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WASTE MANAGEMENT ANALYSIS FOR THE NUCLEAR FUEL CYCLE
II. RECYCLE PREPARATION FOR WASTEWATER STREAMS

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SUBJECT DESCRIPTORS

Actinides
Adsorption
Decontamination
Ion Exchange
Ozonization
Reverse Osmosis
Separation Processes

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WASTE MANAGEMENT ANALYSIS FOR THE NUCLEAR FUEL CYCLE

II. RECYCLE PREPARATION FOR WASTEWATER STREAMS

C. Michael Smith, James D. Navratil, and Carl E. Plock

Abstract. Recycle preparation methods were evaluated for secondary aqueous waste streams likely to be produced during reactor fuel fabrication and reprocessing. Adsorption, reverse osmosis, and ozonization methods were evaluated on a laboratory scale for their application to the treatment of wastewater. Activated carbon, macroreticular resins, and polyurethanes were tested to determine their relative capabilities for removing detergents and corrosive anions from wastewater. Conceptual flow sheets were constructed for purifying wastewater by reverse osmosis. In addition, the application of ozonization techniques for water recycle preparation was examined briefly.

INTRODUCTION

A Rocky Flats project called Actinide Recovery and Recycle Preparation for Waste Streams was a subtask of an Oak Ridge National Laboratory (ORNL) program entitled Waste Management Analysis for the Nuclear Fuel Cycle. The purpose of the subtask was to determine the feasibility of removing actinides from secondary aqueous waste streams likely to be produced during reactor fuel fabrication and reprocessing. The waste streams are part of two proposed flow sheets titled "Salt Waste Management" and "Acid and Waste Water Management."^{1,2}

Evaluation of methods on a laboratory scale for the salt waste and wastewater streams was the major emphasis of this subtask. Results of method evaluation for the salt waste streams are given in Part I of this series of reports.³ This report deals with evaluation of techniques for the wastewater streams.

The problem of recycle preparation involves the selective removal of organic impurities, detergent in particular, and corrosive anions from the wastewater streams prior to actinide removal. Adsorption,

ion exchange, ozonization, and reverse osmosis are possible systems for removing the organics and anions. Recent work on this problem dealt primarily with the laboratory evaluation of adsorbents and ion exchange resins. The evaluation involved a determination of the detergent and chloride breakthrough capacities for these materials and then determining the elution volume needed for regeneration.

As part of an effort to incorporate complete water recycle at Rocky Flats, much of the work on reverse osmosis purification of wastewater had been done prior to the ORNL task. From this work, described elsewhere in the literature,⁴ conceptual flow sheets were developed for the use of reverse osmosis in recycle preparation of wastewater streams.

A determination of the feasibility of ozonization for the removal of organics also was initiated. This process was considered since, under optimum conditions, it oxidizes organics to carbon dioxide and water; thus, it does not introduce an additional waste stream. Furthermore, some metals such as iron and lead are oxidized to insoluble oxides or hydroxides.

EXPERIMENTAL

Materials

A description of the adsorbents that were evaluated is listed in Table 1. All the granular adsorbents are commercially available except for Amoco® carbon, which is in a developmental stage and is distributed only for experimental purposes. The open-pore polyurethane (OPP) had been prepared in 0.4-cm-diameter glass columns with a bed height of 10 cm. Preparation was by precipitation-polymerization of 2.0 g isocyanate (Mondur MR) and 4.0 g of polyol (LA-475) in 25 ml of 60-40 vol % toluene-carbon

