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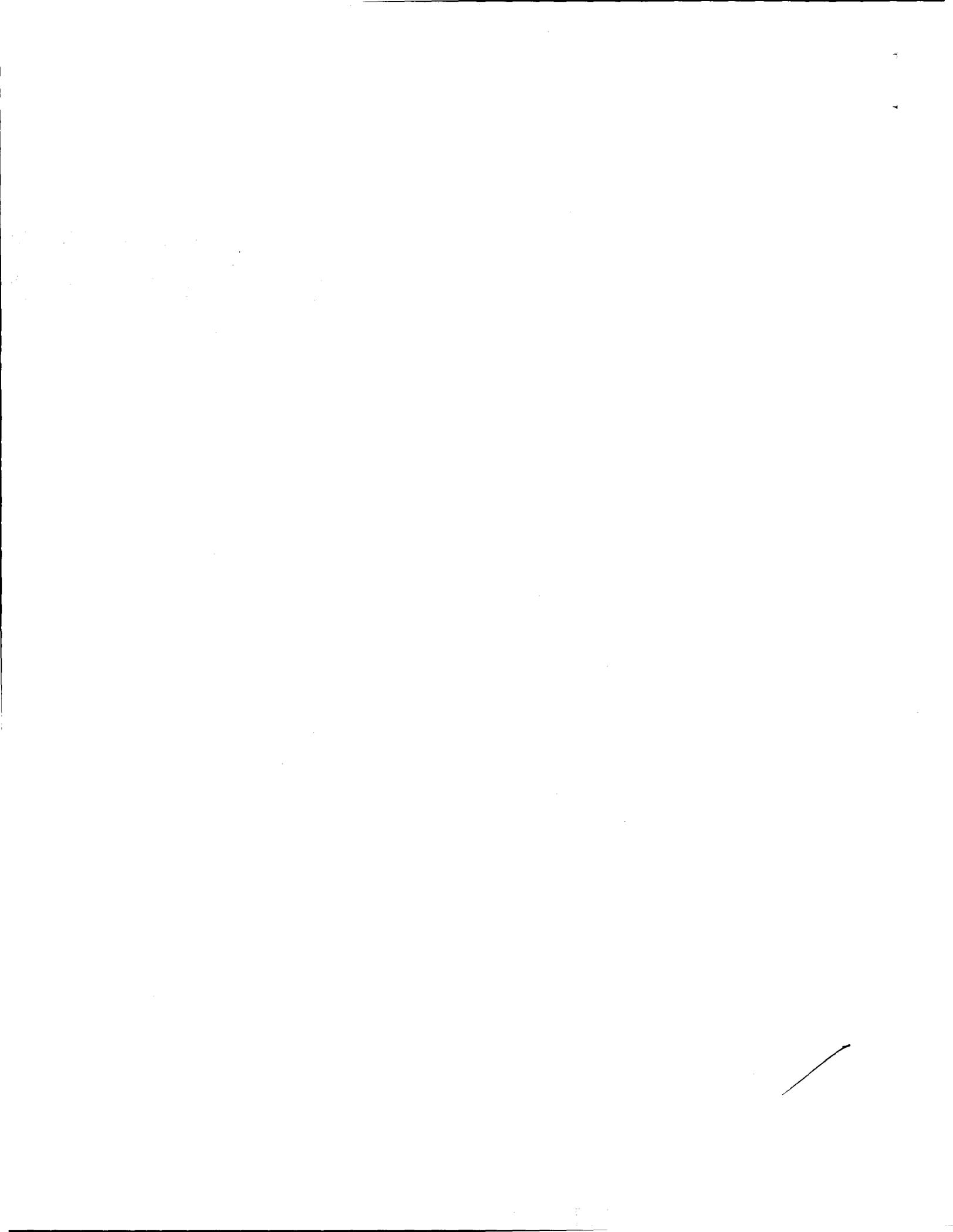
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**Mercury Separation From Mixed Wastes:
Annual Report**

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CHEMICAL TECHNOLOGY DIVISION
MERCURY SEPARATION FROM MIXED WASTES:
ANNUAL REPORT

P. A. Taylor, K. T. Klasson, S. L. Corder, T. R. Carlson, K. R. McCandless

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TABLE OF CONTENTS

LIST OF FIGURES	v
LIST OF TABLES	vii
ABSTRACT	ix
1. INTRODUCTION	1
2. MATERIALS AND METHODS	1
2.1 IDENTIFICATION OF MERCURY-CONTAINING WASTE STREAMS	1
2.2 ADSORBENTS TESTED	6
2.3 ANALYTICAL METHODS	8
2.4 EXPERIMENTAL METHODS	8
3. EXPERIMENTAL RESULTS	11
3.1 SCREENING TESTS	11
3.2 BATCH ISOTHERM TESTS	15
3.3 LABORATORY-SCALE COLUMN TESTS	15
3.3.1 Y-12 LiOH Solution	20
3.3.2 SRS Simulant	20
3.3.3 INEL Simulant	24
3.4 PILOT-SCALE COLUMN TESTS	30
4. CONCLUSIONS	32
REFERENCES	33
APPENDIX A—FORMULATION OF SIMULANT SOLUTIONS	34



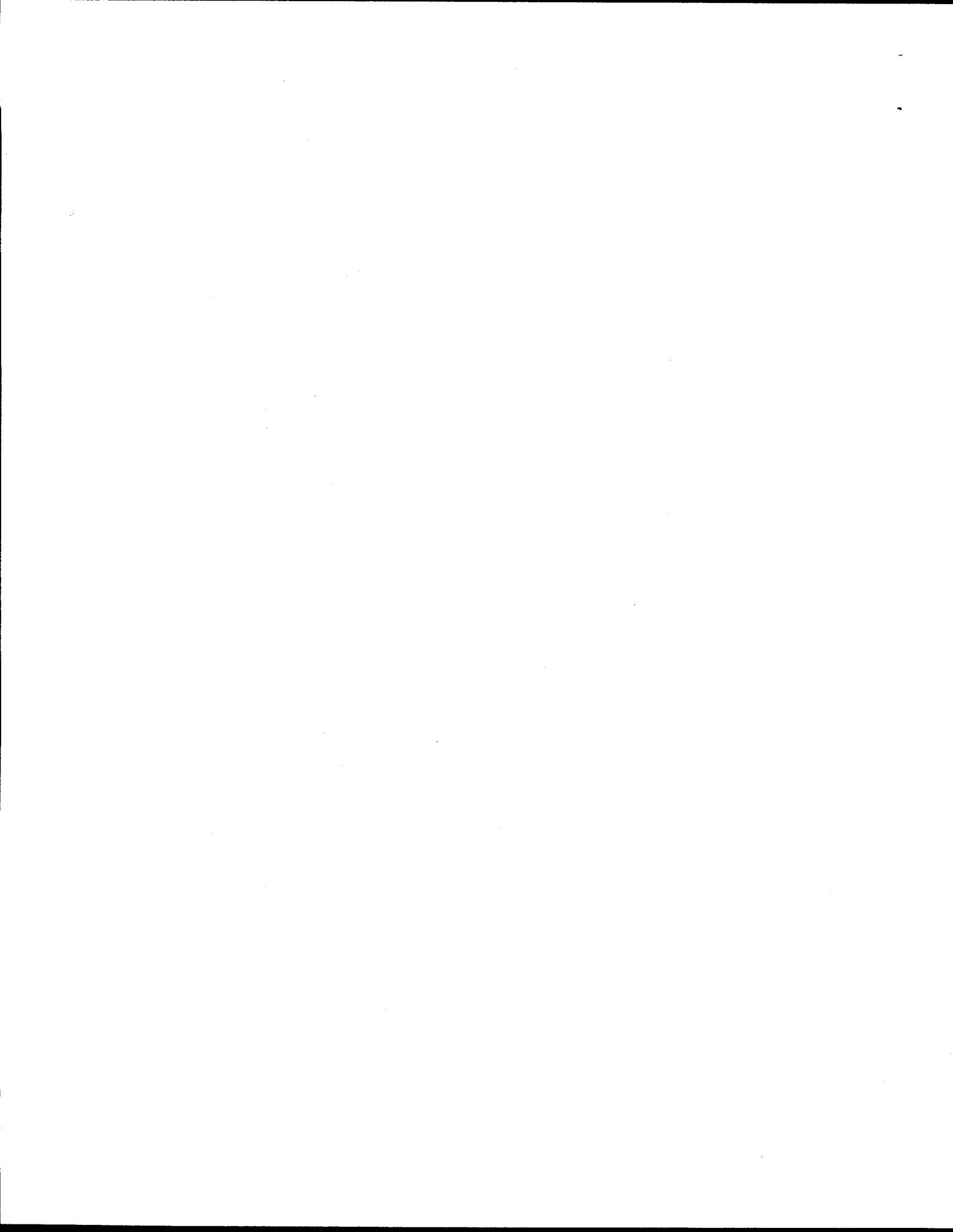
LIST OF FIGURES

<u>Table</u>		<u>Page</u>
1	Flow diagram of pilot-scale system used to treat Y-12 sump water	10
2	Screening test results for three sorbents in Y-12 sump water	14
3	Batch isotherm results for Y-12 sump water	16
4	Batch isotherm results for Y-12 LiOH solution	17
5	Batch isotherm results for SRS tank waste simulant	18
6	Batch isotherm results for INEL tank waste simulant	19
7	Breakthrough curve for treating Y-12 LiOH solution using Ionac SR-3	21
8	Breakthrough curve for treating Y-12 LiOH solution using Durasil 70	22
9	Breakthrough curve for treating SRS tank waste simulant using Mersorb	23
10	Breakthrough curve for treating SRS tank waste simulant using Ionac SR-3	25
11	Breakthrough curve for treating INEL tank waste simulant using Ionac SR-4	26
12	Breakthrough curves for treating INEL tank waste simulant using SuperLig 618	28
13	Regeneration curves for SuperLig 618 use to treat INEL tank wast simulant	29
14	Breakthrough curve for pilot-scale treatment of Y-12 sump water using Mersorb	31



