This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U. S. Department of Energy.

WSRC-TR-2002-00046, Rev. 0

keywords: Mercury, Kd-test, TCLP
retention: Permanent

Mercury Removal Performance of Amberlite™ GT-73A, Purolite™ S-920, Ionac™ SR-4 and SIR-200™ Resins

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January 16, 2002

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ABSTRACT

Testing looked at the mercury removal performance of various resins: Amberlite™ GT-73A from Rohn & Haas, Purolite™ S-920 from Bro-Tech Corporation, Ionac™ SR-4 from Sybron Chemicals, and SIR-200™ from Resin Tech. Larger than explained variations from the SIR-200™ testing is due to one data point being one order of magnitude larger than the rest of the data. Analysis in another lab verified the accuracy of this data point. Additional studies must address the chemical stability of SIR-200™ (a possible source for the one outlier data point) in this solution. This study found that the resin SIR-200™ from Resin Tech performed similarly to the resin GT-73A from Rohn & Haas.

INTRODUCTION

The Effluent Treatment Facility (ETF) receives and treats the overhead stream solution from the evaporators. The treatment involves mercury removal with organic resin in a fixed bed configuration. The organic resin typically used for this operation is Amberlite™ GT-73 from Rohn & Haas. Two previous studies[1, 2] investigated and recorded the performance of Amberlite™ GT-73A resin. Recently, ETF resin inventory has ran low and ETF personnel asked Savannah River Technology Center (SRTC) investigators to identified a substitute resin to replace Amberlite™ GT-73A. To this end, ETF personnel provided SRTC investigators with three different resins: Purolite™ S-920 from Bro-Tech Corporation, Ionac™ SR-4 from Sybron Chemicals, and SIR-200™ from Resin Tech. All of these resins have a polystyrene backbone crosslinked with divinyl benzene.[3] The functional group, which contains the thiol (-SH) group responsible for removing mercury in solution, is covalently attached to the styrene of the backbone. Given the chemical similarity between these resins we expect similar mercury removal performance. For example, we expect similar loading isotherm and uptake kinetics (diffusion) of mercury in these resins. Therefore, we decided to evaluate the resins with a simple batch "K_d" test.

This study evaluated the mercury removal performance of these resins in batch tests. Results from the three resins were compared against Amberlite GT-73A resin. In addition, the mercury-loaded resins were submitted for Toxicity Characteristic Leach Procedure (TCLP). Selection of a candidate resin will be based on performance similarity to GT-73A resin in these two tests. The candidate resin must also prove stable in solutions typically seen in the ETF. Because of similarity in chemistry between the resins and GT-73A, we expect no instability issues.

EXPERIMENTAL

Pretreatment

Personnel located samples from four resins: Amberlite™ GT-73 from Rohn & Haas, Purolite™ S-920 from Bro-Tech Corporation, Ionac™ SR-4 from Sybron Chemicals, and SIR-200-RTI6664™ from Resin Tech. We determined the amount of water in each resin by thermal-gravimetric analysis (see Figures 1-4 in Appendix A). The estimated water content in each resin is shown in Table 1.

Table 1. The Water content (wt%) of the four resins studied here.

