TREATMENT OF RADIOACTIVE LABORATORY WASTE FOR MERCURY REMOVAL (U)

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ABSTRACT

Routine analyses of Savannah River Laboratory wastes at the Savannah River Site (SRS) occasionally reveal mercury concentrations in the waste in excess of the 0.200 μg/L RCRA limit. A polystyrene/divinylbenzene ion exchange resin with thiol functional groups, Duolite™ GT-73, has been demonstrated effective, through a special, permitted decontamination project, for the removal of dissolved mercury from this laboratory waste. As a result of this demonstration, the resin is in use or under consideration for use with several other SRS radwaste streams as a reliable medium for mercury removal.

INTRODUCTION

Mercury, used as a catalyst for dissolution of some spent uranium-aluminum alloy fuel elements at Savannah River Site (SRS), remains with the fission products after their separation from uranium and plutonium. Consequently, mercury is found in both the high- and low-activity liquid radwaste streams resulting from subsequent processing of fission product waste. Mercury is also present in Savannah River Laboratory (SRL) waste, as a result of the research associated with testing of technology for site waste management.

At SRL, low activity waste is collected and stored in RCRA (Resources Conservation and Recovery Act) permitted tanks before shipment by truck to an on-site evaporator that is not RCRA permitted. Occasionally the concentrations of mercury in SRL waste composites exceed the 0.200 mg/L RCRA limit for hazardous wastes, requiring removal of the mercury before shipment to the evaporator. A successful, permitted mercury decontamination of a batch of hazardous SRL waste was accomplished using Duolite™ GT-73 cation exchange resin. Mercury removal from a variety of SRS waste streams using GT-73 ion exchange resin had already been studied extensively in Savannah River Laboratory.(1) Laboratory tests on this particular laboratory waste confirmed that the mercury could essentially be eliminated by sorption on GT-73, generating a treated waste suitable for shipment to the evaporator.

This demonstration constituted the first large-scale test of the resin on a radioactive SRS waste stream. Its success has led to the use of GT-73 for mercury removal in SRS processes across the site. Corrosion studies in the laboratory generate liter quantities of mercury waste that have been decontaminated with GT-73. Columns of the resin are in use in the F/H Effluent Treatment Facility to prevent mercury from being dispensed to the environment by that facility.(2) Melter offgas condensate and waste streams from the SRS Integrated Defense Waste Processing Facility (DWPF) Melter System (IDMS) facility at TNX will be processed through GT-73 resin to remove mercury from simulated, non-radioactive defense waste. Treatment of aqueous laboratory waste with the resin will be an essential step in a proposed treatment facility for SRL liquid waste. Other, novel uses of GT-73 are being considered at SRS for removal of mercury from contaminated soil and water associated with formerly used seepage basins.

TANK L DECONTAMINATION

Routine analyses of SRL waste indicated the mercury concentrations in Tank L, one of five low-activity, radioactive laboratory waste holding tanks, exceeded the 0.200 mg/L RCRA toxicity limit. Tank L, at that time was not a RCRA permitted tank. Thus, a permit for temporary storage of toxic waste in the tank had to be obtained from the South Carolina Department of Health and Environmental Control (SCDHEC). In addition, the on-site evaporator that processes laboratory waste was, and still is, not RCRA permitted and was unable, by law, to receive toxic waste for treatment. This meant that a second permit, for waste water treatment, had to be negotiated with SCDHEC. The detailed treatment and quality assurance plan required by that permit was devised by SRL personnel and coordinated by Department of Energy (DOE) and SCDHEC representatives.

Tank L and Its Contents

Tank L is an 11,230 gallon above-ground tank, 12 feet in diameter and 13 feet high. The walls are 0.5 inch stainless steel and the tank is equipped with an agitator, a sampling system, and a dip-line extending to 1 inch from the bottom for transfer of liquid from the tank.

At the time of treatment, approximately 8,000 gallons of liquid and suspended solids were contained in Tank L.

Table I reflects analyses of samples of the contents before and after filtration through a 0.45 μm filter. A portion of both the total mercury and uranium (and thus, total alpha) concentrations were associated with the suspended solids.

Treatment

A dipleg was installed through a spare flange in Tank L with the tip of the dipleg resting on the bottom of the tank. Waste was pumped from the dipleg through bag filters to remove solids and then upflow through Duolite™ GT-73 ion exchange resin for mercury removal. (See Fig. 1). Treated waste was collected in a 4,000 gallon fiberglass tank fitted with an agitator. The holding tank was installed to assure a well-mixed sample and to provide for recycle, if necessary.

