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REMOVAL OF MERCURY FROM WASTE WATER: LARGE-SCALE PERFORMANCE OF AN ION EXCHANGE PROCESS

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ABSTRACT

Duolite™ GT-73 ion exchange resin routinely reduces the mercury content of a waste water stream to less than the permitted level of 10 ppb. Effluent concentrations from the ion exchange facility (IEF) are consistently between 1 to 5 ppb, even though the feed contains a varying concentration of mercury (0.2 to 70 ppm). Two operational problems have been encountered at that facility, however. Firstly, the stated capacity of the resin for mercury was not being achieved. The abnormally low capacity was traced to analytical laboratory waste which was intermittently treated by the resin. That waste contained hydrochloric acid, stannous chloride, and potassium permanganate, among other chemicals, which presumably eluted sorbed mercury from the resin and also oxidized the thiol (SH) functional groups on the resin and rendered them inactive. The net effect was that the resin had to be replaced more frequently than anticipated. Secondly, the IEF was temporarily shut down because the mercury content of the waste water could not be reduced to below the permitted level, even with fresh resin. That problem was caused by slow settling solids composed mainly of iron which apparently adsorbed some of the mercury and allowed it to pass through the resin untreated. The solids were presumably a result of processing waste water abnormally high in iron which may have co-precipitated with mercury and other elements in the feed and caused a residual buildup of solids throughout the IEF. The problem was remedied by installing a 0.2 µm cartridge filter between the feed tank and the columns.

KEYWORDS

Ion Exchange; Duolite™ GT-73; mercury removal; waste water.

INTRODUCTION

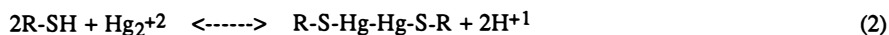
The Integrated Defense Waste Processing Facility (DWPF) Melter System (IDMS), located at the Savannah River Site (SRS), provides an engineering scale, non-radioactive demonstration of the DWPF. The DWPF will soon be used to immobilize high level radioactive waste (HLW) in borosilicate glass. Part of the IDMS charter is to demonstrate the removal of mercury from simulated HLW on an engineering scale. An ion exchange facility (IEF), utilizing Duolite™ GT-73 ion exchange resin, was designed to treat the mercury laden waste water (condensate and sump water) generated during the IDMS process demonstrations.

The IEF is permitted as a treatment facility by the South Carolina Department of Health and Environmental Control (SC DHEC) to reduce the mercury concentration to below the permitted level of 10 ppb (µg/l) for subsequent processing. The IEF became operational in January of 1990 and routinely reduces the mercury content of the waste water from a feed concentration ranging from 0.2 to 70 ppm (mg/l) down to an effluent concentration ranging from 1 to 5 ppb. However, two operational problems have been encountered: 1) the stated capacity of the resin for mercury was not being achieved, and 2) the IEF was temporarily shut down because the mercury content of the waste water could not be reduced to below the permitted level, even with fresh resin. The primary purpose of this paper is to present some specific details on these two problems along with general information on the process characteristics and performance. A secondary purpose is to

advocate the use of Duolite™ GT-73 ion exchange resin as it has proven to be a reliable means to remove mercury and other heavy metals from SRS waste water streams which vary considerably in composition (Osteen and Bibler, 1990; Bibler, *et al.*, 1986; Bibler and Wallace, 1987); yet there is a paucity of information in the literature on Duolite™ GT-73.

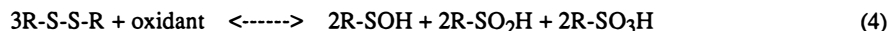
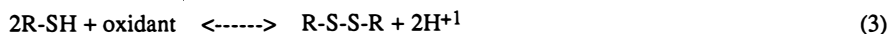
RESIN CHARACTERISTICS

Duolite™ GT-73 ion exchange resin is a macroporous, weakly acidic, polystyrene/divinylbenzene, cation resin with thiol (SH) functional groups. It is selective to many different cations some of which are listed here in order of decreasing selectivity: $\text{Hg} > \text{Ag} > \text{Cu} > \text{Pb} > \text{Cd} > \text{Ni} > \text{Co} > \text{Fe} > \text{Ca} > \text{Na}$. GT-73 has the most pronounced selectivity for mercury in either of its two common oxidation states (Hg^{+1} and Hg^{+2}). The following ion exchange reactions can occur with Hg in these states:



Based on experimental evidence, GT-73 can also remove Hg^0 from waste water, although the mechanism was not clear at that time (Bibler, *et al.*, 1986). Two plausible mechanisms which effectively explain the sorption of Hg^0 are proposed here: 1) The solubilities of Hg^0 and HgO in air-free water are respectively 60 ppb and 52 ppm (Aylett, 1973). However, the solubility of Hg^0 in an aqueous solution with dissolved air (oxygen) increases by a factor of 700 compared to its solubility in air-free water, and the final solubility is nearly the same as that for HgO (Aylett, 1973). These facts suggest that Hg^0 can be partially ionized by O_2 in an aqueous solution and thus be converted into a form that can be removed by GT-73. 2) Sorption of Hg^0 by GT-73 may also be explained by van der Waals attraction between metallic mercury (Hg^0) and the matrix of the resin, thereby interacting with the resin by physical adsorption rather than ion exchange.

GT-73 operates over a very broad pH range (1 to 13) and is insoluble in most solvents except for nitric acid, where it slowly decomposes in one molar (or greater) solutions. Furthermore, oxidizing agents such as oxygen in the presence of ferric ions (Fe^{+3}) or chlorine can cause chemical damage by oxidizing the thiol functional groups. The thiol groups can be oxidized based on the following two step mechanism:



The first oxidation reaction forms a disulfide linkage, which then reacts further (eq. 2) to form various oxidized sulfur compounds (namely, sulfenic, sulfinic and sulfonic compounds).

PROCESS CHARACTERISTICS

A schematic of the IEF facility is shown in Figure 1. It consists of two columns operated in series, a waste water collection tank (WWCT) (7,500 liters) to store the feed, two hold tanks (3,700 litres) to store the treated waste water, a monosodium phosphate tank used for neutralization and a 0.2 μm cartridge filter between the WWCT and the first column to filter any solids which may form within the IEF. Note that the filter was installed when, after six months of operation, it became apparent that solids were forming and building up throughout the IEF (see below). The columns are 1.0 m in diameter and the height of each resin bed is 0.85 to 1.0 m, which corresponds to approximately 0.7 m^3 of resin in each column. The flow rate through the columns is maintained at 7 to 13 litres/min (≈ 3 column volumes (CV) per hour).

The feed to the IEF first undergoes pH adjustment (final pH ≈ 12) with 50 wt. % NaOH to precipitate most of the solids as metal oxides. It then passes through a 0.02 μm ultrafilter to remove the precipitated solids along with any metallic mercury. The filtrate is stored in the WWCT and the solids are recycled back to the IDMS. The feed in the WWCT contains a varying concentration of Hg (0.2 to 50 ppm), a considerable amount of Na, and traces of Al, B, Ca, Li, Mg, Mn, Mo, P, Si, W and Zn (see below). It also contains up to a few thousand ppms of organics consisting mostly of phenol, but ppm levels of aniline, diphenylamine, phenylphenol and nitrobenzene are also present. Since the waste water is highly caustic, the resin has to be soaked for 24 hours in 6 M NaOH prior to being charged to the columns. This procedure has been used because GT-73 resin is purchased in the hydrogen form and undergoes a 40% expansion when the hydrogen ions are exchanged with sodium ions.

Normal processing of one batch of waste water consists of pumping the waste water through both columns and into one of the hold tanks until approximately 3,000 litres have been treated. A sample is taken from the hold tank and analyzed for mercury. If it is below the 10 ppb limit, monosodium phosphate is added to lower the pH to between 7 and 9. It is then transferred to the organic removal facility for further processing prior to being transferred to the clarifier system and discharging to the environment. If the sample is above the 10 ppb limit, the waste water in the hold tank is sent back to the WWCT, mixed with untreated waste water, and reprocessed through the columns as usual. When the level of mercury in a hold tank cannot be reduced to below 10 ppb, even after multiple passes through the columns, the resin is replaced.

Fresh resin is jetted into the columns using treated waste water (if possible) to minimize waste production. This method is possible since mercury is essentially irreversibly sorbed by GT-73. In fact, a sample of resin saturated with mercury passed the EP-Toxicity test (Bibler, 1985). As a result, spent resin has been classified as a non-hazardous waste which can be landfilled.