Resin Type	**% water**
SR-4	11.75
SIR-200	1.312
GT-73A	6.78
S-920	40.98

Personnel used the resin as received (i.e., no attempt was made to sodium convert the resins). Although facility personnel at ETF sodium pre-treat their resin, exposing the resin (in hydrogen form) to 1500 ppm sodium nitrate solution will convert all of the resins to the sodium form. Personnel weighed 0.1 grams of material from each resin and placed then in six 60-mL high-density polyethylene bottles. Personnel then added 45 mL of 200 ppm Hg and 1500 ppm $NaNO_3$ solution to the bottles. This is the most concentrated solution these resin may see at the ETF facility. The bottles were placed in a shaker and shook at 400 rpm (to ensure complete levitation of the granules in the bottles) for 14 days at ambient temperature. This duration proved more than sufficient to reach steady state loading[1]. The temperature in the shaker varied from 24.3 °C to 25.8 °C during the testing. At the end of the test, the bottles were removed from the shaker and the slurry filtered from each bottle using a dead-end filtration unit. The filtrate was submitted to ETF (Effluent Treatment Facility) Labs for Cold-Vapor Atomic Absorption (CVAA). The results are given in terms of K_d units (mL/g) instead of the mmoles of Hg per gram of resin units or in decontamination factor units. The use of "K_d" units will allow comparison with previously published data on ion exchange resin performance. In a separate testing, personnel exposed 100 grams of each resin to 250 mL of the 200 ppm Hg (measurements indicated 165 ppm) and 1500 ppm $NaNO_3$ solution for two weeks (the investigator guessed a mercury K_d value of 10^5 mL/g in order to design this experiment for the four resins). The loaded resins were washed with de-ionized water and sent to the Environmental Chemistry & Analysis Group in Charleston, SC for Toxicity Characteristic Leaching Procedure (TCLP).

RESULTS AND DISCUSSION

Figure 1 shows the mercury loading of the four different resins. A closer look at Figure 1 shows large variability in the data collected for the four resins. The largest variable in mercury concentration was obtained with SIR-200™ resin samples. The sources of variability in the data collected derived from; weighting the samples (water content of the resin), weighting the solutions, incomplete filtration of the slurry at the end of the test, temperature variations in the shaker, non-uniform shaking among the samples, and the mercury concentration measurements of the solutions by Cold-Vapor Atomic Absorption (CVAA). The percent error in weighting the samples was 41 % for the S-920™ resin and it ranged from 0.6 to 1 % for rest of the resins. The percent error in weighting the solutions ranged from 0.2 to 0.3 %. The percent error in the determination of mercury in solution usually ranges from 5 to 10 %. According to the law of propagation of errors, the expected error in Kd values should be 42 % for the S-920 resin and 10 % for the rest of the resins.

$$\left(\frac{\Delta K_d}{K_d}\right)^2 = \left(\frac{\Delta Concentration}{Concentration}\right)^2 + \left(\frac{\Delta \text{Re sin } Weight}{\text{Re sin } Weight}\right)^2 + \left(\frac{\Delta Solution\ \ Weight}{Solution\ Weight}\right)^2$$

The percent error in the Kd values observed in this study ranged from 30 to 65 % (65 % was seen in the SIR-200™ testing). One of the data points from the SIR-200™ testing is one order of magnitude higher that the other five data points. We re-submitted the sample to another lab and the same high value was obtained. The investigator believes the outlier data point is due to resin instability. Therefore, in a conservative design the amount of resin in a fixed bed column and the flow-rate of solution through the bed must be determined from the lowest Kd values obtained in the batch test (over-design).

The largest mercury Kd value ($3.53 \pm 1.1 \times 10^6$ mL/g) was obtained with the GT-73A™ resin commonly used at SRS (see Appendix A for the raw data). This number is comparable to the range of values (from 1.24×10^5 to 6.7×10^6) obtained in Reference 1. The resin with performance most similar to GT-73A™ – testing could not discriminate the performance between these two resin – was resin SIR-200™ from Sybortec. The measured mercury Kd value was 2.64 ± 1.7 $x10^6$ mL/g. The other resins tested S-920™ and SR-4™ provided lower mercury K_d values ($2.3 \pm 0.43 \times 10^4$ and $1.4 \pm 0.41 \times 10^6$ mL/g respectively) relative to GT-73A™. The low Kd value from the S-920™ may be an unsteady state value (slower loading kinetics). Testing did not look at variations in mercury loading with solution pH or ionic strength.

The effect of converting the resins to the sodium form reduces the Kd values by 5 to 6 %. For example, GT-73A™ has a capacity of 1.4 eq/L and the resin density is

800 grams of resin per 1.4 L (including a 40 % swelling in going from hydrogen to sodium form). Therefore, 0.1 grams of hydrogen form resin is replaced by 0.1056 grams of sodium form resin.