LIST OF TABLES

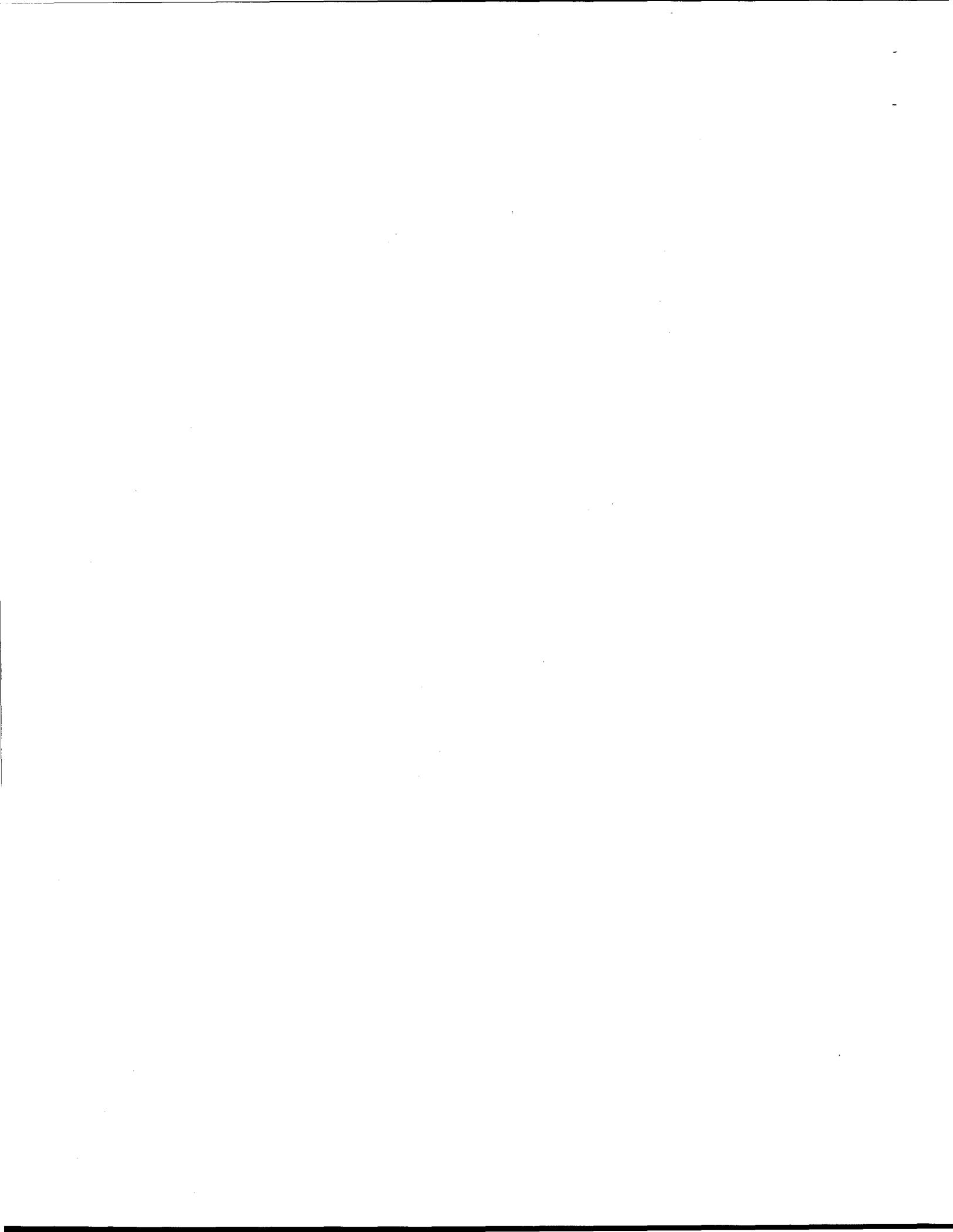
<u>Table</u>		<u>Page</u>
1	Concentration of major contaminants in INEL high-sodium tank waste	4
2	Concentration of major contaminants in SRS tank waste supernate	4
3	Typical metals concentrations in the Oak Ridge Y-12 Plant D-3871 sump water	5
4	Metals analysis of Y-12 LiOH solution sample	5
5	Description of mercury adsorbents tested	7
6	Results of screening tests on Y-12 sump water	12
7	Results of screening tests on Y-12 LiOH solution	12
8	Results of screening tests on SRS tank waste simulant	13
9	Results of screening tests on INEL tank waste simulant	13



ABSTRACT

This project has provided an assessment of new sorbents for removing mercury from wastes at U.S. Department of Energy sites. Four aqueous wastes were chosen for laboratory-scale testing: a simulant of a high-salt, acidic waste currently stored at Idaho National Engineering Laboratory (INEL); a simulant of 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 covering a wide range of cost and capability were identified for testing. Screening tests have been completed, which identify the most promising adsorbents for each waste stream. Batch isotherm tests were completed using the most promising adsorbents, and column tests were performed using at least two adsorbents for each waste stream. 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 and 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.



1. INTRODUCTION

This project, which was supported by the Efficient Separations and Processing Cross-Cutting Program of the U.S. Department of Energy (DOE) Office of Technology Development, has provided an assessment of state-of-the-art sorbent technologies for removing mercury from aqueous waste streams. The project included a characterization of mercury-contaminated aqueous waste streams at DOE facilities and testing of selected technologies for treating those streams to remove mercury. The laboratory studies produced equilibrium data, 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 describes the results achieved in evaluating new sorbents.

DOE facilities produce or store a wide range of mercury-containing aqueous wastes, many of which contain radionuclides in addition to other Resource Conservation Recovery Act hazardous constituents. Various adsorbents were tested for removing 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; therefore, it may be desirable to remove mercury from the wastes prior to stabilization 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

survey was used as a starting point for our project. 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 were identified at DOE facilities. Idaho National Engineering Laboratory (INEL) has about 7.5×10^6 L of a high-salt, acidic waste that contains about 400 mg Hg/L. The Savannah River Site (SRS) has about 3.8×10^8 L of a high-salt, alkaline waste that contains about 440 mg Hg/L. [Oak Ridge National Laboratory (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 Li/L) 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 (VOCs), other heavy metals, and trace levels of radionuclides.

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

Several other mercury-containing waste streams have recently been 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), which hold about 40,000 L of aqueous waste that contains heavy metals including mercury, VOCs, 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, perchloroethylene, and mercury. SRS currently has about 35,000 L of this wastewater stored. The

other waste stream consists of analytical samples and associated solutions that were sent to off-site laboratories and are now 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: the INEL and SRS tank wastes, the Y-12 LiOH solution, and a Y-12 groundwater stream. Since the INEL and SRS wastes contain very high concentrations of radionuclides, simulants were used in the laboratory-scale tests. Simulant formulations were obtained from INEL⁴ and SRS.⁵ The major contaminants in these waste streams are shown in Tables 1 and 2. Water from the D-3871 sump (collected groundwater) at the Y-12 Plant, which contains traces of nitrate and VOCs as well as mercury, and the Y-12 LiOH solution were also 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 the results of 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 ORNL has shown that the Y-12 sump water contains a mixture of ionic mercury and dissolved elemental mercury. The form of mercury in the other solutions has not been determined, but it is assumed to be ionic mercury. The maximum concentration of mercury that could be 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).⁶ 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.⁴ The reason for the differences in mercury solubility between these two waste solutions and their associated simulants is not known at this time. The simulant formulations are shown in Appendix A.

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

Contaminant	Conc. (M)
NaNO ₃	1.78
HNO ₃	1.66
Al(NO ₃) ₃	0.55
KNO ₃	0.23
HF	0.05
Ca(NO ₃) ₂	0.04
H ₂ SO ₄	0.03
Fe(NO ₃) ₃	0.02
H ₃ BO ₃	0.02
HCl	0.02
H ₃ PO 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 ₂ CO ₃	0.16
Na ₂ SO ₄	0.14
NaF	0.015
KNO ₃	0.015
Na ₃ PO ₄	0.008
Na ₂ SiO ₃	0.004
Na ₂ CrO 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

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 on these products is summarized below.

The isothiuronium active site of Ionac SR-3 resin (Sybron Chemicals, Inc., Birmingham, N.J.) 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 cannot be regenerated. The cost is \$390/ft³. 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/ft³. 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/ft³.

Mersorb (NUCON International, Inc., Columbus, Ohio) 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

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	^a
Mersorb	Sulfur
Filtersorb-300	Activated Carbon
SuperLig 608 & 618	^a

^a Proprietary information.

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/ft³.

Activated carbon can adsorb mercury, but it has relatively low capacity and 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/ft³.

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/ft³.

SuperLig 608 (IBC Advanced Technology, American Fork, Utah) uses a macrocycle ligand to selectively bind mercury, based on the size and chemical properties of mercury ions (molecular-recognition technology). It has a selectivity for mercury of $>10^{10}$ over a wide range of other heavy metals. The ligand is effective in a pH range of 2 to 14, and the polymeric support material that the ligand is bound to 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 ethylenedinitrilotetraacetic (EDTA), citrate, or thiourea. The cost of the SuperLig materials is about \$30/g. Production quantities would be less expensive, but a price was not quoted.

2.3 ANALYTICAL METHODS

Mercury analyses were performed as described in Environmental Protection Agency Method 245.1⁷ using a Perkin-Elmer (Norwalk, Conn.) 1100B atomic absorption instrument with a Flow Injection Analysis System 400 attachment. Calibration solutions of 1, 10, and 20 µg Hg/L were prepared from a 1.00-mg Hg/mL standard solution (J. T. Baker, Inc, Phillipsburg, N.J.). Samples and standards were preserved in a solution of 0.01 wt % K₂Cr₂O₇ in 5 wt % HNO₃, 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 measured 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 20 × 50 mesh for the batch tests. All of the other adsorbents were used as received from the manufacturers. For the Y-12 sump water, 200 mL of wastewater was contacted with 0.1 g adsorbent in glass bottles placed on a jar mill roller at 50 rpm. Samples were taken after 1, 6, 24 and 48 h, and then filtered and analyzed for

mercury. All of the other batch tests were conducted in Teflon bottles, using 0.1 or 0.2 g of adsorbent in 50 mL of solution. For each of these experiments, a control test (same type of 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 h, which the screening tests had shown was long enough to permit samples 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 laboratory-scale 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 samples at preselected intervals.

A pilot-scale column test was conducted using Ionac SR-3, Mersorb, and activated carbon to treat sump water at the Y-12 Plant (See Fig. 1). Three columns of activated carbon, each containing 860 g (1570 cm^3), were operated in series. The Ionac SR-3 column contained 250 g (325 cm^3) of resin, and the Mersorb column contained 350 g (670 cm^3) of adsorbent. This experiment was a joint effort between the Development Division of the Y-12 Plant, supported by Y-12 Waste Management, and ORNL, supported by the Efficient Separations and Processing Cross-Cutting Program. The Y-12 Plant is planning to build a centralized treatment facility to remove mercury from various sump water streams. The pilot-scale facility is providing a side-by-side comparison of activated carbon, which is the Y-12 baseline technology, with Ionac SR-3 and Mersorb. The Y-12 Plant supplied the

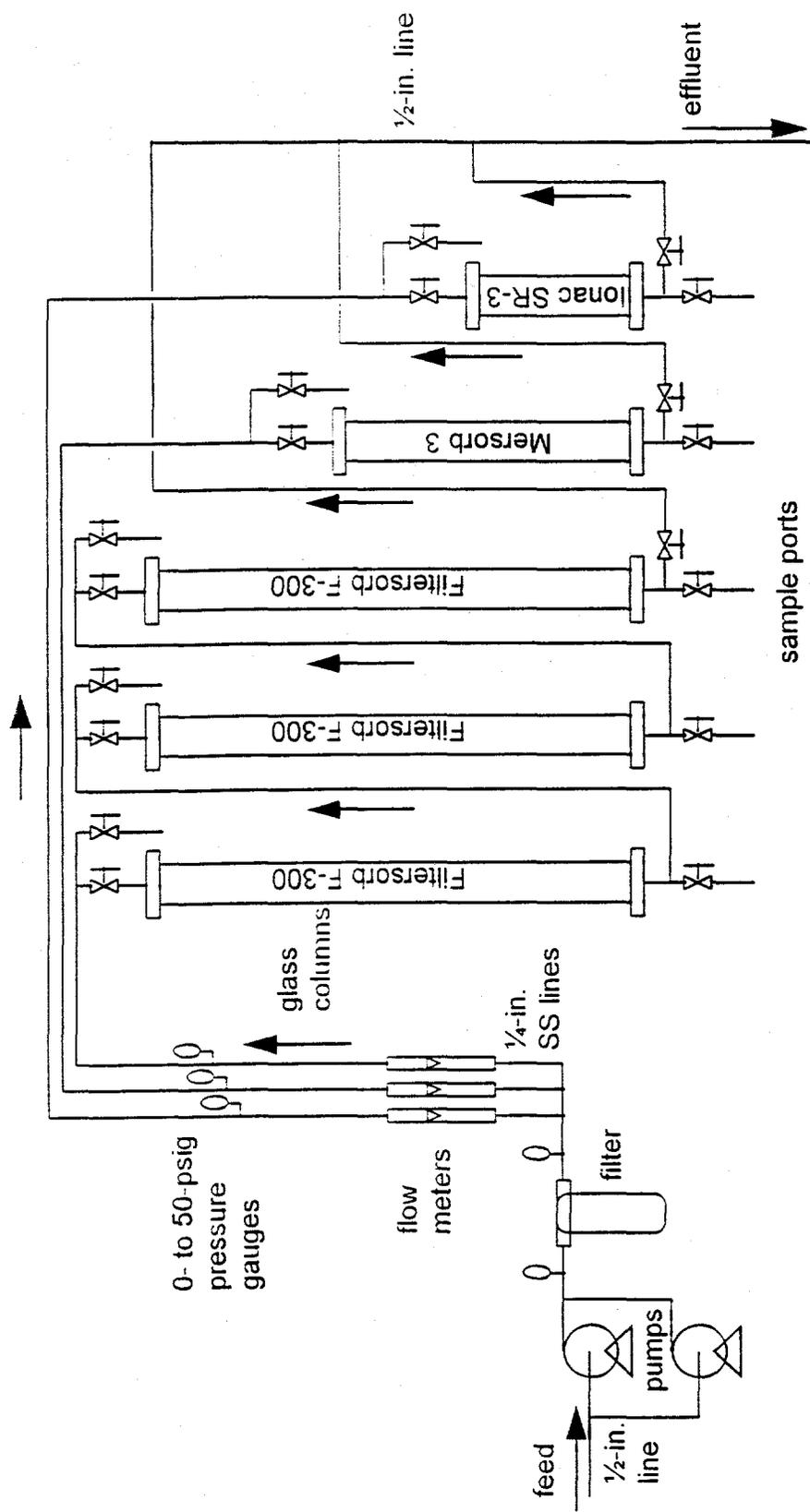


Fig. 1. Flow diagram of pilot-scale system used to treat Y-12 sump water.

equipment and ORNL assembled the pilot-scale system. The system was operated primarily by Y-12 Development Division personnel, with support from ORNL.

