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Treatability Studies and Large-Scale Treatment of Aqueous Mixed Waste Containing Heavy Metals

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ABSTRACT

Wastes have accumulated at the Idaho National Engineering Laboratory through routine laboratory practices, experimental engineering operations, and decommissioning and decontamination of nuclear reactor facilities. A storage tank at the Test Area North held approximately 129,000 L (34,000 gal) of acidic wastewater (pH = 2.8) and contained prohibited levels of lead (15.0 mg/L) and mercury (0.24 mg/L). Radioactive constituents were also present; the most predominant being radiocesium Cs-137 (340 pCi/mL) and radiocobalt Co-60 (35.6 pCi/mL). Bench-scale studies were undertaken to evaluate ion exchange as a means of removing the contaminants. A set of breakthrough curves was obtained and identified capacity constraints, selectivities, and operating requirements of candidate resins. Treatment studies indicated that Purolite S-920 resin could effectively remove mercury, while Rohm and Haas' Amberlite 200-CH was used for lead and radionuclide removal. Based on these laboratory tests a full-scale facility, using multiple ion exchange columns, was designed and operated in the spring of 1994. The liquid effluents were discharged to an onsite evaporation pond [Resource Conservation and Recovery Act (RCRA) Subtitle D equivalent] and met RCRA disposal limits for hazardous metals and self-imposed radionuclide limits. All secondary wastes and residues were sampled and subjected to the toxic characteristic leaching procedure. The resulting leachate concentrations were below RCRA discharge limits and, therefore, these will be disposed of at the onsite low-level disposal facility.

After concluding the tank wastewater operations, enough reserve resin capacity was available to treat three additional mixed wastes residing onsite. These totaled about 1,900 L (500 gal) and contained prohibited levels of chromium, cadmium, and barium. Laboratory studies demonstrated that these heavy metals could also be removed by the existing resins. Treatment was performed at the full-scale facility with the effluents discharged to the evaporation pond.

INTRODUCTION

Much of the current effort at the Idaho National Engineering Laboratory (INEL) is focused on cleanup of old reactor facilities and remediation of contaminated areas onsite. The Test Area North (TAN) facility has been used since the mid-1950s to conduct a variety of activities, ranging from tests on nuclear-powered aircraft to simulated off-normal conditions in nuclear reactors. As these facilities are decommissioned and decontaminated, wastes are generated that must be treated and disposed of before the facility can be permanently closed. One such waste accumulated in a storage tank at TAN and was composed of about 129,000 L (34,000 gal) of wastewater. In addition to lead and mercury above Resource Conservation and Recovery Act (RCRA) discharge limits, this water contained radiocesium and radiocobalt, and was, therefore, classified as a mixed waste. To carry out closure of the tank facility, it was necessary to treat this waste and remove all residues from the site.

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Samples of the wastewater underwent laboratory treatability studies to determine the appropriate processing scheme. The results of the studies were used to redesign an existing ion exchange facility located in a process building next to the tank system. The upgrades included extensive piping modifications, a multistage filtering system, and replacement of the old ion exchangers with columns packed with the resins preferred for treatment of the TAN wastewater.

Environmental and Regulatory Issues

Large-scale treatment of the TAN tank waste was performed in a process building operated under "interim status." This facility had been granted a RCRA Part A permit in 1987 for ion exchange treatment of chromate water. It was determined that the tank waste could also be treated under the existing permit, provided that ion exchange be used as specified in the Part A application.

The approach to treatment was to remove lead and mercury to below RCRA discharge limits and dispose of the water to an onsite evaporation pond (RCRA Subtitle D equivalent). A project specific radionuclide discharge level was established based on Derived Concentration Guidelines (DCG) as outlined in DOE Order 5400.5 (1). The DCG is the radionuclide concentration that, under conditions of continuous exposure for one year, would result in an equivalent dose of 100 mrem to an individual. The disposal limits for Co-60 and Cs-137 was set at five times the DCG for exposure via ingestion of the water and corresponded to radionuclide concentrations of 25 and 15 pCi/mL, respectively.