TABLE 1. Description of Adsorbents

Adsorbent ^a	Type ^b	Density (g/cm ³)	BET Surface Area (m ² /g)
Amoco® GX-31	C-petroleum	0.29	2800-3500
Anasorb® GCA-005	C-coconut shell	0.48	1200-1300
Calgon® F-400	C-bituminous coal	0.42	1050-1200
Amberlite® XAD-4	M-N-P	0.54	750
Amberlite IRA-93	M-W-P	0.61	50
Amberlite IRA-900	M-S-P	0.67	50
OPP	OH/NCO = 2.2	0.20	—

a. Amoco - Amoco Research Corp., P. O. Box 5910A, Chicago, Illinois
 Anasorb - Analabs, Inc., 80 Republic Dr., North Haven, Connecticut
 Calgon - Calgon Corp., 4800 W. 34th St., Houston, Texas
 Amberlite - Rohm & Haas Co., Independence Mall West, Philadelphia, Pennsylvania

b. C - active carbon; M - macroreticular resin; N - neutral (nonion exchange); W - weak base anion exchange; S - strong base anion exchange; P - polystyrene matrix; OH - Union Carbide LA-475 (polyoxypropylene polyether); NCO - Mondur MR Mobay Chemical Co. (p,p'-diphenylmethane diisocyanate); OH/NCO - monomer ratio.

tetrachloride.⁵ Attempts at producing new OPP columns of similar bed volume as granular adsorbent columns were unsuccessful. The OPP columns were washed with 20 bv (bed volumes) of hexane, 20 bv methanol, and 200 bv of distilled-deionized water before use.

All granular adsorbents were dry-sieved to obtain a particle size of 40 to 50 mesh. Columns with an inner diameter of 0.6 cm were filled with a weighed portion of adsorbent to give a bed height of 10 cm. Bed volumes were 2.8 cm³ for the granular adsorbent columns and 1.3 cm³ for the OPP. Before use, the columns were washed with 20 bv of methanol, 20 bv of 1M HNO₃, and finally with 200 bv of distilled-deionized water. Stored columns contained water for preconditioning. This allowed adsorbents to swell and thus avoided a decrease in flow rate prior to evaluation runs being done.

A 2.5 g/l Pierce laundry detergent solution, adjusted to pH 5.0 with 12M hydrochloric acid, was prepared for use as the synthetic waste stream. This solution was filtered through Whatman® No. 42 paper to remove colloidal particles. The slightly acidic pH

was chosen for its compatibility with reverse osmosis (a possible post-adsorbent waste treatment) and the OPP column.

Equipment and Procedures

One-liter quantities of the detergent solution were pumped through each column at an average flow rate of 5.0 ± 0.3 ml/min. Forty-five fractions of 20 ml each were collected with a Scientific Manufacturing Industries drop-counting fraction collector. A schematic of the experimental setup is shown in Figure 1. A selected number of fractions were analyzed for total organic carbon (TOC) and chloride ion.

The elution behavior of the Amoco carbon, the XAD-4 resin, and the OPP was studied by pumping anhydrous methanol through these columns at 1.5 ml/min. Five fractions of 2 ml each were collected. The residue remaining after room temperature evaporation of the methanol was redissolved in distilled deionized water and analyzed for TOC.

FIGURE 1. Breakthrough Evaluation Apparatus

Ozonization Procedure

A synthetic waste solution, prepared the same as previously described except for no pH adjustment, was treated with ozone through the courtesy of Ozone Treatment Systems, Inc. of Ferndale, Michigan. Ozone was produced at 2 g/hr with a Schaefer ozone generator (corona discharge). The ozone was then contacted with the waste solution by means of a frit-type gas diffuser placed at the bottom of the stirred solution. Five samples were taken over an 8-hr period and were analyzed for TOC.

Analyses

The analysis for TOC was carried out with a Beckman® Model 915 Total Organic Carbon Analyzer. Aliquots of 20 ml were run in duplicate, first for inorganic carbon (carbonate), then for total carbon. The difference (total carbon minus carbonate carbon) was reported as TOC.

Chloride ion was determined by an Orion solid state chloride ion electrode with a double junction

reference electrode. Samples and sodium chloride standards were made 1M in potassium nitrate to eliminate matrix effects.