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 completed, and it was unlikely that these expensive, high-performance adsorbents would be cost effective on this dilute waste stream. The removal percentages listed in Table 6 were calculated based on the mercury concentration left in the associated control solution after 24 h. The control solution showed significant loss of mercury, probably by adsorption on the surface of the glass bottle. Figure 2 shows the mercury concentrations over time for the control solution and for three of the adsorbents.

The results for the screening tests on the Y-12 LiOH solutions are shown in Table 7. Durasil 70, Ionac SR-3, and Amberlite IRC-718 were the three most effective adsorbents for the LiOH solution. Table 8 shows the results of the screening tests on the SRS tank waste simulant. Mersorb was by far the most effective adsorbent for this solution. The screening results for the INEL tank waste simulant are shown in Table 9. SuperLig 618 and Ionac SR-4 were the only adsorbents that were effective in this acidic solution. For all of these experiments, the SuperLig materials were tested after the other adsorbents, since they were not received until late March 1995. For all of the screening test results, the removal percentages were calculated using the associated control sample mercury concentration, which was measured at the same time as the sample concentrations.

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

Sorbent	Final Hg Concentration ^b ($\mu\text{g/L}$)	% 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

^a24-hr batch test. 0.1 g sorbent in 200 mL sump water.

^bInitial mercury concentration of about 300 $\mu\text{g/L}$.

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

Sorbent	Final Hg Concentration ^b (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

^a24-hr batch test. 0.2 g sorbent in 50 mL LiOH solution.

^bInitial mercury concentration of 23.3 mg/L .

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

Sorbent	Final Hg Concentration ^b (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

^a24-hr batch test, 0.1 g sorbent in 50 mL SRS simulant.

^bInitial mercury concentration of 108 mg/L Hg.

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

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

^a24-hr batch test, 0.1 g sorbent in 50 mL INEL simulant.

^bInitial mercury concentration of 278 mg/L.

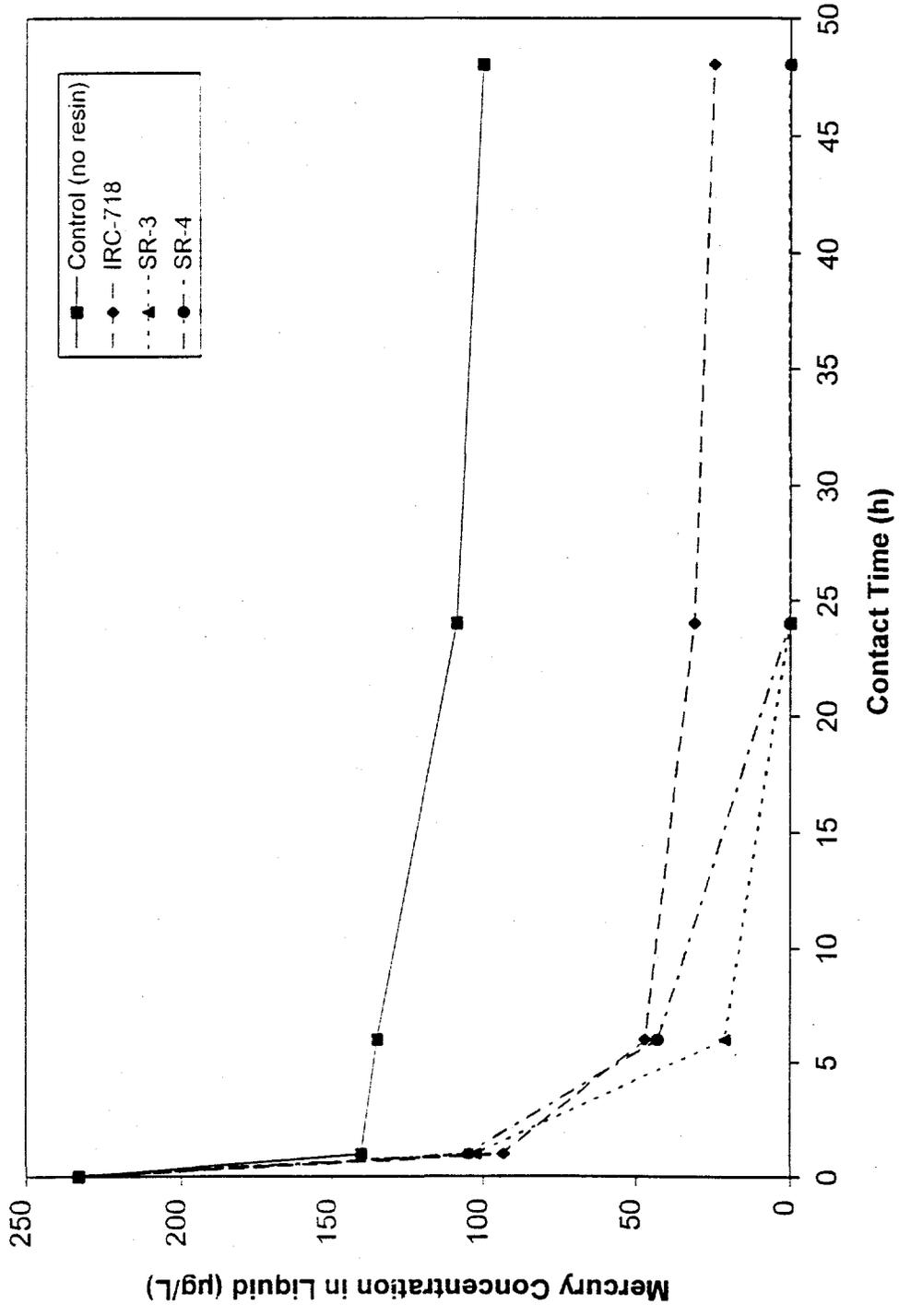


Fig. 2. Screening test results for three sorbents in Y-12 sump water.

In some cases the screening tests were conducted in two separate batches, each with their own control sample.

3.2 BATCH ISOTHERM TESTS

Isotherm tests were performed using the most promising adsorbents identified by the screening tests for each solution. The results are shown in Figs. 3–6. In all cases the mercury loading on the sorbent is plotted against the mercury concentration remaining in the solution after 24 h of contact. The isotherms for the Y-12 sump water (Fig. 3) 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. 4) show that Durasil 70 is slightly more effective than Ionac SR-3, particularly at higher loadings; however, neither adsorbent would reduce the mercury concentration below 1.8 mg/L, even at an extremely high adsorbent concentration of 100 g/L. The isotherm for the SRS simulant solution (Fig. 5) 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 liquid mercury concentrations. For the INEL simulant (Fig. 6), Ionac SR-4 and SuperLig 618 produced essentially identical results.

3.3 LABORATORY-SCALE COLUMN TESTS

Laboratory-scale column tests were conducted for the Y-12 LiOH solution, the SRS simulant solution, and the INEL simulant solution. Because of the continual loss of mercury from stored samples of the Y-12 sump water and the long run times that would be required to load a

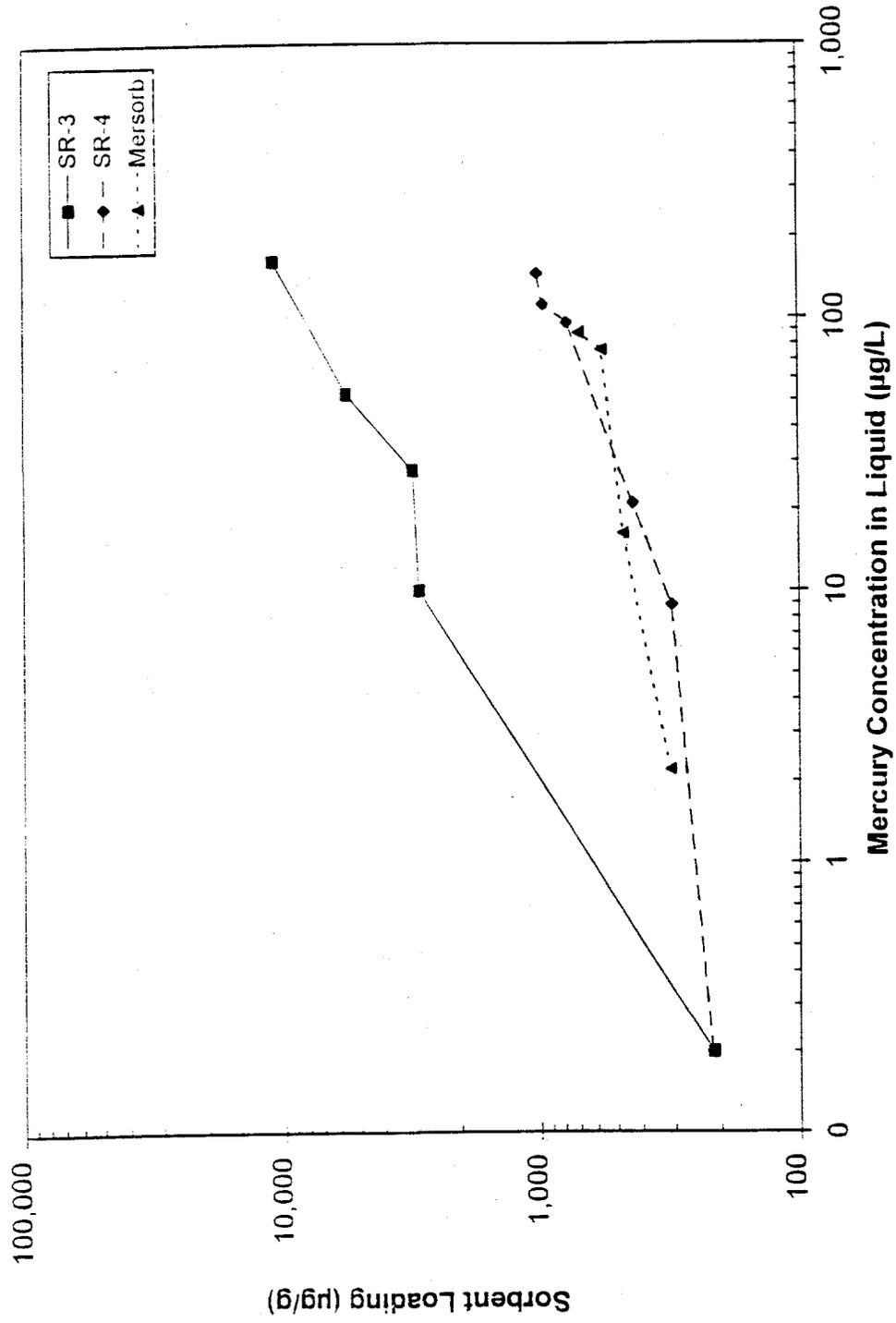


Fig. 3. Batch isotherm results for Y-12 sump water.