The closure plan for the tank system required that all wastewater and secondary wastes, including spent ion exchange resins, spent filters, and personnel protective equipment, be removed from the site. This required extensive sampling to properly characterize each of these wastes. To ensure that reliable data were obtained, sampling and analysis activities followed the quality assurance/quality control requirements as specified by the Environmental Protection Agency (2,3).

TAN WASTE STREAM CHARACTERISTICS

Treatability Studies

The TAN tank wastewater was acidic (pH \approx 2.8) and contained several regulated heavy metals, although only lead (15.0 mg/L) and mercury (0.24 mg/L) were in excess of RCRA disposal limits. A complete list of the regulated metals concentrations is given in Table 1, while Table 2 summarizes the concentrations for common nonregulated metals in the wastewater. A gamma-ray analysis revealed radiocesium (Cs-137) and radiocobalt (Co-60) as the primary gamma-emitting radionuclides; their activities are listed in Table 3.

Samples of the waste underwent laboratory treatability studies in accordance with 40 CFR Part 261.4. It was initially believed that a logical treatment train would be to adjust the pH, remove the ensuing precipitates by filtering, and then ion exchange the clarified liquid. Laboratory tests confirmed that simple pH adjustment and the resulting precipitation would remove lead and Co-60 to below disposal limits. However, it was determined by INEL regulatory personnel that this would constitute a "simple neutralization" in the RCRA sense, and was not allowed under the existing Part A permit. To remain within the permit's

guidelines, the hazardous constituents (lead and mercury) would have to be removed by ion exchange before any neutralization.

The laboratory studies were then reduced to determining the resin(s) necessary to remove lead and mercury from the unaltered wastewater. Previous lab work had shown Purolite S-920 to effectively remove lead and mercury from neutral and alkaline solutions (4). The Purolite S-920 is a hydrogen-form, chelating-type resin with thiouronium functional groups. Wastewater was filtered through a 0.45- μm membrane and then run through a column packed with this resin at a rate of about 11 bed volumes per hour (BV/hr). Mercury was very efficiently removed to below 0.4 $\mu\text{g/L}$ (ppb), but lead and the radionuclides passed unaffected through the column.

Amberlite 200-CH, a strong acid, cationic (hydrogen form) resin was then used in the column. With a flow rate of about 13 BV/hr, this resin showed excellent lead and radionuclide removal. Effluent concentrations are shown in Table 4 and correspond to the leakage of these ions through a column of fresh Amberlite resin.

It was suspected that the Amberlite resin would not show a high selectivity for the ions of interest (lead, mercury, cobalt, and cesium) over other commonly found "interference" ions such as sodium, calcium, and iron. It was desirable to obtain the resin capacity for the targeted ions so that enough reserve capacity would be designed into the large-scale system. Breakthrough curves were obtained by passing a controlled amount of wastewater through the column. At regular intervals, effluent samples were withdrawn and analyzed for pH, lead, mercury, Cs-137, and Co-60. Figures 1-4 show these breakthrough curves.

The breakthrough curve for lead (Figure 1) shows a relatively low, but gradually increasing leakage rate until about 140 BV. The curve then steepens until about 200 BV, at which point the effluent concentration becomes nearly constant at about 0.55 mg/L (ppm). Accompanying the increased leakage is a corresponding increase in effluent pH, indicating that exchange of hydrogen is no longer occurring. The lead concentration in the effluent remained nearly constant beyond 200 BV, presumably due to the establishment of a new steady state leakage value corresponding to lead displacing another, less preferred, ion from the resin. The primary interest for process design is that the leakage value (up to at least 260 BV) was still well below the 5.0 mg/L RCRA level for lead.

Inspection of the cesium breakthrough (Figure 2) shows some interesting behavior. Cesium is bound effectively until about 120 BV, then the onset of breakthrough occurs and a fairly steep rise in cesium leakage follows, along with an accompanying rise in pH. After about 150 BV, the cesium level in the effluent is higher than in the feed, suggesting that cesium is being eluted by more preferred ions, such as lead.

