

Mercury Removal from SRP Radioactive Waste

Streams Using Ion Exchange

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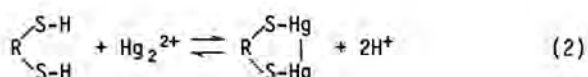
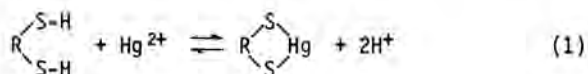
ABSTRACT

Mercury is present in varying concentrations in some Savannah River Plant (SRP) waste streams as a result of its use as a catalyst in the dissolution of fuel elements composed of uranium-aluminum alloys. It may be desirable to remove mercury from these streams before treatment of the waste for incorporation in glass for long-term storage. The glass forming process will also create waste from which mercury will have to be removed. The goal of mercury removal would be to eliminate ultimate emission of this toxic substance into the environment. This paper describes tests that demonstrate the feasibility of using a specific cation exchange resin, Duolite®GT-73 for the removal of mercury from five waste streams generated at the SRP. Two of these streams are dilute; one is the condensate from a waste evaporator while the other is the effluent from an effluent treatment plant now under development. The three other streams are related to the Defense Waste Processing Facility (DWPF) that is being built at SRP. One of these streams is a concentrated salt solution (principally sodium nitrate and sodium hydroxide) that constitutes the soluble fraction of SRP waste and contains 20% mercury in the waste. The second stream is a slurry of the insoluble components in SRP waste and contains 80% of the mercury. The third stream is the offgas condensate from the glass melter system in the DWPF.

Mercury is used as a catalyst in the dissolution of uranium-aluminum alloy fuel elements at the Savannah River Plant (SRP). As a result, mercury is found in several waste streams on the SRP site. These streams differ greatly from each other, not only in the concentrations of mercury they contain, but in their overall physical and chemical composition. Depending on the stream, mercury may be present in solution as Hg^0 , Hg^{2+} , or Hg_2^{2+} . Ion exchange using Duolite® (Diamond Shamrock International) GT-73 cation exchange resin has been demonstrated to selectively remove mercury, in any oxidation state, from each of the streams. In all cases, the mercury displaces radioactive species such as Cs-137 and Sr-90 that also sorb. A sodium nitrate wash removes residual cesium and strontium, which may allow the spent resin to be treated as nonradioactive waste rather than mixed waste. The ultimate result is an effluent that could be properly introduced into the environment, with a mercury concentration reduced to less than 2 ppb.

Duolite®GT-73 is a macroporous, weakly acidic polystyrene/divinylbenzene cation resin with thiol functional groups that have a pronounced selectivity for mercury in any of its three common oxidation states. The distribution coefficients (K_d in mL solution/gram of dry resin at pH=8), determined in laboratory equilibrium experiments, are 7.0×10^4 for Hg^{2+} , 3.6×10^3 for Hg_2^{2+} , and 8.9×10^3 for Hg^0 . The sorption reactions of the resin for these three species are believed to be the following:

For $Hg(II)$ and $Hg(I)$, a simple ion exchange reaction is expected.



The mechanism for sorption of Hg^0 is not clearly understood at this time.

The resin operates over a pH range of 1-13, a much broader range than that for other commercially available, mercury-selective resins. The resin remains physically and chemically stable when exposed to ionizing radiation, having sustained a total dose of 3.2×10^8 rad in a Co-60 source with little change in its efficiency. GT-73 is insoluble in most common solvents but decomposes slowly in nitric acid solutions of greater than one molar concentration. The manufacturer's reported capacity of the resin for Hg^{2+} is 1.4 meg/mL or 140 g Hg/L. We have observed a capacity of 1.45 meg/mL in saturation studies using 1.0×10^{-4} M $Hg(NO_3)_2$.

Two of the SRP waste streams are very dilute solutions that could be treated by conventional ion exchange using GT-73. Since these streams will eventually enter the environment, it is desirable to remove as much mercury as possible before release. The first stream, which is currently sent to a seepage basin, consists of overheads from evaporators that operate regularly on the site. Mercury concentrations in the overheads average 500 ppb at a pH of 10; Cs-137 is present in very low concentrations ($<1 \times 10^2$ dpm/mL). A solution containing 500 ppb Hg^{2+} at pH=10 was passed through a 2 mL column of GT-73, Na form, at a flow rate of 50 column volumes per hour to describe breakthrough. After 110,000 column volumes had been processed, sharp breakthrough was observed. Until that point, effluent from the column contained less than 2 ppb Hg. Based on these results, a five-liter column was tested on actual evaporator overheads at SRP. The test column was operated continuously for two months, and never reached mercury breakthrough.