The entire contents of Tank L were first treated. Clean water was then used to flush the lines and the sump from the building in which the waste had originated back to Tank L. More clean water was introduced from a hose to wash Tank L. Wash water was treated by filtration and ion exchange in exactly the same way the original waste had been treated.

A once-through treatment was sufficient to render the waste non-toxic. Mercury concentration in the waste water was reduced to less than 0.200 mg/L after coarse filtration and ion exchange. At the same time, alpha radiation was reduced to less than 10^3 d/m/ml. This treated waste water was transported as low-activity waste to the general purpose evaporator for processing. Tank L was returned to service.

Used filters were collected in 55-gallon drums and sent to mixed waste storage on-site. Spent resin was slurried out of the column into a 55-gallon drum and sent to hazardous waste storage on-site. Samples of the resin will be subjected to the EP Toxicity test for Hg to determine whether it is a toxic waste. Inasmuch as leaching tests (EP toxicity and Toxic Characteristic Leaching Procedure) on laboratory samples have shown the spent resin to be non-toxic, it is expected that the results will be the same for this waste resin and that it will be removed from hazardous waste storage and disposed of as non-hazardous, solid waste.

DECONTAMINATION OF CORROSION STUDY WASTE

The presence of mercury in SRS waste leads to concerns about mercury-assisted corrosion of waste tanks and equipment associated with waste processing facilities (see Table III). Corrosion studies are ongoing at SRL to assist in the selection of materials of construction for these facil-

TABLE I

L-Tank Analysis Sample 4/29/87

	FILTERED				UNFILTERED			
Analyses	1	2	3	4	1	2	3	4
Ag	0.88	0.90	0.88	0.94				
As	0.04	0.03	0.03	0.03				
Ba	0.18	0.18	0.18	0.18				
Cd	0.03	0.03	0.03	0.03				
Cr	1.5	1.6	1.57	1.65				
Ni	0.76	0.78	0.76	0.76				
Pb	1.83	1.82	1.79	1.86				
Se	<0.02	<0.02	<0.02	<0.02				
Zn	2.73	2.66	2.72	2.66				
pH	3.69	3.68	3.64	3.64				
U235	6.9	7.2	6.9	6.7	9.1	8.5	9.4	9
Mercury	1.43	1.62	1.52	1.56	1.81	1.8	1.56	1.99
Alpha	1420	1450	1410	1440	2340	2340	2460	2430
Beta Gamma	73	75	78	70	468	478	4890	4670
Total U	687	640	687	823	1070	1200	937	1300
TIC	0.46	0.60	0.81	0.24	6.61	8.54	8.94	8.20
TOC	552.78	566.89	565.29	577.07	584.11	594.44	612.23	615.47

All chemical analyses in PPM
All radioactive analyses in DPM/ML

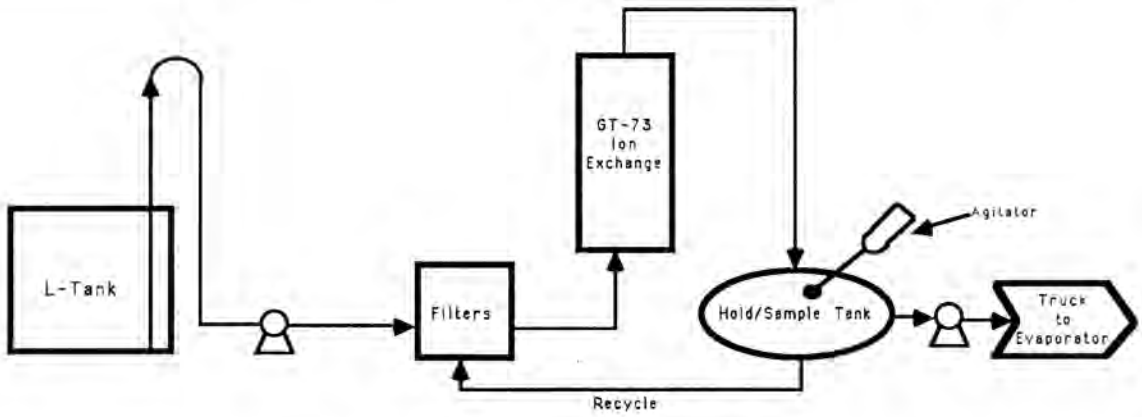

Fig. 1. Tank L Decon Process Schematic.