Figures 3 and 4 show the breakthroughs for mercury and Co-60. Cobalt is more selectively bound than Cs-137, as indicated by the later breakthrough, and thus successful Cs-137 removal would ensure Co-60 removal. Mercury is not bound well by the Amberlite 200-CH, as shown by the nonsharp breakthrough pattern and the low removal efficiency (see Table 4) by the fresh resin.

Large-Scale Design and Treatment

The ion exchange columns were selected to give a throughput so that treatment could be completed within a two- to three-week period. Standard-sized fiberglass columns, each with a 445 L (15.7 ft³) capacity, were procured and placed in the permitted process building. A flow rate of 12 BV/hr was recommended, which equated to an effluent flow of 87 L/min (23 gal/min). Two types of resins were used: Purolite S-920 to ensure mercury removal and Amberlite 200-CH to remove lead, Co-60, and Cs-137. Prior to wastewater entering the columns, it was filtered through a bank of filters with pore sizes of 10, 1, and 0.3 μm .

The total capacity of Amberlite required for treatment was based on the breakthrough for cesium because its breakthrough would occur earlier than lead or cobalt. Based on a breakthrough volume of 110 BV, a total resin capacity equivalent to just over two columns was necessary. Three Amberlite columns were connected in series and valved so that effluent from the first (primary) column would flow directly into the second (polishing) column. When the primary column became saturated, it was removed from service and the second column assumed the lead position, with the third becoming the polishing column. Bypassing the spent column prevented cesium from being eluted and carried downstream.

Amberlite column breakthrough was determined by monitoring the effluent pH from the primary column. When pH rose above a predetermined value (pH \approx 2.6), flow was diverted so that the spent column could be taken off-line. During field activities, it was found that the active mass transfer zone, and therefore the degree of saturation, could also be located by placing a hand-held beta-gamma detector along the side of the active column. By moving the detector vertically along the column's length, the highest dose rate would be found at and behind the mass transfer zone. At the conclusions of operations, the two spent columns had average contact readings of 50 and 65 mrem/hr. The third Amberlite column only had a detectable dose reading at the column's entrance, indicating that a large reserve exchange capacity was still available.

A single column of Purolite S-920 was also used to ensure adequate removal of mercury. This column had a very large excess exchange capacity, owing to the resin's exclusive selectivity for mercury. This column was placed upstream and in series with the Amberlite columns.

A schematic diagram of the treatment process is shown in Figure 5. In addition to the filter banks and resin columns, the system included two open-topped polyethylene tanks used to adjust the effluent pH. The pond discharge criteria required the pH to be within the range of 5 to 9; this was performed via caustic addition. From the polyethylene tanks, treated water was routed to a 189,000 L (50,000 gal) tank where samples were drawn at the conclusion of operations. Validated analytical results are given in Tables 1 and 3. All RCRA discharge and self-imposed radionuclide criteria were met. Treatment of the 129,000 L (34,000 gal) required approximately nine days to complete.

Secondary Wastes and Residues

Residual wastes from primary treatment included spent resins, spent filter cartridges, and miscellaneous items such as rags, wipes, and gloves. Resin from the two spent Amberlite columns were sent for toxic characteristic leaching procedure (TCLP) metals analysis, along with samples from spent filter cartridges and miscellaneous items. All samples were below

disposal limits (see Table 5) and, therefore, all secondary wastes can be disposed of at the onsite low-level waste facility. Samples were not drawn from the third Amberlite column or Purolite column because these still had exchange capacity available and were not considered waste.

ADDITIONAL WASTES TREATED

Small quantities (typically less than 4,000 L) of mixed waste generated onsite are routinely sent to the Mixed Waste Storage Facility. At the conclusion of the TAN waste studies, several of this facility's liquid wastes were targeted as being potentially treated by ion exchange, and were sampled and sent to the laboratory to undergo testing. Three of the targeted wastes were verified to be treatable by ion exchange with the resins already residing in the TAN treatment process. These three wastes are described below.