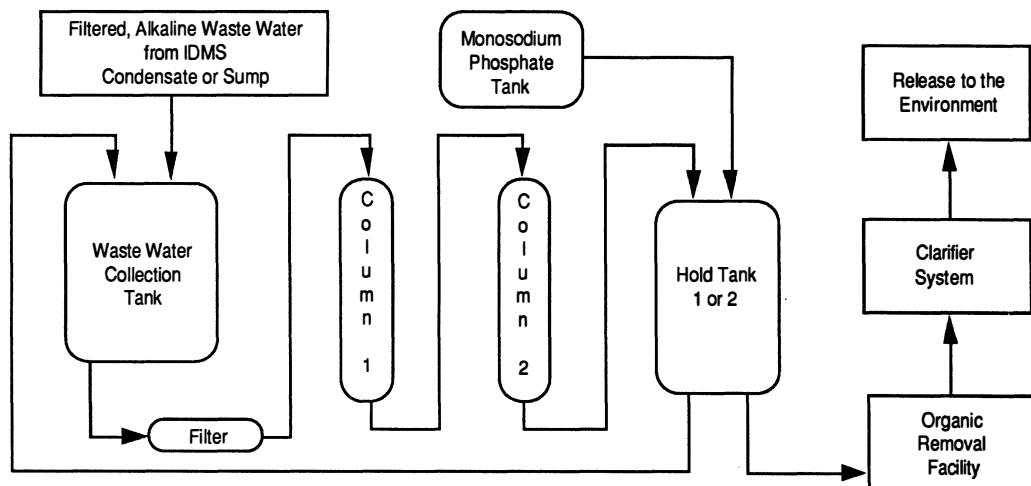


Fig. 1. Ion exchange facility schematic.

ION EXCHANGE FACILITY PERFORMANCE

Initial Process Performance

The initial process performance discussed below pertains to the first six months of operation of the IEF. During that time, the IEF routinely reduced the mercury content of the waste water to less than the permitted level of 10 ppb. However, the design flow rate had to be reduced almost immediately from 10 to 3 CV/hr in order to meet the permitted level. This process adjustment indicated that the waste water being treated required a longer retention time than that stated by the resin manufacturer. As more experience was gained by operating the IEF, it became apparent that the operating capacity of the resin for removing mercury from this waste water was also much lower than that stated by the resin manufacturer. More details of the first six months of operation of the IEF are given below.

A typical set of IEF samples obtained while processing a batch of waste water consisted of a WWCT sample, a between the columns sample and a hold tank sample. Typical mercury concentrations in these samples were respectively 1.00, 0.03, and 0.01 ppm. This IEF profile exemplifies an important fact about the process performance at that time: it was taking both columns to reduce the concentration of mercury in the effluent to less than 10 ppb. It is shown later that only one column is presently required to reduce the concentration of Hg in the effluent to 10 ppb and that the second column is needed only as a polishing step in the treatment of the waste water.

The resin has also been replaced four times; a charge of resin is suppose to last about two years. Since a cubic meter of resin costs \approx \$17,000, the frequent change-outs of the resin significantly increased the operating costs of the IEF. It is shown later that a charge of resin is currently lasting considerably longer.

Moreover, there is still a possibility that the spent resin can be reused (see below); accordingly, it has been transferred to drums, dewatered and stored in a designated staging area until it can be tested.

A charge of resin would process approximately 35,000 litres of waste water containing an average Hg concentration of 10 ppm before being changed-out. This data corresponds to utilizing only 2% of the capacity of the resin, based on a stated operating capacity of 30 g Hg/l resin. However, because the IEF was treating waste water from a research facility (IDMS) and, accordingly, the composition of the waste water varied from batch to batch, a low operating capacity was not considered unusual at first and was thought to be due to competitive sorption between Hg and other metals which were selective for GT-73.

Competitive sorption was ruled out, however, based on comparing a between the columns (BC) sample, a WWCT sample and a hold tank (HT) sample all obtained from the same batch of waste water. These samples exhibited little difference in their metal content except for mercury (see Table 1, samples 377, 379 and 381). Other explanations for the low capacity were 1) something in the waste water may have been oxidizing the thiol functional groups and rendering them inactive, 2) the presence of ppm levels of heavy organics in the waste water may have been fouling the resin by blocking pores, and 3) channeling may have been occurring in the columns. At the time 2 and 3 were ruled out, it was discovered that small volumes of waste from an analytical laboratory were being treated intermittently in the IEF.