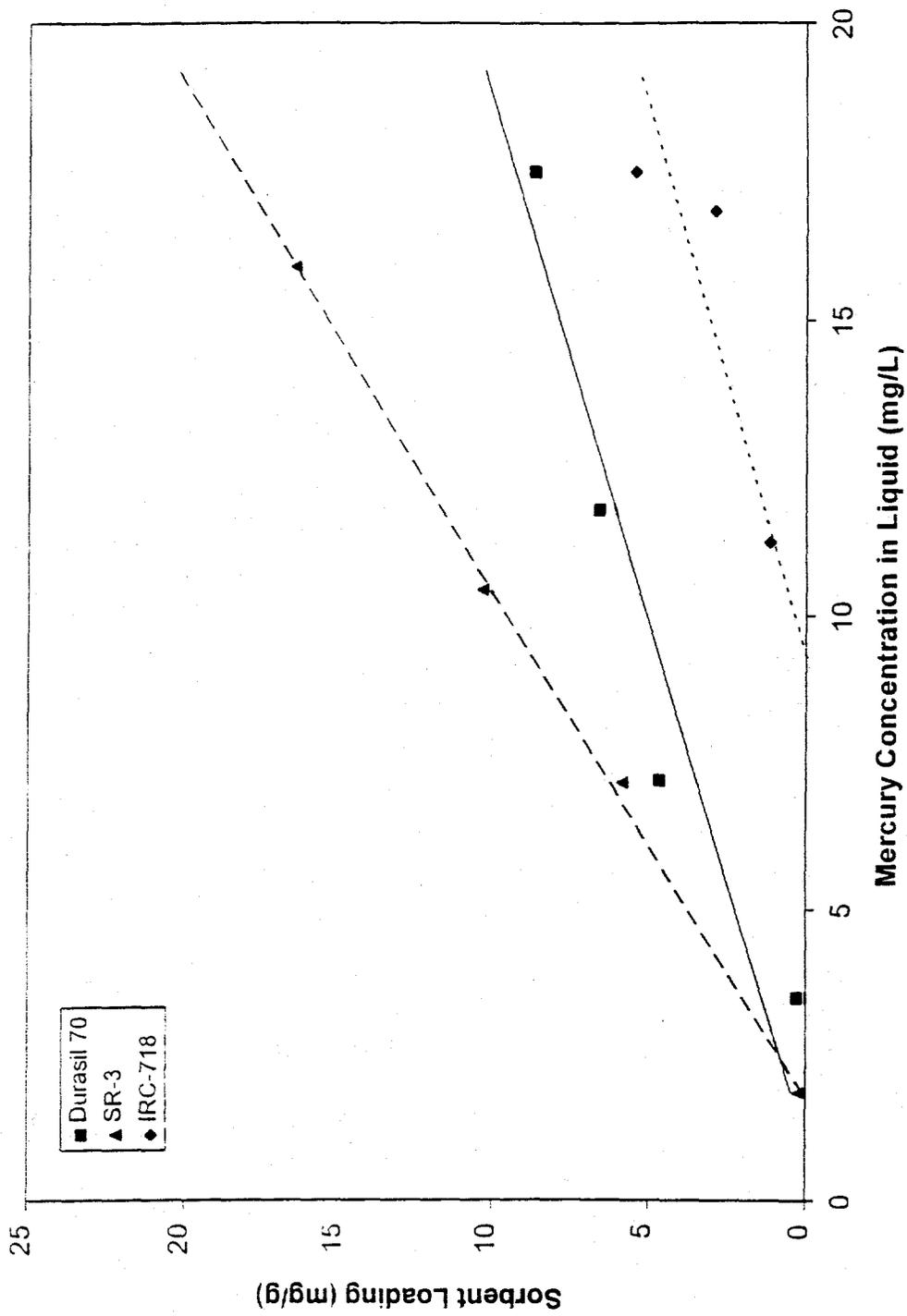


Fig. 4. Batch isotherm results for Y-12 LiOH solution.

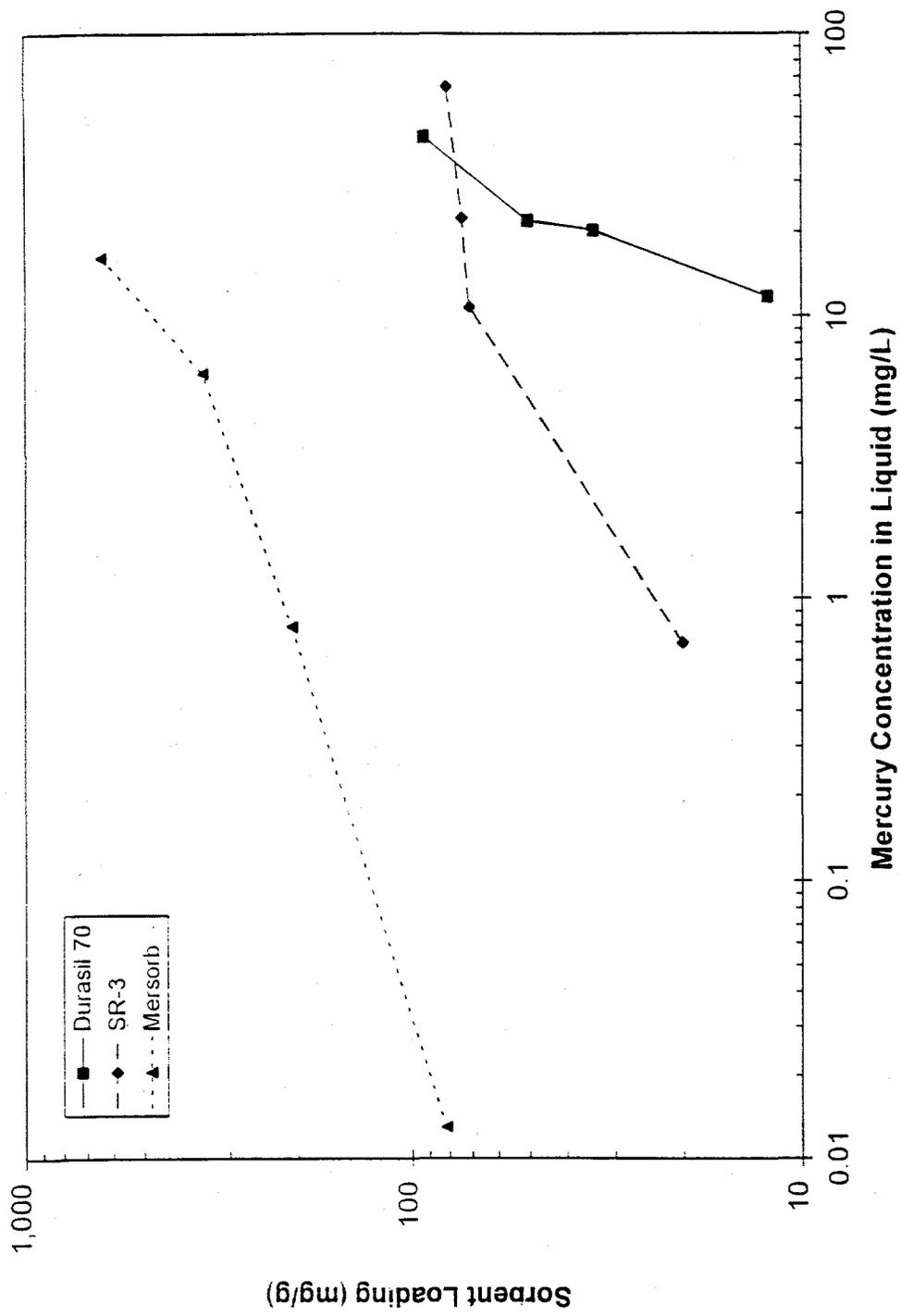


Fig. 5. Batch isotherm results for SRS tank waste simulant.

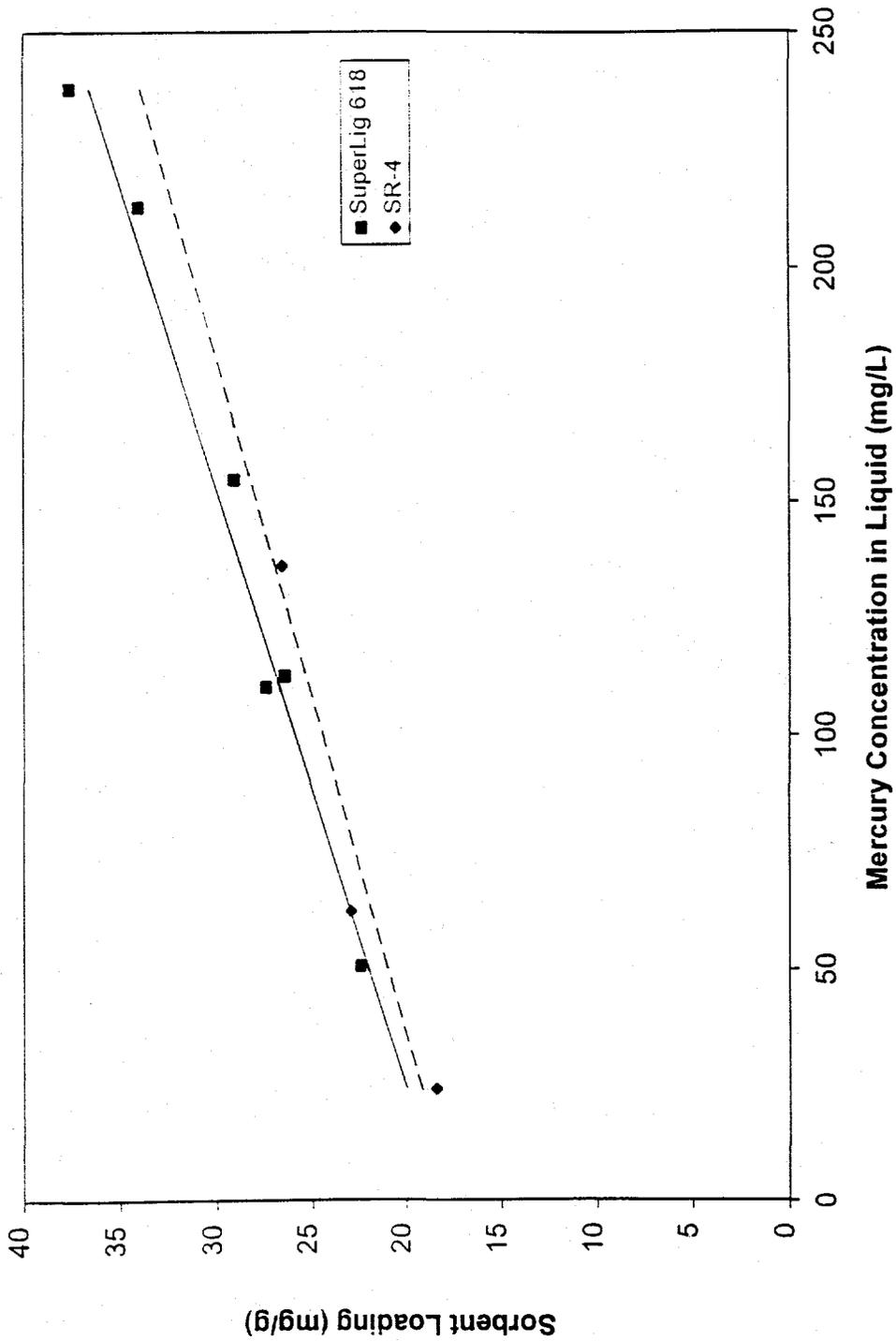


Fig. 6 Batch isotherm results for INEL tank waste simulant.

column using this dilute wastewater. laboratory-scale column tests were not conducted using the Y-12 sump water. A pilot-scale column test, described below, is in progress at one of the Y-12 sumps.