In Situ Vitrification Scrubber Water

This waste was generated during a pilot-scale in situ vitrification (ISV) test at the INEL and totaled about 1,300 L (350 gal). Scrubber water used in the ISV offgas system was found to contain cadmium (3.6 mg/L) above RCRA disposal limits, in addition to trace amounts of Pu-239 and Am-241. Treatability studies demonstrated that the strong acid, cationic Amberlite resin, would remove cadmium as well as the radionuclides.

Biotechnology Water

This waste originated within the biotechnology group at the INEL and was generated from experiments involving uranium mill tailings. The waste, which totaled less than 380 L (100 gal), contained high levels of barium and cadmium, and a small amount of naturally occurring uranium and thorium. Laboratory tests demonstrated that either the Amberlite or Purolite S-920 chelating resin would remove the heavy metals.

Chromate Water

This single drum of waste, comprised of 144 L (38 gal), was from the Navy's nuclear reactor facility and resulted from chromate being added to process water to act as a corrosion inhibitor. Prior to being discarded as waste, the chromate was reduced in a series of chemical processes to Cr^{+3} . The radioactive constituent in the waste was Cr-51, which having a short half-life had decayed to undetectable levels during its five-year stay at the waste storage facility. The Amberlite resin proved ineffective at removing chromium, indicating that chromium was probably bound as an anionic (chloride) complex. Subsequent tests proved that an anionic resin would remove chromium, but it was also found that the Purolite S-920 chelating resin, which was already available in the TAN treatment process, would also remove chromium.

There was a generous amount of exchange capacity available in the third Amberlite column and in the Purolite S-920 column. The three wastes were sent by truck to the TAN facility and processed in the existing system. The effluent from the three streams, totaling less than 1,900 L (500 gal), were aggregated in a single tank from which samples were drawn. The water met RCRA disposal limits, as shown by the results in Table 6, and was discharged to the evaporation pond.

CONCLUDING COMMENTS

Treatment of mixed wastes will continue to be emphasized at DOE sites as nuclear facilities undergo decommissioning. Closure of the TAN tank facility required that all wastes and residues in the tank system be treated and removed from the site. A permitted ion exchange facility was available at TAN, and its use expedited processing; however, it did constrain the allowable pretreatment options available.

Laboratory treatability studies positively demonstrated that ion exchange could remove the RCRA-regulated metals and radionuclides. These laboratory studies also provided design information for modifying the existing process and included resin selection, column sizing, column change-out criterion, and piping and filter system modifications. Full-scale treatment was completed within two weeks, with the liquid effluents being discharged to an onsite evaporation pond. In addition to the TAN tank waste, three smaller waste streams stored onsite were also involved in treatability studies and found to be treatable with the resins specified for the TAN treatment. These were treated after completion of the TAN waste.

ACKNOWLEDGMENTS

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Table 1. Hazardous metals in Test Area North tank wastewater.

Hazardous metal	Concentrations (mg/L)		
	Raw wastewater	Treated water	RCRA discharge
Arsenic	ND	ND	5.0
Barium	0.230	ND	100.0
Cadmium	0.170	ND	1.0
Chromium	1.40	0.20	5.0
Lead	15.0	0.08	5.0
Mercury	0.240	0.023	0.2
Selenium	ND	ND	1.0
Silver	ND	ND	5.0

ND = none detected

Table 2. Nonhazardous metals in the Test Area North tank wastewater.

Metal	Concentrations (mg/L)
	Raw wastewater
Calcium	82.0
Copper	2.1
Iron	43.0
Magnesium	30.0
Manganese	0.87
Phosphorus	ND
Potassium	40.0
Sodium	47.0

ND = none detected

Table 3. Activities of the radionuclides in the Test Area North tank wastewater.

Radionuclide	Raw wastewater (pCi/mL)	Treated water (pCi/mL)	Self-imposed discharge limit (pCi/mL)
Co-60	37.0	1.34	25
Cs-137	320	11.6	15

Table 4. Key constituent concentrations from the laboratory column packed with fresh Amberlite 200-CH resin.

Component	Wastewater	Effluent
Lead	15.0 mg/L	<0.036 mg/L
Mercury	0.24 mg/L	0.141 mg/L
Co-60	37.0 pCi/mL	0.29 pCi/mL
Cs-137	320.0 pCi/mL	0.03 pCi/mL

Table 5. TCLP metals analysis for secondary wastes: spent Amberlite 200-CH resin and filters.