TABLE 1. Elemental Analyses of IEF Samples (ppm)

Element	BC-377	WWCT-379	HT-381	WWCT-398	WWCT-409
Al	3.72	1.75	2.07	1.92	1.95
B	16.17	7.88	8.59	6.97	7.45
Ca	1.0	0.07	0.22	0.75	0.55
Fe	0.00	0.00	0.00	1.62	0.46
Hg	0.18	14.34	0.35	0.25	0.22
Li	5.72	3.50	2.83	1.46	1.49
Mg	0.01	0.00	0.07	0.20	0.14
Mn	0.00	0.00	0.00	0.11	0.07
Mo	1.47	1.17	0.96	0.81	0.85
Na	2161.60	1047.50	1866.20	1357.00	1382.40
P	13.18	17.21	550.13	314.32	324.82
Si	33.68	27.31	23.52	20.40	20.17
Sn	0.03	1.80	0.03	4.76	1.53
W	0.25	0.17	0.17	0.14	0.14
Zn	0.83	0.73	0.50	0.60	0.46

Treatment of Analytical Laboratory Waste

The analytical laboratory waste contained hydrochloric acid, stannous chloride, and potassium permanganate, among other chemicals. Note that the unusually high levels of Sn found in samples 379, 398 and 409 (see Table 1) were due only to treating laboratory waste. Hydrochloric acid can be used to regenerate the resin by complexing the mercury ions with chloride ions to form HgCl_4^{2-} , an anion complex which is repelled by the cation resin. It was, therefore, suspected that part of the poor performance was due to the HCl levels in the waste water being high enough to effect partial elution of the mercury from the resin. Moreover, potassium permanganate is a very strong oxidizing agent and so is chlorine which was apparently formed from mixing different laboratory waste chemicals together. A strong chlorine odor was apparent in laboratory waste which was typical of that treated in the IEF. These oxidizers presumably rendered the thiol functional groups inactive according to either of the reactions given previously (eqs. 3 and 4). It was unfortunate, however, that at about the time the treatment of the laboratory waste was discontinued, the IEF was temporarily shut down because the mercury content of the waste water could not be reduced to below the permitted level, even with fresh resin. Thus, the effect of treating the laboratory waste on the IEF performance could not be independently ascertained. Nevertheless, it was presumed that the poor performance observed during the first six months was at least partially attributable to treating that waste.

Presence of Mercury Laden Solids

In July of 1990 the mercury content of the waste water could not be reduced to below 200 ppb, even after the resin was replaced. The problem with the performance of the IEF became apparent only after the resin was replaced, and the fresh resin failed to reduce the mercury content of the waste water to below 200 to 300 ppb. Prior to this, the behavior of the process was typical of previous experiences with spent resin. It was

immediately apparent, however, that the level of mercury (200 to 300 ppb) in the hold tanks was far above that observed in any of the previous batches which were processed with spent resin (usually 20 to 50 ppb Hg), and the waste water whether treated or not was cloudy and contained a solid which did not readily settle (days to weeks). Some solids have always been present in both untreated and treated waste water; however, they always settled fairly rapidly (within hours).

Table 1 displays the metal content of samples taken from the WWCT prior to this problem (sample 379) and after the problem had occurred (samples 398 and 409). This data shows that the levels of Fe, Li, Mg, Mn and P were significantly different after the problem had occurred. The concentrations of these elements were higher afterwards, except for Li. This indicated that the feed to the IEF was not typical of previous batches. The high level of Fe in the waste water and, to a lesser extent, the Mg and Mn most likely resulted from an IDMS cooling water spill into the IDMS sump (the process water contains a high level of iron). It should be noted that the high levels of P in samples 398 and 409 were due to residual monosodium phosphate (see above): since the untreatable waste water was recirculated through the system several times, the P was distributed throughout the IEF tanks.

