

DECONTAMINATION OF A BENZENE WASTE STREAM CONTAINING Cs-137 AND DIPHENYLMERCURY

Jane P. Bibler
Westinghouse Savannah River Company
Savannah River Laboratory
Aiken, SC 29808

J. Paul Deininger
Analytical Development Corporation
44053 North Chestnut Street
Colorado Springs, Colorado 80907

ABSTRACT

A secondary waste stream from the Defense Waste Processing Facility at the Savannah River Site will contain benzene and entrained higher boiling organic derivatives of benzene, Cs-137, and diphenylmercury. This stream constitutes a mixed waste that will have to be decontaminated before disposal. Removal of both diphenylmercury and Cs-137 represents the optimum decontamination of the mixture.

Decontamination studies have been conducted on this organic product waste stream to remove both Cs-137 and diphenylmercury. Cesium can be effectively removed by conventional ion exchange techniques using zeolite as the ion exchange medium. It can also be extracted from the benzene phase by washing with water or dilute caustic solution. Diphenylmercury is much more difficult to separate from the benzene. Treatment of the benzene waste with Tru Clear™, a stabilized ferrate (FeO_4^{2-}) system in dilute KOH, allowed extraction of nearly all of the cesium ion and 1-2% of dissolved mercury into an aqueous phase where they can be more easily managed.

INTRODUCTION

At the Savannah River Site (SRS), sodium tetraphenylborate (TPB) is used to precipitate cesium ion from a high level waste supernate prior to the vitrification process in the Defense Waste Processing Facility (DWPF). (1) The precipitate, including mercury precipitated as diphenylmercury on addition of TPB, is hydrolyzed with formic acid to remove 90% or more of the organic material before the cesium stream is sent to the glass melter. This is done to reduce the burden on the melter offgas system caused by the presence of large amounts of organics and to prevent reduction of metals in the glass melt. An end product of the acid hydrolysis of tetraphenylborate precipitates will be the Recovered Organic Process Stream, a condensed stream of benzene. Dissolved in the benzene will be entrained impurities of diphenylmercury (approximately 90 ppm Hg), Cs-137 (approximately 0.5 nCi/mL), and high-boiling organics. The eventual fate of this waste stream is to be incineration when a permitted site incinerator is online.

The incinerator will not be ready in time to process the first batches of Recovered Organic Process Stream, meaning that SRS will have an inventory of mixed waste that will require alternative disposal. Management of the stream until the incinerator is ready will require decontamination of the waste before any disposal. If only cesium is removed, the benzene is still a hazardous waste, though no longer a mixed waste, and could then be transported offsite and incinerated in a permitted facility. Removal of both cesium and diphenylmercury would greatly simplify disposal, but

diphenylmercury is very difficult to separate from benzene due to its solubility.

A novel use of Linde™ IE-96 zeolite ion exchange has been demonstrated effective in removing most of the Cs-137 from the Recovered Organic Process Stream with no interference from dissolved organics. Another method of Cs decontamination involved washing the waste with water or 3% KOH solution, a process which extracted Cs-137 efficiently into the aqueous phase. Attacking diphenylmercury by rapid mixing with Tru Clear™, a very reactive ferrate material, in 3% KOH solution had a net effect of extracting nearly all of the Cs-137 and a fraction of the diphenylmercury into the aqueous phase.

DISCUSSION

The Recovered Organic Process Waste Stream

A sample of Recovered Organic Process Stream waste was obtained from the SRS Precipitate Hydrolysis Experimental Facility. This material did not initially contain any Cs-137 or diphenylmercury. Both were added at the Savannah River Laboratory after receipt of the waste. Cs-137 was added as an aqueous CsNO_3 solution (300 and 600 $\mu\text{L/L}$ benzene waste in feeds #1 and #2, respectively) followed by stirring to ensure good mixing. An analysis of the composition of two complete samples treated in these studies is given in Table I.

TABLE I

Analyses of the Recovered Organic Product
Process Stream
 $\mu\text{g/mL}$ benzene^a

Component	Feed #1	Feed #2
Formanilide	18	18
Phenol	9,388	9,388
Aniline	1,237	1,237
4-phenylphenol	40	40
2-phenylphenol	261	261
diphenylamine	15,166	15,166
biphenyl	65,318	65,318
o-terphenyl	140	140
m-terphenyl	101	101
p-terphenyl	175	175
diphenylmercury	250	250
Cs-137 ^b	8.0 E-4	1.2 E-2

a Determined by high performance liquid chromatography (HPLC).

b Determined by gamma counting from 655.2-667.7 KEV. Units are $\mu\text{Ci/mL}$ benzene solution.