Hazardous metal	Amberlite column 1 (mg/L)	Amberlite column 2 (mg/L)	Filter cartridges (mg/L)
Arsenic	ND	ND	ND
Barium	ND	ND	ND
Cadmium	0.049	0.050	ND
Chromium	1.6	0.68	0.17
Lead	3.5	0.55	0.13
Mercury	ND	ND	0.026
Selenium	ND	ND	ND
Silver	ND	ND	ND

ND = none detected

Table 6. Heavy metals in the three additional wastes treated from the Mixed Waste Storage Facility.

Hazardous metal	Chromate water (mg/L)	Biotechnology water (mg/L)	In situ vitrification water (mg/L)	Treated water (mg/L)
Arsenic	-	-	-	ND
Barium	-	220	-	ND
Cadmium	-	49	3.6	ND
Chromium	230	-	-	0.04
Lead	-	4.8	1.9	ND
Mercury	-	-	-	ND
Selenium	-	-	-	ND
Silver	-	-	-	ND

ND = none detected

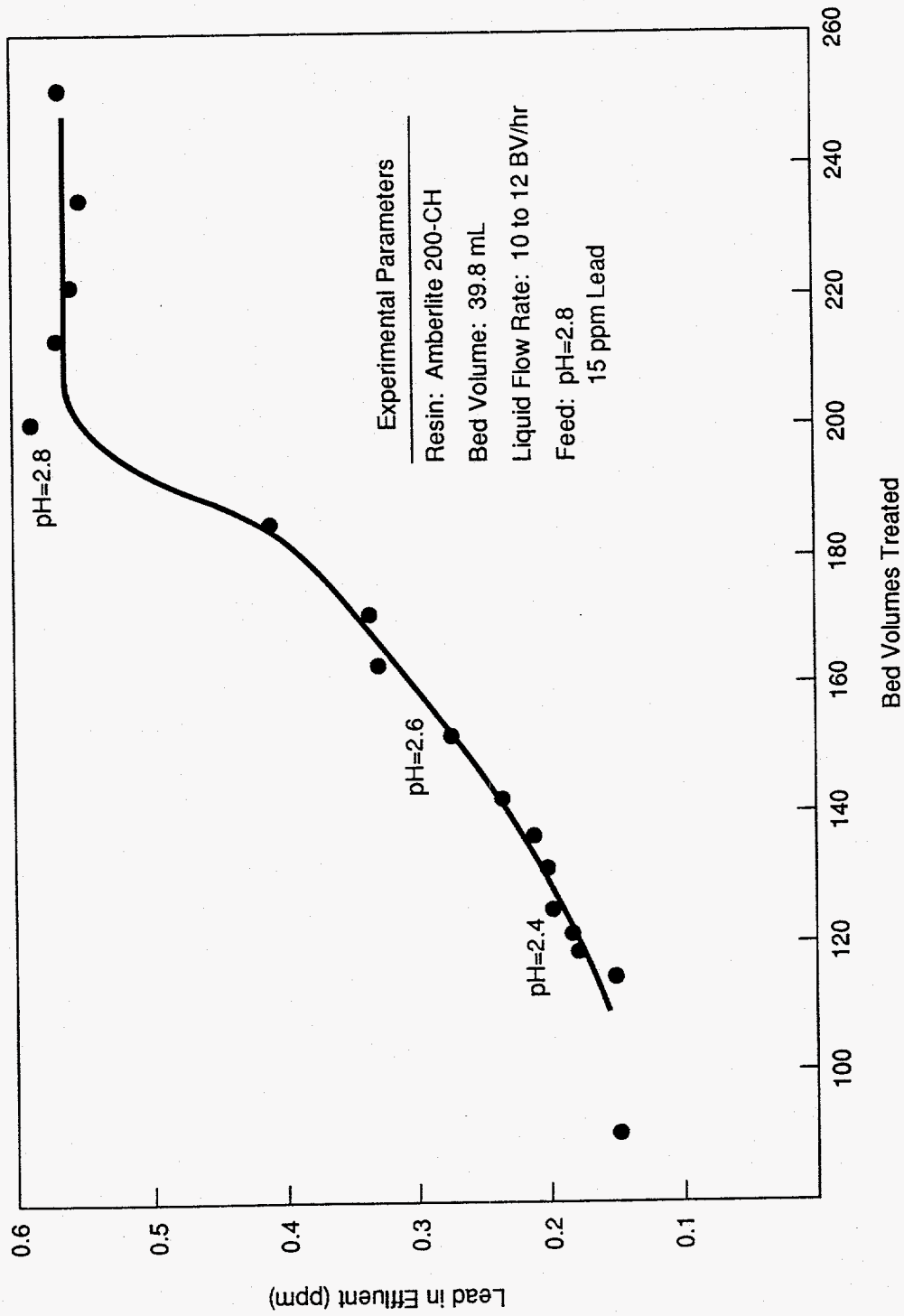
Figure 1. Breakthrough of lead on Amberlite 200-CH.