RESULTS AND DISCUSSION

Adsorbents

The adsorption of surfactants by active carbon from wastewaters (both real and synthetic) has been well researched.⁶⁻⁸ When considering one dominant contaminant, such as surfactants, the adsorptive capacity of a carbon is found to be dependent on specific surface area. The carbon capacity is even more dependent on the nature of the carbon surface, i.e., the kinds and populations of functional groups that are a result of production variables such as raw material and activation method.⁹ These organic and inorganic residual groups give rise to chemical adsorption in addition to the physical (van der Waal) adsorption common to all adsorbents. The characteristics of the carbon surface are not well defined, however, which makes it necessary to evaluate an assortment of carbons.¹⁰ Thus, three carbons of different raw materials and manufacture were used in this study.

The macroreticular, polymeric adsorbents are relatively new to the field of adsorption—introduced primarily for the preconcentration of trace organics from natural waters.¹¹ In that application, the adsorbents have proved more efficient than carbon.¹² A recent industrial use of macroreticular resin has been in the treatment of waste effluent from insecticide manufacture. The resin, XAD-4, surpassed an active carbon of greater surface area both in terms of adsorptive capacity and elution efficiency.¹³ Furthermore, that work indicated an economic advantage of the XAD-4 with chemical regeneration over granular active carbon with thermal regeneration.¹³ In contrast to carbon, the chemistry of the inert, nonactivated surface of the resin is well defined and easily varied.¹⁴

The addition of ion exchange functional groups to the macroreticular resin matrix provides the possibility of removing both organics and anions, the latter species being resistant to adsorption on carbon.¹⁰ The macroreticular resins evaluated in

TABLE 2. Breakthrough and Elution Data on Adsorbent Materials

Adsorbent Material	Breakthrough Capacity		Elution (ml MeOH/g mat) ^c
	(ml det/g mat) ^a	(mg Cl ⁻ /g mat) ^b	
Anasorb	225	7	--
Amoco GX-31	240	--	>12
Calgon F-400	215	--	--
Amberlite XAD-4	250	--	1
Amberlite IRA-93	16	9	--
Amberlite IRA-900	11	47	--
OPP ^d	100	48	8

a. Milliliter of detergent passed per gram of adsorbent at breakthrough of 0.30 total organic carbon (TOC) in effluent. Feed = 89 mg/l TOC.

Breakthrough defined as concentration of solute in effluent divided by concentration of solute in feed.

b. Milligrams of chloride passed per gram of adsorbent at breakthrough of 0.30. Feed = 1 mg/l Cl⁻.

c. Milliliters of methanol passed per gram of adsorbent at 30% TOC eluted.

d. Open-Pore Polyurethane.

this project included a high-surface-area neutral resin and two anion exchange resins—a weak base and a strong base.

The OPP, like the macroreticular resin, was introduced in the field of chromatography and preconcentration.^{5,15} As an agglomeration of spherical particles, the OPP is prepared *in situ* by a solution polymerization, and it adheres tightly to the walls of the column. Channeling at the adsorbent-wall interface, which is a potential problem with granular adsorbents in small bore columns, is thus prevented.¹⁵ Previous studies have dealt with quantitative and preparative application of this polymer. No work has been reported in which OPP was investigated for the removal of organics from wastewater, as was done with foamed polyurethane,¹⁶ although a reported column with the dimensions of 6 × 245 cm suggests the feasibility of a large-scale application.¹⁵

Results of the detergent and chloride breakthrough capacities and the elution behavior of the adsorbents are summarized in Table 2. These data are taken

from graphs of the breakthrough and elution curves that appear in Appendix A. The data at $C/C_0 = 0.3$ were used for adsorbent capacity evaluation since the breakthrough curves were not sufficiently resolved at $C/C_0 = 0.1$, which is the usual criterion for adsorbent evaluation. The abbreviation C/C_0 is defined as concentration of solute in effluent divided by concentration of solute in feed.

In spite of a smaller surface area (750 m²/g), the neutral, inactive surface of XAD-4 has a definite advantage over the large surface area of Amoco active carbon (3000 m²/g). This evidences the effect on adsorption had by the functional groups that originate during the activation process.

