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Evaluation of Concentrations of Hazardous Components to Support Removal of the Tank 48 Thermowell (U)

by

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INTRODUCTION

In support of start-up activities for the In Tank Precipitation (ITP) process, a thermowell is scheduled to be removed from Tank 48. Disposal of the thermowell in the Solid Waste Disposal Facility (SWDF) requires manifesting the quantities of several radioisotopes and, equally important, declaring that the waste package is nonhazardous. Sampling of the waste in the package (i.e., the thermowell) to determine quantities of hazardous materials or to perform a Toxicity Characteristic Leaching Procedure (TCLP) is not prudent or practical. Extremely high dose rates due to contamination of the thermowell preclude any close contact to obtain smear samples, and obtaining a representative sample of the various parts of the thermowell for a TCLP is not feasible.

Alternatively, the TCLP can be simulated using a limited amount of data supplemented with process knowledge. This information can be further developed into a conservative screening tool to provide guidance on declaring whether the waste package is hazardous or not. This report documents the information and calculations of hazardous component concentrations used to support the possible disposal of the Tank 48 thermowell.

SUMMARY

Calculations were performed to evaluate if a thermowell to be removed from Tank 48 will be hazardous due to contamination from waste in that tank. Process knowledge and historical analytical data were used to simulate the TCLP determination for the waste package, using conservative scaling factors relating benzene and mercury to ^{137}Cs. Benzene (as a result of hydrolysis of precipitate during a TCLP) was determined to exceed the hazardous threshold at a lower ^{137}Cs level than for mercury and as such, is the more restrictive hazardous component. In order to declare that the liquid waste from Tank 48 will not cause the package to be hazardous, the ^{137}Cs contamination of the thermowell must be less than 0.072 Ci.

DISCUSSION

Tank 48 is the main processing vessel for the ITP operations, where sodium tetraphenylborate (NaTPB) will be added to HLW salt solutions to decontaminate the solution by removal of soluble ^{137}Cs. Potassium (typically present in the salt solution at about 20 times the ^{137}Cs concentration) and mercury also react with tetraphenylborate (TPB). Potassium and cesium TPB and diphenylmercury are, for practical purposes, insoluble and precipitate from solution. The resulting solids initially float on the liquid surface due to the relatively high density of the salt solution, and eventually settle as the salt solution is diluted during the washing stages of the ITP process.

A full scale demonstration of the ITP process was conducted in 1983 [1] using 427,000 gal of reconstituted salt solution from Tank 24. Sodium tetraphenylborate was added to precipitate the ^{137}Cs in the solution, and the resulting precipitate has remained in Tank 48. Tank histories reflect that, since the demonstration, only nonradioactive process chemicals, water, and, in October 1990, RBOF waste (126,000 gal) have been added to Tank 48 [2].

The hazardous components of concern in Tank 48 are benzene (Bz) and mercury (Hg). Benzene is formed when the TPB precipitate radiolytically and chemically degrades, but benzene has a very small solubility in salt solution. More importantly though, benzene would be generated during the TCLP on waste contaminated with precipitate, due to the hydrolysis caused by the leaching solution (acetic acid). Mercury is present in High Level Waste (HLW) supernate at varying concentrations, and was transferred into the tank in the Tank 24 solution. Mercury reacts with

TPB to form diphenylmercury, which decomposes to some degree upon contact with acetic acid in the TCLP. (Nitrobenzene has been observed during a TCLP of a filter plugged with nonirradiated simulant to evaluate the future disposal of ITP filters [3]. Nitrobenzene is generated by reaction of nitrite with TPB in acidic conditions. The nitrobenzene limit of 2 mg/l was exceeded by a small amount, although there was some uncertainty regarding the quality of the result. For the Tank 48 thermowell, the nitrite concentration and the quantity of solids would be considerably lower than in the conditions of the filter TCLP. The nitrobenzene concentration in the leachate would be much less and is, therefore, not considered to be of concern.)

Method Description

The thermowell in Tank 48 will be contaminated with TPB solids and supernate. Much of the contamination can be removed by spraying with water as the equipment is being drawn out of the tank. Because of the high radiation rate associated with the thermowell, the quantity of waste that remains on the surface (or trapped inside) cannot be determined by conventional measurement techniques. However, the quantity of the slurry can be estimated by taking advantage of the radioactive decay of ^{137}Cs by using the inventory to "trace" other components.