The presence of radioactive cesium raises the question of the need for shielding determined by the extent of cesium sorption by the resin. Batch experiments using the sodium form of GT-73 and a solution that was 1.0×10^{-5} M $Hg(NO_3)_2$ and 9.4×10^3 dpm/mL Cs-137 showed that the K_d for Cs under these conditions was 472 mL/g. When the same solution was adjusted to

0.01 M NaNO₃, the Kd for cesium dropped to 112 mL/g, whereas the Kd for mercury remained unchanged. Thus, it appeared that any buildup of cesium on the resin would not become a problem because a sodium nitrate wash would selectively remove cesium ion without removing sorbed mercury. A column run in the laboratory confirmed this. A two milliliter column was run to cesium breakthrough with the Cs/Hg solution; fifteen column volumes of 0.1 M NaNO₃ were needed to strip virtually all the cesium (0.74 μ Ci Cs-137/g resin) from the resin. Similarly, sodium nitrate solution washed residual Cs-137 from resin used in the five-liter test column.

A second dilute stream that will be released into the environment at SRP is effluent from a treatment plant called the F/H Effluent Treatment Facility (F/H ETF). This facility will treat waste streams that now empty into seepage basins scheduled to be closed in 1988. Treatment is a three-stage process of filtration, reverse osmosis, and ion exchange. Mercury will still be present in the waste going to ion exchange, and GT-73 is a reasonable candidate for removing mercury to levels below regulatory limits before final release of the stream.

The three remaining streams of interest all relate to the processes of the Defense Waste Processing Facility (DWPF) that is under construction at SRP. An estimated 80-90 tons of mercury are present in existing waste that will be processed in the DWPF. One-fifth of the amount will be present in soluble high-level waste (HLW) supernate. Supernate is a concentrated salt solution containing about 5.6 M Na+(primarily as nitrate and nitrite), 1.5 M NaOH, an average concentration of 57 ppm Hg²⁺ as Hg(OH)₂, and several radionuclides, particularly Cs-137 and Sr-90. In the DWPF, supernate will be treated first with sodium tetraphenylborate to precipitate cesium, and then with sodium titanate to remove strontium. Mercury also precipitates during this process as diphenylmercury. Precipitation is followed by filtration and formic acid hydrolysis to destroy tetraphenylborate. The mercury species remaining after acid hydrolysis of diphenylmercury are metallic mercury, phenylmercuric ion, and diphenylmercury. We have demonstrated that GT-73 will not sorb diphenyl mercury but will quantitatively react with its hydrolysis product, C₆H₅Hg+.

Tests on simulated and actual SRP HLW supernate, as they exist before the precipitation step, indicate that a column of GT-73 resin would be capable of removing greater than 99% of dissolved mercury from this highly concentrated and caustic waste stream. There is no apparent negative physical or chemical reaction of the resin to the substantial hydroxide concentration in supernate; the high concentration of sodium ion actually has a beneficial effect in that it preferentially displaces cesium and strontium from the resin (the resin also shows no significant retention of plutonium or ruthenium). Washing spent resin with 2 M NaNO₃ was sufficient to remove residual Cs-137 to a measured level of 0.60 μ Ci Cs-137/mL resin, below the 1 μ Ci Cs-137/mL allowed for classification as a Class A waste.

According to the current DWPF flowsheet, cesium, strontium, and any remaining mercury in the treated supernate are sent to be blended with the second of the remaining streams, the solid waste called sludge. Sludge is a concentrated slurry (16-19 weight percent solids, principally iron, aluminum, and manganous hydroxides) containing the remaining 80% of waste mercury in concentrations that range as high as 2000 mg Hg per liter of wet slurry. The resulting mixture

is adjusted to pH 4 with formic acid (formated), and heated to reduce dissolved mercury to its elemental form. Steam stripping is then utilized to remove as much metallic mercury as possible. Glass frit is added to the mixture and the concentration is adjusted by evaporation to 45-49% solids, by weight. This blend is then fed as a slurry to a melter where glass containing radioactive waste is produced for long-term storage. Any mercury remaining will proceed with the sludge to the melter and ultimately to the melter offgas system. In the event that it should become necessary to remove the mercury from the sludge, a resin-in-sludge process has been demonstrated as effective in mercury removal using GT-73 with both formated sludge and steam-stripped formated sludge.

Removal of mercury found in SRP sludge is a more difficult problem than removal of mercury from other waste streams discussed here, and must be addressed differently. First, there is a much greater quantity of mercury to be removed from sludge than from dilute streams or supernate. Second, sludge is a very concentrated slurry and its nature serves to hinder the sorption process by protectively coating both resin and mercury particles in suspension. Third, chemical processes, carried out on the sludge to effect removal of mercury by steam stripping, reduce the mercury to forms (Hg metal and mercurous ion) that are not soluble and, hence, more difficult to remove by ion exchange than the mercuric ion.