Earlier studies with OPP showed a high capacity for linear alkylate sulfonates (LAS), the anionic surfactant constituent of detergent.¹⁷ A repeat of this work, detailed in Appendix B, confirmed these results. The LAS is preferentially sorbed while the remainder of the organic constituents pass through, thus giving the low value for total organic capacity. The anion exchange properties of OPP,

FIGURE 2. Osmosis -- Normal Flow From Low to High Concentration.

FIGURE 3. Reverse Osmosis -- Flow Reversed by use of Pressure Upon High Concentration Solution

which make possible the good adsorption of LAS, also aids in chloride removal. The OPP, along with the Amberlite IRA-900, has the highest capacity for chloride.

Elution data show the regeneration of XAD-4 to be more efficient than that of carbon and OPP. The inefficiency of the chemical regeneration of active carbon stems from chemisorption effects of the carbon surface.¹⁸ For this reason, thermal methods are commercially favored for renewing the surface of carbon.¹⁹ This, however, requires the installation of a regeneration furnace and results in the gradual loss of carbon from volatilization. Both add to the overall expense of applying carbon adsorption. Similarly, the functional groups that give OPP its anion exchange properties may also interfere with the elution process.

Reverse Osmosis

Reverse osmosis (RO) is a separation process that depends upon a suitable semipermeable membrane. The membrane allows water flow under pressure but effectively prevents the passage of dissolved and suspended substances.^{20, 21}

The conventional concept of osmosis refers to the spontaneous flow of a solvent from a dilute to a more concentrated solution across a semipermeable membrane (Figure 2). This transfer continues until a concentration-dependent osmotic pressure becomes great enough to prevent further transfer of the solvent to the more concentrated solution.

If a pressure greater than the equilibrium osmotic pressure is applied to the more-concentrated-solution side of the membrane (Figure 3), the solvent flows in reverse (from the more concentrated solution to the dilute solution). Thus, the RO process effects removal of substances by forcing the water-solvent through a suitable membrane.

The RO method is capable of reducing the volume of a waste stream by as much as 98%. Reduction of the waste stream will depend on osmotic pressure of impurities in the generated brine and on the composition of impurities in the waste stream. If the concentration of impurities is high, osmotic pressure will be high, which will result in a decrease in the flux and desired water recovery. If impurities in the waste stream are substances with low solubilities, such as silica and the salts of calcium, barium, and strontium, the possibility of scaling the membranes is increased. If scaling does take place, the flux will be reduced.

FIGURE 4. Conceptual Flow Sheet for Purification of Wastewater Containing Negligible Quantities of Anions and Low Concentrations of Impurities and Radioactivity

The advantages of RO are that it is a low-energy-consuming process, wastewater stream adjustment is minimal, and the quantity of combustible waste generated is small.

Figure 4 shows a conceptual flow sheet for purification of wastewater containing significant quantities of anions and/or detergents. The flow sheet applies to both tritiated and nontritiated waste streams.

Ultrafiltration (UF), another membrane separation technique that is similar to RO, was also suggested for the removal of detergents. The UF membrane pores are larger, however, than those of RO membranes (5-10 nm for UF versus 0.5-1.0 nm for RO); consequently the UF method would only effect a nominal removal of detergent or detergent-actinide complexes. The UF could be used as a "prefilter" that would increase the RO efficiency. Use of RO methods with or without UF would greatly reduce the quantities of waste materials

FIGURE 5. Reduction of Total Organic Carbon (TOC) With Ozone

for evaporation-incineration as compared with adsorption-ion exchange methods.

Ozonization

Ozone, an allotropic form of oxygen, is one of the most powerful oxidizing agents; it has an oxidation potential of -2.07 V. Ozone has long been used for the disinfection of water supplies in Europe and recently, with the advent of modern, more efficient, and less expensive ozone generators, it has been gaining importance in the treatment of waste effluents.

