Separation, Concentration, and Immobilization of Technetium and Iodine from Alkaline Supernate Waste

**Final Report
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**By
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List of Acronyms

ABEC	aqueous biphasic extraction chromatographic
ABEC-5000	aqueous biphasic extraction chromatographic, with 5000 MW PEG
ABS	aqueous biphasic system
ANL	Argonne National Laboratory, E. P. Horwitz, Ph.D. and co-workers
AW-101	a Hanford tank
BNFL	British Nuclear Fuels
BV	bed volume
Ci	curie
Cl	chloride
cm	centimeter
CRADA	Cooperative Research and Development Agreement
Cs	cesium
CST	crystalline silica titanates, Sandia/UOP
DI	deionized (water)
DOE	Department of Energy
DSC	differential scanning calorimetry
D _w	weight distribution ratio
dwcf	dry weight conversion factor
EDTA	ethylenediaminetetraacetic acid, a chelant
EPA	Environmental Protection Agency
FAA	flame atomic absorption
fcv	free column volume
FP	finished product
g	gram
GRAS	generally recognized as safe
HTiO	hydrous titanium oxide
HLW	high level waste
I	iodide/iodate
KCoCF	potassium cobalt hexacyano ferrate
L	liter
LLW	low level waste
mL	milliliter
MW	molecular weight
NCAW	a Hanford waste form
NIU	Northern Illinois University, Robin D. Rogers, Ph.D. and co-worker
NRC	Nuclear Regulatory Commission
ORNL	Oak Ridge National Laboratory
PEG	polyethylene glycol
PEG-5000	5000 molecular weight polyethylene glycol, methyl capped
Re	perrhenate, rhenium
Sn	tin
Sr	strontium
SRR	resorcinol-formaldehyde resin (Savannah River)

SST	single shelled tank (Hanford)
SY-101	a Hanford tank
Tc	per technetate, technetium
Tc/I	technetium/iodine
THF	tetrahydrofuran
UT	University of Tennessee, Spiro Alexandratos, Ph.D. and co-workers
W-3	a Melton Valley tank
W-29	a Melton Valley tank

Executive Summary

Development of remediation technologies for the characterization, retrieval, treatment, concentration, and final disposal of radioactive and chemical tank waste stored within the Department of Energy (DOE) complex represents an enormous scientific and technological challenge. A combined total of over 90 million gallons of high-level waste (HLW) and low-level waste (LLW) are stored in 335 underground storage tanks at four different DOE sites. Roughly 98% of this waste is highly alkaline in nature and contains high concentrations of nitrate and nitrite salts along with lesser concentrations of other salts. The primary waste forms are sludge, saltcake, and liquid supernatant with the bulk of the radioactivity contained in the sludge, making it the largest source of HLW.

The saltcake (liquid waste with most of the water removed) and liquid supernatant consist mainly of sodium nitrate and sodium hydroxide salts. The main radioactive constituent in the alkaline supernatant is cesium-137, but strontium-90, technetium-99, and transuranic nuclides are also present in varying concentrations. Reduction of the radioactivity below Nuclear Regulatory Commission (NRC) limits would allow the bulk of the waste to be disposed of as LLW. Because of the long half-life of technetium-99 (2.1×10^5 y) and the mobility of the pertechnetate ion (TcO_4^-) in the environment, it is expected that technetium will have to be removed from the Hanford wastes prior to disposal as LLW. Also, for some of the wastes, some level of technetium removal will be required to meet LLW criteria for radioactive content. Therefore, DOE has identified a need to develop technologies for the separation and concentration of technetium-99 from LLW streams. Eichrom has responded to this DOE-identified need by demonstrating a complete flowsheet for the separation, concentration, and immobilization of technetium (and iodine) from alkaline supernatant waste.

Both technetium, as pertechnetate, and iodine, as iodide and/or iodate, are strongly absorbed from concentrated salt solutions, such as the alkaline tank wastes, by Eichrom's Aqueous Biphase Extraction Chromatographic (ABEC[®]) resin. The separation of technetium and/or iodine from such waste solutions has been clearly demonstrated for a number of simulant and actual waste streams. These waste streams include actual Hanford tank waste from tank AW-101, (a cesium decontaminated double shell slurry feed composite), three different Hanford tank waste simulants, actual waste samples from ORNL Melton Valley Storage Tanks W-29 and W-3, and waste simulant solutions from two British Nuclear Fuel (BNFL) locations—Capenhurst and Sellafield—in the United Kingdom. All of these waste streams contain high salt concentrations. Alternative technologies for the separation of technetium from tank wastes utilize anion exchange resins to sorb pertechnetate. The high concentrations of anions present in tank wastes will compete with pertechnetate and iodide/iodate for uptake by the anion exchange resin. Thus, high salt concentrations in tank wastes pose a serious potential problem for the alternative separation technologies utilizing anion exchange resins. A distinct advantage of the ABEC resin separation technology is that the high salt concentrations do not interfere with uptake of technetium and iodine (Tc/I). In fact, greater salt concentrations

actually enhance the uptake of Tc/I by ABEC resin. Therefore, ABEC resin offers a significant advantage for the separation of Tc/I from alkaline supernate waste streams.

It has also been clearly demonstrated that Tc/I are rapidly and efficiently stripped and ABEC resin is regenerated by eluting the loaded resin with water. This offers another significant advantage over alternative technologies which require concentrated acid solutions or solutions of chelating agents (e.g., EDTA) and reductants (e.g., Sn^{2+}) to remove technetium from anion exchange resins. The ability to strip Tc/I from ABEC resin with water results in no additional wastes added to the concentrated Tc/I solution. It is expected that at least a 100-fold concentration of Tc/I will be achieved by loading Tc/I from tank wastes onto ABEC resin and stripping with water. For example, a capacity of 76 mmol technetium per liter of ABEC resin has been determined as part of this effort. Assuming only a 50% loading of the resin, 1,000 liters of alkaline supernatant waste containing 5×10^{-5} M technetium would require 1.3 liters of ABEC resin to load the technetium. Greater than 95% of the technetium can be stripped in approximately 5 bed volumes (BV) of water. Thus, the original 1,000 liters of alkaline waste can be reduced to 6.5 liters of water containing 7.7×10^{-5} M technetium for a concentration factor of 150.

The selectivity of ABEC resin for Tc/I over other tank waste constituents, combined with the ability to regenerate the resin with water, provides a clean, concentrated solution of Tc/I which may be treated further in a variety of ways. One possibility is to evaporate the water strip solution for additional concentration to any desired level prior to grouting for final waste disposal. A second option being considered by management at the BNFL Capenhurst facility is to dispose of the technetium-loaded ABEC resin as the final waste form. As stated in the example above, 1.3 liters of ABEC resin are required to load technetium from 1,000 liters of waste containing 5×10^{-5} M pertechnetate. Assuming that the resin volume will decrease by 50% when dried before disposal, the original 1,000 liters of waste can be reduced to 0.65 liters for a final concentration factor of approximately 1,500.

Another option for technetium stabilization and disposal has been demonstrated in this research effort as part of a complete technetium control flowsheet. First, the Tc/I which has been stripped from ABEC resin with water is loaded onto a commercial silica-based anion exchange resin, NUCLEOSIL. An average D of 1×10^4 was demonstrated for this process with greater than 99.5% uptake of technetium and a concentration factor of approximately 70. Given the extremely high D value, concentration factors of at least several hundred should be obtainable. Continuing the example given for ABEC resin above, the stated capacity for NUCLEOSIL is 1 mmol/g. Assuming only 50% loading, 100 g (50 mL) of NUCLEOSIL are required to sorb the 50 mmol of technetium contained in 6.5 liters of water strip solution after the ABEC resin separation step. This yields a concentration factor of 130 for the NUCLEOSIL loading step. The combined concentration factor for these two steps is approximately 20,000.

As a final step, the NUCLEOSIL is then encapsulated within a hydrous titanium oxide (HTiO) matrix at a level which yields 40% NUCLEOSIL by volume after drying.

The result is a highly stable waste form from which less than 1% of the encapsulated technetium was leached in either of two different leachability tests. Continuing the examples from above, the original 1000 liters of alkaline supernate can be reduced to approximately 125 milliliters of stable waste for an 8,000-fold reduction of initial waste volume.

Advantages of this new flowsheet are:

- ABEC-resin exhibits high retention of Tc/I and high selectivity for Tc/I over other species in the alkaline supernatant wastes
- Tc/I are eluted quickly and efficiently from ABEC-resin with water
- Tc/I are sorbed strongly by silica-based anion exchange resin from the water strip solution
- high concentration factor (~ 8000) minimizes volume of final immobilized waste form
- final waste form is stable and amenable to disposal without additional treatment or can be further incorporated in a grout matrix

The successes of this development effort are summarized as follows:

- improved, large particle ABEC-resins exhibiting less shrinking and swelling and greater bed densities than earlier versions have been developed
- type of resin support polyethylene glycol (PEG) molecular weight, and synthetic parameters have been optimized to produce the desired ABEC-resins more economically
- tetrahydrofuran (THF), the original solvent for the PEG addition step, was successfully replaced with a safer solvent
- the improved ABEC-resins exhibit greater than required uptake performance and loading capacity and can be rapidly stripped with water
- successful demonstration of ABEC-resin synthesis at the 110-liter pilot reactor scale
- cost for manufacturing ABEC-resin at the 110-liter scale demonstrated as comparable to other specialty resins
- demonstrated loading of technetium onto commercial silica-based anion exchange resin from simulated strip solutions

- demonstrated an improved, simplified procedure for encapsulation which greatly minimizes risks of radioactive contamination and worker exposure, and reduces costs of the process
- demonstrated high stability of the encapsulated waste form to leaching
- performed theoretical heating and shielding calculations which indicate the surface dose rate and heating from radioactive decay of the encapsulated, final waste form should be insignificant for all geometries and loading levels examined

Based on observations made during this phase of the effort, recommendations are made for additional studies to be accomplished as part of the next phase of the program. These additional studies can be performed within the scope and budget of the second phase.

The base phase of the program was successfully completed within a 15-month time frame. Details of the research effort are presented in this report.

I. Introduction

Alkaline waste constitutes the largest portion of the HLW tank inventory at both Hanford and ORNL Melton Valley. Nearly 160 million liters of liquid, alkaline waste are currently being held in either single- or double-shelled tanks at the Hanford site. The supernate at Hanford has nitrate and nitrite concentrations ranging from 1 to 4 molar, hydroxide concentrations from 2 to 4 molar, and somewhat lower levels of other salts, such as sulfate and carbonate. The Melton Valley waste, estimated to contain 1.6 million liters of supernate, is similar to Hanford supernate with slightly higher nitrate, higher carbonate, and much lower hydroxide levels. Similar in composition to the Melton Valley waste, the ORNL Bethel Valley evaporator tanks are estimated to contain an additional 0.26 million liters of alkaline supernatant waste.