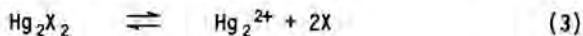
Early batch experiments showed that GT-73 cation exchange resin removes >90% of mercury found in formated simulated sludge and formated SRP aluminum dissolved, washed, high-level radioactive sludge. These same experiments demonstrated that abrasion from vigorous stirring of the sludge/resin mixture caused the resin to degrade into particles too small to separate from the slurry after reaction. To protect the resin from abrasion, a fluidized bed contactor was designed wherein the sludge slurry contacts the resin by circulating several times through a resin bed retained between two screens in a column. It was necessary to pretreat the sludge by sieving to remove particles that could plug the screens. The process has been demonstrated with simulated and actual radioactive sludge using a 0.5"-internal-diameter upflow column containing two milliliters of resin. In both cases, using formated sludge, 99.6% of the mercury present was removed from the sludge in 12 hours. Removal of mercury by ion exchange from the sludge after steam stripping would be advantageous because it would permit recovery of the bulk of the mercury as metal and put less of a burden on the ion exchange system. Experiments using formated simulated sludge which has been steam stripped indicated that the resin is capable of removing about 75% of the mercury in the system in an eight-hour period; 90% could be removed from sludge which had not been steam stripped in the same time. This was expected because of the less tractable nature of mercury species believed to exist in steam stripped sludge. The percent mercury removed can be improved by operating at higher temperatures (50°C-90°C).

A 6.4"-internal-diameter stirred-bed downflow fluidized bed-column has been tested with mercury-containing steam-stripped synthetic sludge. After initial sieving, that column operated for seven hours, with 80% mercury removal.

The offgas condensate from the melter constitutes the third DWPF waste stream that can be treated for mercury removal by GT-73 cation resin. This is a more complicated stream containing elemental mercury, mercurous chloride and iodide, and dissolved mercuric

salts. It is scheduled to be recycled through the DWPF and will ultimately find its way back to the melter. Thus, mercury removal from the offgas condensate may be desirable before it has a chance to be recycled.

Simulated offgas condensate and condensate from an extended run of a minimelter with mercury containing feed were treated on a column of the sodium form of GT-73. In both cases the resin removed all but a small fraction of the initial mercury, leaving what is believed to be suspended, solid mercurous halides in the effluent. Although sorption of Hg^{2+} , Hg_2^{2+} , and Hg^0 is straightforward, when mercurous ion must be supplied to the resin from undissolved Hg_2Cl_2 or Hg_2I_2 , sorption is not as efficient because the equilibrium regulating dissolution of the solid does not favor formation of the ions.



If only a cation exchange resin is used to remove the mercurous ion, halide ion concentration gradually increases in solution and the equilibrium in Eq. (3) is shifted to the left. But, if an anion exchange resin is added to the resin bed to simultaneously remove X^- as it forms, the dissolution of Hg_2X_2 is ultimately complete and removal of all of the mercurous ion from solution is possible. Duolite® GT-73 (H^+ form) and Dowex® (Dow Chemical Co.) 1x8 (OH^- form) were mixed equally by mass, and used to treat simulated and minimelter offgas condensates such that the final pH of the effluent would not differ from that of the influent. Results indicate that such a mixed-bed system will induce dissolution and sorption of mercury to give an effluent concentration at or below the 2 ppb level. The dissolution process, as would be expected, requires some residence time in the column. We have determined that operation of the column at a flow rate of 10 column volumes per hour or less is required to allow sufficient contact time.

Ultimately, the disposal or storage of the mercury form of GT-73 must be addressed. Three alternatives have been studied: storage of mercury-containing resin as such, storage of mercury-containing resin incorporated in grout, and recovery of sorbed mercury from the resin.

Samples of GT-73 were saturated with mercury and sent to an EPA-sanctioned laboratory for an EP-toxicity test. The spent resin passed the test, indicating that simple storage is a viable option.

Similar resin samples were incorporated in Portland Type II grout and subjected to structural integrity tests and the EP-toxicity test. These samples passed the structural integrity test but not the EP-toxicity test. It is expected that the nature of the EP-toxicity test, where the sample is maintained at pH 5 with acetic acid, and the high concentration of calcium ions in grout resulted in some exchange of calcium ions for mercuric ions during leaching. Thus storage of spent resin without incorporation into grout is preferred.

Regeneration of the spent resin is possible but not desirable. Mercury can be eluted from the resin using 3 M HCl or 2 M NaSCN, neither of which is chemically compatible with materials of construction or processes at SRP. Dissolution of the resin and reclamation of mercury by chemical means such as precipitation as the sulfide or reduction to the metal is an attractive alternative to storage, should recovery and removal become desirable.

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