Cs-137 Decontamination Using Linde™ IE-96 Zeolite

Zeolites are commonly used (2) to remove cesium ion from aqueous solutions. Since it was suspected that contaminant Cs-137 in the Recovered Organic Process Stream might be associated with very small entrained amounts of water, the first attempt at effecting Cs⁺ decontamination utilized treatment of the organic stream on an inorganic sorbant, Linde™ IE-96 zeolite.

The benzene solution, maintained at 35°C in a water bath, was processed through an 18 mL column of zeolite in a downflow mode at a flow rate of 180 mL/hr (10 column volumes/hr). The linear flow rate through the column was 0.9 gpm/ft². Samples of effluent from the column were collected in 180 mL fractions. These were analyzed by gamma counting and by HPLC. The results of gamma counting for Cs-137 are given in Table II. Analyses of the dissolved organic components are not tabulated but showed no change in their respective concentrations in the effluent relative to the feed. The zeolite did not retain organic molecules or diphenylmercury but it did sorb cesium ion.

The desired decontamination limit for Cs-137 was 1.0 E + 3 d/m/mL (disintegrations per minute per milliliter) in the treated waste. The zeolite was able to reduce Cs-137 levels from 1.8 E + 3-2.6 E + 4 d/m/mL in the feeds to less than 5.8 E + 2 in the effluent, thus meeting the desired limit.

TABLE II

Cs-137 Concentrations in Feeds and Effluents From a Linde™ IE-96 Zeolite Column

Sample	$\mu\text{Ci/mL}$ Cs-137	d/m/mL Cs-137
Feed #1	8.0 E-4	1.8 E+3
Effluent fraction 1-1	2.5 E-5	5.5 E+1
Effluent fraction 1-2	4.4 E-5	9.6 E+1
Effluent fraction 1-3	6.8 E-5	1.5 E+2
Effluent fraction 1-4	2.4 E-5	5.3 E+1
Effluent fraction 1-5	4.5 E-5	9.8 E+1
Effluent fraction 1-6	5.0 E-5	1.1 E+2
Feed #2	1.2 E-2	2.6 E+4
Effluent fraction 2-1	2.6 E-4	5.8 E+2
Effluent fraction 2-2	2.3 E-4	5.1 E+2
Effluent fraction 2-3	1.6 E-4	3.5 E+2
Effluent fraction 2-4	below blank	-----
Effluent fraction 2-5	3.3 E-6	7.2 E+0
Effluent fraction 2-6	1.5 E-4	3.3 E+2

Note: Each effluent fraction represents 10 column volumes (180 mL) of treated waste.

Cs-137 Decontamination by Washing With Water or Caustic

The ability of zeolite to remove cesium ion from an organic matrix reinforced the rationale that Cs^+ is associated with very small amounts of entrained water. It was reasoned that it might be possible to simply wash the cesium away from the benzene using water or an aqueous solution.

Ten milliliter samples of contaminated Recovered Organic Process Stream solutions were stirred vigorously with different volumes of water and 3% KOH solution. The Cs-137 levels in the benzene layer was determined by gamma counting. A typical result is shown in Fig. 1. The data represented in that series of experiments were generated by vigorously stirring 10 mL samples of organic waste with 10, 5, 3, 2, and 1 milliliters of water or KOH for five minutes. The Cs-137 levels remaining in the organic layer were 0- 20 d/m/mL, after correcting for background. This represents a better decontamination than that afforded by ion exchange. There does not appear to be a significant difference between the efficiency of water or KOH. Further, use of one volume of aqueous phase for each ten volumes of organic can result in adequate decontamination.

Decontamination of Diphenylmercury and Cs-137 Using Chemical Reaction with Tru Clear™

The most desirable decontamination of the Recovered Organic Process Stream would effect removal of both cesium ion and diphenylmercury from the waste. Early experiments to chemically attack the diphenylmercury so that Hg could also be removed from the benzene were not successful. Acidic permanganate, persulfate, and periodate had no effect on diphenylmercury in a benzene matrix. Promising

results have been achieved, however, in attacking the organomercury compound using a new product named Tru Clear™.