Fission products (Cs-137, Sr-90, Tc-99 and I-129) are the major problem radioisotopes in the alkaline supernate. The most promising technologies being tested to date have been developed for the separation of cesium and strontium. The Sandia/UOP crystalline silica titanates (CST's) have undergone broad testing and have been shown to have the high selectivity required for concentrating the cesium and achieving volume reduction targets. Similarly, a number of other inorganic absorbers, such as the hexacyanoferrates, cobalt dicarbollide, and sodium titanates, and organic absorbers, such as the Savannah River resorcinol-formaldehyde resin, have been shown to be effective in removing cesium and strontium from a number of wastes

Technetium (as TcO_4^- , pertechnetate) and, to a somewhat lesser extent, iodine (as I^- , iodide, or, possibly, IO_3^- , iodate) separations have relied primarily on anion exchange resins, notably the ReillexTM-HPQ, Reillex 420, and certain Purolite and Amberlite resins. Technetium (and possibly iodine) is absorbed readily by anion exchange resins, but difficulties with elution of activity from the resin, radiolytic stability, and selectivity for pertechnetate over nitrate have been identified by a number of researchers. N. Schroeder at Los Alamos has developed an improved elution method for the most promising anion exchange resin, ReillexTM-HPQ, which utilizes Sn^{2+} as a reductant and the chelating group, EDTA. This new elution process is a great improvement over the 8 M nitric acid elution that had previously been suggested to remove technetium from anion resins.

Additional improvements in technetium (and iodine) separation, concentration and immobilization are still required. Foremost among these are a high selectivity for technetium over other anions present in the alkaline supernate due to the high nitrate and nitrite concentrations and an effective elution scheme which does not contribute to the waste volume. Elution of technetium from anion resins with the reductant Sn^{2+} and chelating agent EDTA, for example, will likely require an additional separation step to eliminate Sn^{2+} and EDTA before the technetium can be placed into a final waste form.

Eichrom Industries, Inc. has a new technetium and iodine selective resin which meets the above-mentioned requirements. This new resin, developed jointly at Argonne National Laboratory and Northern Illinois University, shows remarkable selectivity for

technetium and iodine over other constituents present in alkaline supernate. Most importantly, this resin has the unique advantage of being regenerated by eluting the bound technetium and iodine with water. A flowsheet based on this new Tc/I selective resin is presented in Figure 1.

As described above, a number of promising technologies already exist for the separation of cesium and strontium from alkaline supernate and other waste streams. However, significant improvements are still required in the separation processes of technetium and iodine. Our efforts with regard to this research program are concentrated on the separation, concentration and immobilization of technetium and iodine from alkaline supernate. The technologies employed will be shown to be applicable to technetium and iodine problems in a number of other waste streams. Eichrom's Tc/I selective resin works well with highly salted alkaline and neutral solutions.

In designing the flowsheet shown in Figure 1, we have combined the selectivity and the simplicity of the water elution of the Tc/I selective resin with compatible, known technologies to yield a process that delivers a Tc/I encapsulated waste in a form suitable for storage. The preparation of a stable waste for the immobilization of technetium and iodine is based on three separate but closely integrated processes. The first step involves the separation of technetium as pertechnetate and iodine as iodide or iodate from the alkaline supernatant solution contained in high-level waste storage tanks using the new Tc/I selective resin. As mentioned, the unique features of the new resin are its very high retention and selectivity for pertechnetate salts as well as iodide/iodate salts from highly alkaline salt solutions of the type and composition found in HLW storage tanks and that the technetium and iodine can be effectively and completely eluted from the resin with water.

The water elutability property of the new resin is particularly important because it enables one to quantitatively (>99.9%) sorb the pertechnetate and iodide/iodate species onto a small quantity of silica strong-based ion exchange resin. In this second step, a silica strong-based resin in the chloride form is used as a slurry to sorb the Tc/I from the water strip solution. Laboratory studies indicate that a presence of chloride in the strip solution has no effect on the Tc/I selective resin's performance enabling a recycle of the strip solution.

Because both Eichrom's Tc/I selective resin and the silica strong-based resin concentrate the technetium and iodine from the alkaline supernate and water strip solution, respectively, both radioisotopes should be concentrated by a factor of at least one thousand, thus minimizing the volume of the final immobilized waste form.

The third step in the immobilization process is the encapsulation of the silica strong-based anion material containing the technetium and iodine in a titania or zirconia

Figure 1. Flowsheet for the separation, concentration and immobilization of Tc/I from alkaline supernate wastes.

shell. The encapsulation process is an adaptation of the work performed at ORNL by J.L. Collins in the production of composite microspheres by internal gelation. The encapsulated composite microspheres are finally heated to collapse the outer shell of titania or zirconia onto the encapsulated silica strong-based resin containing technetium and iodine. The heating also reduces the porosity of the outer shell making any leaching of technetium or iodine from the inner encapsulated particles unlikely.

Figure 1 assumes that cesium and strontium treatment is done initially by one of the technologies outlined in the prior section. The Savannah River resorcinol-formaldehyde resin, the Sandia CST's, the titanates, and several other inorganic absorbers are all being tested and show promise as cesium and strontium removal technologies. The removal of cesium and strontium in an initial alkaline supernate treatment module has the obvious economic advantage of minimizing shielding requirements in subsequent technetium and iodine waste treatment systems. The Tc/I selective resin will also work in a stand-alone flowsheet. The presence of cesium and strontium have no effect on the separation of technetium and iodine by the resin.

The Technology Supporting the Flowsheet

Loading and Elution of Tc/I Selective Resin.

The new Tc/I selective resin development was based upon the observed chemistry of polyethylene glycol (PEG) based aqueous biphasic systems (ABS). ABS consist of two immiscible phases formed when certain water soluble polymers (i.e., PEG's) are combined with certain inorganic salts in specific concentrations. In ABS, the major component of each of the two phases is water. It has been observed by R. D. Rogers and co-workers at Northern Illinois University (*Aqueous Biphasic Separations: Biomolecules to Metal Ions* edited by R. D. Rogers and M. A. Eiteman, Plenum Press, New York, 1995, "Metal Ion Separations in Polyethylene Glycol-Based Aqueous Biphasic Systems") that a PEG-based ABS would have great potential as a viable metal separations technique. In particular, technetium, as pertechnetate, is observed to partition to the PEG-rich phase. In evaluating this process as a potential separation technique, it is important to note that PEG-ABS are virtually nontoxic and nonflammable. PEG is classified as a GRAS (generally recognized as safe) compound by the Food & Drug Administration.

There are, however, two major drawbacks to aqueous biphasic separations operating in a liquid-liquid mode. These are the loss of phase forming components, PEG and salt, due to their high solubility in water and the difficulty in stripping partitioned solutes. These two drawbacks are eliminated when the PEG is attached to a polymeric support. Rogers and co-workers have found that PEG's of molecular weight between 2,000 and 5,000 could be attached to polystyrene particles and that the resultant materials would exhibit separation behavior of a magnitude similar to that observed for the liquid-liquid system. Figure 2 shows weight distribution ratios (D) for technetium versus molality of several salts. The Tc/I selective resin designated as ABEC-5000, aqueous biphasic extraction chromatographic material with PEG of molecular weight 5000, was

made by the nucleophilic replacement of chloride on a chloromethylated polystyrene bead by a PEG-anion.

Figure 2. D_w for TcO_4^- vs. molality of salt with Tc/I selective resin (ABEC-5000).

Biphase-formation is believed to be a function of the water-structure-making or lyotropic property of an anion. An anion with a Gibbs free energy of hydration (ΔG_{hyd}) of less than -300 kJ/mole will cause biphasic behavior and other anions, such as pertechnetate and iodide or iodate, will be “salted-out” to the PEG-rich phase.

A selected list of biphase-forming anions is shown below:

hydroxide	fluoride	carbonate
sulfate	phosphate	silicate
citrate	molybdate	thiosulfate
formate		

An examination of Figure 2 and the list of biphase-forming anions given above shows that the Tc/I selective resin is ideally suited for removing technetium and iodine from HLW tank supernate. Figure 3 shows the D_w 's for TcO_4^- from three simulated Hanford tank wastes: NCAW, SST, and SY-101. The designations ABEC-5000, ABEC-2000, etc. refer to the molecular weight of the PEG attached to the polystyrene support. Comparable behavior is observed for both resins based on both the 2,000 and 5,000 molecular weight PEG's.

Figure 3. D_w for TcO_4^- from three Hanford HLW tank simulants vs. MW of PEG on Tc/I selective resin (e.g., ABEC-5000 $\equiv$ PEG-5000 on polystyrene).

The results, illustrated in Figure 3, with Hanford tank simulants have been confirmed in a preliminary, unpublished report by J. L. Collins at ORNL with actual waste samples from the ORNL Melton Valley Storage Tank W-29 supernate. In Collins' work, the supernate is first treated with resorcinol-formaldehyde resin (Savannah River technology) and potassium cobalt hexacyanoferrate (KCoCF) to remove all cesium and strontium activity. Ammonium pertechnetate is added to the treated samples to achieve a technetium concentration of 4.0 mg/L. The adjusted technetium concentration in these studies corresponds to an average technetium concentration in several Hanford tanks. In these small-scale batch studies, technetium distribution ratios ranged from 240 mL/g at 0.25 hours to 930 mL/g at 72 hours. These values were slightly higher than the values obtained for the anion exchange resins included in Collins' studies. Elution studies at ORNL have not yet been completed, but preliminary results confirm our observations that the Tc/I selective resin strips efficiently and completely with water.

The Collins' ORNL results with the Tc/I selective resin are particularly interesting when one considers the hydroxide concentration of the Melton Valley tanks, 0.3 M, versus the hydroxide concentration in the Hanford tanks, 2-4 M. Figure 2 shows increasing distribution ratios with increasing hydroxide concentration and it can be expected that the performance of the Tc/I resin will only improve with actual Hanford waste.

Additional studies with the Tc/I selective resin have been performed at ORNL by A. Meeks and reported on at the Thirty-Sixth ORNL/DOE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, TN, October 1995, "Isolation and Determination of I-129 in Waste Tank Samples Using Extraction Chromatography". In this report, there is a discussion of the development of an analytical method for iodide and iodate. Meeks examined both synthetic salt solutions and actual waste in her studies. A sample designated as Melton Valley W-3 supernate, comprised of interstitial liquid from a W-3 waste tank sludge sample and the liquid on top of the sludge in tank W-3, that was spiked with I-131 was used as a sample matrix. A 1-mL column of Eichrom's Tc/I selective resin was loaded with 1 mL of spiked supernate, rinsed with 10 mL of 3.5 M K_2CO_3 , and eluted with deionized (DI) water to generate the chart shown in Figure 4. Recovery of the spike in the elution stream was >98% for each sample tested. In a separate experiment with synthetic solutions, 96% of an I-129 spike was recovered in 5 free column volumes (fcv) during elution with water.