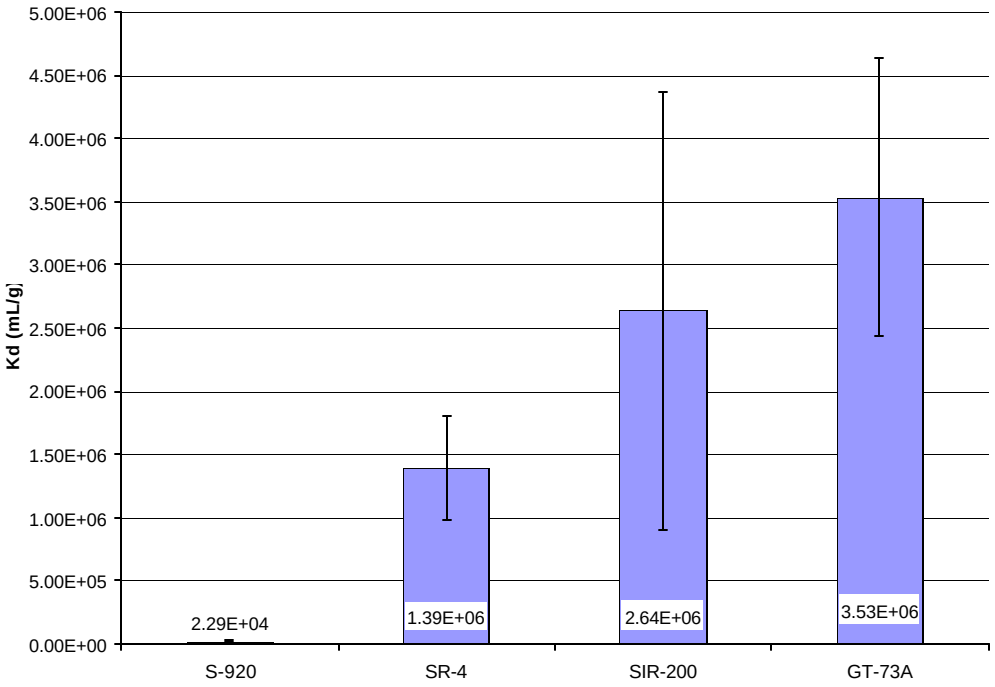

Figure 1. The mercury loading on resins from Sybron (SR-4), Resin Tech™ (SIR-200), Amberlite™ (GT-73) and Purolite™ (S-920)

The cause of the poor performance of the SR-4™ and S-920™ resins is unknown at this time. A possible explanation is higher sodium loading in the resins or resin degradation (loss of capacity) or fouling of the resin. Future testing should include spectroscopy and microscopy analysis of these resins (SR-4™ and S-920™) for fouling material. In addition, sodium analysis of the solution should be considered since sodium is a competitor. At the molecular level, the difference between the four resins exists on the molecule where the thiol group (-SH) resides. For example, the functional group in the resin S-920 is RCH_2—S—C—N_2H_3. In the resin SIR-200, the thiol group is attached next to an aromatic ring (styrene—R-SH). Similarly, the resin GT-73 has its thiol group next to an aromatic ring. In the other hand, the resin SR-4 has its thiol group next to an aliphatic molecule (R—SH). The similarity in chemistry between SIR-200 and GT-73A may explain the similar mercury removal performance in this solution. The large performance variability of the SIR-200™ resin introduces large uncertainty in the prediction and design with this resin. Therefore, additional studies should be conducted to examine the chemical stability of this resin in this

solution. The final Kd value from the TCLP testing (100 grams of resin in 1.5 L of 200 ppm mercury) follows (see Table 2).

Table 2. The Mercury Kd values of the TCLP test solutions.	
Resin Type	Kd (mg/L)
SIR-200	8787
S-920	16843
SR-4	4809
GT-73A	5396

Looking at Table 2, it is noted the Kd values obtained in the TCLP test are two to three orders of magnitude lower than the values obtained in the 0.1 grams test (One exception is the Kd value from the S-920 resin test). The reason for this difference is the liquid to solid ratio used in this test. In the TCLP test the ratio was 2.5 mL/g while in the 0.1 grams test the ratio was 450 mL/g. In addition, the large amount of resin used in the test (100 grams) limited uniform mixing (complete levitation of the granules) of the slurry. The effect of non-uniform mixing is to lengthen the time for loading the resin. Since the diffusion of the mercury ions through a “thick” boundary layer outside the individual granules is the rate-controlling step. Therefore, the Kd values will be lower.