The ^{137}Cs content of the waste package will be obtained by converting field exposure rate readings (the only "sample" information available) to the number of curies of ^{137}Cs. Based on process knowledge of the operations associated with Tank 48, the inventory of components of interest can be estimated. Combined with a knowledge of the chemistry occuring in the tank and in the TCLP, the quantities of hazardous components can be related to the ^{137}Cs concentration in the form of scaling factors. The concentrations of the hazardous components in the leachate from a TCLP are then calculated using the ^{137}Cs content of the waste package and the scaling factors. At the hazardous threshold concentration, the maximum amount of ^{137}Cs that could be included in the package is then calculated.

Component Inventory in Tank 48

The ^{137}Cs inventory in Tank 48 is almost entirely due to the waste transferred into the tank for the full scale demonstration. Approximately 110,000 Ci of ^{137}Cs were transferred from Tank 24 [1]. Transfer of RBOF waste into Tank 48 introduced less than 190 Ci of ^{137}Cs (based on the highest ^{137}Cs concentration of RBOF waste in the past 3 years [4]). The present inventory, after adjusting for decay, is estimated to be 85,000 Ci.

No data were available on the mercury concentration in the salt solution from Tank 24, so the maximum value of 340 mg/l for Tank Farm supernate [5] was assumed. The typical Hg concentration in RBOF waste is <0.001 mg/l [6], so the quantity introduced in 1990 was insignificant. Thus, the mercury inventory in Tank 48 was conservatively estimated to be 550 kg.

During the 1983 demonstration, a total of 36,000 lb of NaTPB was added to Tank 48 [1]. Initial testing with cold chemicals consumed approximately 1,300 lb of the NaTPB, and decontamination of the Tank 24 supernate consumed another 8,800 lb (both forming potassium TPB). After the demonstration, 500 lb of insoluble and 1,300 lb of soluble NaTPB remained in Tank 48. The balance was transferred to Tanks 49 and 50 during the dewatering and washing phases of the demonstration. Recently, run-in testing of the ITP facility has also introduced as much as 14,000 lb of NaTPB [7] into the system. Conservatively assuming that none of the precipitate has decomposed, the inventory of TPB in Tank 48 was estimated to be 24,000 lb (93 wt% of NaTPB is due to the TPB ion).

Evaluation of TCLP Leachate

Benzene

Based on the inventory described above, the ratio of TPB to ^{137}Cs is

$$R_{TPB/Cs} = \left(\frac{24{,}000 \text{ lb}}{85{,}000 \text{ Ci}}\right) = 0.28 \frac{\text{lb TPB}}{\text{Ci}} \quad (1)$$

As indicated above, this conservatively assumes that all TPB is still present (i.e., has not decomposed) and takes into account decay of ^{137}Cs.

Tetraphenylborate compounds, when contacted with the acetic acid specified in the TCLP [8], hydrolyze releasing benzene according to the reaction [9]

$$\Psi(C_6H_5)_4B + CH_3COOH + 2H_2O \text{ --> } 3C_6H_6 + C_6H_5B(OH)_2 + \Psi OOCCH_3$$

where Ψ represents either sodium, potassium or cesium. The stoichiometry reflects that 3 moles of benzene are released for every mole of TPB reacted. In mass terms, 234 gm of benzene are produced for every 319 gm of TPB reacted. Combining this ratio with Eqn. (1) and converting units results in a ratio of

$$R_{Bz/Cs} = \left(\frac{234 \text{ gm Bz}}{319 \text{ gm TPB}}\right)\left(\frac{24{,}000 \text{ lb}}{85{,}000 \text{ Ci}}\right)\left(\frac{454 \text{ gm}}{\text{lb}}\right) = 94 \frac{\text{gm Bz}}{\text{Ci}} \quad (2)$$

This conservatively implies that all of the TPB in the TCLP sample will react within the time frame allowed for the TCLP (18±2 hrs).