Figure 4. I-131 rinse and elution curve. Melton Valley W-3 tank supernate sample on Tc/I selective resin.

In an experiment similar to the I-131 study referenced above, a separation of Tc-99m from its parent ion Mo-99 is shown in Figure 5. During the resin loading phase of the experiment, the activity due to Mo-99, which does not load on the resin and reports to the eluent, is plotted on the graph. Mo-99 activity in the column eluent drops rapidly

Figure 5. Elution curve for Mo-99, loading Tc-99m. Rinse and elution of Tc-99m from Tc/I selective resin, ABEC-5000.

Figure 6. Effect of increasing perrhenate concentration on technetium distribution ratio from 2 M $(NH_4)_2SO_4$ solution on Tc/I selective resin.

during the carbonate rinse with no observation of Tc-99m breakthrough. The data in Figure 5 again confirm the efficient and complete water elution of activity from the Tc/I selective resin.

Capacity and Concentration Factor of the Tc/I Selective Resin.

An estimate of the Tc/I selective resin's capacity for iodide of 0.05 mmol I/g dry resin was obtained from the A. Meeks' ORNL analytical work referenced above. Loading studies for technetium were performed as part of this research effort. Using perrhenate (ReO_4^-) as a cold surrogate for pertechnetate, the effect of increasing perrhenate concentration on distribution ratio for technetium has been determined. The results of this study are shown in Figure 6. Both Figure 6 and the results of the ORNL study indicate that the Tc/I selective resin meets the capacity requirements expected of a commercial separation resin.

The estimated capacity and the efficient and complete water elution of the Tc/I selective resin have been referred to in the previous discussion and charts. These two properties provide a basis for estimating the concentration factor that can be achieved in the first step of the flowsheet shown in Figure 1. We expect an overall concentration factor for Tc/I activity of between 50 and 100 during the resin load and water elution steps.

Sorbing Tc/I onto a Silica Strong-Based Resin.

The pertechnetate and iodide/iodate species will sorb strongly onto a small quantity of silica strong-based ion exchange resin. The chemistry of the second step of the flowsheet is the well understood exchange of a more strongly bound anion, pertechnetate or iodide/iodate, for another weaker bound anion, chloride (Cl^-). Exchange of technetium and iodide/iodate for chloride on a strong base anion resin exhibits distribution ratios that increase linearly with increasing pH. Distribution ratios $>5 \times 10^4$ are anticipated, and quantitative pick-up of the technetium and iodine on the silica strong-based resin will be achieved. Use of Eichrom's Tc/I selective resin in the prior separation and concentration step ensures that matrix constituents, e.g., nitrates and nitrites, which otherwise compete for loading on anion resins, will not interfere with technetium and iodine sorption. The flowsheet shown in Figure 1 lists a silica-based strong anion resin named NUCLEOSIL. This particular modified silica gel, particle size $45 \mu\text{m}$, is available commercially and produced in Germany by Macherey-Nagel. The general form of the resin is $\text{Si-O-}(\text{CH}_2\text{N}^+(\text{CH}_3)_3\text{Cl}^-)$. A silica gel based resin was chosen for the flowsheet to address the obvious radiolytic stability concerns.

The capacity of the NUCLEOSIL resin is listed as ca. 1 mmol/g. The prior separation step of loading Tc/I selectively on the resin and eluting with water ensures an additional concentration of activity onto the silica strong-based resin. The combined concentration of Tc/I activity on the first two steps of the flowsheet should be increased by at least a factor of 1,000.

A determination of the concentration factor achievable at each of the three steps in the proposed separation, concentration and immobilization flowsheet described in Figure 1 is a task of this project. All of the available data indicate that a significant reduction in waste volume will be achievable, and this will be confirmed in the bench-scale and pilot testing programs as a requirement for an engineering scale-up of the flowsheet.

Encapsulation of the Silica Strong-Based Anion Material Containing Tc/I in a Titania or Zirconia Shell

In the report No. ORNL/TM-12315 entitled "Development and Testing of Ion Exchangers for Treatment of Liquid Wastes at Oak Ridge National Laboratory" J.L. Collins describes a procedure of encapsulation of inorganic particles that will be included as the final step of Tc/I waste immobilization in the flowsheet described in Figure 1.

In Collins' work, a broth is prepared by addition of silica particles with sorbed technetium and iodine together with hexamethylenetetraamine and either a TiCl_4 or ZrCl_4 solution. The temperature of the broth is maintained at 0° C. The fine silica particles, NUCLEOSIL, are available as either 5 or 10 μm particles, and precipitated titania or zirconia gels are kept homogeneously suspended using an agitator. Air pressure is used to transfer the suspension out of the container through the end of a flat-tipped 20 gauge needle. Droplets of the suspension are introduced into and sheared by a perpendicular flow of hot silicone oil flowing past the needle tip. To control drop formation, the needle is positioned near the center of the tube. The size of the microsphere is controlled by adjusting the flow through the tube and the air pressure provided as the driving force for expulsion of the suspension broth. Droplets of the aqueous broth begin to gel and entrap the suspended silica particles within seconds of contacting the hot silicone oil. After an aging process, the formed microspheres are filtered from the silicone oil. The silicone oil is recycled. The filtered microspheres are washed to remove traces of silicone oil and urea, and are then dried at 200° C. The final drying step collapses the outer shell of titania or zirconia onto the silica strong-based resin containing the sorbed technetium and iodine. The reduced porosity of the outer shell makes any leaching of the inner encapsulated particles unlikely.

This approach for preparing a final waste form is not limited to titania or zirconia. Other inorganic coatings, such as zirconium phosphate, are also feasible with the internal gelation technique and may prove to be suitable as encapsulation materials. The basic concept of protecting the primary location of technetium and iodine sorbed on silica particles is the same.

An important part of this research effort will be the evaluation of the stability of the encapsulated silica as a waste form for technetium and iodine to leaching by simulated groundwater and brine solution and the effect of prolonged radiolysis on the particles. Because the final waste form should contain fairly high levels of technetium and iodine

loading, the detection of a breakdown in the integrity of the encapsulated particles should be relatively simple.

Concentration Factor and Final Waste Volume Estimation

Earlier it was stated that a concentration factor of at least 1000 is expected from the loading and elution of Tc/I on the resin and from the sorbing of technetium and iodine from the water strip solution onto the silica strong-based resin. The encapsulation step allows a final dilution control of the final waste form. The internal gelation work by J.L. Collins referred to above cites examples of substrate encapsulation such that the weight percent of substrate is between 6 and 32% in hydrous titanium oxide microspheres.

As an example, consider the treatment of 1,000 liters of alkaline supernate containing 5×10^5 M technetium and 5×10^5 M iodine (I and IO_3^-). This solution is loaded onto a Tc/I selective resin column, 20 liters in bed volume. After loading, the column is rinsed with 2 bed volumes of $NaCO_3$ and stripped with 50 liters (5 fcv) of water. (The A. Meeks work referenced on page 7 indicated a 96% recovery of activity in 5 fcv.) The resulting concentration of technetium and iodine in the strip solution will be 1.0×10^3 M, or a 20-fold concentration increase.

The stated capacity of NUCLEOSIL resin, the silica strong-based resin, is 1 mmol/g. If the NUCLEOSIL resin is loaded to stated capacity, 50 grams of resin are required to sorb the technetium and iodine. As a conservative estimate, we assume only a 50% loading of the NUCLEOSIL and specify 100 grams of resin to load the technetium and iodine. Assuming a density similar to silica gel of 2.0 g/cm^3 , the volume of resin with sorbed technetium and iodine will be approximately 50 cm^3 .

Using these assumptions, the original 1,000 liters of alkaline supernate can be reduced to 50 cm^3 of technetium and iodine loaded silica resin, for a reduction factor of 20,000. If one then assumes that an encapsulation of the silica strong-based resin with sorbed technetium and iodine at a level of 10% in titania or zirconia microspheres will provide a stable final waste form, one can estimate that a 2,000-fold reduction from the initial waste volume can be achieved.

II. Objectives

The objective of this work is to synthesize an improved version of the Tc/I selective resin that resolves the performance issues of the original resin known as ABEC-5000. The overall objective is broken into specific items as described below:

The first task is designed to optimize the chemical reactions used to produce the Tc/I selective resin, perform a preliminary cost evaluation, and perform the initial scale-up synthesis of the resin. The specific subtasks are:

- (1) study alternative substrates,
- (2) optimize the reaction time of the PEG addition step,
- (3) study alternative molecular weight PEG materials,
- (4) study alternatives to using sodium hydride as catalyst in the PEG addition step,
- (5) perform scale-up to the 110-liter reactor, and
- (6) perform cost evaluation.

The second task is designed to test the newly prepared resin and demonstrate the second and third steps of the flowsheet. These tests involve:

- (1) determining the batch uptake properties and column load/strip behavior of technetium/iodine on the resin,
- (2) load technetium/iodine from simulated strip solutions onto commercial silica-based anion exchange resins,
- (3) encapsulate the technetium/iodine loaded silica-based anion exchange resin by internal gelation, and
- (4) perform stability studies on the encapsulated waste form.

III. Experimental - Laboratory Scale Synthesis

The general synthetic scheme for ABEC resins consisted of two distinct parts: (1) the suspension copolymerization of styrene, vinylbenzyl chloride (VBC), and divinylbenzene (DVB) monomers using benzoyl peroxide (BPO) as the initiator to give the substrate (the support to which the functional groups are attached), and (2) the attachment of polyethylene glycol monomethyl ether (PEG) to this copolymer substrate via nucleophilic substitution to yield ABEC resin (Figure 7). The syntheses are discussed in detail in the following sections.

Copolymer Substrate Synthesis: The substrates to which the PEG units were attached during Step 2 of the ABEC resin synthesis were prepared by suspension copolymerization. In this technique there is an aqueous phase (continuous phase), consisting of various stabilizers dispersed in water, and an organic phase (discontinuous phase), consisting of the monomers and a monomer-soluble initiator. During copolymerization the organic phase is suspended in the aqueous phase as droplets of monomer/initiator solution. The suspension is maintained by mechanical agitation and by the presence of the stabilizers, which coat the surface of the monomer droplets and help prevent their agglomeration.

VBC: VinylbenzylChloride
 DVB: Divinyl Benzene
 BPO: Benzoyl Peroxide
 PEG: Polyethylene Glycol

Figure 7. Synthetic route to make ABEC resins.

