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MERCURY SEPARATION FROM AQUEOUS WASTES

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ABSTRACT

This project is providing an assessment of new sorbents for removing mercury from wastes at U.S. Department of Energy sites. Four aqueous wastes were chosen for lab-scale testing; a high-salt, acidic waste currently stored at Idaho National Engineering Laboratory (INEL); a high-salt, alkaline waste stored at the Savannah River Site (SRS); a dilute lithium hydroxide solution stored at the Oak Ridge Y-12 Plant; and a low-salt, neutral groundwater generated at the Y-12 Plant.

Eight adsorbents have been identified for testing, covering a wide range of cost and capability. Screening tests have been completed, which identified the most promising adsorbents for each waste stream. Batch isotherm tests have been completed using the most promising adsorbents, and column tests are in progress. Because of the wide range of waste compositions tested, no one adsorbent is effective in all of these waste streams. Based on loading capacity and compatibility with the waste solutions, the most effective adsorbents identified to date are SuperLig 618 for the INEL tank waste simulant; Mersorb followed by Ionac SR-3 for the SRS tank waste simulant; Durasil 70 and Ionac SR-3 for the LiOH solution; and Ionac SR-3 followed by Ionac SR-4 and Mersorb for the Y-12 groundwater.

solutions that were sent to off-site laboratories, and now are being returned to SRS for disposal. This waste solution contains low concentrations of acetonitrile and mercury, and the volume generated is currently about 14,000 L/year.

Four waste solutions were chosen for laboratory-scale testing for this project, the INEL and SRS tank wastes, the Y-12 LiOH solution, and the Y-12 groundwater stream. The INEL and SRS wastes contain very high concentrations of radionuclides, so simulants are being used in the laboratory-scale tests. Formulations were obtained from INEL[4] and SRS[5] for the simulants. The major contaminants in these waste streams are shown in Tables 1 and 2. Water from the D-3871 sump at the Y-12 Plant, which contains traces of nitrate and VOC's as well as mercury, and the LiOH solution are also being used in our tests. Table 3 gives a typical metals analysis of the sump water, and Table 4 gives the metals concentrations in a sample of the LiOH solution. The selected waste streams cover a wide range of compositions, so this project should provide useful information for other mercury-containing aqueous wastes that may be generated in the future. Previous work by Ralph Turner of the Environmental Sciences Division at Oak Ridge National Laboratory (ORNL) has shown that the Y-12 sump water contains a mixture of ionic mercury and dissolved elemental mercury. All of the other solutions contain only ionic mercury. The maximum concentration of mercury that dissolved in the SRS simulant was 108 mg/L, which is much less than the maximum concentration measured in the SRS tank waste solution (440 mg Hg/L). The solubility of mercury in the INEL simulant was 278 mg/L, which is lower than the maximum value of 400 mg/L measured in the actual waste.

2.2 ADSORBENTS TESTED

Potential adsorbents for mercury were identified from literature sources and contacts with manufacturers. Eight different adsorbents (Table 5) were chosen for testing on the waste streams listed above. Information from the manufacturers of these products is described below.

The isothiouronium active site of the Ionac SR-3 resin (Sybron Chemicals, Inc., Birmingham, NJ) selectively chelates mercury and precious metals such as gold, silver or platinum group metals. It is stable in a pH range of 1 to 6, but the active sites are destroyed by strong oxidizing agents such as chlorine. The resin binds essentially all forms of mercury, ionic, elemental and organic, but it can not be regenerated. The cost is \$390/ft^3. The Purolite Company (Bala Cynwyd, PA) makes a similar resin called S-920 which was not tested.

Ionac SR-4 has a thiol active site that selectively binds mercury and other heavy metals. The selectivity of the resin is dependent on the insolubility of the associated metal sulfide complexes, so mercury is adsorbed preferentially to most heavy metals. The resin can be used in a pH range of 1 to 14 and has good chemical stability. The resin binds ionic forms of mercury, and is regenerable with 30% hydrochloric acid (HCl). The cost is \$470/ft^3. Rohm and Haas (Philadelphia, PA) makes a similar resin called Amberlite GT-73.

Amberlite IRC-718 (Rohm and Haas) is a complexing resin with an iminodiacetate functional group that is selective for heavy metals. The relative selectivity of the resin varies depending on the composition of the solution being treated. It can be used in a pH range of 1.5 to 14, and will bind ionic forms of mercury. The resin is regenerable with 15% HCl, and the cost is \$390/ft^3.

Mersorb (NUCON International, Inc., Columbus, OH) is an activated carbon product that is impregnated with sulfur. The adsorbent is selective for mercury and other heavy metals, based on the insolubility of the associated metal sulfide complexes. Mersorb binds ionic mercury, but could also adsorb elemental and organic forms on the activated carbon substrate. The adsorbent is unstable in strong acid solutions, forming hydrogen sulfide gas. Mersorb is not regenerable, and the cost is \$130/ft^3.

1. INTRODUCTION

This project is providing the U.S. Department of Energy (DOE) with an assessment of state-of-the-art sorbent technologies for processing mercury-containing aqueous waste streams. The project includes a characterization of mercury-contaminated aqueous waste streams at DOE facilities, and the testing of selected technologies for treating those streams to remove mercury. The laboratory studies will produce equilibrium data and correlations, kinetic information, and column breakthrough data, which can be used to design full-scale systems and predict performance and cost for treatment systems using the various sorbents. This report is a semi-annual update of the progress achieved on evaluating new sorbents.

U.S. Department of Energy facilities are producing or storing a wide range of mercury-containing aqueous wastes. Many of the wastes contain radionuclides in addition to other RCRA hazardous constituents. Various sorbents are being tested for removal of mercury from these wastes prior to discharge or further treatment. Several of these wastes are scheduled to be stabilized using vitrification or high temperature calcination, so it may be desirable to remove mercury from the wastes prior to treatment to reduce the potential for air discharges of mercury. Other waste streams need to be treated for mercury to meet discharge permit requirements.