The regulatory limit for benzene is 0.5 mg/l in the leachate, as derived from a 25 gm representative sample contacted with 500 ml of the leaching solution. The amount of benzene in the leachate solution at the TCLP limit is calculated using Eqn. (3).

$$Bz_{TCLP} = \left(0.5 \frac{\text{mg}}{\text{l}}\right)(500 \text{ ml})\left(\frac{1 \text{ l(iter)}}{1000 \text{ ml}}\right) = 0.25 \text{ mg Bz} \quad (3)$$

The amount of ^{137}Cs that would be present in the leachate with the 0.25 mg of benzene is

$$Cs_{TCLP} = \left(\frac{0.25 \text{ mg Bz}}{94 \frac{\text{gm Bz}}{\text{Ci}}}\right)\left(\frac{1 \text{ gm}}{1000 \text{ mg}}\right) = 2.7 * 10^{-6} \text{ Ci} \quad (4)$$

The thermowell to be removed from Tank 48 weighs approximately 1470 lb [10]. The mass of any precipitate slurry trapped on or in the thermowell will be small and can be neglected. The maximum amount of ^{137}Cs that can contaminate the thermowell without the benzene limit being exceeded is

$$Cs_{max,Bz} = \left(\frac{2.7*10^{-6}\ Ci}{25\ gm}\right)(1470\ lb)\left(\frac{454\ gm}{lb}\right) = 0.072\ Ci \qquad (5)$$

Therefore, if the ^{137}Cs content (based on radiation exposure measurements) of the waste package is less than 0.072 Ci, the benzene concentration in the leachate from a TCLP would be less than the regulatory limit of 0.5 mg/l, and the waste package will be nonhazardous with respect to benzene.

Mercury

The mercury inventory in Tank 48 was conservatively estimated to be 550 kg, so the ratio of Hg to ^{137}Cs is

$$R_{Hg/Cs} = \left(\frac{550\ kg}{85{,}000\ Ci}\right)\left(\frac{1000\ gm}{kg}\right) = 6.5\ \frac{gm\ Hg}{Ci} \qquad (6)$$

Mercury reacts with TPB to produce insoluble diphenylmercury, essentially removing all of the mercury from solution. Diphenylmercury reacts to a limited extent with the acetic acid solution used in the TCLP; however, all of the diphenylmercury that would be in the TCLP sample was conservatively assumed to react completely. At the regulatory limit of 0.2 mg/l, the amount of mercury that would be in the leachate from a TCLP sample is

$$Hg_{TCLP} = \frac{\left(0.2\ \frac{mg}{l}\right)(100\ gm * 20)\left(\frac{1\ l(iter)}{1000\ ml}\right)}{1.0\ \frac{gm}{ml}} = 0.4\ mg\ Hg \qquad (7)$$

(Note that a different sample size and execution of the TCLP are used for Hg than for benzene, due to the latter's volatility. The sample size is 100 gm, and the mass of leaching solution is 20 times the mass of the sample.)

The quantity of ^{137}Cs that would be in the TCLP sample was calculated using Eqn. (8).

$$Cs_{TCLP} = \left(\frac{0.4\ mg\ Hg}{6.5\ \frac{gm\ Hg}{Ci}}\right)\left(\frac{1\ gm}{1000\ mg}\right) = 6.2*10^{-5}\ Ci \qquad (8)$$

Finally, the maximum amount of ^{137}Cs that can contaminate the thermowell without the mercury limit being exceeded is

$$Cs_{max,Hg} = \left(\frac{6.2*10^{-5}\ Ci}{100\ gm}\right)(1470\ lb)\left(\frac{454\ gm}{lb}\right) = 0.41\ Ci \qquad (9)$$

Therefore, if the ^{137}Cs content in the thermowell waste package is less than 0.41 Ci, the Hg concentration in the leachate from a TCLP would be less than the regulatory limit of 0.2 mg/l, and the package will be nonhazardous with respect to mercury.

Field Implementation

Comparison of the results of the previous section indicate that benzene will cause the thermowell waste package to exceed the hazardous limit at a considerably lower ^{137}Cs loading than for mercury. The TPB solids included with 0.072 Ci of ^{137}Cs will force the benzene to exceed the 0.5 mg/l regulatory limit, while mercury at the same ^{137}Cs level is only 18% of the 0.2 mg/l TCLP threshold. Thus, benzene is the more restrictive component. In order to declare that the liquid waste from Tank 48 will not cause the package to be hazardous, the ^{137}Cs contamination of the thermowell must be less than 0.072 Ci.

ACTIONS

None

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