One of the objectives of this research was to investigate the influence certain copolymer substrate properties had on the physical properties and uptake performance of ABEC resins. These substrate properties included degree of cross-linking, copolymer bead porosity (i.e., gel-type, or microporous, beads vs. xero gel-type beads, a form of macroporous bead), and number of potential sites for attachment of PEG, as determined by the percentage of VBC units in the copolymer substrate. A second objective of this research effort involved the optimization of certain synthetic variables, or parameters, during the functionalization of the substrate with PEG (Step 2 in Figure 7). The parameters investigated included type of solvent; optimum ratio of solvent, PEG, and NaH to substrate; solvent quantity; reaction temperature; and reaction time.

Two slightly different methods of copolymerization were used for the laboratory scale synthesis of all substrates. The primary differences between the two methods were in the reactor size (500-mL or 2-L), total quantity of organic phase (100 g or 716 g), and the aqueous phase composition. During the course of this project, the decision was made to change the composition of the aqueous phase used initially to one which was already in use for larger scale copolymerizations by the potential toll processor to scale up the synthesis in larger scale 1000-gallon reactors. By using an aqueous phase already proven in large scale reactions for the copolymerization of styrene and DVB, it was hoped that the transition from laboratory scale synthesis to production scale synthesis would be made more easily. It should be noted that the change in aqueous phase composition did not have any significant impact on the chemical composition of the copolymer beads nor on the reaction character of the copolymer beads during the subsequent functionalization step.

The details of the two different copolymerization methods are discussed below. As it turns out, all of the copolymers used in the substrate studies were prepared using the initial aqueous phase (Method A), while all of the copolymers used during the functionalization parameter optimization studies were prepared using the aqueous phase formula supplied by the potential toll processor (Method B).

Copolymerization Method A The copolymerizations were carried out in a 500-mL round bottom flask equipped with a teflon stir blade, condenser and thermometer. The organic phase consisted of VBC, styrene, DVB, diluent (for xero gel-type copolymer only), and BPO as initiator. The total quantity of organic phase was 100 grams, and the percentage of each component is described in the results and discussion section. The aqueous phase was prepared by dissolving 0.5 g of polyvinyl alcohol (PVA) in 100 mL of water by gentle stirring and heating until the PVA was completely dissolved. Then, 20 g $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and 1.0 g calcium phosphate, tribasic ($\text{Ca}(\text{OH})_2(\text{PO}_4)_3$) were added to the mixture with stirring followed by heating the aqueous phase to 30. The stir blade was positioned at the aqueous/organic interface, and the stir speed was adjusted to a value designed to give beads of the desired size. The organic phase was then slowly poured into the round bottom flask, and the formation of a suspension was verified by observing the stirring mixture in a flashlight beam. The appearance of sparkling particles in the flashlight beam indicated that organic droplets had been suspended in the aqueous layer. The

mixture was slowly heated from 50°C to 80°C (5°C/30 minutes) to initiate the polymerization within the suspended droplets, and the temperature was maintained at 80°C for 15 hours. After the polymerization was completed and cooled to room temperature, the product was washed once with 10% solution of isopropyl alcohol (IPA) in water and twice with deionized (DI) water. If the organic phase contained diluent (as when xero gel-type copolymers were prepared), the diluent was removed by azeotropic distillation with methanol before the washing procedures. The resin beads of the desired size fraction were isolated by wet sieving the beads through U.S. Standard screens. After evaporation of water in a hood overnight, the beads were dried in a 60°C oven for at least 2 hours before being used for ABEC synthesis. All of the copolymers used for the substrate studies were prepared by this method.

Copolymerization Method B The copolymer beads were synthesized in a 2-liter, three-neck, cylinder-type flask equipped with a metal, double-paddle stir shaft, condenser, and thermometer. The organic phase consisted of 71.60 g (10%) VBC, 616.20 g styrene, 26.03 g (2%) DVB (technical grade containing 55% DVB), and 2.15 g (0.3%) BPO. The total quantity of organic phase was 716 g. When a higher level of VBC (such as 15% and 20%) was required in the formula, some styrene was replaced by an equivalent mass of VBC to maintain a total of 716 g of organic phase. The formula of the aqueous phase was provided by the potential toll processor to scale up the synthesis in larger scale 1000-gallon reactors. The aqueous phase was prepared by dissolving 2.25 g gelatin in 735 mL DI water by heating the solution to 30°C for 30 minutes followed by adding 7.03 g NaCl, 4.71 g Na₂HPO₄, 0.98 g Na₃PO₄, 7.03 g SA/RE (a polyacrylate solution provided by the potential toll processor), and 0.55 mL of 25% NaOH(aq). The pH of the final aqueous phase was above 10. Both the aqueous and organic phases were gently purged with nitrogen for about 3 minutes to remove dissolved oxygen which, because of the small amount of initiator used, could terminate the free radical copolymerization. The organic phase was added to the flask, and the stirring shaft blade positioned at the interface of the two layers. The stir speed was adjusted to a value designed to give beads of the desired size. The formation of a suspension was verified by observing the stirring mixture in a flashlight beam. The appearance of sparkling particles in the flashlight beam indicated that organic droplets had been suspended in the aqueous layer. The reaction mixture was heated from room temperature to 67°C over a 2 hour time ramp and held at 67°C for 6 hours. The temperature was then raised to 74°C over a one hour time ramp and held at 74°C for another 6 hours. To ensure complete polymerization, the polymer was heated at 93°C for 3 hours. After cooling to room temperature, the copolymer was washed once with a dilute solution of HCl (pH 3 to 4), once with 10% IPA(aq), and twice with DI water. The desired bead size fraction was isolated by wet sieving the beads through U.S. Standard screens. After evaporation of water in a hood overnight, the beads were dried in a 60°C oven for at least 2 hours before being used for ABEC synthesis. All of the copolymers used for parameter optimization studies were prepared by this method.

ABEC Synthesis: The ABEC resin was prepared in a three-neck, 500-mL round bottom flask equipped with a mechanical stir shaft, condenser (capped with a drying tube through the end of reaction), and thermometer. All of the glassware was oven dried to remove all

traces of moisture. The copolymer was preswelled in the solvent with stirring for 15 minutes at room temperature. The PEG was then added to the system, followed by a preheat treatment at 50°C for 1 hour to aid dissolution of PEG and to allow some penetration of PEG into the copolymer beads. After cooling to 30°C, the sodium hydride (NaH, 60% in mineral spirit) was slowly added over a period of approximately 1 hour. The mixture was heated at 70°C for 17 hours, followed by quenching any unreacted NaH with IPA at room temperature. The functionalized ABEC resin was washed twice with IPA and DI water and finally conditioned with 6 bed volumes (BV) of DI water in a column.

Synthesis of ABEC Resins Using PEG-2000 vs. Peg-5000 ABEC resins containing 2% crosslinking agent were prepared using both PEG-2000 and PEG-5000 for parallel comparison of synthetic yield and technetium uptake performance.

Synthetic Parameter Optimization ABEC resins prepared by altering various synthetic parameters were evaluated for synthetic yield and uptake performance. In this way the most economical synthetic route for producing ABEC resin having desirable performance characteristics was determined. The parameters investigated included type of solvent; optimum ratio of solvent, PEG, and NaH to copolymer; solvent quantity; reaction temperature; reaction time; and percentage of VBC in the copolymer.

Replacement of Sodium Hydride with Sodium Methoxide Due to the evolution of hydrogen and any potential hazards in the use of sodium hydride, several attempts were made to replace sodium hydride with sodium methoxide as the base in the PEG addition step. To avoid competition between PEG alkoxide and methoxide during this step, a solution of PEG in either toluene or diglyme was pretreated with a 1:1 molar ratio of sodium methoxide. To drive the reaction to completion, the side product methanol was removed by rotary evaporation as the reaction progressed. When no more methanol could be removed, the contents of the flask were added to a reaction vessel containing copolymer suspended in diglyme and the reaction completed as usual.

Evaluation of Resin Properties and Performance Four criteria that are key to the successful implementation of ABEC resins for the removal of technetium and iodine from the DOE's alkaline radioactive wastes are: (1) uptake performance (2) capacity, (3) expansion of resin bed during stripping and (4) resin density. The first two criteria relate to the separation performance of ABEC resins and the last two are important engineering considerations.

The uptake performance of ABEC resins was evaluated by determining technetium D_w profiles from NaOH solution. Volume distribution ratios (D) were also calculated because these may more accurately predict column performance than D_w values. Experiments to measure the capacity of ABEC resins for technetium are more complicated due to the quantity of radioactive material being handled and were performed only for selected resins.

In order to evaluate the performance of ABEC resins more quickly during the optimization of certain synthetic parameters, rhenium was used as a cold surrogate for technetium to help identify desirable resin formulations. This substitution of rhenium for technetium was justified based on the similarities in the aqueous chemistry of pertechnetate and perrhenate (*The Chemistry of Technetium and Rhenium* R.D. Peacock, Elsevier Publishing Co., New York, 1966 *The Chemistry of Rhenium and Technetium* R. Colton, Interscience Publishers, New York, 1965) and the fact that initial uptake studies of rhenium from both water and 6 M NaOH suggested that it would serve as a reliable substitute for macroquantities of technetium. Figure 8 shows the results of radiotracer studies with ^{188}Re in which similar D_w values were obtained for technetium and rhenium with ABEC-5000 (PEG-5000 attached to 1% crosslinked chloromethylated polystyrene of 100 to 200 mesh particle size) from NaOH solution. Technetium D_w 's in hydroxide solutions were generally higher than those observed for rhenium. For some other salt solutions, however, the measured D_w 's are slightly higher for rhenium than for technetium.

Figure 8. Comparison of $^{188}\text{ReO}_4^-$ and $^{99}\text{TcO}_4^-$ uptake with ABEC-5000 resin from NaOH solution.

An additional observation to support substitution of rhenium for technetium in screening studies is the fact that technetium uptake by ABEC-5000 from 2 M and 4 M NaOH solution decreases as the concentration of NH_4ReO_4 increases (Figure 9). This graph indicates that rhenium competes with technetium for resin sites at metal concentrations approaching the loading capacity of the resin.

Figure 9. TcO_4^- uptake with ABEC-5000 resin from 2 M and 4 M NaOH solution vs. NH_4ReO_4 concentration.

For the evaluation of resins during parameter optimization studies, two different rhenium batch uptake studies were conducted for each resin. One involved an excess of resin (in terms of capacity) relative to rhenium and the other an excess of rhenium relative to resin. This approach allowed both the affinity and the capacity of the resin for rhenium to be evaluated in as little as one day so that a number of parameters could be optimized in a short period of time. The most promising resins were then evaluated for technetium uptake and capacity.