2. MATERIALS AND METHODS

2.1 IDENTIFICATION OF MERCURY-CONTAINING WASTE STREAMS

An initial survey of mercury-containing mixed wastes, including aqueous wastes, was conducted by J. J. Perona and C. H. Brown as part of a technology assessment project in 1993[1]. This report was used as a starting point for our survey. Other DOE reports on technology needs[2,3] were reviewed and contacts were made with personnel at various DOE sites. A variety of mercury-containing aqueous wastes have been identified at DOE facilities. Idaho National Engineering Laboratory (INEL) has about 7.5M L of a high-salt, acidic waste that contains about 400 mg Hg/L. The Savannah River Site (SRS) has about 380M L of a high-salt, alkaline waste that contains about 440 mg Hg/L (ORNL and Hanford have similar waste streams, but with much lower mercury concentrations). All of these wastes contain high concentrations of radionuclides. The Oak Ridge Y-12 Plant has about 80,000 L of dilute lithium hydroxide (LiOH) solution (about 3000 mg/L Li) containing 30 to 60 mg Hg/L. The Y-12 Plant, SRS and the Hanford site all have low-salt, neutral, groundwater and process wastewater streams containing trace quantities of mercury (up to 0.4 mg/L). These low-salt streams may also contain volatile organic compounds (VOC's), other heavy metals and trace levels of radionuclides.

The *DOE Mixed Waste Treatment Technology Needs*[2] report listed the solar pond water at Rocky Flats as the largest mixed waste aqueous stream needing mercury treatment; however, discussions with Rocky Flats personnel indicated that the pond water did not contain any mercury. The *Technology Needs Crosswalk Report*[3] was also examined, but no mercury-containing aqueous mixed waste streams were identified.

Several other mercury-containing waste streams have been recently identified, but the characterization data on these waste streams are limited at the present time. INEL has three mixed-waste tanks (called the V-tanks) that hold about 40,000 L of aqueous waste that contains heavy metals including mercury, volatile organic compounds and high levels of radionuclides. SRS has two dilute waste streams that contain mercury. One stream consists of purge water from sampling groundwater wells. This wastewater is stored in drums and contains low concentrations of trichloroethylene (TCE), perchloroethylene (PCE) and mercury. SRS currently has about 35,000 L of this wastewater stored. The other waste stream is analytical samples and associated

Table 1. Concentration of major contaminants in INEL high-sodium tank waste

Contaminant	*Conc. (M)*
NaNO3	1.78
HNO3	1.66
$Al(NO_3)_3$	0.55
KNO_3	0.23
HF	0.05
$Ca(NO_3)_2$	0.04
H_2SO_4	0.03
$Fe(NO_3)_3$	0.02
H_3BO_3	0.02
HCl	0.02
H_3PO_4	0.01
$Mn(NO_3)_2$	0.01
$Cd(NO_3)_2$	0.002
$Ni(NO_3)_2$	0.002
$Hg(NO_3)_2$	0.002

Table 2. Concentration of major contaminants in SRS tank waste supernate

Contaminant	Conc. (M)
$NaNO_3$	1.95
NaOH	1.33
$NaNO_2$	0.60
$NaAl(OH)_4$	0.31
NaCl	0.22
Na_2CO_3	0.16
Na_2SO_4	0.14
NaF	0.015
KNO_3	0.015
Na_3PO_4	0.008
Na_2SiO_3	0.004
Na_2CrO_4	0.003
$HgCl_2$	0.002

Table 3. Typical metals concentrations in the Oak Ridge Y-12 Plant D-3871 sump water

Metal	Concentration (mg/L)
Al	0.27
Ba	0.18
Ca	58
Cr	0.016
Hg	0.3
Mg	5.4
Mn	0.004
Na	9.3
Si	6.7
Sr	0.16
V	0.004
Zn	0.011

Table 4. Metals analysis of Y-12 LiOH solution sample

Metal	Concentration (mg/L)
Al	2.3
B	0.43
Ba	0.04
Ca	1
Cd	0.008
Co	0.01
Cr	0.11
Cu	0.04
Hg	32
Li	3000
Mg	0.14
Mn	0.015
Na	140
P	0.68
Sb	0.27
Si	142
Sr	0.016
V	0.2
Zn	0.066

Table 5. Description of mercury adsorbents tested

Name/company	Active site
Ionac SR-3	Isothiouronium
Ionac SR-4	Thiol
Amberlite IRC-718	Iminodiacetate
Durasil 70	Proprietary
Mersorb	Sulfur
Filtersorb-300	Activated Carbon
SuperLig 608 & 618	Proprietary

Activated carbon can adsorb mercury, but it has relatively low capacity and it is not selective. Filtersorb 300, an activated carbon manufactured by Calgon Carbon Corp. (Pittsburgh, PA), was included in our tests for comparison with the more selective adsorbents since it is currently being used to treat the sump water at the Y-12 Plant. The cost is about \$62/ft^3.

Durasil-70 (Duratek Corp., Beltsville, MD) is a carbon-based resin that was developed for removing Cobalt-60 from water, but the manufacturer indicates that it would also be selective for mercury. The resin is not regenerable, and the cost is \$1000/ft^3.

SuperLig 608 (IBC Advanced Technology, American Fork, Utah) uses a macrocycle ligand active site to selectively bind mercury, based on the size and chemical properties of mercury ions (molecular recognition technology). It has a selectivity for mercury over a wide range of other heavy metals of $>10^{10}$. The ligand is effective in a pH range of 2 to 14, and the polymeric support material is chemically stable. The adsorbent can be regenerated with >1 M concentrations of any strong acid. SuperLig 618 is a pH independent ligand bonded to a silica gel support. The selectivity is similar to SuperLig 608. The material can be used to remove mercury from acidic to mildly basic solutions. The silica gel support is not stable in strongly basic solutions. The adsorbent can be regenerated with 6 M HCl, 0.5 M HBr, or strong complexing agents such as EDTA, citrate or thiourea. The cost of the SuperLig materials was about \$3000/100 g. Production quantities would be less expensive, but a price was not quoted.