TABLE III

Corrosion Study Simulated Sludge Suspensions Decontaminated by GT-73 Ion Exchange Resin

Component	Ion	Molarity Range	ppm Range
$NaAlO_2$	Al^{3+}	4.5 E-3	120
$Ni(NO_3)_2 \cdot 6H_2O$	Ni^{2+}	1.5 E-3	88
$Fe(NO_3)_3 \cdot 9H_2O$	Fe^{3+}	2.5 E-4	14
$Hg(NO_3)_2 \cdot H_2O$	Hg^{2+}	2.5 E-4	50 [a]
$Cu(NO_3)_2 \cdot 2.5H_2O$	Cu^{2+}	4.3 E-5	2.8
$Co(NO_3)_2 \cdot 6H_2O$	Co^{2+}	3.0 E-5	1.8
$CrCl_3 \cdot 6H_2O$	Cr^{3+}	3.8 E-5	2.2
Na_2CrO_4	Cr^{6+}	5.6 E-4	29
Na_2MoO_4	Mo^{6+}	7.3 E-5	7.0
MnO_2	MnO_2	5.8 E-3	500
$Na_2C_2O_4$	$C_2O_4^{=}$	1.4 E-3	120
$Na_2SiO_3 \cdot 9H_2O$	$SiO_3^{=}$	5.6 E-4	540
$Na_3PO_4 \cdot 12H_2O$	PO_4^{3-}	1.6 E-3	150
$Na_2CO_3 \cdot H_2O$	$CO_3^{=}$	1.7 E-2 - 1.9 E-1	1.0 E+3 - 1.1 E+4
$NaHCO_3$	HCO_3^{-}	4.5 E-2 - 1.7 E-1	2.7 E+3 - 1.1 E+4
NaCl	Cl^{-} [b]	2.6 E-4 - 6.0 E-3	9.2 - 210
NaF	F^{-}	7.4 E-5 - 2.9 E-3	1.4 - 56
Na_2SO_4	$SO_4^{=}$	6.5 E-4 - 2.6 E-2	62 - 2.5 E+3
$NaNO_3$	NO_3^{-}	9.7 E-3 - 3.9 E-1	470 - 1.9 E+4
$NaNO_2$	NO_2^{-}	2.5 E-2 - 1.0	1.2 E+3 - 1.6 E+4
Total Na	Na^{+}	1.1 E-1 - 1.8	2.5 E+3 - 4.1 E+4

[a] After ion exchange the Hg concentration was ≥0.004 ppm

[b] Includes contribution from $CrCl_3$

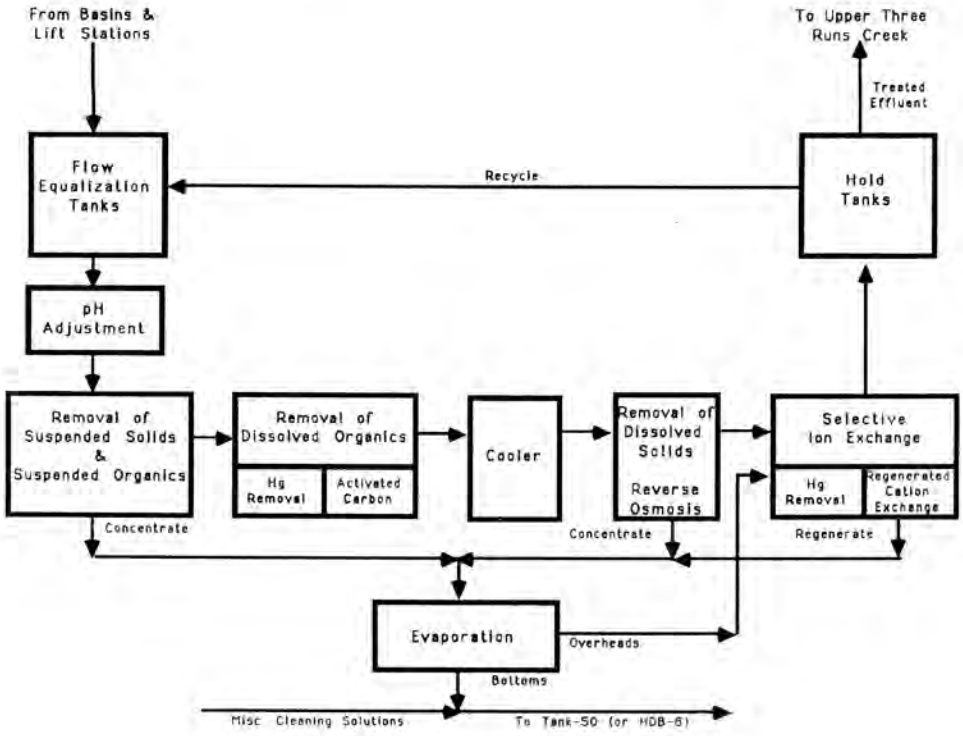

Fig. 2. F/H ETF Process Flowsheet.