The expansion of the resin bed during water stripping was identified early on as a potentially important engineering issue. ABEC resins consist of hydrophilic polyethylene glycols (PEGs) grafted to polystyrene-divinylbenzene crosslinked supports and are extensively hydrated. During loading from concentrated salt solution, the ABEC resin is dehydrated resulting in a decrease in the size of the resin beads and a concurrent decrease in bed volume. Conversely, on crossover to water strip the resin hydrates and the beads swell. Continuous expansion and contraction of the bed could result in diminished chromatographic performance due to bed fracture and channeling. It is also an engineering concern because excessive pressure during expansion could damage the chromatographic apparatus. Therefore, it was desirable to design and synthesize ABEC resins that did not show significant (i.e., greater than 10%) changes in bed density during the load/strip cycle.

Resin density is important because previous ABEC resins floated when contacted with dense solutions like the Hanford and Melton Valley Storage Tank wastes. These resin beds may float in the column during loading, and may, therefore, also present an engineering concern. While it is practically and economically feasible to use an upflow load and downflow strip design in this situation, it is more desirable to increase resin density to eliminate the potential of floating resin.

Physical Properties Analysis

Percent Solids Determination (Moisture Content): The resin was air dried on a Büchner funnel with a coarse filter paper at 660 mm Hg for 5 minutes. Resin dried in this manner is referred to as air dried resin. An air dried sample (0.05 g to 0.1 g) weighed by analytical balance was heated in a 110°C oven until a constant weight was obtained (up to 5 days) and then allowed to cool in a desiccator prior to determination of the dry mass. The relative uncertainty for duplicate percent solids analyses by this technique was typically less than $\pm 5\%$.

Dry weight conversion factors (dwcf = percent solids/100) for some resins were also determined by thermogravimetric analysis (TGA). In this analysis a small amount of resin was heated under a nitrogen stream from ambient temperature to 500°C over a period of approximately 30 minutes while recording any changes in mass over time. The values obtained by TGA analysis were from 1.3 to 2.2 times greater than those obtained by oven analysis (Figure 10). This may indicate that during oven drying some oxidation of resin is occurring such that the weight loss is not entirely due to loss of water. This would be unlikely to occur during the TGA analysis because of the nitrogen atmosphere. At this time it is not completely clear which technique yields more accurate values for dwcf or percent solids. For the time being percent solids have been reported using the data obtained from oven analysis and all weight distribution ratios have been calculated using these values.

Bed Density Determination: The bed density (g of dry resin per mL of resin bed volume) was determined for each resin in both DI water and 4 M NaOH. This was

accomplished by placing a known mass of resin in a column and marking the bed height when eluted with water and then when eluted with 4 M NaOH. The resin was then removed from the column and the volume of water needed to fill the column to each mark determined by mass difference. The bed density (ρ_{bed}) was then calculated as:

Figure 10. Comparison of dwcf's from oven gravimetric analysis and TGA analysis.

$$\rho_{\text{bed}} = \frac{\text{g of air dried resin} \times \text{dwcf}}{\text{mL bed in H}_2\text{O or NaOH}},$$

where dwcf is the dry weight conversion factor (% solids/100).

Evaluation of Percent Resin Swelling During Stripping The extent of swelling that the resin undergoes upon crossover from a load solution of 4 M NaOH to a water

strip was calculated using the bed density data. Owing to the fixed geometric parameters of a chromatographic column, only the bed height changes when the resin swells or contracts. It is then possible to calculate the change in bed height, reported as percent swelling, using the following equation:

$$\% \text{ Swelling} = \left(\frac{\rho_{\text{bed in 4 M NaOH}} - \rho_{\text{bed in H}_2\text{O}}}{\rho_{\text{bed in 4 M NaOH}}} \right) \cdot 100.$$

All of the percent swelling values reported in this work were calculated according to the above equation.

It was also observed following elution of the resin with NaOH that the resin did not swell to its original volume upon elution with water. In this case percent swelling values were calculated as

$$\% \text{ Swelling} = \left(\frac{|V_{\text{NaOH}} - V_{\text{H}_2\text{O}}|}{V_{\text{NaOH}}} \right) \cdot 100,$$

where V_{NaOH} is the resin volume after elution with 5 BV of 4 M NaOH and $V_{\text{H}_2\text{O}}$ is the rehydrated resin volume after elution with 5 BV of DI water. Percent swelling values calculated in this way were usually about half the value of those calculated from the bed density data. This indicates that the percent swelling values calculated from the bed density data are a conservative estimate of the degree of expansion the resins will undergo upon crossover from load solution to strip solution.

Resin Uptake Performance

D_w Measurement of Pertechneate Uptake Pertechneate D_w values (mL/g) for ABEC resins were measured as a function of NaOH concentration by contacting 30 to 50 mg of air dried resin with 1.0 mL of NaOH solution containing $\text{NH}_4^{99}\text{TcO}_4$. A portion of the solution was counted by liquid scintillation before and after contact. The dry weight distribution ratios were calculated as

$$D_w = \left(\frac{A_0 - A_f}{A_f} \right) \left(\frac{V \text{ (mL)}}{W \text{ (g)} \times \text{dwcf}} \right),$$

where A_0 is the aqueous phase activity before equilibration, A_f is the aqueous phase activity after equilibration, W is the weight of air dried resin in grams, and V is the aqueous phase volume in mL. Based on agreement between values obtained for duplicate samples, a conservative estimate of the relative uncertainty associated with this measurement is $\pm 15\%$.

The resins prepared in this project had dwcf values ranging from less than 0.15 to greater than 0.85. These values can have a significant impact on the value of D_w (see equation above and Figure 11). Therefore, it may be misleading to compare D_w values for resins having very different levels of percent solids. For column applications it may be more meaningful to compare volume distribution ratios (D_v) in order to predict resin performance per unit volume rather than per g of dry resin. D_w values (mL/g) from 4 M NaOH solution can be converted to D_v values (mL/mL) from 4 M NaOH solution according to the following equation:

$$D_v = D_w \times \rho_{\text{bed in 4 M NaOH}}.$$

Figure 11. $\text{TcO}_4^- D_w$ in 4 M NaOH solution vs. dwcf by oven gravimetric analysis.

The fact that bed densities are usually proportional to dwcf values results in much less difference between D_v values than between D_w values. This is illustrated by the graph in

Figure 12 which depicts a much narrower range of D_V values ($3 < D_V < 200$) than the range of D_W values in Figure 11 ($8 < D_W < 1100$).

Technetium Capacity and Column Loading/Stripping Behavior ABEC resin capacity for pertechnetate was determined for the ABEC resin produced in the 110-liter reactor. The capacity, in units of $\mu\text{mol/mL}$ bed in water (can be converted to $\mu\text{mol/g}$ dry resin by dividing by the bed density in water), was calculated from the column breakthrough curve where rhenium served as a bulk nonradioactive surrogate for technetium in a spiked solution. A load solution containing $^{95m}\text{TcO}_4^-$ and 0.01 M ReO_4^- in 4 M NaOH was passed through a column containing approximately 3 mL of ABEC resin, and 0.5 mL fractions of eluant were collected in preweighed gamma counting tubes. The column was rinsed with 3 or 4 bed volumes of 4 M NaOH solution and then technetium and rhenium were stripped from the column by elution with DI water. The collection tubes were weighed again to determine the exact amount of each fraction. A plot of loading/stripping behavior was constructed from the data obtained by gamma counting individual fractions of the load and strip solutions. The capacity of the resin at 10% breakthrough was then calculated using the volume and composition of the load solution. The loading/elution curve and capacity value are shown in Figure 23, p. 49.

Figure 12. $\text{TcO}_4^- D_V$ in 4 M NaOH solution vs. dwcf by oven gravimetric analysis.

Rhenium Uptake Performance The sorption of rhenium by ABEC resins during optimization studies was monitored using flame atomic absorption (FAA). Due to flame interference from the high levels of sodium in 4 M NaOH load solutions, uptake studies for rhenium were conducted in 2 M (NH₄)₂SO₄ solution. Two different batch uptake experiments were conducted for each resin. The first consisted of contacting 0.40 g of air dried resin with 10.00 mL of solution containing 250 mg/L rhenium (1.34×10^{-3} M ReO₄⁻). The contact time was one hour (previous kinetic studies indicated no difference in uptake for contact times ranging from 30 minutes to 8 hours). In this experiment the amount of rhenium was small relative to the amount that could actually be loaded onto the resin. The uptake of rhenium, reported in μ mol of rhenium per mL of resin in water, was used to evaluate the resins' relative affinity for rhenium and, therefore, for technetium.

The second experiment involved contacting 0.10 g of air dried resin with 5.00 mL of solution containing 4 g/L rhenium (2.15×10^{-2} M ReO₄⁻). Again, a contact time of 1 hour was found to be sufficient to achieve equilibrium. The purpose of this experiment was to load as much rhenium as possible onto the resins so that the rhenium uptake, reported in μ mol of rhenium per mL of resin in water, was an estimate of the rhenium saturation capacity. Based on repeated analyses of the same resin the relative uncertainty associated with both the relative affinity and saturation capacity measurements was conservatively estimated to be $\pm 15\%$.

Column Loading/Elution Behavior of Rhenium Column studies were performed with two resins in which NaReO₄ was loaded onto ABEC resin from 4 M (NH₄)₂SO₄ solution. The resin was rinsed with 4 M (NH₄)₂SO₄ and then stripped with DI water. All three solutions—load, rinse, and strip—were collected in appropriate sized fractions in preweighed plastic centrifuge tubes. The tubes were weighed a second time and the net weights divided by the appropriate density term to determine the exact volume of each fraction. The concentration of rhenium in each fraction was determined by FAA. From this data the amount of rhenium loaded on the resin and stripped from the resin was determined. Plots of column loading/elution behavior were also constructed from this data.

Technetium Uptake from Simulant Waste Solutions During the course of this project British Nuclear Fuels (BNFL) in Great Britain expressed a keen interest in testing ABEC resins for removal of technetium from waste streams at both their Sellafield and Capenhurst locations. This was an extremely important development in that they may be willing to provide a demonstration site for technetium removal from real waste streams with ABEC resin at their Capenhurst facility.

In an effort to assist them in applying this technology to their applications for removal of technetium, the uptake of technetium from two different simulant waste solutions was investigated. One simulant waste solution, referred to as BNFL Sellafield waste simulant, contained 200 g/L NaNO₃ (2.4 M) and 3 g/L Na₂CO₃ (0.03 M). A second

waste simulant, referred to as BNFL Capenhurst waste simulant, contained 20 g/L $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (0.072 M), 62 g/L $\text{Al}(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ (0.093 M), and 284 g/L Na_2SO_4 (2.0 M). The total sulfate concentration was approximately 2.4 M. The column loading and elution behavior of technetium from the BNFL Capenhurst waste simulant was also investigated. The data are presented in the Results and Discussion Section (pp. 39-43).