2.3 ANALYTICAL METHODS

Mercury analyses were performed as described in EPA Method 245.1[7] using a Perkin-Elmer (Norwalk, CT) 1100B atomic absorption instrument with a Flow Injection Analysis System (FIAS) 400 attachment. Calibration solutions of 1, 10 and 20 ppb are prepared from a 1.00 mg Hg/mL standard solution (J. T. Baker, Inc, Phillipsburg, NJ). Samples and standards were preserved in a solution of 0.01 wt% $K_2Cr_2O_7$ in 5 wt% HNO_3, and dilutions were made using this same solution. The digestion procedure listed in method 245.1 was tested using all of the wastewater solutions and simulants utilized in this project. Only the LiOH solutions showed a significant difference in mercury concentration between digested and undigested samples; thus, the other solutions were not routinely digested prior to mercury analysis.

2.4 EXPERIMENTAL METHODS

Batch screening tests were conducted using each adsorbent in all of the target waste solutions. Mersorb, which is supplied as 3 mm pellets, was crushed and screened to 20X50 mesh for the batch tests. All of the other adsorbents were used as received from the manufacturers. For the Y-12 sump water, 100 mL of wastewater and 0.1 g adsorbent was contacted in glass bottles placed on a jar mill roller at 50 rpm. Samples were taken after 1, 6, 24 and 48 hrs, filtered and analyzed for mercury. For all of the other solutions the batch tests were conducted in teflon bottles, using 0.1 or 0.2 g adsorbent in 50 mL of solution. For each of these experiments a control test (same type bottle, filter and solution, but no adsorbent) was performed for comparison. The batch isotherm tests were conducted at room temperature using the teflon bottles and jar mill roller as in the screening tests. Samples were collected after 24 hrs, which the screening tests showed was long enough to reach equilibrium. The amount of adsorbent was varied as needed to cover the range of the isotherm. Sorbent loadings were calculated from the difference in liquid mercury concentrations between the test bottles and control bottles that did not contain any adsorbent. Except for the Y-12 sump water, the difference in mercury concentration between the controls and the corresponding starting solution was small.

The column tests were performed in glass columns with teflon seals and support screens. For all tests, the column diameter used was at least 20 times larger than the average size of the adsorbent particles, and the height of the adsorbent bed was at least 4 times the column diameter. Solution was pumped up through the column using a peristaltic pump. An in-line filter was used to remove any particulates from the feed solution, and to trap any air that might enter the system. A fraction collector was used to automatically collect new samples at pre-selected intervals.

3. EXPERIMENTAL RESULTS

3.1 SCREENING TESTS

The results of the screening tests on the Y-12 sump water are shown in Table 6. The SuperLig materials were not tested in this solution since they were received after these tests were

3.2 BATCH ISOTHERM TESTS

Isotherm tests were performed with the most promising adsorbents identified by the screening tests for each solution. The results are shown in Figures 2–5. In all cases the mercury loading on the sorbent is plotted against the mercury concentration left in the solution after 24 hours contact. The isotherms for the Y-12 sump water (Fig. 2) show that Ionac SR-3 can adsorb almost ten times more mercury from this solution than Ionac SR-4 or Mersorb. Each of these adsorbents can produce treated water with very low concentrations of mercury. The results for the Y-12 LiOH solution (Fig. 3) show that Durasil 70 is slightly more effective than Ionac SR-3; however, neither adsorbent would reduce the mercury concentration below 1.8 mg/L, even at high sorbent concentrations of 100 g/L. The isotherm for the SRS simulant solution (Fig. 4) shows that Mersorb is by far the most efficient adsorbent, as was the case in the screening tests. Mersorb can achieve high loadings (100 mg mercury/g) even at very low mercury concentrations. For the INEL simulant (Fig. 5), Ionac SR-4 and SuperLig 618 gave essentially identical results.

3.3. COLUMN TESTS

Lab-scale column tests have been completed using Ionac SR-4 and SuperLig 618 to treat INEL tank waste simulant. The first test used a 2.5-cm I.D. column filled to a height of 12.9 cm. with 40 g (65 mL) of Ionac SR-4 resin. INEL simulant was pumped up through the column at a rate of 5 mL/min (4.6 bed volumes/hr), and effluent samples were collected every 30 min. Figure 6 shows

Table 6. Results of screening tests on Y-12 sump water

Sorbent	Final Hg Conc. (μg/L)	% Removal
SR-3	<0.5	>99.8
SR-4	<0.5	>99.8
Mersorb	2.5	99.0
Durasil 70	25.0	90.0
IRC-718	31.0	86.7
Filtersorb	112	60.3

24-hr batch test, 0.1 g sorbent in 200 mL sump water.
Initial concentration about 300 μg/L Hg.

the breakthrough curve for this test. The average mercury loading on the resin at the end of the test was 15.1 mg/g, which is about half of the maximum value measured in the batch isotherm tests. The mass transfer zone (MTZ) for 5% to 50% breakthrough was 2.4 cm. There were some gas bubbles visible in the resin during the test, but at the time the cause could not be identified.

An attempt was made to regenerate the resin with 30 wt% HCl, as recommended by the resin manufacturer, but the column filled with gas bubbles. The gas was determined to be a mixture of SO_2 and NO_x, presumably caused by a reaction between the nitrate ions in the simulant and the thiol groups of the resin. Subsequent tests with the resin showed that it would not adsorb mercury, indicating that the thiol groups on the resin had been destroyed. Since there were some gas bubbles present in the original column while the INEL simulant was being treated, further compatibility testing was performed. The column was filled with new SR-4 resin, and then INEL simulant was pumped through the column until it was full of liquid. The pump was stopped and the column was monitored for gas formation. No gas bubbles were visible for the first two hours, some bubbles were visible after 3 hrs, and the column was full of bubbles after 4 hrs. The SR-4 resin used in the screening tests had not released any mercury back into solution after 24 or 48 hours contact with the INEL simulant, and the sharp breakthrough for the column test did not occur until after 8 hrs run time. These results suggest that thiol groups which have adsorbed mercury or other heavy metals are more resistant to oxidation by the simulant solution than thiol groups associated with sodium ions. The resin used in the compatibility test did not contact enough simulant to load hardly any of the thiol sites with heavy metals. The reaction between the resin and the simulant solution demonstrates that Ionac SR-4 is not a promising resin for treating the INEL tank waste.