A number of tests have been made on sewage and industrial waste effluents in which the concentrations of highly refractory compounds such as phenols,²² cyanides,²³ and polymer manufacturing wastes²⁴ were appreciably reduced. In ozonization tests on detergents, from 80-90% of anionic and

FIGURE 6. Conceptual Flow Sheet for Ozonization Treatment of Wastewater

nonionic detergents were removed from sewage effluents depending on solution pH and temperature, rate of ozone addition, and the amount of additional organics.²⁵

In all tests and applications of ozonization, the major advantage was the absence of a persistent residual. Ozone removed contaminants without producing secondary pollutants and without increasing the inorganic salt concentration. This is an important consideration when the treated stream is to be recycled.

Figure 5 shows the result of a trial ozonization run on a Pierce laundry detergent solution (2.5 g/l detergent). Even though the operating conditions

were not optimized (the method of contact, in particular), 60% of the organics (detergent and detergent residuals) was removed. Further work would be needed to optimize reaction conditions and to ascertain the fate of the anion and actinide constituents of the waste stream. Ozonization appears to be a "cleaner" method than adsorption since (1) under optimum conditions the organics are totally separated from the actinides and are destroyed by oxidation to CO_2 , H_2O , and other inorganic residuals; and (2) another waste stream would not be generated from column regeneration. Figure 6 details a waste management process utilizing ozonization. The amount of ozone required is based on 5.5 grams ozone (O_3) per gram

FIGURE 7. Conceptual Flow Sheet for Wastewater Treatment Using Adsorbents and Reverse Osmosis

alkylbenzene-sulfonate (ABS) for complete oxidation to CO_2 , H_2O , and NaHSO_4 . This assumes only one singlet-oxygen of the ozone is available,²⁶ according to the following:

Efficiency can be increased, however, to about 2 grams ozone per gram ABS by including ultraviolet (uv) irradiation in the process.^{26, 27} Greater than 90% oxidation has been realized with this method. This high percentage is probably caused by the increased amount of highly reactive singlet-oxygen resulting from uv radiation²⁷ in the following reaction:

CONCLUSIONS

Based on results obtained from this work, it appears that a process combining adsorption and reverse osmosis would satisfactorily accomplish the task of treating secondary aqueous waste streams produced during reactor fuel fabrication and reprocessing.

The breakthrough capacity and elution results suggest that XAD-4 would be an efficient and economical method for removing organics. The IRA-900 could be used in conjunction with XAD-4 to remove anions.

Figure 7 shows a conceptual flow sheet in which XAD-4 resin is used to remove organics. Material

balance is based on the assumption that resin selectively removes organics, with actinides passing on through that step. The correctness of this assumption could be determined with column runs using a contaminated waste solution.

As stated before, separation of the organics from actinides would be complete with ozonization by virtue of the organics being oxidized. Lack of experimental work, however precludes consideration of the ozonization process at present.

After removal of the organics (with or without actinides), the waste stream could be reduced to 5% original volume by reverse osmosis. This would greatly facilitate subsequent processing or evaporation of the wastewater.

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APPENDIX A.

EXPLANATION OF BREAKTHROUGH AND ELUTION GRAPHS

Graphic results of organic breakthrough capacity evaluations are shown in Figures A-1 (carbons) and A-2 (resins). The data are presented as C/C_0 , which is defined as the concentration of total organics (TOC) in the column effluent divided by TOC in the column influent ($89 \mu\text{g/ml}$), as a function of the volume of detergent solution passed through the column.

The abrupt rise in the curves for the carbons and resins may be attributed to two factors: (1) the presence of weak or non-adsorbing constituents in the solution—namely sodium pyrophosphate,

metasilicate, carbonate, chloride, and sulfate; and (2) possible channeling caused by a small column diameter, although the use of 40-50 mesh particles and a slow flow rate was intended to prevent this.