During operation with the fresh batch of resin, many side tap and effluent samples were taken from the columns and analyzed for mercury. The locations of the side tap samples are shown in Figure 2, and the resulting column and effluent profiles of mercury are shown in Figures 3A and 3B, respectively. Note that the set of points in Figure 3B at 0.5 hours corresponds to the between the column sample and the effluent sample in Figure 3A. The data in these figures demonstrate two important facts: 1) the resin was removing some of the mercury (Figure 3A), and 2) both columns attained the same performance limit of around 250 ppb (Figure 3B). The later result was very uncharacteristic of fixed bed processes and suggested that some of the mercury must have been attached to a solid which was passing through the columns untreated by the resin. It should be noted that, by this time, many other causes were ruled out: analytical error, resin fouling by organics in the feed, resin fouling by microbial or algae growth, and an improper batch of resin. Moreover, laboratory tests showed that the waste water could be filtered through a $0.45\ \mu\text{m}$ filter. Therefore, both filtered and unfiltered waste water were tested with fresh GT-73 resin.

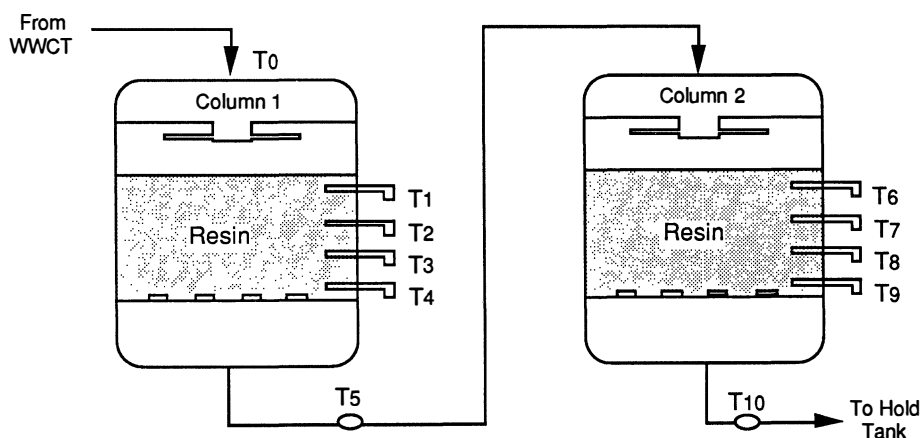


Fig. 2. IEF columns: sample tap numbers and locations.

Untreatable waste water from the WWCT contained 400 ppb mercury prior to being treated overnight with fresh resin and 200 ppb after. Note that the level of Hg remaining in the sample was similar to the level observed in the process (see Figure 3). On the other hand, the filtrate from a $0.45\ \mu\text{m}$ filter contained only 200 ppb mercury prior to being treated overnight with resin and less than 10 ppb after. Clearly, filtering alone removed about 200 ppb of Hg from the sample and, more importantly, GT-73 effectively removed Hg from the filtered waste water. This last result was further verified by generating a sorption isotherm. Two different samples of filtered ($0.45\ \mu\text{m}$) waste water from the WWCT and varying amounts of fresh resin were placed in sample vials and allowed to equilibrate overnight while being shaken. In this way, a sorption isotherm was generated for each sample. They are both displayed in Figure 4. The slopes of these curves are very close to that published in the literature ($K_d = 7.0 \times 10^4\ \text{ml/g}$) (Bibler, *et al.*, 1986). Overall, these results demonstrated that the resin performed as expected for the removal of the soluble mercury but it could not remove the mercury trapped in the solids as the solid particles were too large to be sorbed by the resin.

The amount of solids collected on a $0.45\ \mu\text{m}$ filter corresponded to a concentration in solution of

approximately 50 ppb. A qualitative analysis identified the following elements in the solids: $\text{Fe} \approx \text{Ca} > \text{Hg} > \text{Zn} \gg \text{Cr}$. A more quantitative analysis identified O, S, Ca, Fe, P, Si and Cl respectively at 20, 8, 6, 5, 2, 0.3 and 0.3 wt. %. Based on this information, there is evidence in the literature which suggests that, among other compounds, mercuric sulfide may have co-precipitated with ferric chloride which facilitates flocculation (Singer and Nowak, 1981). Furthermore, the average particle size was $1.44 \mu\text{m}$, and 93% were less than $3 \mu\text{m}$. By definition, a colloid is 1 micron or less in diameter (Hiemenz, 1977); thus, the solids in the waste water formed, in part, a colloidal suspension. This result may explain the unusually slow settling rate which was on the order of days. Also, it further substantiates the formation of mercuric sulfide which forms extremely small particles that generally require a flocculating agent to remove them from an aqueous solution (Singer and Nowak, 1981).