For the next column test, a 1-cm I.D. column was filled to a height of 5 cm. with 1.62 g (3.9 mL) of SuperLig 618. INEL simulant was pumped through the column at 1 mL/min (15 bed volumes/hr). The breakthrough curve is shown in Figure 7. The average loading was 38.2 mg Hg/g resin, which compares well with the batch isotherm results, and the MTZ for 5% to 50% breakthrough was 2.4 cm. The resin was regenerated with 38 mL of 6 M HCl, as recommended by the manufacturer, and 87% of the mercury loaded on the resin was recovered. The regenerated resin was then used for another loading cycle using the same conditions as before (see Fig 7).

The average loading for this test was 34.8 mg Hg/g and the MTZ was 2.3 cm. Regeneration with 44 mL of 6 M HCl recovered 83.1% of the mercury loaded. Another regeneration with 28 mL of 12 M HCl recovered an additional 2.6% of the mercury. This resin will be used for additional loading and regeneration cycles to determine the stability of the resin.

Table 7. Results of screening tests on Y-12 LiOH solution

Sorbent	Final Hg Conc. (mg/L)	% Removal
Durasil 70	6	74.2
Ionac SR-3	7.2	69.1
IRC-718	7.5	67.8
Mersorb	8	65.7
Ionac SR-4	9.6	58.8
Filtersorb	13.8	40.8
SuperLig 608	17.2	26.2

24-hr batch test, 0.2 g sorbent in 50 mL LiOH solution.
Initial concentration 23.3 mg/L Hg.

Table 8. Results of screening tests on SRS tank waste simulant

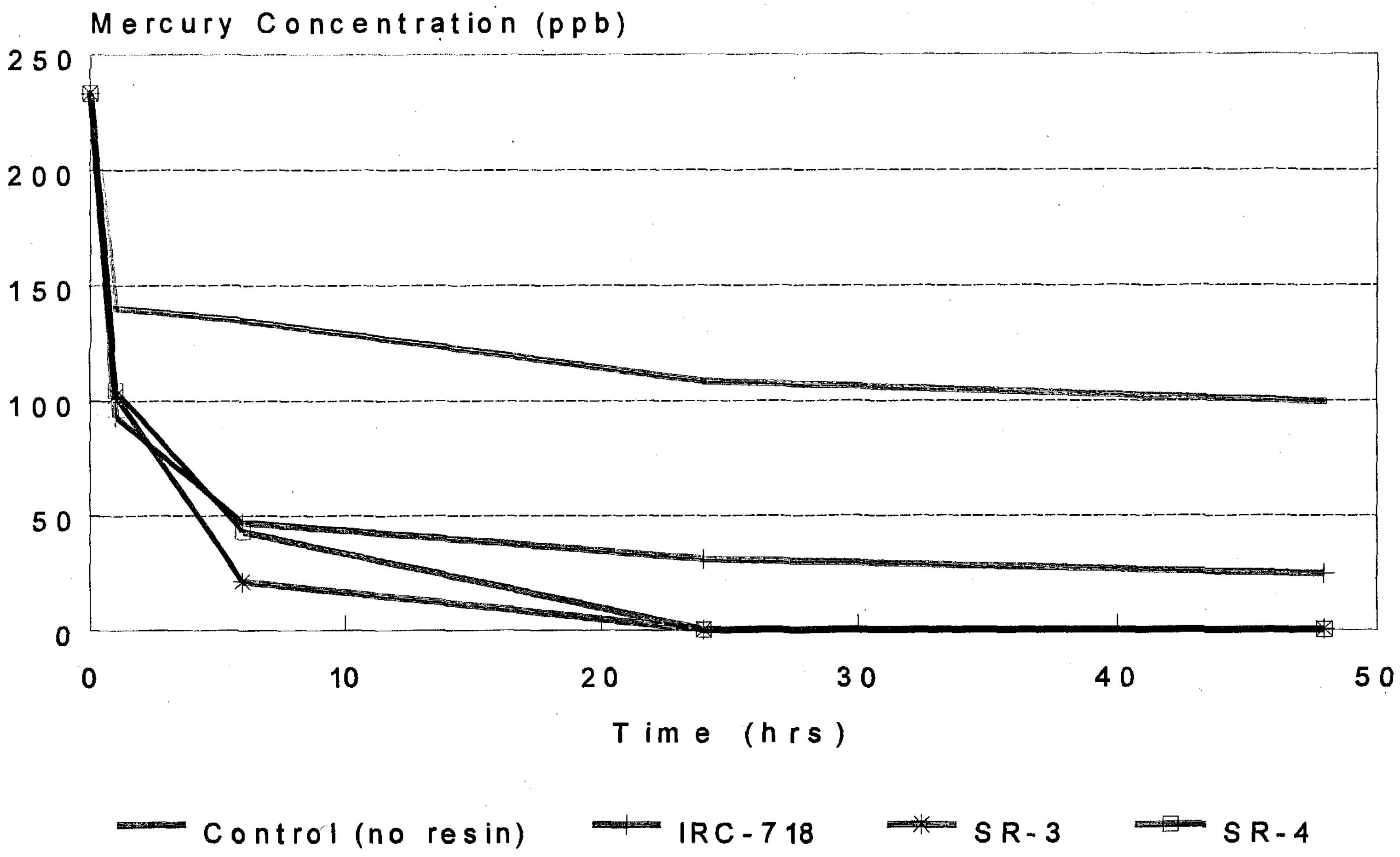
Sorbent	Final Hg Conc. (mg/L)	% Removal
Mersorb	0.8	99.3
Durasil 70	21.9	79.7
SR-3	22.4	79.2
SuperLig 608	24.1	75.1
Filtersorb	60.2	44.1
SR-4	66.6	38.2
IRC-718	68.4	36.5

24-hr batch test, 0.1 g sorbent in 50 mL SRS simulant.
Initial concentration 108 mg/L Hg.

Table 9. Results of screening tests on INEL tank waste simulant

Sorbent	Final Hg Conc. (mg/L)	% Removal
Ionac SR-4	205	25.6
SuperLig 618	213	25.2
Durasil 70	265	3.6
Ionac SR-3	267	3.0
Mersorb	273	0.5
Filtersorb	274	0.4
IRC-718	278	0.0

24-hr batch test, 0.1 g sorbent in 50 mL INEL simulant.
Initial concentration 278 mg/L Hg.



0.1 g resin in 100 mL water

Fig. 1. Screening test results using Y-12 D-3871 sump water.