IV. Results and Discussion of Laboratory Scale Synthesis

Study of Substrates The study of substrates was initially focused on ABEC resins prepared using a set of copolymers classified as xero gel resins. Xero gel resins are a form of macroporous resin produced by suspension polymerization when an organic solvent, or diluent, which is a solvent for both the monomers and the copolymer is present in the organic phase. The presence of the diluent during copolymerization results in a more porous bead structure than that obtained for copolymer beads prepared when a diluent is not present (regular gel-type beads). Xero gel substrates were the initial focus of this work because it was thought that, due to their more porous structure, more complete and homogeneous functionalization of the beads with the bulky PEG molecules would be obtained.

A series of copolymer beads was synthesized using varying levels of divinylbenzene (1% and 2%), vinylbenzyl chloride (10%, 15% and 20%), and toluene (0%, 10%, 20% and 30%). The rest of the formula was composed of styrene and a low level of initiator, BPO. Divinylbenzene is the crosslinking agent which usually provides the primary control of the swelling property for the copolymer beads. Vinylbenzyl chloride is the unit which reacts with PEG in the subsequent functionalization reaction. Using varying amounts of toluene as the diluent in the substrate synthesis yields copolymer beads with different porosities. The presence of diluent in the copolymer synthesis also influences the swelling property of the copolymer beads. The yield of copolymerization and the swelling ratio of these copolymer beads in THF are summarized in Table 1. In general, all of the copolymerization yields are higher than 90%, while the quantity of the copolymer prepared from the same size reactor decreases as the amount of diluent increases. Moreover, the copolymers prepared with more diluent show higher swelling ratios than the copolymers prepared with less diluent.

All of the substrates studied at this stage were functionalized to ABEC-2000 resins using THF as the solvent with scalable amounts of PEG-2000 and sodium hydride depending on the percentage of VBC in the copolymer. The reagent quantities are summarized as follows:

Solvent:	20 mL / g of copolymer,
PEG-2000	1.5 mole / mole of theoretical VBC unit,
NaH	5 mole / mole of theoretical VBC unit.

Table 1. Copolymerization Yield and Swelling Ratios for Copolymer Beads Prepared in Substrate Studies

Lot# Copolymer (Substrate)	Resin Type	% Diluent (Toluene)	% DVB (Crosslinking)	% VBC	Yield of Copolymerization	Copolymer Swelling Ratio in THF
FC-54-009-A	Xero-gel	30%	1%	10%	90.0%	7.3X
FC-54-009-B	Xero-gel	30%	1%	15%	90.2%	7.3X
FC-54-009-C	Xero-gel	30%	1%	20%	92.3%	6.9X
FC-54-011-A	Xero-gel	20%	1%	10%	94.0%	5.9X
FC-54-011-B	Xero-gel	20%	1%	15%	97.5%	5.9X
FC-54-011-C	Xero-gel	20%	1%	20%	90.3%	6.0X
FC-54-012-A	Xero-gel	10%	1%	10%	93.8%	4.6X
FC-54-012-B	Xero-gel	10%	1%	15%	97.1%	5.1X
FC-54-012-C	Xero-gel	10%	1%	20%	95.4%	4.7X
FC-54-013-A	Gel	0%	1%	10%	94.3%	5.2X
FC-54-013-B	Gel	0%	1%	15%	94.6%	4.8X
FC-54-013-C	Gel	0%	1%	20%	93.8%	5.1X
FC-54-018-A	Xero-gel	30%	2%	15%	98.9%	4.4X
FC-54-018-B	Xero-gel	10%	2%	15%	99.4%	3.4X
FC-54-016-A	Xero-gel	20%	2%	10%	99.3%	3.7X
FC-54-016-B	Xero-gel	20%	2%	15%	98.9%	3.6X
FC-54-016-C	Xero-gel	20%	2%	20%	95.8%	3.7X

The functionalization yields were measured both by weight and by volume and are listed in Table 2. The data indicate that the yield of functionalization increases with the content of VBC units on the copolymer. This is because there are more sites for PEG-2000 to attach to the substrate. Moreover, the yield also increases with the quantity of diluent used in copolymerization. Because the substrate prepared with a higher level of diluent can swell more during functionalization, there is a better chance for PEG molecules to penetrate deeper into the polymer network and to give more homogeneously functionalized ABEC resin.

The physical properties and technetium uptake data from 4 M NaOH are also summarized in Table 2, and technetium D profiles from NaOH solution are given in Figure 13. All of these resins show a high affinity for technetium as indicated by their D and D_v values. The ABEC-2000 resins prepared from 1% crosslinked xero gel substrates generally showed a very high percent swelling during stripping compared to the 2%

Table 2. Formulations and Yields of ABEC-2000 Resins Prepared for Substrate Studies

Lot# (ABEC-2000)	Lot# for Copolymer (Substrate)	Yield* of PEG Addition g(mL)	% Swelling During Stripping	% Solids	Bed Density in H ₂ O (g.mL)	Bed Density in 4 M NaOH (g.mL)	Dw of Tc in 4 M NaOH (mL/g)	Dv of Tc in 4 M NaOH (mL/mL)
FC-54-014-A	FC-54-009-A	52.2 (71)	40.6%	21.0%	0.139	0.234	640	150
FC-54-014-B	FC-54-009-B	77.6 (110)	43.1%	15.5%	0.107	0.187	440	82
FC-54-014-C	FC-54-009-C	106.8 (154)	55.1%	14.2%	0.095	0.211	410	87
FC-54-015-A	FC-54-011-A	49.2 (76)	32.6%	22.5%	0.153	0.227	630	140
FC-54-015-B	FC-54-011-B	70.1 (116)	38.7%	14.2%	0.119	0.194	670	130
FC-54-015-C	FC-54-011-C	93.8 (146)	48.2%	13.7%	0.098	0.189	690	130
FC-54-017-A	FC-54-012-A	43.7 (68)	29.2%	24.5%	0.153	0.216	550	120
FC-54-017-B	FC-54-012-B	64.1 (102)	42.3%	17.9%	0.118	0.205	790	160
FC-54-017-C	FC-54-012-C	78.0 (120)	45.8%	17.0%	0.115	0.212	840	180
FC-54-019-A	FC-54-013-A	44.9 (70)	29.7%	24.4%	0.205	0.292	590	170
FC-54-019-B	FC-54-013-B	57.3 (88)	27.8%	20.7%	0.140	0.193	710	140
FC-54-019-C	FC-54-013-C	70.8 (108)	36.8%	18.8%	0.116	0.186	710	130
FC-54-020-A	FC-54-018-A	29.0 (43)	7.5%	36.9%	0.240	0.26	250	65
FC-54-020-B	FC-54-018-B	16.4 (27)	11.7%	64.3%	0.376	0.426	120	51
FC-54-021-A	FC-54-016-A	18.1 (27)	0%	55.8%	0.384	0.384	370	140
FC-54-021-B	FC-54-016-B	18.0 (29)	0%	60.2%	0.366	0.366	340	120
FC-54-021-C	FC-54-016-C	23.2 (34)	3.0%	35.2%	0.226	0.226	560	130

*All of ABEC-2000 resins are prepared from 10 grams of copolymer beads and the yields are measured after the ABEC-2000 resins are dried on a Buchner funnel for 5 minutes.

crosslinked resins. The 2% crosslinked resins show somewhat lower D_w values than the 1% crosslinked resins, but the D_v values are very similar (Table 2). Due to the fact that it can be more difficult to work with the resins if they undergo dramatic volume changes during loading and stripping, the substrate study was continued focusing on the 2% crosslinked xero gel and regular gel copolymers.

Figure 13. $\text{TcO}_4^- D_w$ vs. [NaOH] for ABEC resins prepared for substrate studies.

The characterization results of 2% crosslinked xero gel and regular gel ABEC-2000 resins are summarized in Table 3 and technetium D_w profiles for these resins are included in Figure 14. Both products exhibit much lower percentage swelling during stripping—approximately 10% compared to between 25% and 50% for 1% crosslinked resins. Additionally, the distribution ratios measured for these 2% crosslinked resins compare very favorably with those measured for 1% crosslinked resins (see Figure 13). The xero gel resins show a slightly better weight distribution ratio, however, the observed difference in D_w values is mainly due to the fact that the xero gel resins have lower percent solid values than the regular gel resins. The D_w values are much closer, indicating that column behavior should be quite similar. Because the diluent used for making xero

gel resins needs to be removed by an azeotrope distillation, which can make a significant cost difference between xero gel and regular gel resins, the 2% crosslinked regular gel copolymer was chosen for further parameter studies.

Table 3. Comparison of Xero Gel and Regular Gel ABEC-2000 Resins.

ABEC Lot#	Resin Type	DVB Content	VBC Content	% Solids	Bed Density in Water (g/mL)	Bed Density in 4M NaOH (g/mL)	D _w of TcO ₄ in 4 M NaOH mL/g	D _v of TcO ₄ in 4 M NaOH mL/mL	% Swelling During Stripping
FC-54-021-C	xero gel	2%	20%	35.2%	0.224	0.231	560	130	3.0%
FC-54-044-A	xero gel*	2%	10%	34.2%	0.213	0.245	517	126	12.0%
FC-54-026-B	gel	2%	20%	41.4%	0.296	0.328	320	105	9.8%
FC-54-044-B	gel	2%	20%	44.2%	0.301	0.333	310	103	9.4%

* Prepared with 20% toluene as the diluent in copolymer synthesis.

Figure 14. TcO₄⁻ D_w vs. [NaOH] for xero gel and regular gel ABEC-2000 resins.

Study of PEG Molecular Weight: The PEG used for ABEC synthesis was studied at two molecular weight ranges, PEG-2000 and PEG-5000. The copolymer containing 2% crosslinking agent and 20% VBC was functionalized to ABEC-2000 and ABEC-5000 respectively in experiments FC-54-038-C and FC-54-038-D. The results shown in Table 4 indicate that both the yield of ABEC-2000 synthesis and the uptake performance of ABEC-2000 resin are better than that of the 2% crosslinked ABEC-5000. This could be due to the fact that the activated alkoxide group on the less bulky PEG-2000 molecule has better opportunity to react with the VBC unit on the substrate. Additionally, the synthesis of ABEC-5000 requires more solvent to dissolve the PEG-5000. The use of PEG-2000 for the synthesis of 2% crosslinked ABEC resin proved to be more economical and yielded a resin with higher D_w 's for technetium. Therefore, further parameter studies were based upon the synthesis of ABEC resin functionalized with PEG-2000.

Table 4. Comparison of ABEC-2000 and -5000 Resins Prepared from 2% Crosslinked, 20% VBC Substrate.