After the initial rise, breakthrough curves for the granular adsorbents flatten out, the effluent concentration increasing only slightly over the range of solution volume used. A similar behavior has been noticed in column studies with pure surfactants and has been explained in terms of secondary adsorption—the formation of micelles of the surfactant with the adsorbed phase.⁷ Figure A-3

FIGURE A-1. Breakthrough Curves for Carbon Adsorbents

shows curves, based on Weber's work,⁸ that represent three types of breakthrough behavior. The "S"-shaped curve (solid line) is typical for ideal monolayer adsorption. Secondary adsorption (e.g., micelle formation), which eventually goes to saturation, is represented by the dotted line. The curve shown as a line of dashes represents the effect of non-adsorbing constituents of the influent or possible channeling.* This third curve best represents the breakthrough curves generated in these evaluations of carbons and resins. Repeating these experiments but with wider column diameters or

*Channeling and non-adsorbing constituents of the influent are sometimes referred to as "leakage."

the development of adsorption isotherms⁴ would differentiate the effects of non-adsorbers from channeling.

Breakthrough results for the Open-Pore Polyurethane (OPP) column are shown in Figure A-4. The organic curve shows a similar "leakage" plus secondary adsorption behavior. The small column volume predicated the early breakthrough, even though the capacity was still less than the carbons and neutral resin. The OPP eventually reached saturation (100% C/C_0) at 860 ml.

Figure A-5 gives graphic results of the chloride capacity evaluation. Only four curves are shown, both for clarity and because the other adsorbents

FIGURE A-2. Breakthrough Curves for Macroreticular Resins

FIGURE A-3. Theoretical Breakthrough Curves Showing Types of Adsorption Behavior

FIGURE A-4. Breakthrough Curve for Open-Pore Polyurethane

FIGURE A-5. Breakthrough Curves for Chloride Adsorption on Various Adsorbents

FIGURE A-6. Elution Curves for the Three Best Adsorbents

did not remove any chloride. As stated earlier, only the IRA-900 resin and the OPP effected any noticeable removal. Except for IRA-900, the adsorbents shown here exhibit the same leakage-secondary or competitive adsorption characteristics for chloride as for TOC.

Elution curves for the best adsorbent in each of the three categories—carbon, resin, and foam—are shown in Figure A-6. The neutral inactive surface of the XAD-4 accounts for the efficiency of elution since only physical adsorption is concerned.

APPENDIX B.

ADSORPTION OF LINEAR ALKYLATE SULFONATE BY OPEN-PORE POLYURETHANE

Results contained in the body of this text indicated a low capacity for organics by the Open-Pore Polyurethane (OPP). This could be due to poor column design or the selective adsorption of a component of the detergent. The former possibility may be ruled out on the grounds that in the column "synthesis," the OPP becomes bonded to the column walls. Considering the latter possibility, much better results are obtained if the behavior of OPP with only the LAS (linear alkylate sulfonate) constituent of the detergent is studied. Figure B-1 gives graphic data for LAS breakthrough and the recovery of LAS eluted, with methanol, from the column.

Fractions for LAS determination were collected simultaneously and under the same conditions as

those for total organic carbon (TOC) and Cl^- . The LAS was determined spectrophotometrically after reaction with methylene blue.²⁸ The weak anion exchange properties of the polymer,⁵ coupled with its macroporous surface, permits good removal of LAS from the test waste solution, whereas the nonionic constituents are poorly adsorbed. These results confirm preliminary results from a comparison of OPP to XAD-4 and carbon¹⁷ (Figure B-2). From Figures B-1 and A-6, it appears that only the LAS is adequately eluted from the OPP, whereas the other organic components of the detergent remain adsorbed. The LAS constitutes 40% of the detergent organics, and after 12 ml methanol has passed through the column, only about 20% of the nonionic have eluted.

FIGURE B-1. Breakthrough and Elution Behavior of Linear Alkylate Sulfonate (LAS) on Open-Pore Polyurethane (OPP)

FIGURE B-2. Breakthrough Curves for Adsorbents With Acidified Detergent (pH 3.5)

$C_o = 34$ mg/l LAS (Linear Alkylate Sulfonate)
 C/C_o = LAS concentration in effluent divided
by LAS in Influent
Flow Rate = 10 ml/min