4. FUTURE PLANS

Column tests will be performed on the other waste solutions that are being examined. Laboratory-scale tests will be used for the SRS tank waste simulant with Mersorb and Ionac SR-3, and the Y-12 LiOH solution will be tested using Durasil 70 and Ionac SR-3. A pilot-scale column test is being planned for the Y-12 sump water, in conjunction with Y-12 personnel. Equipment for this system has been procured using Y-12 Waste Management Division funds, and the system is being assembled at ORNL. The system will be installed at a sump in the basement of Building 9201-5 at Y-12, and operation will be a joint effort, with Y-12 Development Division taking the lead role. This test will provide a direct comparison of three adsorbents for treating the Y-12 sump water. This test will provide Y-12 with the information needed to design a full-scale mercury treatment system.

The results from these tests are being provided to personnel at the appropriate sites (INEL, SRS and Y-12) on a continuing basis. The data will allow informed choices to be made on the types of adsorbents that are appropriate for various waste streams and the relative costs involved.

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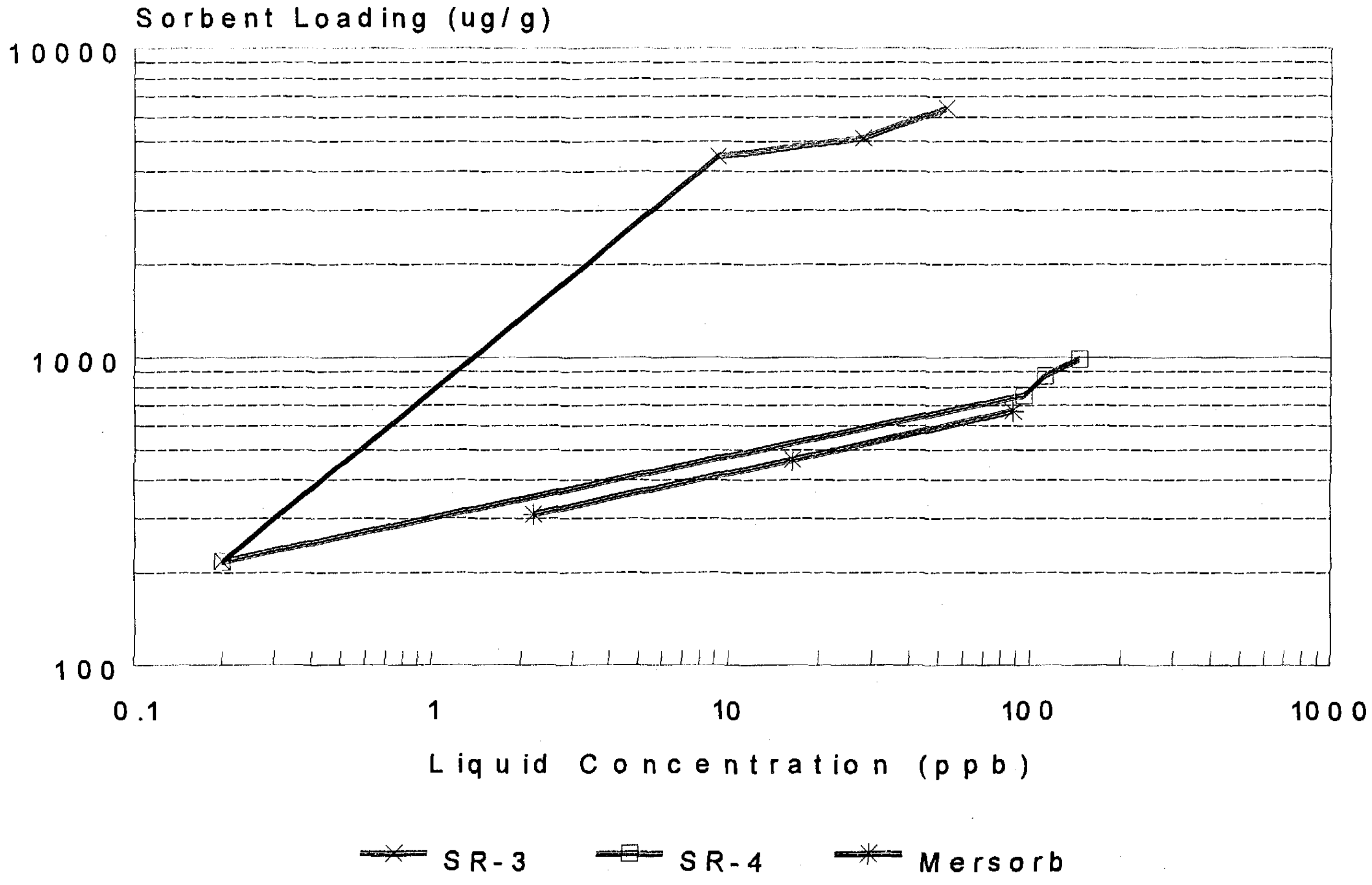

Fig. 2. **Batch isotherm results in Y-12 sump water.** 24-hr batch tests, 220 ppb Hg initially.