TCLP results

All resins leached less than regulatory levels of RCRA metals in the TCLP test as shown in Table 3.

TABLE 3. THE METAL CONCENTRATION OF THE LEACHATE SOLUTION FROM GT-73A, S-920, SR-4 AND SIR-200 RESINS					
RCRA Metal	SR-4	SIR-200	S-920	GT-73A	RCRA Limit
Mercury	0.000	0.0000	0.0001	0.0001	0.2
Arsenic	0.0306	0.0015	0.0001	0.0001	5.0
Barium	0.00885	0.012	0.011	0.0102	100
Cadmium	0.002	0.0006	0.00172	0.0001	1.0
Chromium	0.0051	0.0016	0.00316	0.00445	5.0
Lead	0.0024	0.0042	0.0001	0.00473	5.0
Selenium	0.0000	0.0126	0.0001	0.0001	1.0
Silver	0.0040	0.0036	0.0000	0.00223	5.0

CONCLUSION

This study evaluated the mercury removal performance of four different resins: Amberlite™ GT-73A from Rohn & Haas, Purolite™ S-920 from Bro-Tech Corporation, Ionac™ SR-4 from Sybron Chemicals, and SIR-200™ from Resin Tech. Larger than explained variations from the SIR-200™ testing is due to one data point being one order of magnitude larger than the rest of the data. This sample was re-analyzed by another lab and its mercury concentration was verified. Therefore, a plausible explanation of this outlier data point is resin instability and additional studies must be conducted. This study found similar performance between SIR-200™ and GT-73A. The user can replace GT-73A resin with SIR-200™ but it must be keep in mind that chemical instability of this resin can play a role. All four resins successfully passed the TCLP test.

References:

[1] W. R. Wilmarth, "Duolite™ GT-73 Resin Testing in Support of the Salt Disposition Alternatives," WSRC-TR-98-00361, October 2, 1998.

[2] L. N. Oji, "Evaluation of Crystalline Silicotitanate and Self-Assembled Monolayers on Mesoporous Support for Cesium and Mercury Removal From DWPF Recycle", WSRC-RP-99-00331, September 22, 1999.

[3] Ionac™ SR-4 Selective Ion Exchange Resin from Sybron Chemicals, MSDS # 28803-1.
SIR-200™ from ResinTech, MSDS # 28801-1.
Purolite™ S-920 Ion Exchange Resin from Bro-Tech Corp. MSDS # 14077-1.
Amberlite™ GT-73A Ion Exchange Resin from Rohn & Haas, MSDS # 969-1.

Appendix A

The Thermogravimetry analysis of the four resins follows.