Figure 2. Breakthrough of Cs-137 on Amberlite 200-CH.

Figure 3. Breakthrough of Co-60 on Amberlite 200-CH.

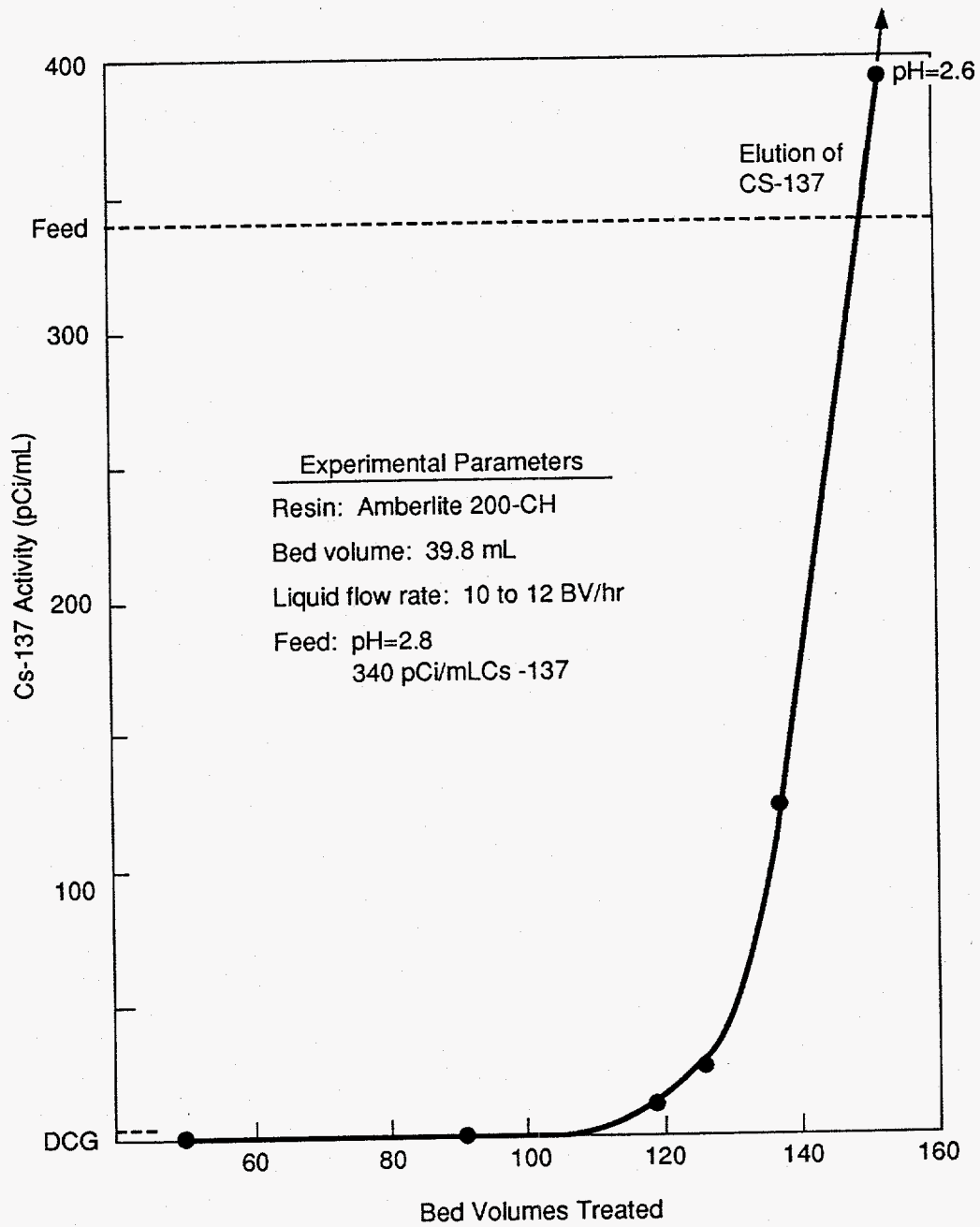
Figure 4. Breakthrough of mercury on Amberlite 200-CH.