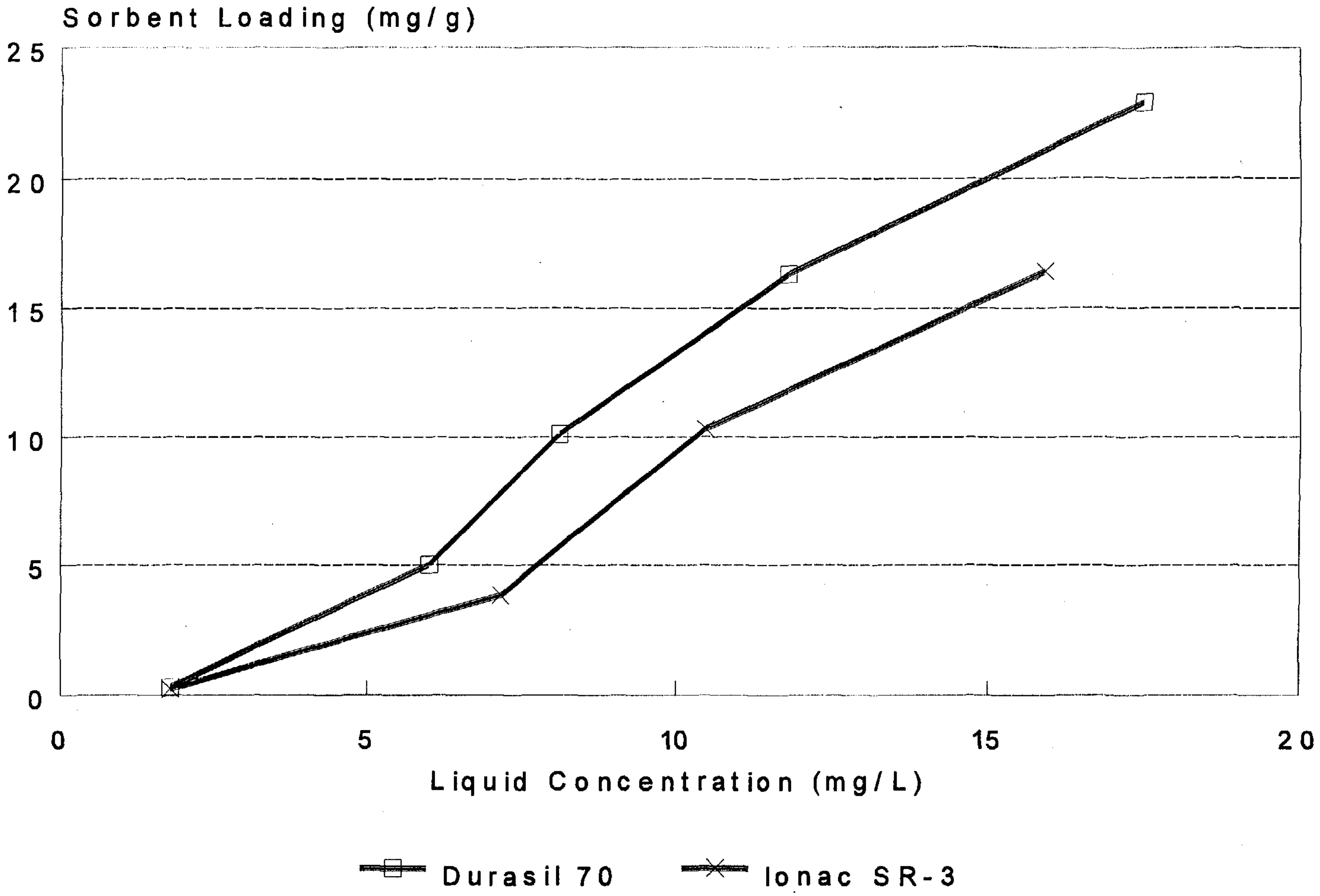

Fig. 3. Batch isotherm results in Y-12 lithium hydroxide solution. 24-h batch tests, 28 mg/L Hg initially.

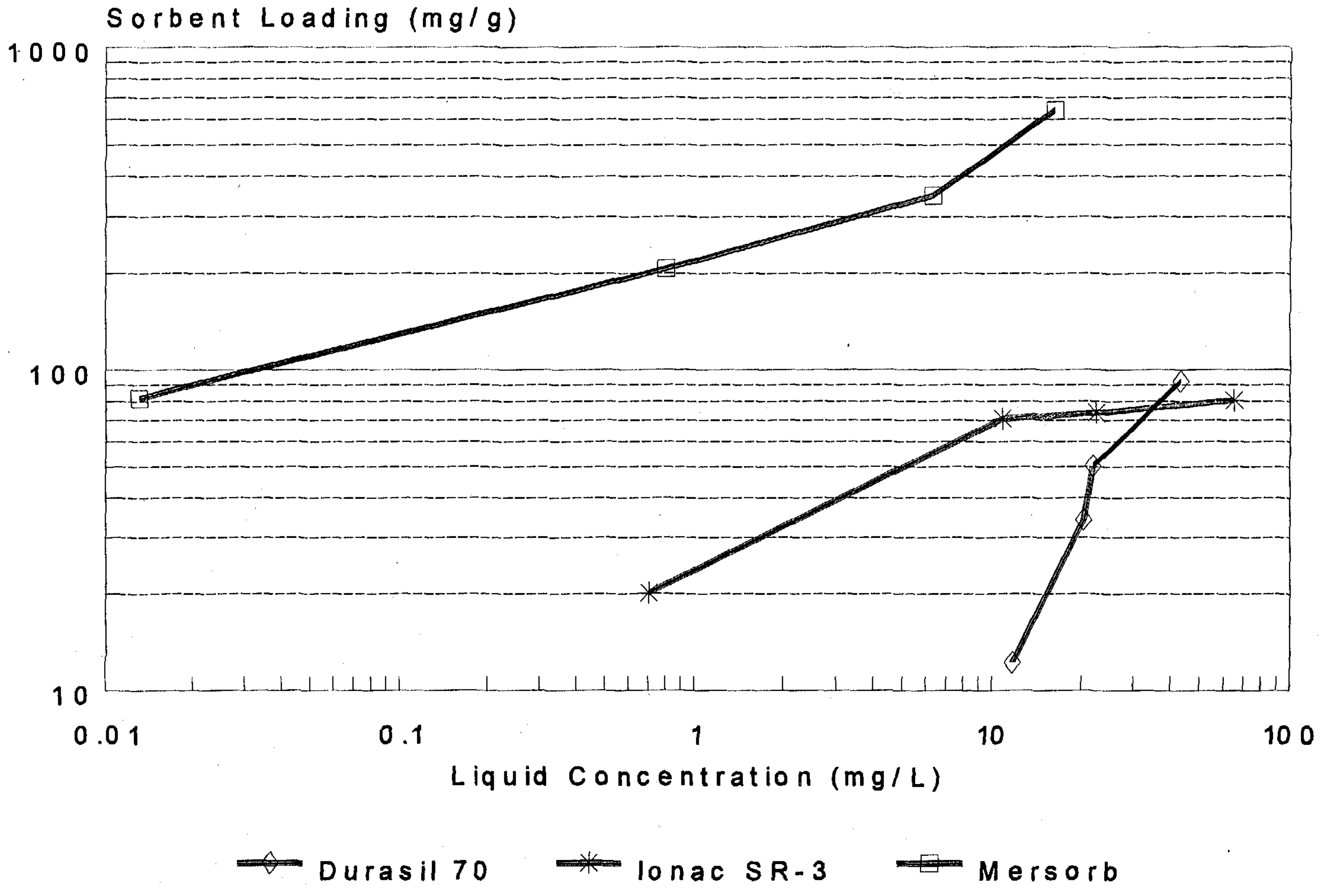

Fig. 4. Batch isotherm results in SRS tank waste simulant. 24-h batch tests, 97 mg/L Hg initially.