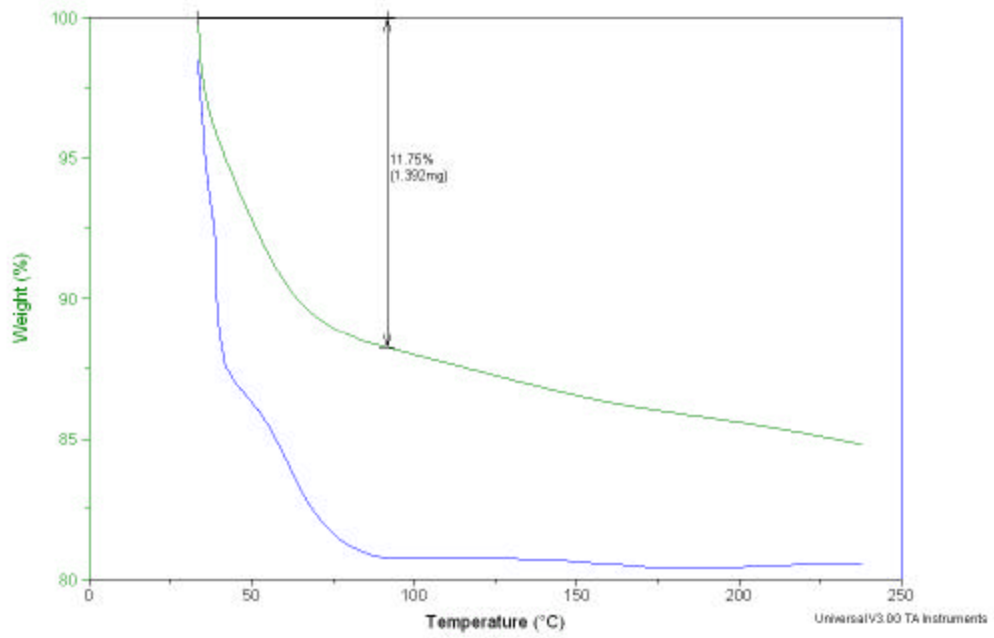

Figure 2. Weight loss (green) and differential weight loss curve (blue) of the resin from IONAC ™ SR-4.

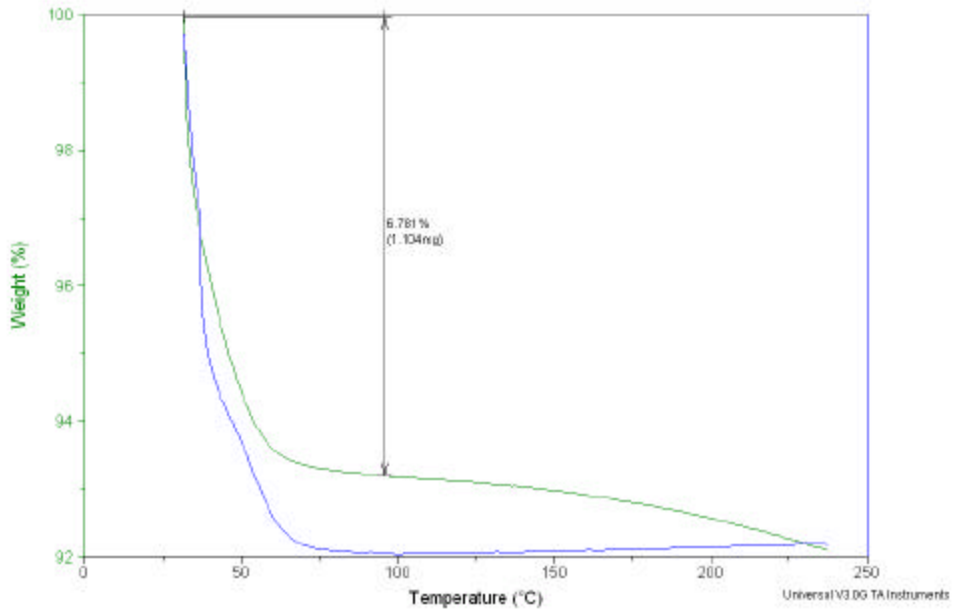

Figure 3. The weight loss and the derivative of the weight loss curve of GT-73A resin from Rohn & Haas.