Figure 5. Schematic diagram of the Test Area North treatment process.



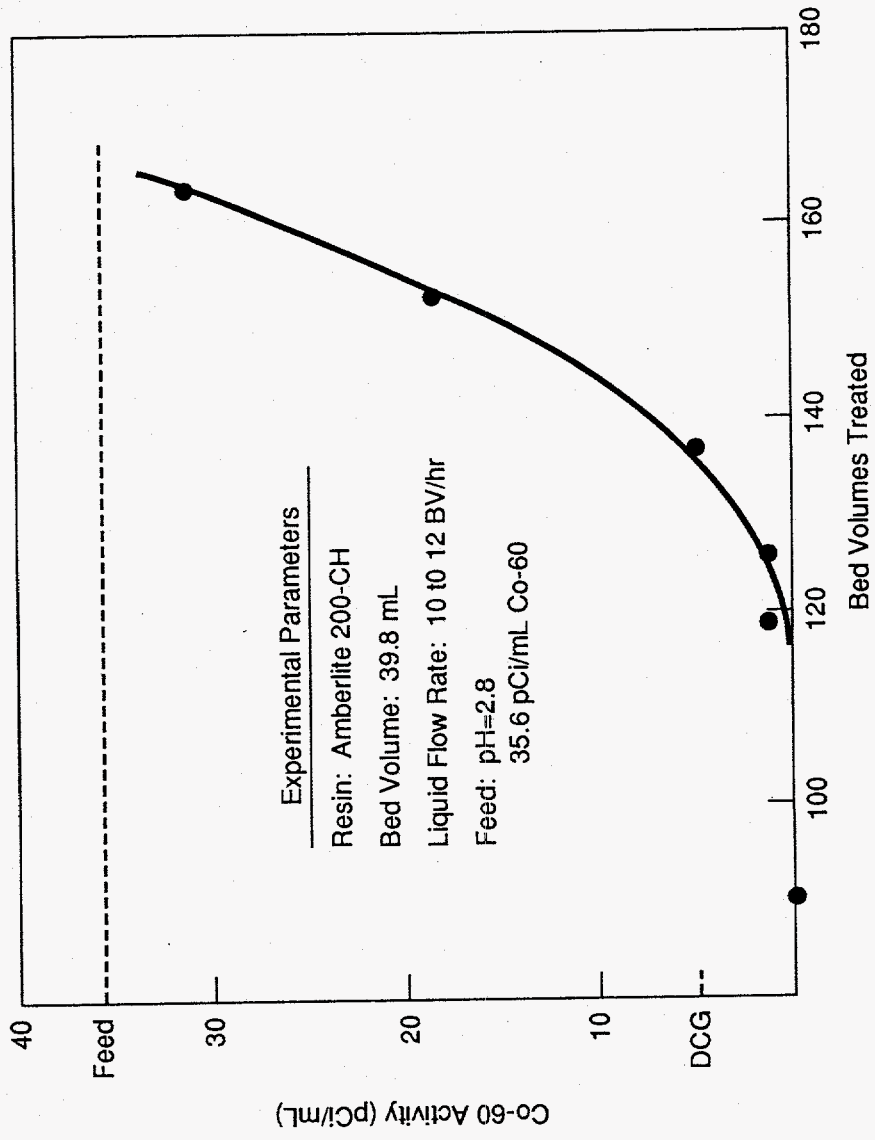
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Figure 1. Breakthrough of Lead in Amberlite 200-CH.