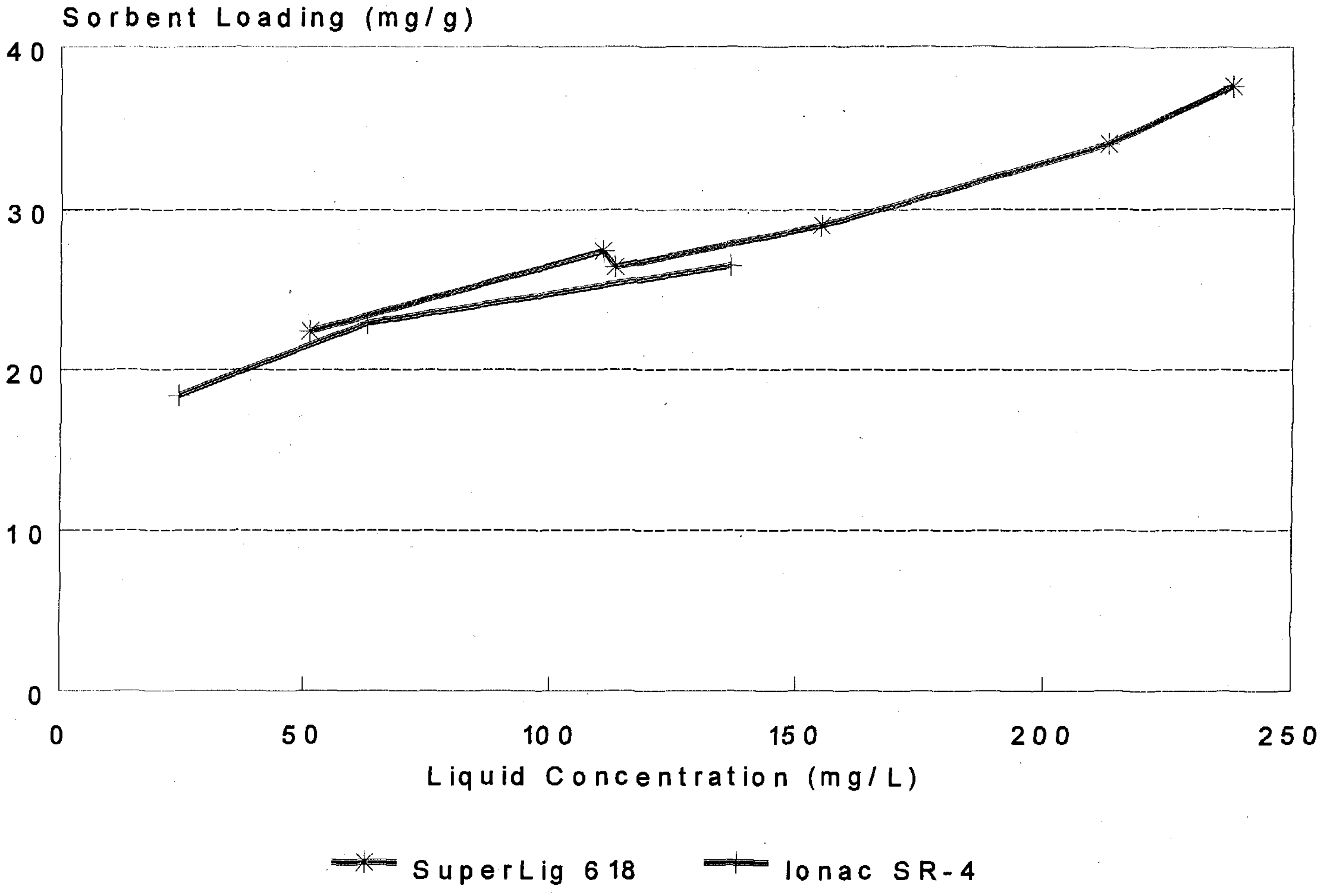

Fig. 5. **Batch isotherm results in INEL tank waste simulant.** 24-h batch tests, 285 mg/L Hg initially.