ABEC Lot #	M.W. of PEG	Yield of PEG addition g (mL)	%Solids	Bed Density in Water (g/mL)	Bed Density in 4M NaOH (g/mL)	Dw of TcO ₄ - in 4 M NaOH g/mL	Dv of TcO ₄ - in 4 M NaOH mL/mL	% Swelling During Stripping
FC-54-038-C	2000	49.1 (72)	48.8%	0.21	0.255	579	148	17.7%
FC-54-038-D	5000	32.2 (50)	62.5%	0.372	0.372	111	48	0%

Study of the Alternate Solvent, Diglyme: Due to the potential safety concern of peroxide accumulation in the system when running the reaction in THF, the PEG addition reaction was studied side-by-side using THF and diglyme as the reaction solvents (JW-53-065-A and B). The reaction conditions and results shown in Table 5 indicate that diglyme gives a product with better yield and comparable rhenium uptake character. Since diglyme is a safer solvent in production scale operations, the reaction solvent was changed from THF to diglyme for further studies.

Effect of Reducing Solvent/PEG/NaH: In this set of experiments, the quantities of solvent, PEG and NaH were studied in the same ratio with respect to each other but at different levels relative to the amount of copolymer (JW-53-085-A, B, C). Both the synthesis yield and rhenium uptake character (Table 6) decrease when a lower level of solvent/PEG/NaH combination is used. Because the reaction conditions used for JW-53-085-B gave ABEC-2000 with the best compromise of yield, affinity for rhenium, percent swelling, and process quantity in reaction vessel, the parameters chosen for experiment JW-53-085-B were used for further studies.

Effect of Solvent Quantity: In order to increase the concentration of PEG in the reaction mixture and thus the production yield, the synthesis was further explored with decreasing quantities of solvent (JW-53-085-B, JW-53-106-A and B). In Table 7, the results indicate that the distribution of rhenium to the resin phase under conditions not

Table 5. Effect of Solvent on PEG Addition Reaction

Part A: Synthesis Parameter and Yield

	% DVB in Copolymer	% VBC in Copolymer	Solvent	mL of Solvent per g of Copolymer	g of PEG-CH ₃ per g of copolymer	g of 60% NaH per g of copolymer	mg of 60% NaH per g of PEG-CH ₃	Reaction Temp and Reaction Time	Yield of ABEC wet in g per g of copolymer	Yield of ABEC wet in mL per g of copolymer
JW-53-065-A	2%	20%	THF	20 mL	3.83 g	260 mg	67.8 mg	reflux / 17 hrs	2.45	3.53
JW-53-065-B*	2%	20%	Diglyme	20 mL	3.83 g	260 mg	67.8 mg	70°C / 17 hrs	2.98	4.40

Part B: Characterization and Uptake Property

	Bed Density in H ₂ O (g/mL)	Bed Density in 4 M NaOH (g/mL)	%Solid	% Swelling During Stripping	Re Capacity μmole of Re per ml of wet resin	Re Affinity μmole of Re per ml of wet resin
JW-53-065-A	0.300	0.330	43.1%	9.1%	129	15.0
JW-53-065-B*	0.242	0.313	35.5%	22.5%	137	15.2

*Bold type indicates the experiment selected for further optimization studies.

Table 6. Effect of Reducing Solvent/PEG/NaH on PEG Addition Reaction

Part A: Synthesis Parameters and Yield

	% DVB in Copolymer	% VBC in Copolymer	Solvent	mL of Solvent per g of Copolymer	g of PEG-CH ₃ per g of copolymer	mg of 60% NaH per g of copolymer	mg of 60% NaH per g of PEG-CH ₃	Reaction Temp and Reaction Time	Yield of ABEC wet in g per g of copolymer	Yield of ABEC wet in mL per g of copolymer
JW-53-065-A	2%	20%	THF	20 mL	3.83 g	260 mg	67.8 mg	reflux / 17 hrs	2.45	3.53
JW-53-085-A	2%	20%	Diglyme	20 mL	2.60 g	104 mg	40.0 mg	70°C / 17 hrs	1.91	2.80
JW-53-085-B*	2%	20%	Diglyme	10 mL	1.30 g	52 mg	40.0 mg	70°C / 17 hrs	1.58	2.33
JW-53-085-C	2%	20%	Diglyme	5 mL	0.65 g	26 mg	40.0 mg	70°C / 17 hrs	1.42	2.07

Part B: Characterization and Uptake Property

	Bed Density in H ₂ O (g/mL)	Bed Density in 4 M NaOH (g/mL)	% Solid	% Swelling During Stripping	Re Capacity μmole of Re per ml of wet resin	Re Affinity μmole of Re per ml of wet resin
JW-53-065-A	0.300	0.330	43.1%	9.1%	129	15.0
JW-53-085-A	0.372	0.439	54.5%	15.2%	125	13.0
JW-53-085-B	0.437	0.489	64.4%	10.7%	71	11.1
JW-53-085-C	0.484	0.494	70.0%	2.0%	84	9.6

*Bold type indicates the experiment selected for further optimization studies.

Table 7. Effect of Solvent Quantity on PEG Addition Reaction

Part A: Synthesis Parameters and Yield

	% DVB in Copolymer	% VBC in Copolymer	Solvent	mL of Solvent per g of Copolymer	g of PEG-CH3 per g of copolymer	mg of 60% NaH per g of copolymer	mg of 60% NaH per g of PEG-CH3	Reaction Temp and Reaction Time	Yield of ABEC wet in g per g of copolymer	Yield of ABEC wet in mL per g of copolymer
JW-53-065-A	2%	20%	THF	20 mL	3.83 g	260 mg	67.8 mg	reflux / 17 hrs	2.45	3.53
JW-53-085-B	2%	20%	Diglyme	10 mL	1.30 g	52 mg	40.0 mg	70°C / 17 hrs	1.58	2.33
JW-53-106-A*	2%	20%	Diglyme	6.7 mL	1.30 g	52 mg	40.0 mg	70°C / 17 hrs	1.76	2.60
JW-53-106-B	2%	20%	Diglyme	5.0 mL	1.30 g	52 mg	40.0 mg	70°C / 17 hrs	1.60	2.40

Part B: Characterization and Uptake Property

	Bed Density in H ₂ O (g/mL)	Bed Density in 4 M NaOH (g/mL)	%Solid	% Swelling During Stripping	Re Capacity μmole of Re per ml of wet resin	Re Affinity μmole of Re per ml of wet resin
JW-53-065-A	0.300	0.330	43.1%	9.1%	129	15.0
JW-53-085-B	0.437	0.489	64.4%	10.7%	71	11.1
JW-53-106-A	0.403	0.464	58.0%	13.0%	118	11.7
JW-53-106-B	0.441	0.480	63.4%	8.3%	85	11.3

*Bold type indicates the experiment selected for further optimization studies.

approaching the loading capacity of the resin is similar for the three resins (11.1, 11.7, and 11.3 $\mu\text{mol/mL}$ of resin, respectively), but JW-53-106-A exhibits a greater capacity for rhenium (118 $\mu\text{mol/mL}$ of resin vs. 71 and 85 $\mu\text{mol/mL}$). The reaction yield was slightly improved in experiment JW-53-106-A. This was attributed to a greater concentration of PEG in the reaction vessel. However, the yield decreased when the solvent was further reduced in experiment JW-53-106-B. Because the fluidity of the mixture was reduced to an unacceptable level in experiment JW-53-106-B, the quantity of diglyme solvent used for experiment JW-53-106-A (6.7 mL/g copolymer) was chosen as the standard level for further parameter studies.

Effect of Reaction Temperature: The reaction temperature was studied at 70°C, 85°C and 100°C (Table 8). The changes of reaction temperature between 70°C and 100°C did not have any significant impact on either the reaction yield or the rhenium uptake of the resulting product. Therefore, a reaction temperature of 70°C was used in subsequent studies.

Effect of Reaction Time: The impact of reaction time was studied with three reaction periods: 17 hours (JW-53-106-A), 12 hours (JW-53-139-A) and 6 hours (JW-53-139-B). The analysis results shown in Table 9 indicate that the resins prepared with shorter reaction period have similar affinity for rhenium but the loading capacities for rhenium decreased significantly. Also, more floating beads were observed during the transfer with water for the resins prepared with lower reaction time. Since PEG-2000, though not as bulky as PEG-5000, is still a relatively large molecule, more time may be required for the activated alkoxide to contact the methylene chloride group on the substrate, and a longer reaction time for PEG addition should yield resin with better uptake properties. Therefore, a reaction time of 17 hours (experiment JW-53-106-A) was chosen for subsequent copolymer functionalizations.

Study of Substrates with Various levels of VBC: Up to this point, the 2% crosslinked substrate used for the parameter studies contained 20% VBC, the functional group for attaching the PEG molecule in the addition reaction. Since the PEG-2000 is moderately bulky, it is very important to leave enough space between the VBC units on the substrate for attaching the PEG molecules. A series of ABEC resins was prepared using copolymers prepared with lower VBC levels (15% and 10%). The data summarized in Table 10 show that reducing the VBC content in the substrate from 20% down to 10% does not compromise the rhenium uptake performance of ABEC-2000 resin. The resin synthesized with the substrate containing 10% VBC shows similar affinity character and loading capacity for rhenium compared to the resin made from the substrate with 20% VBC. Due to the relatively high cost of VBC monomer (\$110/kg) compared to the cost of the styrene and DVB monomers (\$6.57/kg and \$8.52/kg, respectively), it is advantageous from an economic perspective to reduce the amount of VBC used in the copolymerization. Therefore, a VBC level of 10% (experiment JW-53-140-C) was chosen for future work.

Table 8. Effect of Reaction Temperature on PEG Addition Reaction

Part A: Synthesis Parameters and Yield

	% DVB in Copolymer	% VBC in Copolymer	Solvent	mL of Solvent per g of Copolymer	g of PEG-CH3 per g of copolymer	mg of 60% NaH per g of copolymer	mg of 60% NaH per g of PEG-CH3	Reaction Temp and Reaction Time	Yield of ABEC wet in g per g of copolymer	Yield of ABEC wet in mL per g of copolymer
JW-53-065-A	2%	20%	THF	20 mL	3.83 g	260 mg	67.8 mg	reflux / 17 hrs	2.45	3.53
JW-53-106-A*	2%	20%	Diglyme	6.7 mL	1.30 g	52 mg	40.0 mg	70°C / 17 hrs	1.76	2.60
JW-53-133-A	2%	20%	Diglyme	6.7 mL	1.30 g	52 mg	40.0 mg	85°C / 17 hrs	1.81	2.53
JW-53-133-B	2%	20%	Diglyme	6.7 mL	1.30 g	52 mg	40.0 mg	100°C / 17 hrs	1.77	2.53

Part B: Characterization and Uptake Property

	Bed Density in H ₂ O (g/mL)	Bed Density in 4 M NaOH (g/mL)	%Solid	% Swelling During Stripping	Re Capacity μmole of Re per ml of wet resin	Re Affinity μmole of Re per ml of wet resin
JW-53-065-A	0.300	0.330	43.1%	9.1%	129	15.0
JW-53-106-A	0.403	0.464	58.0%	13.0%	118	11.7
JW-53-133-A	0.404	0.436	57.4%	7.4%	110	12.0
JW-53-133-B	0.399	0.435	58.8%	8.3%	96	11.7

*Bold type indicates the experiment selected for further optimization studies.