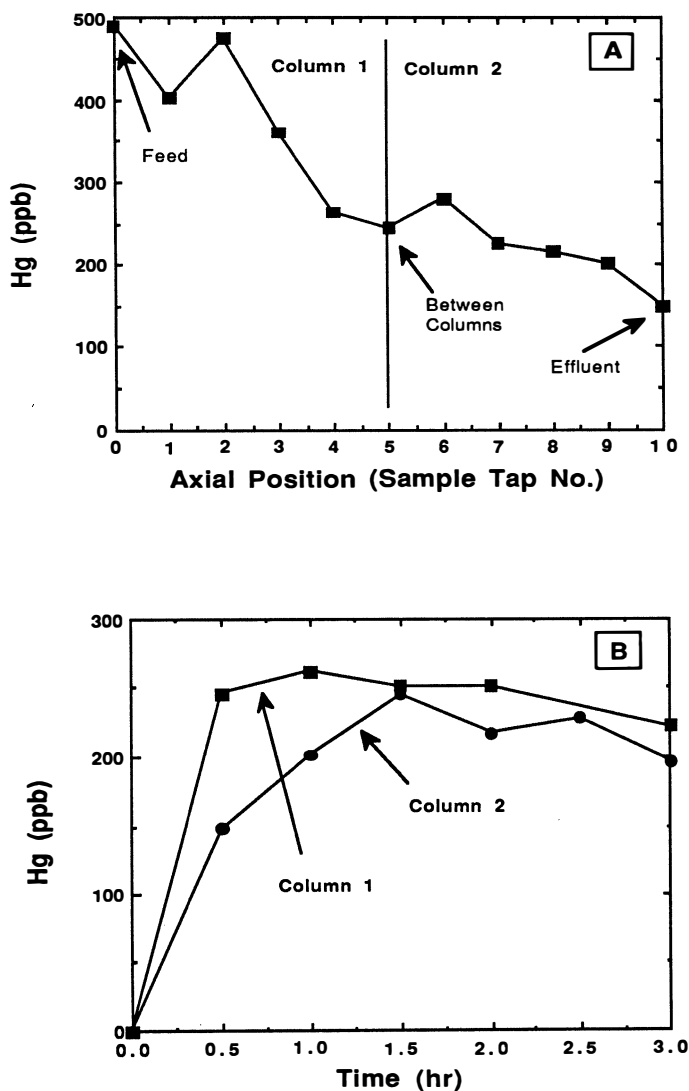


Fig. 3. Column (A) and effluent (B) profiles during operation of the IEF with mercury laden solids in the waste water.

It also appears that the solids are most likely a result of post precipitation in the feed to the IEF since

adequate time for precipitation prior to filtering is not available. The time between pH adjustment and complete precipitation can be 30 minutes, whereas the retention time between pH adjustment and filtering can be seconds. Moreover, although there have always been some solids in IEF samples, they apparently did not contain much Hg otherwise the 10 ppb limit would not have been met. There are two possibilities as to why the solids only recently adsorbed a considerable amount of Hg: 1) the solids may have been slowly building up throughout the IEF, especially since treated waste water in the hold tanks has been recycled numerous times back to the WWCT with no further means of filtering, and 2) as stated previously, the composition of the waste water suddenly changed due to a spill, which may have immediately caused the problem. In either case, it is known that Hg forms amalgams with many different metals, so amalgamation, co-precipitation or both phenomena occurring in the WWCT and throughout the IEF were entirely plausible. For these reasons, a 0.2 μm cartridge filter was installed between the WWCT and the first column.

Improved Process Performance

Figure 5 displays column profiles of mercury obtained after treatment of the laboratory waste was discontinued and the 0.2 μm cartridge filter was installed. The data in these figures show that the first column alone was capable of reducing the mercury content of the waste water to below the permitted level and that the second column was acting only as a polishing step in the waste water treatment process. The level of performance exhibited by the first column has never been observed in the IEF. Moreover, to date, the same batch of resin has processed $\approx 100,000$ litres of waste water, which is three times that observed in the past, and column 1 still has enough capacity to reduce the mercury concentration to below 10 ppb. The cost savings are obvious: the process performance has improved 300% and is expected to increase even further. In addition, because there is some speculation that the mercury laden solids may have contributed to the poor performance of the IEF during the first six months of operation, the previous four batches of supposedly spent resin are being tested for residual mercury capacity, as they may still be used in the IEF.