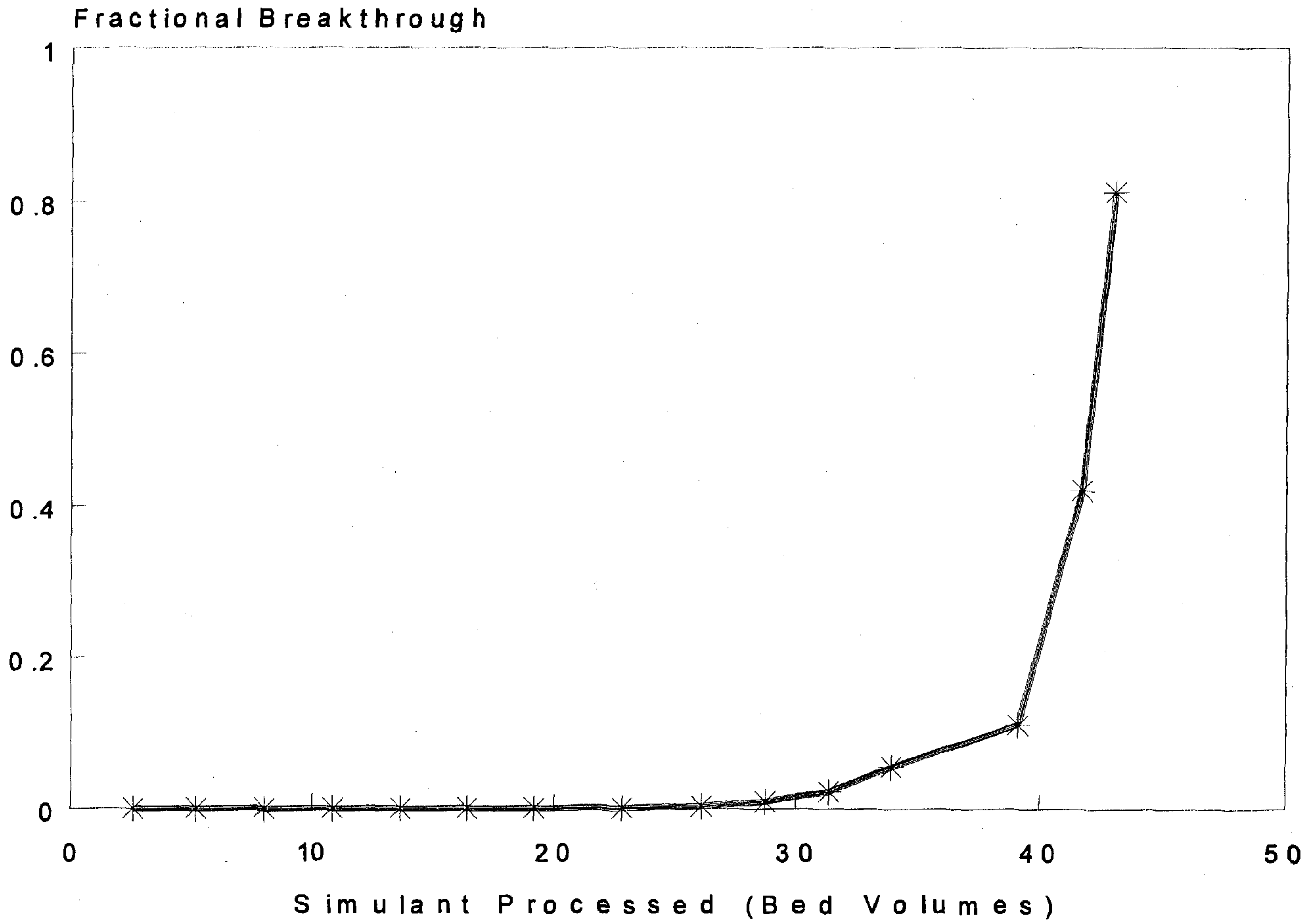

Fig. 6. Treatment of INEL simulant column test using Ionac SR-4 resin.

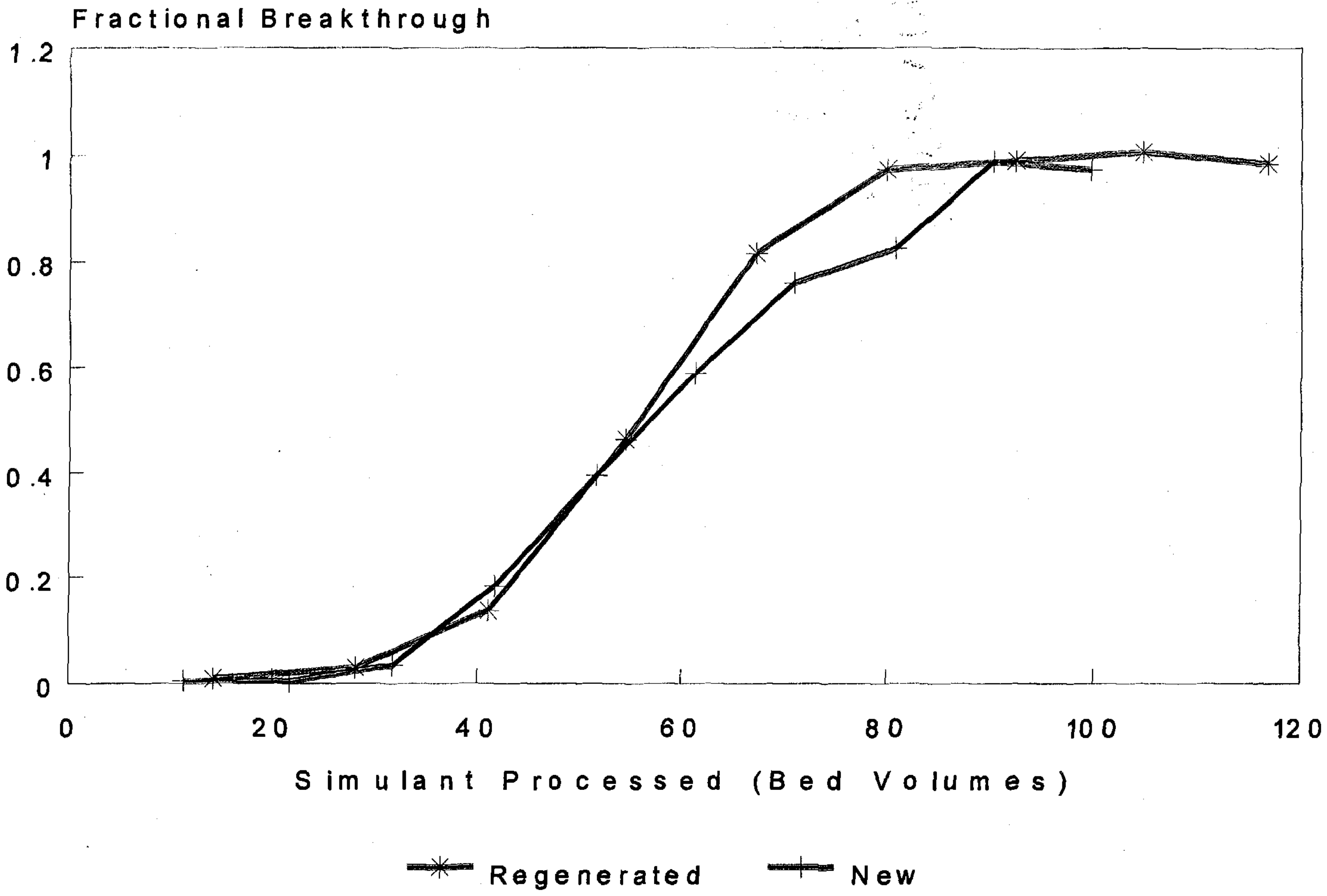

Fig. 7. Treatment of INEL simulant. New vs. regenerated SuperLig 618.