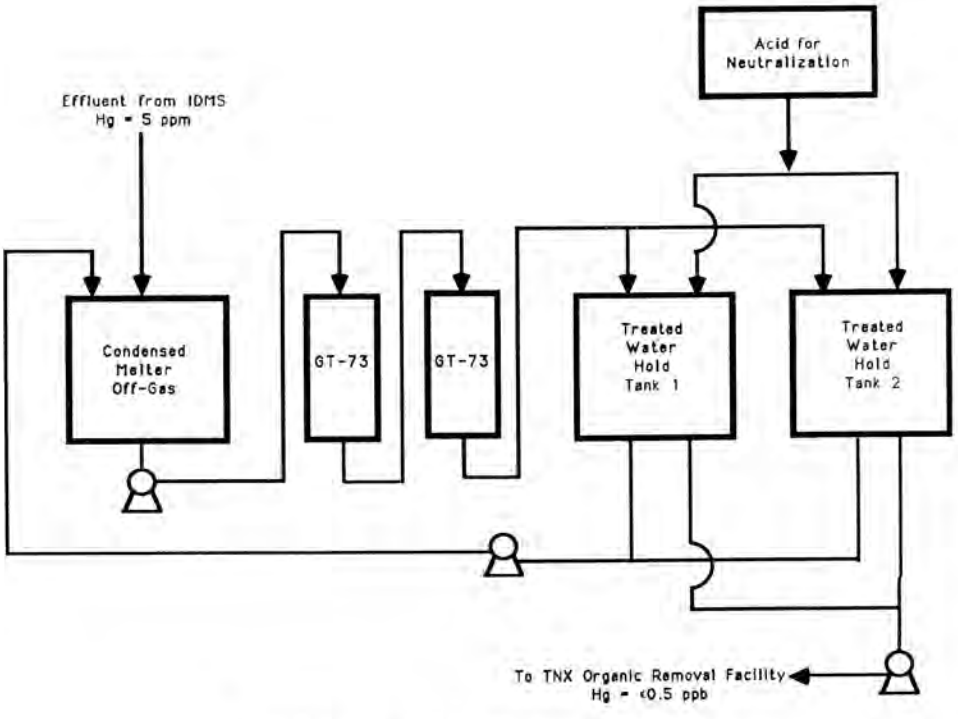

Fig. 3. The IDMS Ion Exchange System.

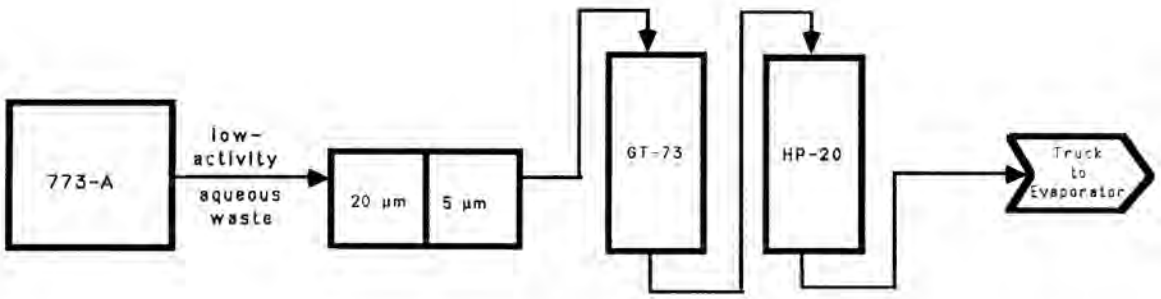

Fig. 4. Low-Activity Laboratory Waste Treatment Test Schematic.

TABLE IV

Mercury Removal Resin Effluent in ETF[a]

		Organic Removal Columns			Final IX Columns	
	Feed	#1	#2	#3	#1	#2
Minimum[b]	0.002	0.002	0.002	0.002	0.002	0.002
Average	0.127	0.018	0.017	0.018	0.005	0.005
Maximum	1.26	0.370	0.370	0.250	0.060	0.070

[a]Samples = 378

[b]ppm Hg; detection limit = 0.002 ppm

ities and to identify ways to prevent corrosion of existing process materials. As a result, tens of liters of aqueous mercury waste, containing approximately 50 ppm Hg, has been generated in the laboratory. Mercury was removed from this waste by contacting it with GT-73 resin in a small (about 1.5 L) column. The concentration of Hg in the effluent from the column was never allowed to exceed 4 ppb Hg without replacing the resin. In the test of the resin the entire volume of laboratory waste was rendered non-hazardous relative to mercury by ion exchange.