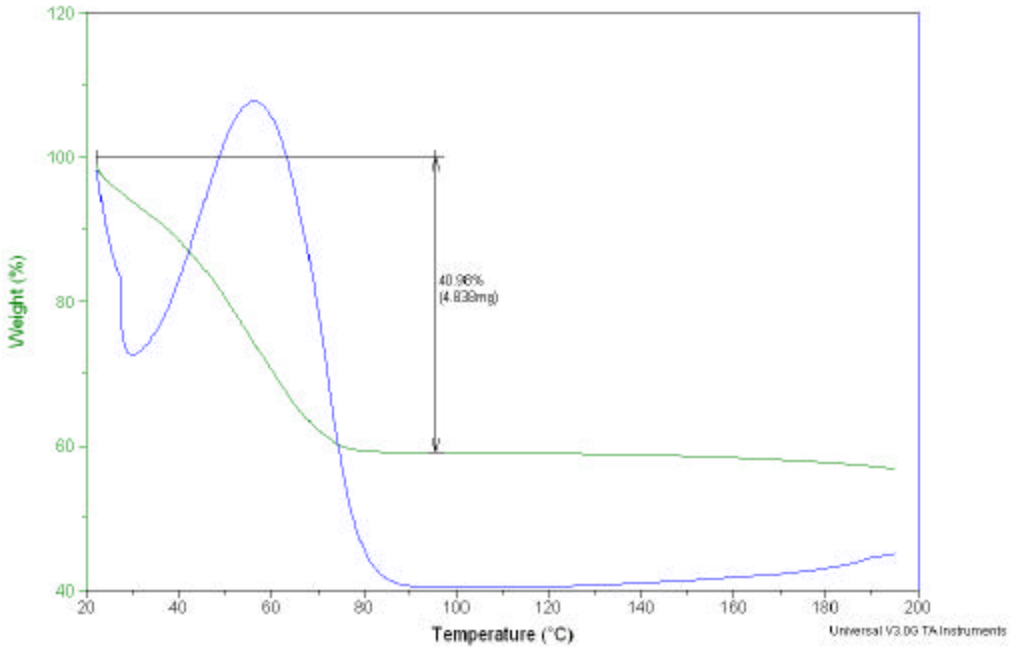

Figure 4. Weight loss (green) and the derivative of the weight loss curve of the S-920 resin from Purolite™.

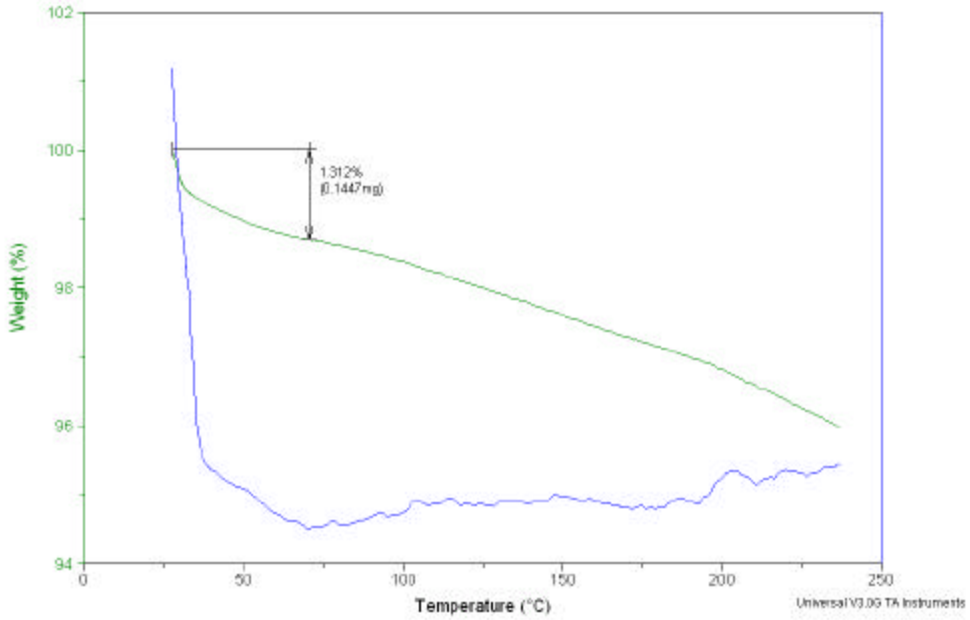

Figure 5. The weight loss and the derivative of the weight loss curve of SIR-200 resin from Resin Tech.

Appendix B

A list of the measured mercury levels in solution after exposure to the four resins in the batch test (see Table 4).

Table 4. Mercury concentration (mg/L) of the solutions from the K_d test after contacting the different resins.

GT-73A	S-920	SR-4	SIR-200
0.06	5.114	0.075	0.407
0.021	5.676	0.088	0.06
0.018	3.76	0.072	0.047
0.024	5.796	0.069	0.018
0.016	6.141	0.04	0.022
0.022	5.922	0.045	0.014

The K_d values was obtained from the concentration given in Table 2, the initial concentration (165 ppm), the sample weight and the volume of solution used as indicated in the equation below:

$$K_d = \left(\frac{C_{Initial}}{C_{final}} - 1 \right) \times \frac{45 mL}{0.1 \text{grams} \times (1 - \text{fraction of water in the resin})}$$