium (VI) and might be extracted into the strong nitric acid. Thus, W25 could contain soluble chromate, while W27 contains the reduced chromium (III). It is also possible that a matrix is binding chromate to be released into the strong acid. Since cadmium is a cation and chromate is an anion, it is not likely both are bound chemically in the same matrix, although at least one could be bound physically. It seems more likely that cadmium is bound on an ion exchange site of clay or aluminosilicates and reduced chromium (III) accounts for the increased resistance to dissolution for W27.

Table V. Thermal properties of mercury and mercury compounds (Ref. 4)

Compound	Property	Temperature (°C)
Elemental mercury	Melting point (MP)	-39
	Boiling point (BP)	357
	Significant vapor pressure even at room temperature	
	Log p(mm)=7.752-2803/T(°K)	0-1300
Mercurous fluoride	MP (decomposes)	570
Mercurous chloride	Sublimes (decomposes)	383
Mercurous bromide	Sublimes (decomposes)	390
Mercurous iodide	MP	290
	BP (decomposes)	357
Mercurous carbonate	Decomposes into Hg^0, HgO, and CO_2	130
Mercurous sulfate	Decomposes into Hg^0, O_2, and SO_2	Upon heating
Mercurous chlorate	Decomposes into O_2, HgO, and $HgCl_2$	250
	Hot water hydrolyzes into basic salts	
Mercurous iodate	Decomposes	200
Mercuric fluoride	MP (decomposes)	645
	BP	647
Mercuric chloride	Vapor pressure 10 mm	180
	Vapor pressure 100 mm	235
	MP	277
	BP	304
Mercuric bromide	Vapor pressure 10 mm	180
	Vapor pressure 100 mm	238
	MP	241
	BP	319
Mercuric iodideHgI_2	Vapor pressure 10 mm	204
	Vapor pressure 100 mm	252
	MP	257
	BP	354
Mercuric cyanide	Decomposes into mercury and cyanogen	320
Mercuric thiocyanate	Decomposes	165
Mercuric oxide	Decomposes	
	Vapor pressure $2.8x10^{-4}$ mm	20
	Vapor pressure 108 mm	370
	Vapor pressure 760 mm	447
Mercuric sulfide	Decomposes	
	MP @ 120 atm	1450
	Vapor pressure 760 mm	584
Mercuric nitrate	Hemihydrate MP (decomposes)	145
	Decomposes in boiling solution to HgO	
Mercuric sulfate	Decomposes into Hg^0, O_2, SO_2, and SO_3	600
Mercuric chlorate	Decomposes into $HgCl_2$, HgO, and O_2	On warming
Mercuric bromate	Decomposes into Br_2, HgO, and O_2	140
Mercuric iodate	Decomposes into HgI_2 and O_2	175
Organomercury Compounds		
Mercuric acetate	Decomposes	180
Dimethyl mercury	BP	93
Diethyl mercury	BP	159
Dipropyl mercury	Vapor pressure 10 mm	63
	BP	190
Dibutyl mercury	Sublimes	100
	Vapor pressure 7 mm	105
	BP	206
Di(n-pentyl) mercury	Vapor Pressure 10 mm	133
Di(n-hexyl) mercury	Vapor Pressure 10 mm	158
Divinyl mercury	Vapor Pressure 20 mm	60
Diphenyl mercury	Sublimes	122
	Vapor pressure 10 mm	204
Methyl mercury chloride	Sublimes	100
	MP	170
Ethyl mercury chloride	Sublimes	40
	MP	193
Butyl mercury chloride	MP	130
Phenyl mercury chloride	MP	271

Table VI. Testing thermal desorption of mercury

Compound	Vaporized (wt %)
105ºC	
Elemental Hg	7.1
Mercuric nitrate	23.5
Mercuric oxide	0.00
W-25	33.3
W-25 Dup	43.9
W-27	2.21
200ºC	
Elemental Hg	70.5
Mercuric nitrate	42.8
Mercuric oxide	0.00
W-25	86.6
W-25 Dup	80.0
W-27	93.0
300ºC	
Elemental Hg	97.8
Mercuric nitrate	33.0
Mercuric oxide	8.2
W-25	98.9
W-25 Dup	98.9
W-27	99.1

These results are suggestive but not definitive. They suggest that elemental mercury, cadmium oxide, and both chromate and chromium (III) are in the MVST sludge. Other mercury species are also likely present, for example mercuric oxide. It also seems likely a binding matrix is present in part of the sludge that alters the extractability or mobility of some contaminants of concern.

SUMMARY AND CONCLUSIONS

A vendor proposes treating high pH tank waste at ORNL by adding a commercial stabilizing agent for mercury and evaporating the supernate and wet sludge to dryness. Laboratory testing indicated that the commercial mercury stabilizer had problems stabilizing the mercury in this high pH tank waste. Testing with a solution of mercuric chloride confirmed that both this commercial stabilizer and the traditional sulfide precipitation of mercury do not adequately stabilize mercury at the high pH of these tank wastes. Studies of the speciation of the mercury in this tank waste hint that the mercury is not present as mercuric oxide, as expected, but rather may be present as elemental mercury. Elemental mercury is stable; hence, its conversion to the mercuric oxide predicted by thermodynamics may be slow. It is likely the mercury is distributed among two or more species in this tank waste, perhaps even distributed into solids in the sludge and resistant to extraction until this solid matrix is destroyed by a strong acid extractant. Evidently enough of this mercury is extractable from some of the sludge by the weak acid used in TCLP to fail this regulatory test. The high pH salty chemistry of these wastes apparently frustrate efforts to precipitate this mercury using techniques that are usually quite effective at precipitating mercury dissolved in wastewaters. A better understanding of the mercury chemistry in these tank wastes is needed and the vendor's process needs to be changed to ensure that the treated tank waste is not characteristically hazardous.

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