3.3.1 Y-12 LiOH Solution

Ionac SR-3 and Durasil-70 were tested for treating the Y-12 LiOH solution. Each adsorbent was crushed and screened to between 100 and 200 mesh size for use in a 0.5-cm-I. D. column. The LiOH solution was pumped at a flow rate of 0.2 mL/min (23.5 bed volumes/h) up through a column containing 0.72 g (0.51 mL) of SR-3 resin. The mercury breakthrough curve for this test is shown in Fig. 7. (Note that the fractional breakthrough numbers plotted are the effluent mercury concentrations divided by the feed concentration of 25.3 mg Hg/L.) Initial breakthrough of mercury occurred very rapidly, and there was then a slow increase in the mercury concentration of the column effluent. The resin accumulated 18.4 mg Hg/g resin, which is consistent with the results from the isotherm tests. The mass transfer zone (MTZ) for 5 to 50% breakthrough, which is the portion of the column where mercury loading actively occurs, was 1.9 cm. A lower MTZ indicates a sharper breakthrough curve and better utilization of the adsorbent. A 0.5-cm-I. D. column containing 0.90 g (0.80 mL) of Durasil-70 was used to treat the Y-12 LiOH solution at a flow rate of 0.2 mL/min (15.1 bed volumes/h). The breakthrough curve is shown in Fig. 8. The resin loading was 14.5 mg Hg/g resin, which is slightly lower than the results from the isotherm tests, and the MTZ was 3.9 cm. The initial mercury breakthrough for the Durasil-70 column was even higher than for the SR-3 column, and the effluent concentrations were somewhat erratic.

3.3.2 SRS Simulant

A 0.5-cm-I. D. column containing 0.78 g (0.98 mL) of Mersorb was used to treat the SRS simulant at a flow rate of 0.2 mL/min (12.2 bed volumes/h). The simulant solution used in this test contained 112 mg Hg/L. The breakthrough curve is shown in Fig. 9. The loading on the resin was 218 mg Hg/g resin, which is significantly lower than was shown in the isotherm tests, and the

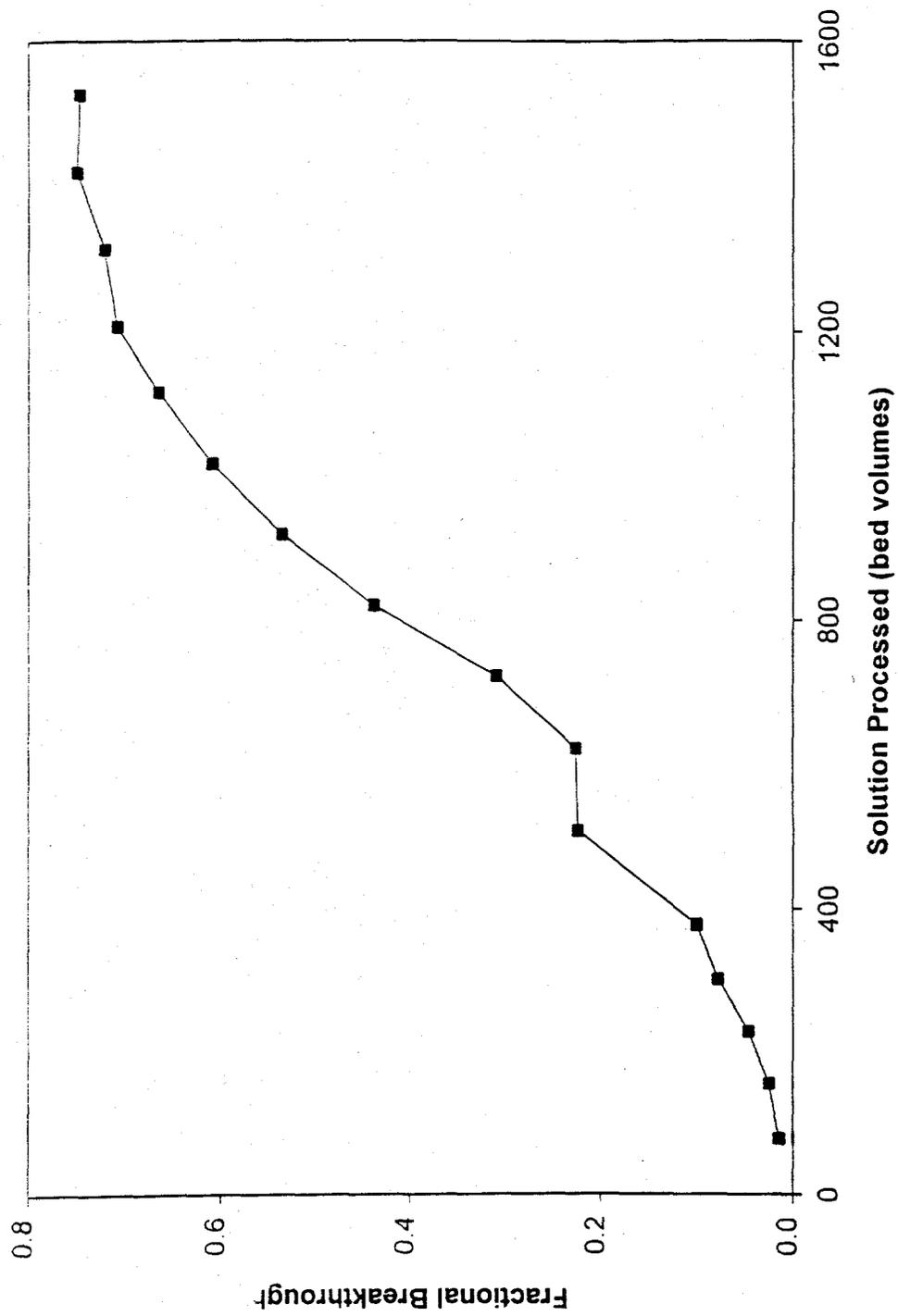


Fig. 7. Breakthrough curve for treating Y-12 LiOH solution using Ionac SR-3.

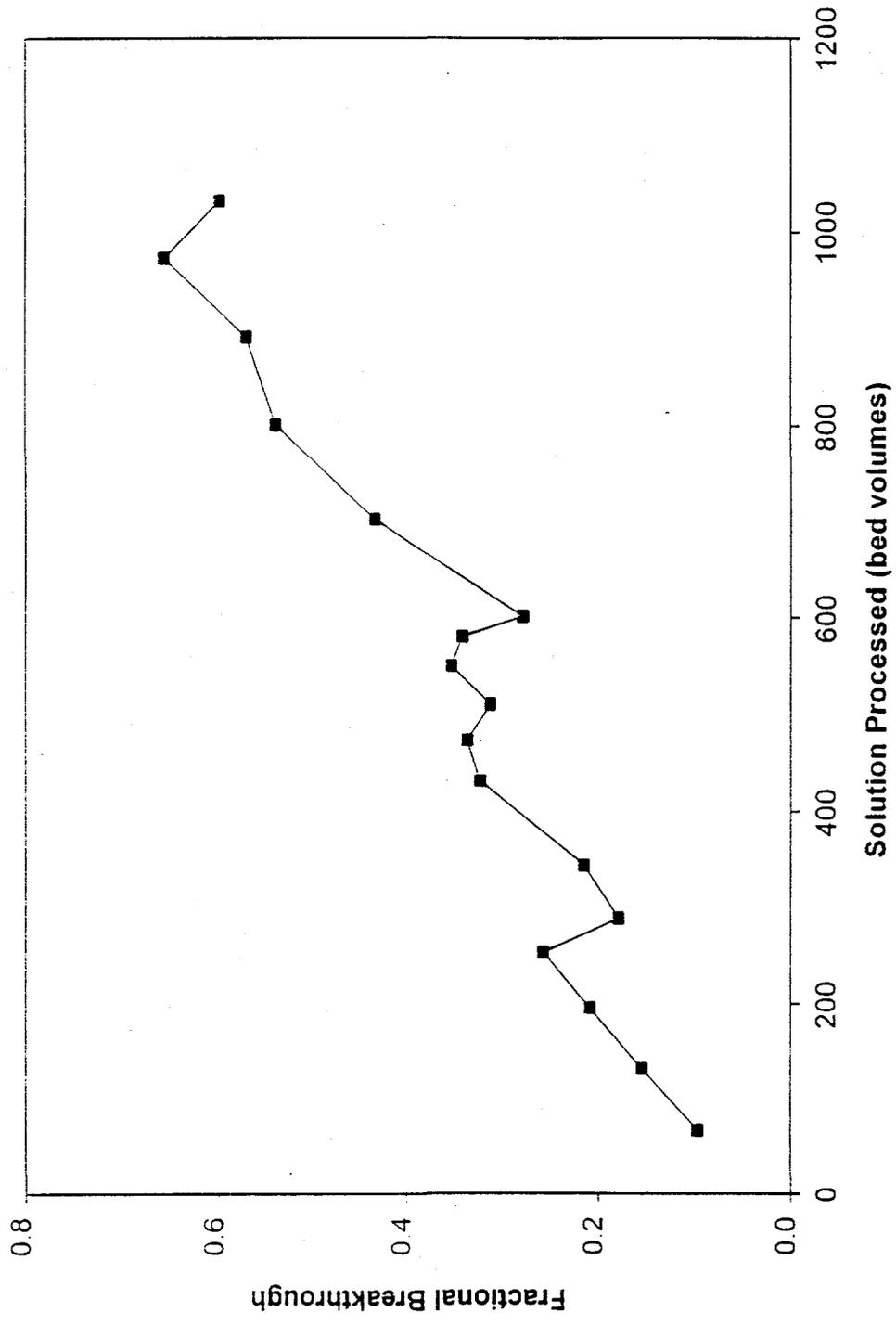


Fig. 8. Breakthrough curve for treating Y-12 LiOH solution using Durasil 70.