MERCURY REMOVAL IN THE F/H EFFLUENT TREATMENT FACILITY

The F/H Effluent Treatment Facility (ETF) treats dilute radwaste streams, formerly diverted to seepage basins at SRS, to remove toxic and radioactive species before they reach the environment (Fig. 2). Mercury concentrations in the waste streams entering the ETF average 0.122 mg Hg/L. An initial pH adjustment to 7 and a subsequent microfiltration step generate insoluble mercury compounds that are sent to an evaporator in the filter concentrate. Soluble mercury proceeds in the filter permeate to an organic removal step.

In the organic removal step, carbon columns are used to protect reverse osmosis (RO) membranes from tri-n-butyl phosphate (TBP) that can cause premature flux loss and fouling in the RO treatment step. Unfortunately, the carbon will also sorb mercury and thereby become a hazardous secondary waste. To prevent dissolved mercury from reaching the carbon columns, three columns of GT-73 were

inserted between the filtration and carbon removal process steps.

A second set of two GT-73 columns operate to remove mercury from the ETF evaporator overheads before a final ion exchange polishing step using a sulfonic acid resin. Mercury is present in the condensate stream because it is reduced in the evaporator by ammonia or bisulfite used in the cleaning or disinfecting of RO membranes. Once reduced, all of the mercury in the evaporator will volatilize and appear in the overheads. The resin has demonstrated consistently in the laboratory that it can remove dissolved Hg^{o} as well as the ionic species $Hg2^{2+}$ and Hg^{2+1}. Approximately twelve months of operating data from these columns in the ETF indicate (Table IV) that the resin efficiently removes mercury, whatever its oxidation state.

MERCURY REMOVAL IN THE IDMS

The Integrated DWPF Melter System (IDMS) is a one-ninth-scale demonstration of the DWPF feed preparation, melter, and off-gas systems. The IDMS is the first engineering-scale melter system at SRL to process mercury and flowsheet levels of halides and sulfates. The demonstration will generate an aqueous off-gas condensate that contains mercury. In order to safely dispense this waste, two columns of GT-73 resin have been permitted by SCDHEC and installed as a polishing step so that the treated waste can be disposed of as non-hazardous waste.

MERCURY REMOVAL FROM LOW-ACTIVITY LABORATORY WASTE

A process has been proposed for treatment of both low- and high-activity SRL laboratory waste. An important step in that process will be mercury removal using GT-73 resin. In April 1990, an experimental filtration/ion exchange apparatus, representing a part of the total treatment, will be installed and tested on the low-activity aqueous waste from the technical area. A schematic of that apparatus shown in Fig. 4. Suspended solids will be removed by filters. Then a column of GT-73 will treat the waste to remove mercury. Finally, a second column, containing Diaion™ HP-20 nonfunctionalized resin, will be used to remove benzene and its derivatives, generated in DWPF research on sodium tetraphenylborate at SRL.

MERCURY REMOVAL STUDIES IN CONTAMINATED SOIL AND GROUNDWATER

The dispensing of waste to seepage basins at SRS was discontinued with startup of the ETF in November 1988. Current efforts involved with closure of the basins have identified the presence of mercury in basin mud and in groundwater below the basins. A novel adaptation of ion exchange technology is under consideration for mercury removal in the basin systems. GT-73 resin, incorporated in Isolock 100™, a hydrophilic polymeric support [3], has been used successfully in preliminary tests in the laboratory to sorb mercury away from contaminated SRS soil samples. Larger-scale field tests of this technology are being planned for the second quarter of 1990.

CONCLUSION

The demonstration of GT-73 cation exchange resin for mercury removal from contaminated Tank L waste at the Savannah River Site proved what earlier laboratory experiments had predicted. The resin renders hazardous waste non-hazardous by effectively sorbing all three simple oxidation states of mercury from waste streams. After sorption, the spent resin is itself non-hazardous, making disposal of this secondary waste environmentally safe. The resin has since been used to decontaminate a variety of waste streams and is being considered for decontamination projects that cannot utilize traditional ion exchange column operations.

REFERENCES

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2. BIBLER, J.P., and WALLACE, R.M., "Ion Exchange Processes for Clean-up of Dilute Waste Streams by the F/H Effluent Treatment Facility at the Savannah River Plant", Recent Developments in Ion Exchange-Proceedings of Ionex '87 Meeting, Clwyd, Wales, 1987, p.173.
3. ISOLOCK 1000™ is a proprietary product of ISOTRON, Inc. Patents have been applied for by ISOTRON, Inc. for this technology.

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