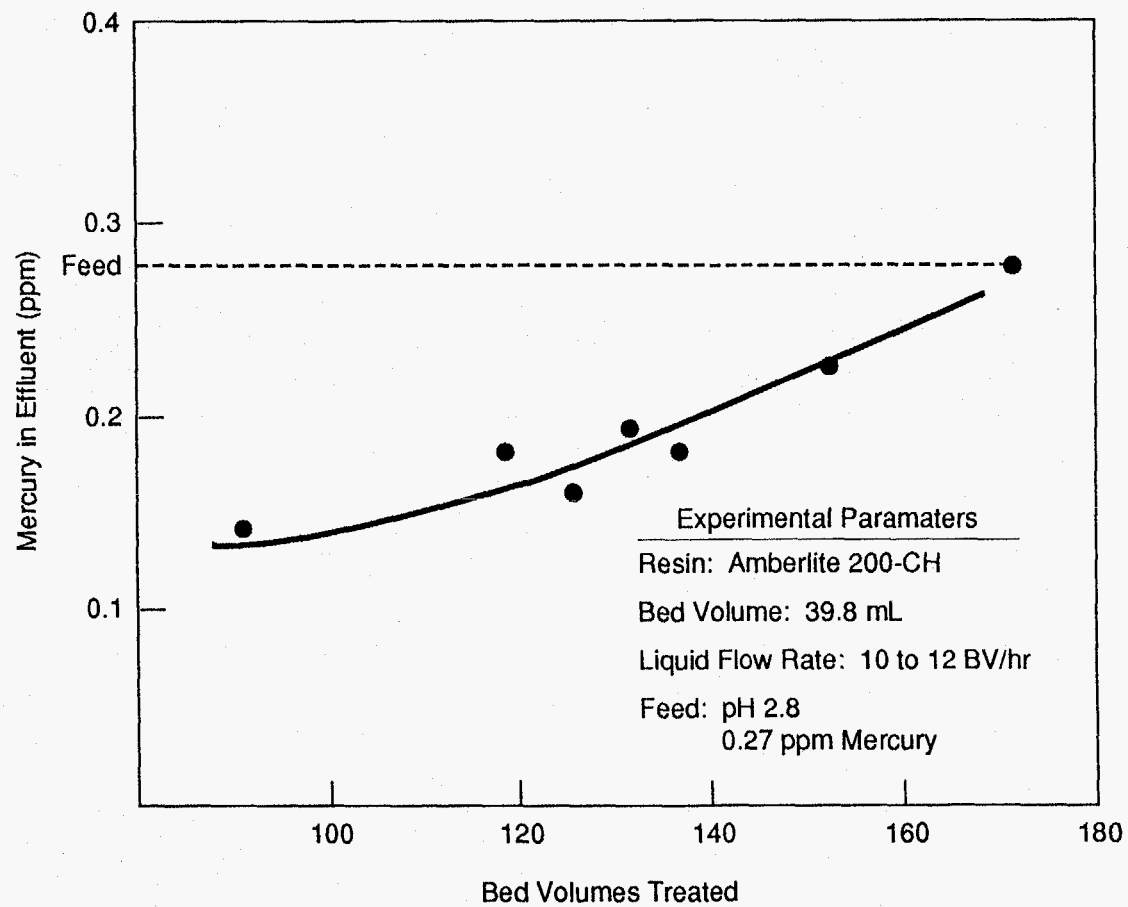
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Figure 2. Breakthrough of Cs-137 on Amberlite 200-CH.



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Figure 3. Breakthrough of Co-60 on Amberlite 200-CH.



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Figure 4. Breakthrough of mercury on Amberlite 200-CH.