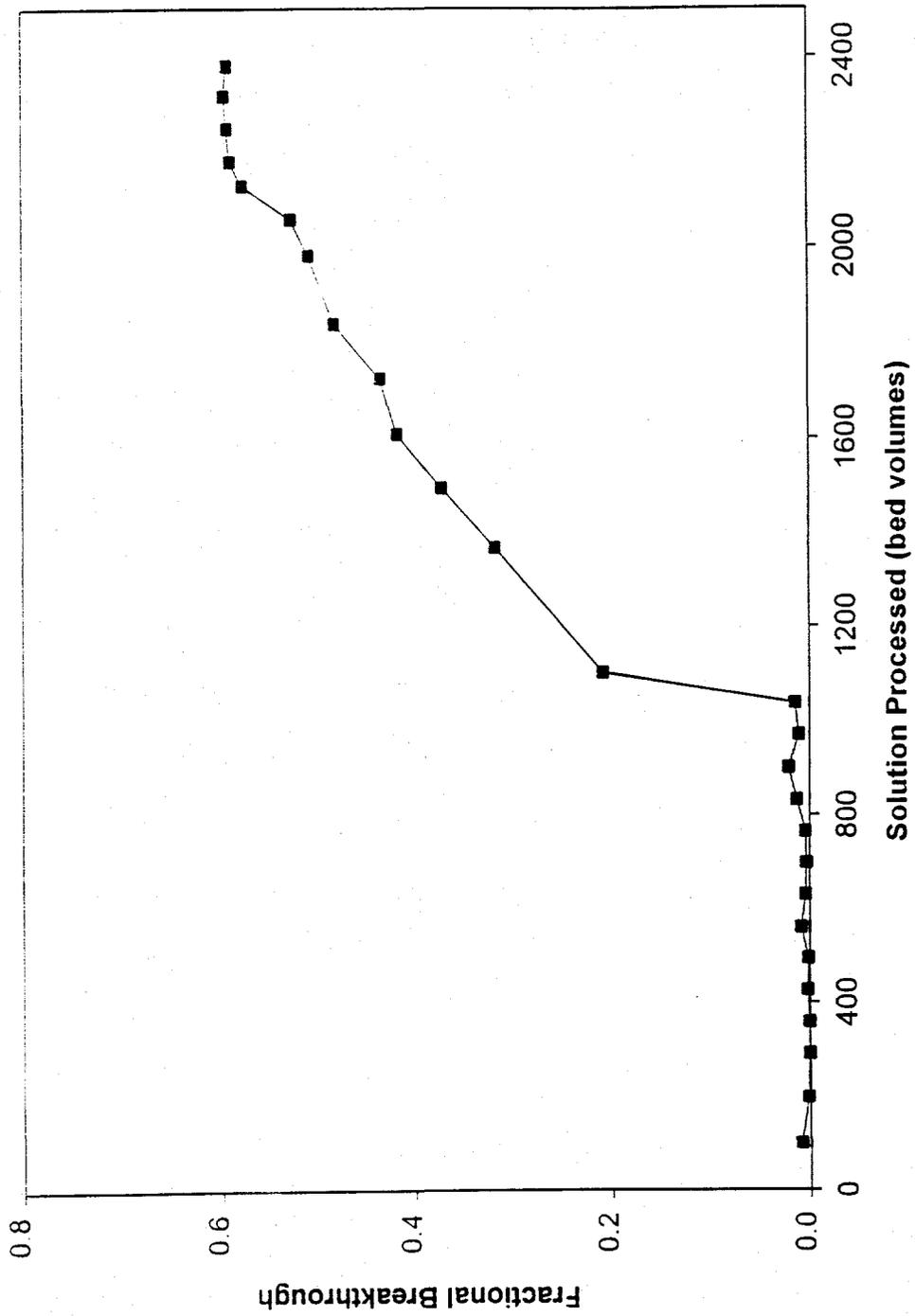


Fig. 9. Breakthrough curve for treating SRS tank waste simulant using Mersorb.

MTZ was 2.3 cm. The column test was repeated, and the results were very similar, with a loading of 239 mg Hg/g resin. The next column test used 1.3 g (1.12 mL) of Ionac SR-3 resin and an SRS simulant flow rate of 0.2 mL/min (10.7 bed volumes/h). The simulant solution contained 85 mg Hg/L. The breakthrough curve for this test was very sharp (see Fig. 10). The resin loading was 180.7 mg Hg/g resin, which is much higher than was measured in the isotherm tests, and the MTZ was 0.62 cm.

3.3.3 INEL Simulant

Laboratory-scale column tests were 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 11 shows 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 MTZ for 5% to 50% breakthrough was 2.4 cm. Some gas bubbles were visible in the resin bed during the test, but at the time the cause could not be determined.

An attempt was made to regenerate the SR-4 resin with 30 wt % HCl, as recommended by the resin manufacturer, but the column immediately filled with gas bubbles. The gas was determined to be a mixture of SO₂ and NO_x, presumably caused by a reaction between nitrate ions from the Simulant still present in the column 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 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

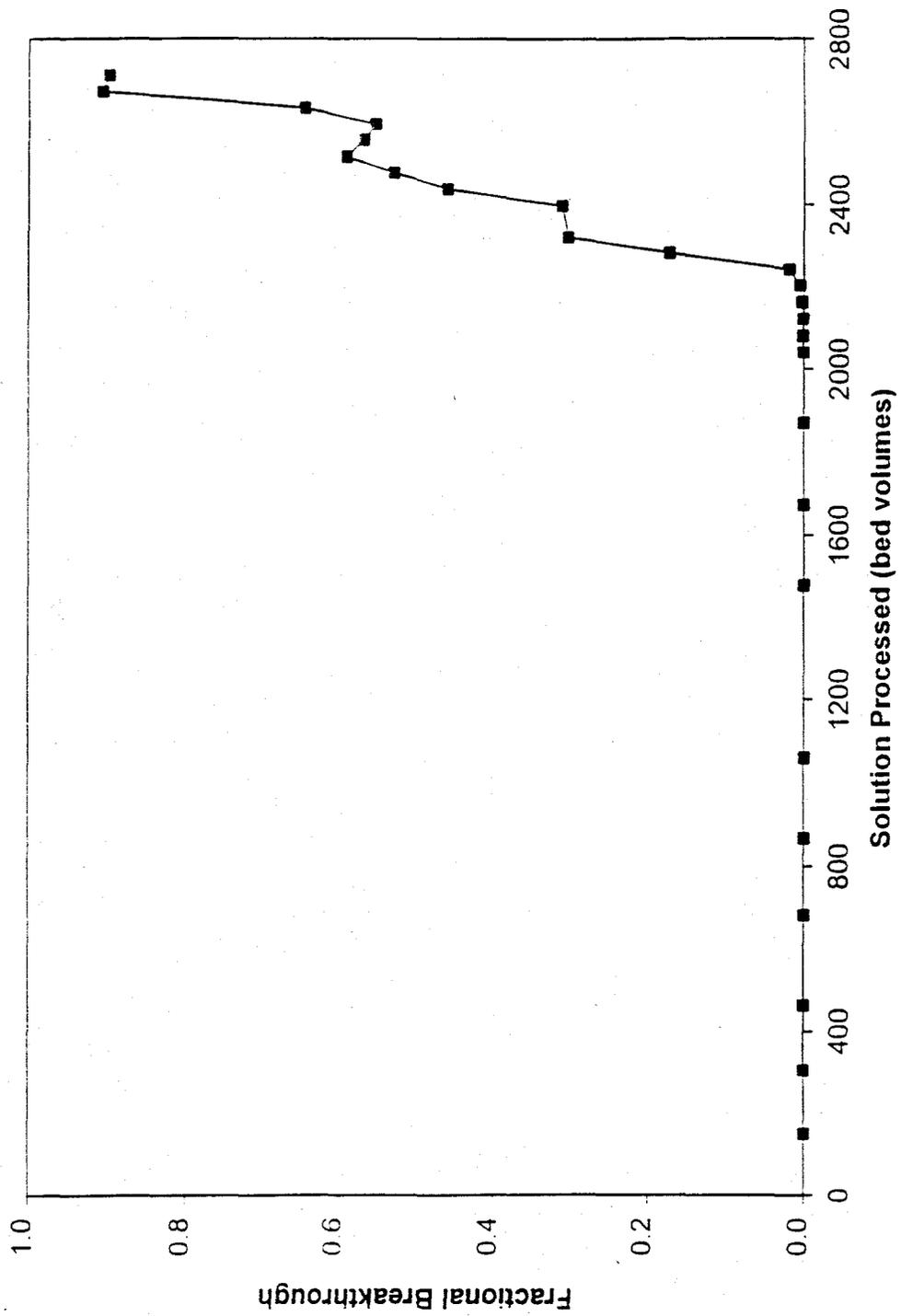


Fig. 10. Breakthrough curve for treating SRS tank waste simulant using Ionac SR-3.

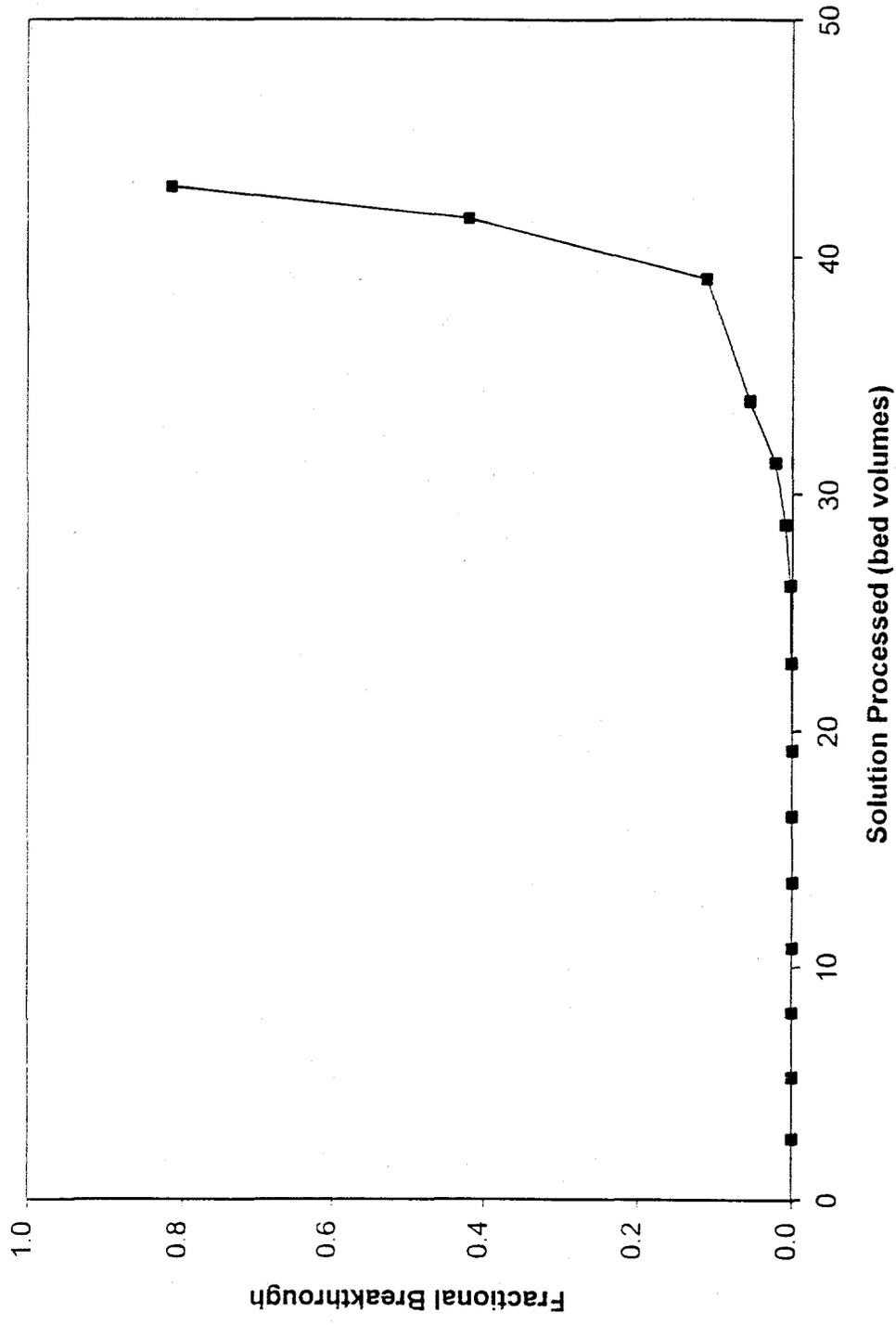


Fig. 11. Breakthrough curve for treating INEL tank waste simulant using Ionac SR-4.

were visible for the first 2 h, some bubbles were visible after 3 h, and the column was full of gas after 4 h. The SR-4 resin used in the screening tests (previously described) had not released any mercury back into the solution after 24 or 48 h of contact with the INEL simulant, and the sharp breakthrough for the column test did not occur until after 8 h of run time. These results suggest that thiol groups which have adsorbed mercury or other heavy metals, as was the case for the SR-4 resin used in the batch and first column tests, are more resistant to oxidation by the simulant solution than thiol groups that are still associated with sodium ions. The resin used in the compatibility test did not contact enough simulant to load many 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 series of column tests, 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 up through the column at 1 mL/min (15 bed volumes/h) for the loading cycles, and 6 M HCl was used at a flow rate of 0.5 mL/min to regenerate the sorbent. A series of five loading and regeneration cycles was completed. The breakthrough curves for the loading cycles are shown in Fig. 12. The first four loading cycles showed mercury uptake of 50 to 60 mg Hg, but the fifth loading cycle only removed 34 mg Hg from the simulant. The first three regenerations were very effective, recovering all of the mercury from the resin in 3 to 4 bed volumes of acid. The fourth and fifth regeneration cycles left about 20 mg Hg on the resin (Fig. 13).