Tru Clear™ is a stabilized ferrate (FeO_4^{2-}) system that has shown promise in removing heavy metals from aqueous streams. (3) Volumes of mixtures of Tru Clear™ in 3% (w/w) KOH were vigorously reacted with equivalent volumes of solutions of diphenylmercury in benzene and with the Recovered Organic Process Stream. Reaction was presumed complete when the purple color of the Tru Clear™ solution disappeared. Samples of the aqueous layers were analyzed for their Cs-137 and Hg content after reaction. Some typical results are tabulated in Table III.

Clearly, Cs-137 is taken up in the aqueous layer and its concentration in the benzene matrix is reduced below the desired limit of decontamination of $1.0 \text{ E} + 3$. The greatest diphenylmercury decontamination experienced has been about 2% removal into the aqueous layer. The degree of reaction between the Tru Clear™ material and diphenylmercury in benzene is a function of how well the two phases are mixed. A large amount of solid material is generated, particularly when the Recovered Organic Product Stream is reacted. Analysis of the acidified solids for inorganic Hg has been difficult due to the presence of organic matter that interferes in a cold vapor atomic absorption analysis. Further, HPLC and gas chromatographic analysis for diphenylmercury in the reacted benzene layer is complicated due to the presence of organic oxidation products that appear to generate spurious results. The efficiency and optimization of the mercury decontamination will be more clearly defined when ongoing studies designed to improve analytical techniques are completed.

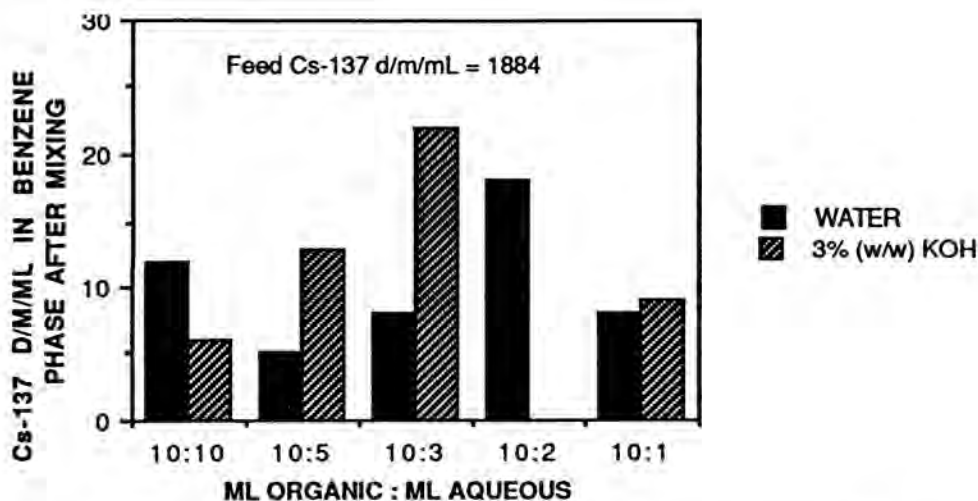


Fig. 1. Cs-137 decon of organic product stream by stirring with an aqueous phase.

TABLE III

Cesium and Mercury Decontamination of a Benzene Solution

Solution	Tru Clear wt % in KOH	Initial, Organic Phase		Final, Aqueous Phase	
		ppm Hg	d/m/mL Cs-137	ppm Hg	d/m/mL Cs-137
Benzene	0.50	90	6.1 E + 3	0.12	5.8 E + 3
Benzene	1.0	90	6.0 E + 3	1.3	7.1 E + 2
ROPS ^a	2.0	90	3.4 E + 7	2.1	1.2 E + 0
ROPS ^a	1.0	90	7.6 E + 2	0.25	1.6 E + 0

^a Recovered Organic Product Stream

CONCLUSIONS

SRS benzene waste that is contaminated with diphenylmercury and radioactive Cs⁺ can be treated on a zeolite or washed with water (or an aqueous solution) to remove the radionuclide. Diphenylmercury is not removed during either of these processes, however. Chemical reaction with a KOH solution of the strong ferrate oxidant in Tru Clear™, a commercially available material, leads to degradation of diphenylmercury to a water-soluble form. On treatment of the benzene waste with the Tru Clear™ product, nearly all of the cesium and about 2% or less of the mercury have been extracted into the aqueous phase, which can easily be decontaminated using conventional methods such as ion exchange.

These methods have possible application in decontaminating other organic mixed waste systems and mercury-containing streams that result from nonradioactive operations.

ACKNOWLEDGEMENT

The information contained in this article was developed during the course of work done under Contract No. DE-AC09-89SR18035 with the U.S. Department of Energy.

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