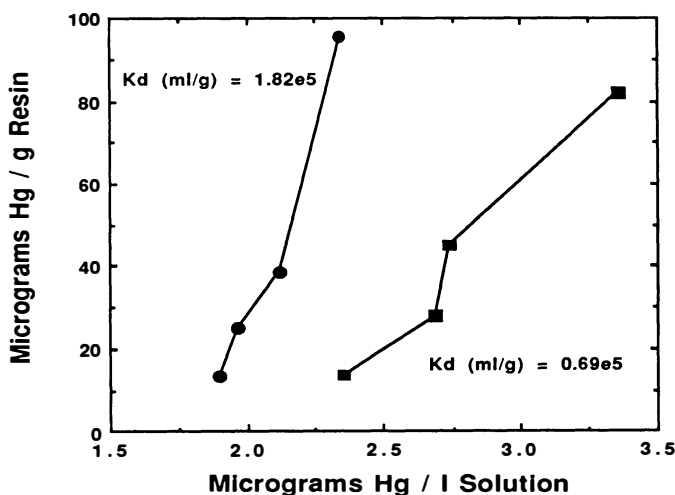


Fig 4. GT-73 sorption isotherms: removal of Hg from the filtrate of waste water containing the Hg laden solids.

As an aside, the mercury profile in the second column (Fig. 5) suggests that 1 to 5 ppb Hg may be a lower limit for the removal of mercury from this waste water by GT-73. This range was further substantiated with bench-scale testing: effluent concentrations below 1 ppb have never been observed. However, since the waste water contains up to a few thousand ppms of organics, there is a possibility that this apparent lower limit is caused by organomercury compounds, which the resin can not remove.

CONCLUSIONS

Duolite™ GT-73 ion exchange resin routinely reduces the mercury content of a SRS waste water stream to

less than the permitted level of 10 ppb. However, two operational problems have been encountered with the IEF. Firstly, the stated capacity of the resin for mercury was not being achieved. This problem was presumably caused by the intermittent treatment of analytical laboratory waste. Secondly, the IEF was temporarily shut down because the mercury content of the waste water could not be reduced to below the permitted level. This problem was caused by solids in the waste water which contained mercury and passed through the resin untreated. After these two problems were solved by 1) discontinuing the treatment of the analytical laboratory waste, and 2) installing a 0.2 μm cartridge filter between the WWCT and the first column, the process performance increased 300% and is still improving. It is anticipated that the stated operating capacity of 30 g Hg/l resin will at least be attained, if not exceeded. Overall, this IEF effectively and efficiently removes mercury from waste water down to a very low level (1 to 5 ppb). It also avoids complications associated with column regeneration and then disposal of mercury in a different medium, especially since Hg laden GT-73 can be landfilled as a non-hazardous waste.

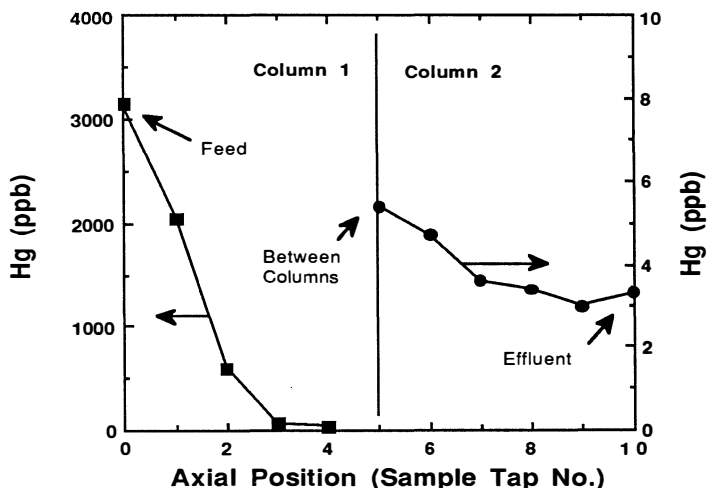


Fig 5. Column profiles during operation of the IEF after treatment of the laboratory waste was discontinued and the cartridge filter was installed. Note the scale changes.

ACKNOWLEDGEMENT

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