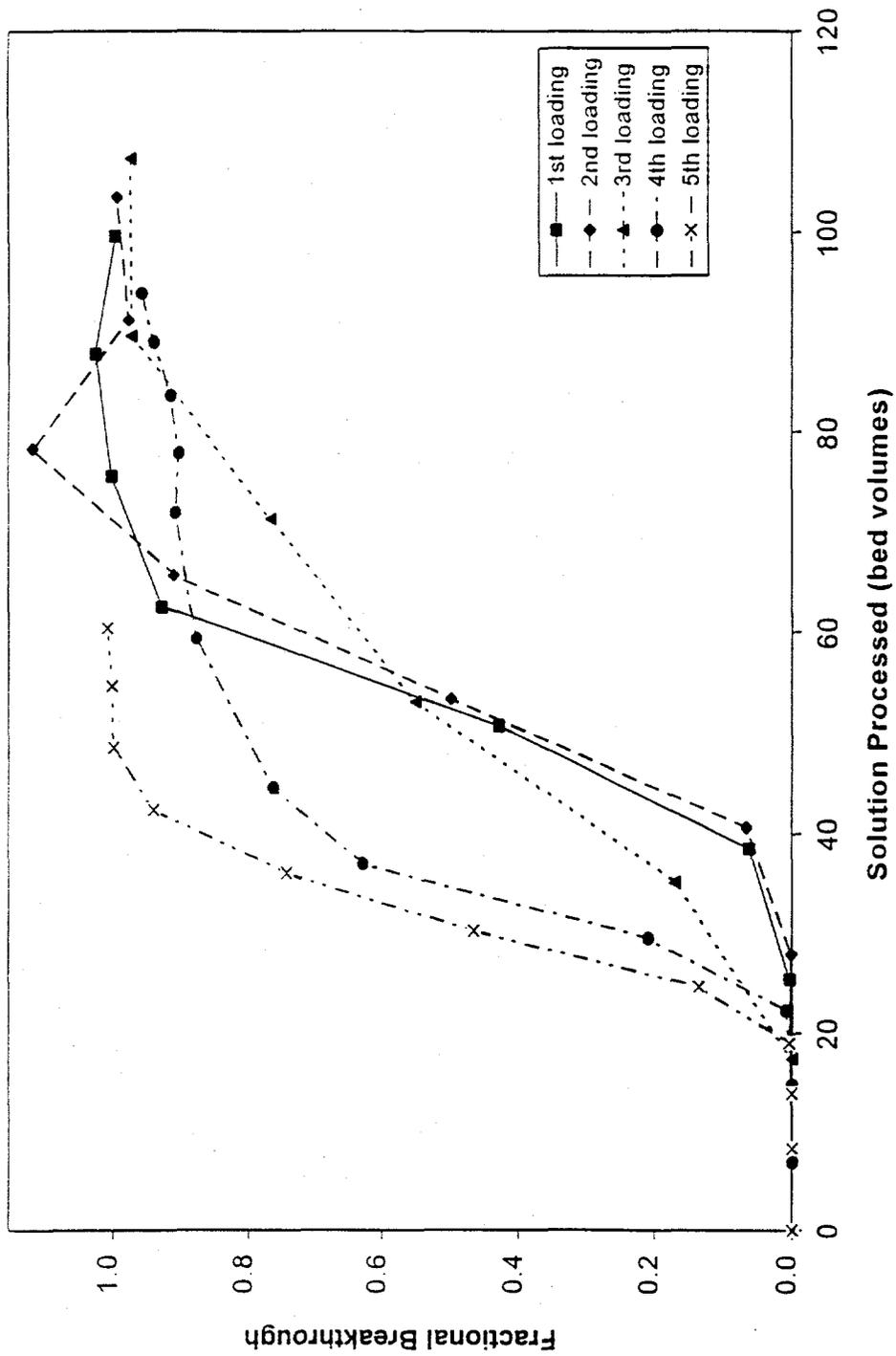


Fig. 12. Breakthrough curves for treating INEL tank waste simulant using SuperLig 618.

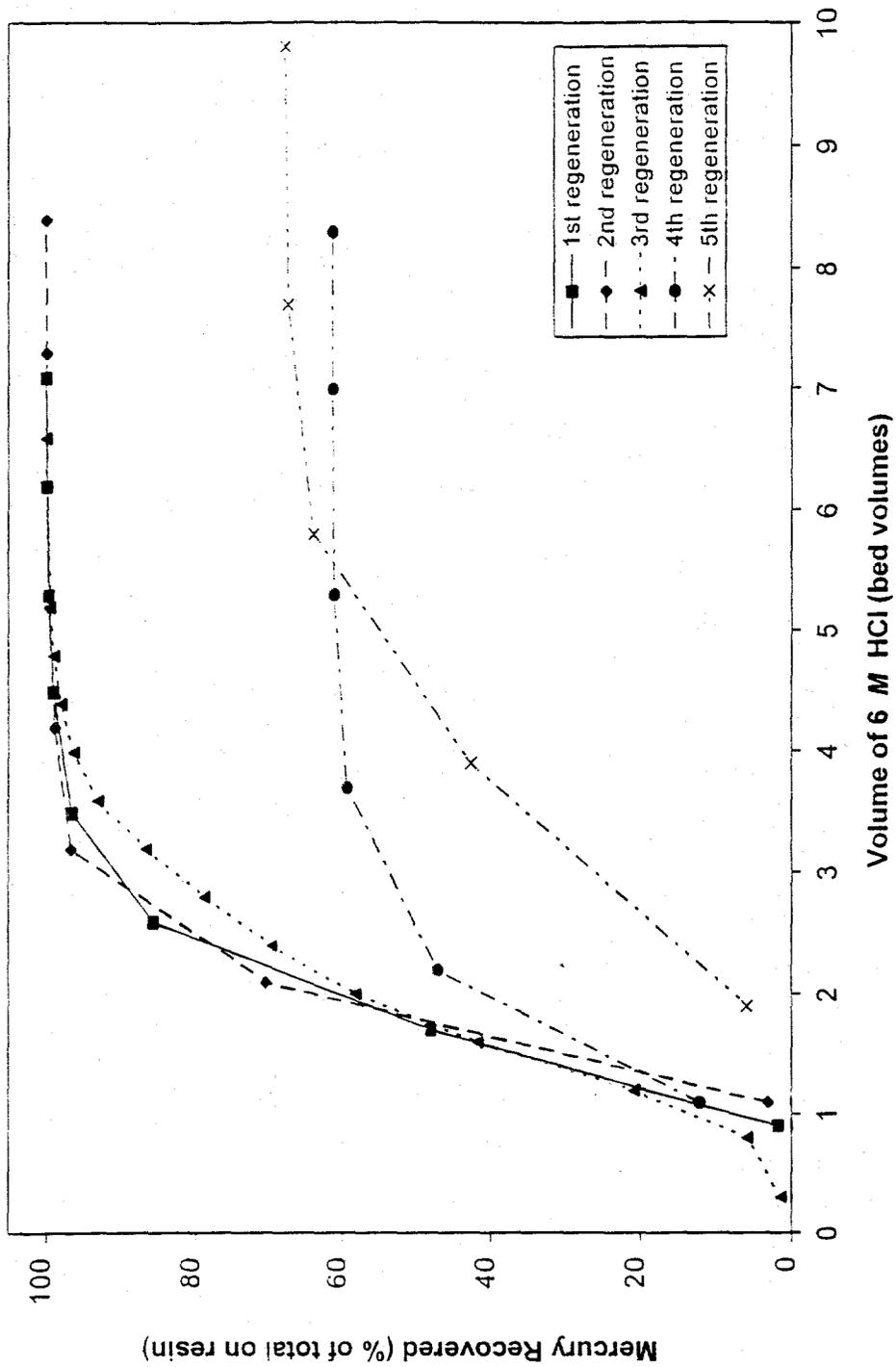


Fig. 13. Regeneration curves for SuperLig 618 use to treat INEL tank waste simulant.

3.4 PILOT-SCALE COLUMN TESTS

A joint project is being conducted with researchers from the Development Division of the Y-12 Plant to test three different adsorbents in a pilot-scale system located at a mercury-containing sump in the basement of Building 9201-5. The test system has 4.8-cm-I. D. columns with 250 g (325 mL) of Ionac SR-3, 350 g (670 mL) of Mersorb, and three columns in series with 860 g (1570 mL) each of activated carbon. The pilot-scale system had been in operation for 96 days, as of 10/30/95. The SR-3 column has treated 14,040 L (43,200 bed volumes) of sump water, at an average flow rate of 107 mL/min (19.8 bed volumes/h). The Mersorb column has treated 10,900 L (16,300 bed volumes) of water and has averaged 83 mL/min (7.4 bed volumes/h). The activated carbon columns have treated 18,500 L (11,800 bed volumes for the first column) at an average flow rate of 147 mL/min (5.6 bed volumes/h). The inlet mercury concentration has ranged between 70 and 90 $\mu\text{g/L}$. The SR-3 column and the first activated carbon column have shown a small leakage of mercury in their effluents (0 to 2 $\mu\text{g Hg/L}$), but no sign of breakthrough. The Mersorb column has shown a steadily increasing concentration of mercury in its effluent. The breakthrough curve for this column is shown in Fig. 14. The SR-3 column has adsorbed 1081 mg Hg (4.32 mg Hg/g resin), the Mersorb column has adsorbed 660 mg Hg (1.89 mg Hg/g sorbent), and the first activated carbon column has adsorbed 1413 mg Hg (1.64 mg Hg/g sorbent) to date. The mercury loadings achieved to date by the SR-3 and Mersorb columns are consistent with the results shown in the batch isotherm tests. Development Division personnel will continue to operate the pilot-scale equipment, and the results will be used by the Y-12 Plant to design a full-scale treatment system for treating the sump waters.

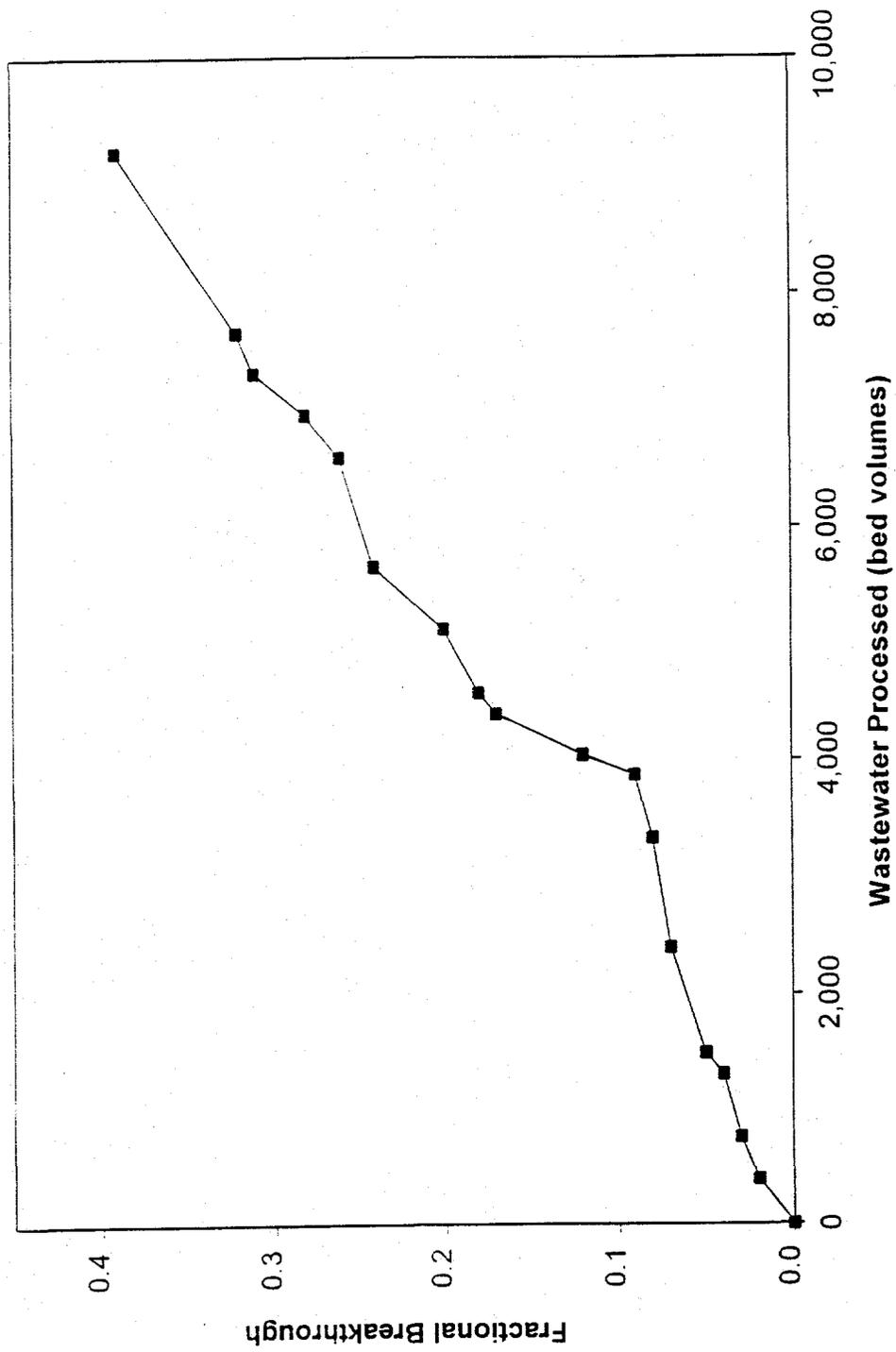


Fig. 14. Breakthrough curve for pilot-scale treatment of Y-12 sump water using Mersorb.

4. CONCLUSIONS

This project has provided an assessment of new sorbents for removing mercury from wastes at U. S. DOE sites. Four aqueous wastes were chosen for laboratory-scale testing: a simulant of a high-salt, acidic waste currently stored at INEL; a simulant of a high-salt, alkaline waste stored at the 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 were identified for testing, covering a wide range of cost and capability. Screening tests measured the potential of each of these sorbents to remove mercury from the four waste streams. The sorbents that showed promise in the screening tests were used in batch isotherm tests to better define the capabilities of the selected sorbents. Column tests were then conducted using the few best sorbents identified for each waste stream to determine the breakthrough characteristics and loading capacity of each sorbent. A pilot-scale test is continuing using three sorbents (activated carbon, Ionac SR-3, and Mersorb) to treat the Y-12 groundwater.

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 and 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. The Mersorb column tests showed a very gradual breakthrough curve for both the SRS simulant solution and the Y-12 groundwater, which would make it difficult to achieve a high loading on the sorbent while still attaining low mercury concentrations in the effluent stream. The Y-12 LiOH solution, which is a low-salt, high-pH wastewater, was much more difficult to treat than the high-salt, high-pH SRS simulant solution. The two best sorbents for the LiOH solution (Durasil 70 and Ionac SR-3) both showed relatively low mercury capacity and very gradual breakthrough curves.

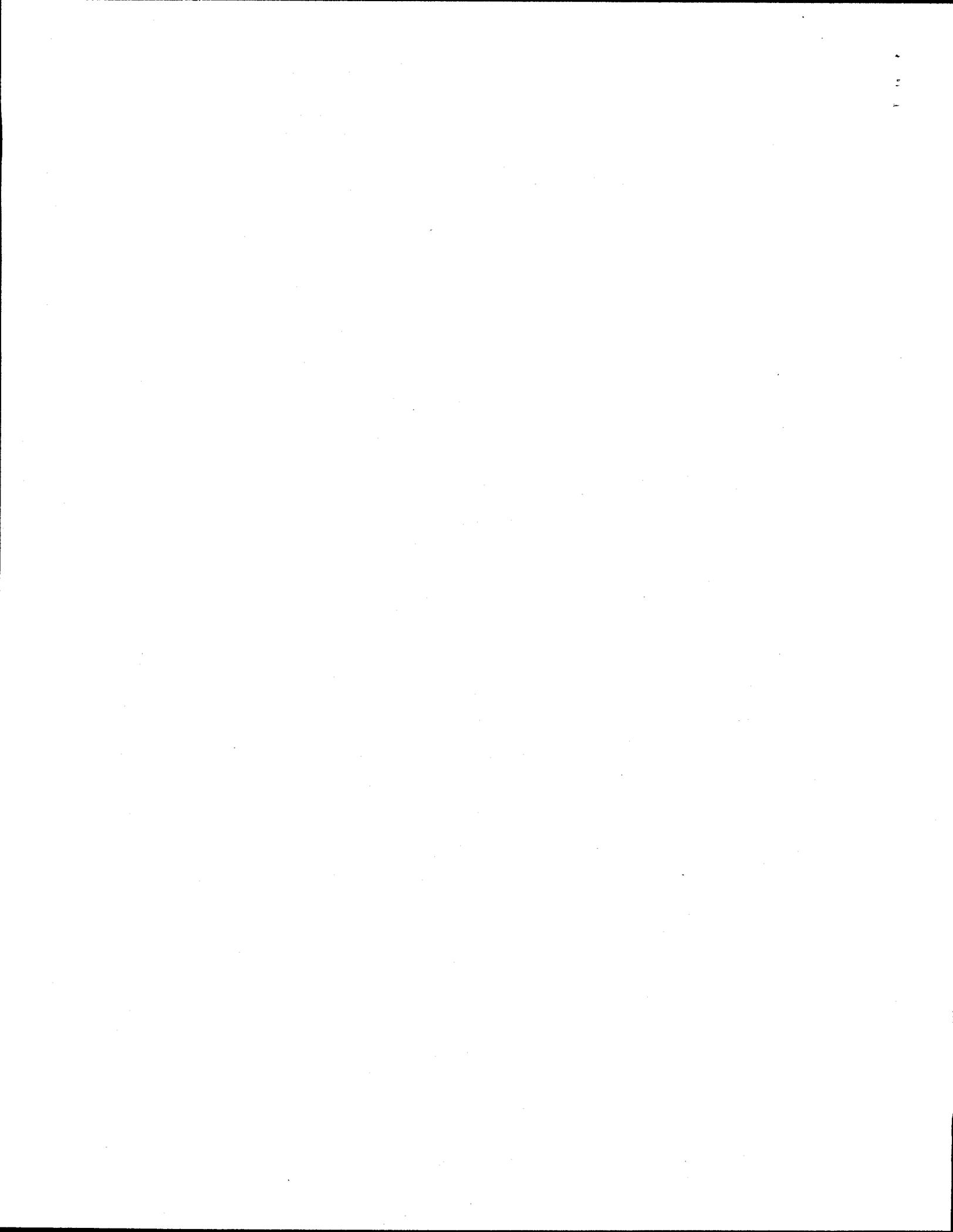
REFERENCES

1. Perona, J. J., and C. H. Brown, *A Technology Assessment for Mercury-Containing Mixed Wastes*, DOE/MWIP-9, Oak Ridge National Laboratory, March 1993.
2. Borduin, L. C., *DOE Mixed Waste Treatment Technology Needs, Phase I: MLLW Analyses and Historical Perspective*, LA-UR-94-3500, Los Alamos National Laboratory, October 1994.
3. *Technology Needs Crosswalk Report*, DOE/ID/12584-117, ed. 1, Chem-Nuclear Geotech, Inc., January 1993.
4. Kent, C., and L. G. Olson, Idaho National Engineering Laboratory, personal communication, Feb. 4, 1993, and Dec. 5, 1994.
5. Hobbs, D. T., *Composition of Simulants Used in the Evaluation of Electrochemical Processes for the Treatment of High-Level Wastes*, WSCR-TR-94-0286, Westinghouse Savannah River Company, June 27, 1994.
6. Ondrejcin, R. S., *Chemical Composition of Supernates Stored in SRP High Level Waste Tanks*, DP-1347/UC-70, E. I. duPont de Nemours & Co., Savannah River Laboratory, August 1974.
7. Lobring, L. B. and B. B. Potter, eds., *Determination of Mercury in Water by Cold Vapor Atomic Absorption Spectrometry*, Revision 2.3, Analytical Method 245.1, Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio, April 1991.



APPENDIX A

FORMULATION OF SIMULANT SOLUTIONS



INEL high-sodium tank waste simulant^a

Chemical	Amount for 1 L solution
NaNO ₃	151 g
KNO ₃	23.3 g
Ca(NO ₃) ₂	7.2 g
50% Mn(NO ₃) ₂	5.0 g solution
Pb(NO ₃) ₂	0.33 g
Cd(NO ₃) ₂ · 4H ₂ O	0.62 g
Ni(NO ₃) ₂ · 6H ₂ O	0.58 g
Hg(NO ₃) ₂ · H ₂ O	0.68 g
2.2M Al(NO ₃) ₃	250 mL
Fe(NO ₃) ₃ · 9H ₂ O	10.1 g
H ₂ MoO ₄	0.16 g
H ₃ BO ₃	1.48 g
Cr(NO ₃) ₃ · 9H ₂ O	2.40 g
Zr(NO ₃) ₂ · 3H ₂ O	0.28 g
27.6 M HF	1.81 mL
12.0 M HCl	1.75 mL
18.0 M H ₂ SO ₄	1.72 mL
14.8 M H ₃ PO ₄	0.68 mL
CsNO ₃	0.029 g
Sr(NO ₃) ₂	0.0038 g
Ce(NO ₃) ₃ · 6H ₂ O	0.16 g
13.0 M HNO ₃	124 mL

^aSource: Kent, C., and L. G. Olson. Idaho National Engineering Laboratory, personal communication, Feb. 4, 1993, and Dec. 5, 1994.



SRS tank waste simulant^a

Chemical	Amount for 1 L solution (g)
NaNO ₃	165.8 g
NaOH	53.2 g
Na ₂ CO ₃	17.0 g
Na ₂ SO ₄	19.9 g
KNO ₃	1.52 g
K ₂ Cr ₂ O ₇	0.48 g
NaNO ₂	41.4 g
NaH ₂ PO ₄ ·H ₂ O	1.14 g
HgCl ₂	0.54 g
NaCl	1.28 g
NaAlO ₂	26.0 g
NaF	0.63 g
Na ₂ SiO ₃ ·9H ₂ O	1.08 g

^aSource: Hobbs, D. T., *Composition of Simulants Used in the Evaluation of Electrochemical Processes for the Treatment of High-Level Wastes*, WSCR-TR-94-0286, Westinghouse Savannah River Company, June 27, 1994.



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