Table 9. Effect of Reaction Time on PEG Addition Reaction

Part A: Synthesis Parameters and Yield

	% DVB in Copolymer	% VBC in Copolymer	Solvent	mL of Solvent per g of Copolymer	g of PEG-CH3 per g of copolymer	mg of 60% NaH per g of copolymer	mg of 60% NaH per g of PEG-CH3	Reaction Temp and Reaction Time	Yield of ABEC wet in g per g of copolymer	Yield of ABEC wet in mL per g of copolymer
JW-53-065-A	2%	20%	THF	20 mL	3.83 g	260 mg	67.8 mg	reflux / 17 hrs	2.45	3.53
JW-53-106-A*	2%	20%	Diglyme	6.7 mL	1.30 g	52 mg	40.0 mg	70°C / 17 hrs	1.76	2.60
JW-53-139-A	2%	20%	Diglyme	6.7 mL	1.30 g	52 mg	40.0 mg	70°C / 12 hrs	1.81	2.40
JW-53-139-B	2%	20%	Diglyme	6.7 mL	1.30 g	52 mg	40.0 mg	70°C / 6 hrs	1.77	2.47

Part B: Characterization and Uptake Property

	Bed Density in H ₂ O (g/mL)	Bed Density in 4 M NaOH (g/mL)	%Solid	% Swelling During Stripping	Re Capacity μmole of Re per ml of wet resin	Re Affinity μmole of Re per ml of wet resin
JW-53-065-A	0.300	0.330	43.1%	9.1%	129	15.0
JW-53-106-A	0.403	0.464	58.0%	13.0%	118	11.7
JW-53-139-A	0.434	0.460	61.7%	5.7%	89	11.8
JW-53-139-B	0.431	0.461	61.6%	6.5%	52	11.5

*Bold type indicates the experiment selected for further optimization studies.

Table 10. Study of PEG Addition Reaction Using Copolymers with Various Levels of VBC**Part A: Synthesis Parameters and Yield**

	% DVB in Copolymer	% VBC in Copolymer	Solvent	mL of Solvent per g of Copolymer	g of PEG-CH ₃ per g of copolymer	g of 60% NaH per g of copolymer	mg of 60% NaH per g of PEG-CH ₃	Reaction Temp and Reaction Time	Yield of ABEC wet in g per g of copolymer	Yield of ABEC wet in mL per g of copolymer
JW-53-065-A	2%	20%	THF	20 mL	3.83 g	260 mg	67.8 mg	reflux / 17 hrs	2.45	3.53
JW-53-106-A	2%	20%	Diglyme	6.7 mL	1.30 g	52 mg	40.0 mg	70°C / 17 hrs	1.76	2.60
JW-53-140-A	2%	20%	Diglyme	6.7 mL	1.30 g	52 mg	40.0 mg	70°C / 17 hrs	1.91	2.70
JW-53-140-B	2%	15%	Diglyme	6.7 mL	1.30 g	52 mg	40.0 mg	70°C / 17 hrs	2.25	2.83
JW-53-140-C*	2%	10%	Diglyme	6.7 mL	1.30 g	52 mg	40.0 mg	70°C / 17 hrs	1.77	2.67

Part B: Characterization and Uptake Property

	Bed Density in H ₂ O (g/mL)	Bed Density in 4 M NaOH (g/mL)	% Solid	% Swelling During Stripping	Re Capacity μmole of Re per ml of wet resin	Re Affinity μmole of Re per ml of wet resin
JW-53-065-A	0.300	0.330	43.1%	9.1	129	15.0
JW-53-106-A	0.403	0.464	58.0%	13.0%	118	11.7
JW-53-140-A	0.401	0.449	56.5%	10.7%	97	13.5
JW-53-140-B	0.346	0.436	48.3%	20.6%	132	13.8
JW-53-140-C	0.416	0.454	58.0%	8.3%	127	13.3

*Bold type indicates the experiment selected for further optimization studies.

Sodium Methoxide as a Substitute for Sodium Hydride: Several batches of ABEC-2000 resin were prepared from 2% crosslinked substrate using sodium methoxide to activate the PEG. However, in each case the resin percent solids was higher and the synthetic yield and rhenium uptake performance lower than for resin JW-53-140-C, which was prepared using sodium hydride to activate the PEG (Table 11). All of these factors indicate that a lower level of substrate functionalization was obtained when sodium methoxide was used instead of sodium hydride. Additional work is needed in order to improve the level of functionalization obtained when sodium methoxide is used to replace sodium hydride as the activating agent.

Table 11. Results of Replacing Sodium Hydride with Sodium Methoxide

Lot #	Yield of ABEC wet in g per g of copolymer	Yield of ABEC wet in mL per g of copolymer	Bed Density in H ₂ O (g/mL)	Bed Density in 4 M NaOH (g/mL)	% Solid	Re Capacity μ mol of Re per mL of wet resin	Re Affinity μ mol of Re per mL of wet resin
JW-53-140-C ^a	1.77	2.67	0.416	0.454	58.0%	127	13.3
JW-53-118 ^b	1.27	1.87	0.522	0.564	76.6%	---	3.4
JW-53-146 ^b	1.58	2.37	0.444	0.466	64.0%	21	8.9
JW-53-148 ^b	1.33	1.97	0.499	0.529	73.7%	68	4.2
CD-73-005 ^b	1.46	2.00	0.484	0.498	70.7%	78	2.7

- a. Sodium hydride used to activate PEG.
- b. Sodium methoxide used to activate PEG.

Synthesis Summary: The substrate synthesis and composition and the parameters of the PEG addition reaction have been optimized in this project. Based on compromises between physical characteristics, uptake performance, and production safety and cost considerations, the ABEC-2000 resin produced in experiment JW-53-140-C was selected as the model for the scale up syntheses. The substrate characteristics and reaction conditions follow:

Substrate:	regular gel-type copolymer with 2% DVB and 10% VBC,
Particle Size:	30 to 60 mesh,
Solvent:	6.7 mL of Diglyme / g of copolymer,
PEG-2000:	1.30 g / g of copolymer,
NaH (60%):	52 mg / g of copolymer,
Reaction Temp.:	70°C,
Reaction Time:	17 hours.

Uptake and Column Loading/Elution Studies of Technetium-Spiked Waste Simulants

Uptake studies for removal of $^{99}\text{TcO}_4^-$ from waste simulant solutions (see discussion on p. 21) were conducted to demonstrate removal of technetium from simulants of actual waste streams generated at two BNFL sites. The solution referred to as BNFL Sellafield waste simulant contained only a very low concentration of biphasic forming anion (0.03 M carbonate ion) and a high concentration of nitrate ion (2.4 M). The uptake of technetium by ABEC-5000 (100 to 200 mesh, 1% crosslinked chloromethylated polystyrene beads functionalized with PEG-5000) from the BNFL Sellafield waste simulant was determined as the NaNO_3 concentration was increased from the initial concentration of 0.03 M to 1.0 M (Figure 15). The technetium distribution was found to increase with increasing Na_2CO_3 concentration, but in every case the D values were less than 100.

Figure 15. TcO_4^- D_w with ABEC-5000 vs. total $[\text{Na}_2\text{CO}_3]$ in BNFL Sellafield waste simulant solution.

Next, higher concentrations of biphas-forming salts (1.3 M K_2CO_3 , 1.4 M Na_2CO_3 , and 1.7 M $(\text{NH}_4)_2\text{SO}_4$) were added to the waste simulant and D_w values greater than 100 were obtained in each case (Figure 16). The highest D_w value was from the simulant to which 1.3 M K_2CO_3 had been added. The technetium uptake will likely increase as the K_2CO_3 concentration is increased even further (see Figure 2). The addition of carbonate salts to the waste stream to enhance the uptake of technetium by ABEC resins is acceptable to BNFL because the treated waste will be released to the ocean, which already contains high concentrations of carbonate species.

Figure 16. TcO_4^- D_w with ABEC-5000 vs. molarities of different biphas-forming salts added to BNFL Sellafield waste simulant solution.

The technetium distribution ratio for the BNFL Sellafield simulant ~~wh~~ had been made 1.3 M in K_2CO_3 was also measured for the ABEC-2000 resin FC-54-026-B, the most promising ABEC-2000 resin which had been produced at the time this work was performed. An average D_w value of 67 was obtained. While this is less than the D_w value of 180 measured for ABEC-5000 resin, the difference is largely due to the the fact that ABEC-5000 resin has a dwcf value of 0.12 compared to a dwcf of 0.42 for resin FC-54-026-B. Based on the differences in the bed densities in 4 M NaOH (see Figure 11) for these resins, the D_w 's for ABEC-5000 resin and resin FC-54-026-B would convert to

D_V 's of approximately 20 and 22, respectively. This indicates that on a volume basis, the resins were equally effective in removing technetium from this waste solution.

Technetium D_w values from the BNFL Capenhurst waste simulant solution were also measured for ABEC-5000 resin and resin FC-54-026-B. This simulant solution contained relatively high concentrations of the biphas-forming anion sulfate. The solution also contained moderate concentrations of aluminum and iron(II) cations, both of which were shown to enhance the uptake of technetium. The average D_w value for ABEC-5000 resin was 3552 while resin FC-54-026-B gave an average D_w of 728. Again, using the bed densities in 4 M NaOH, these values convert to approximate D_V values of 391 for ABEC-5000 resin and 239 for resin FC-54-026-B. Based on these results, both resins exhibit very good uptake of technetium from the Capenhurst waste simulant.

The loading and elution behavior of $^{99}\text{TcO}_4^-$ on ABEC-5000 resin (100 to 200 mesh) and resin FC-54-026-B (50 to 100 mesh) for the BNFL Capenhurst waste simulant solution were also investigated (Figures 17 and 18, respectively).

Figure 17. Column loading and elution of TcO_4^- in BNFL Capenhurst waste simulant with ABEC-5000 resin.

The initial concentration of pertechnetate in the ABEC-5000 resin load solution was 2.92 mM, and 100% breakthrough was reached at 18 bed volumes (0.644 mL/BV) of load solution (Figure 17). The loading capacity, based on the amount of technetium stripped from the column was $43 \mu\text{mol/mL}$ of resin bed in water (4.3 g technetium per liter of resin). Essentially all of the technetium was stripped in 5 bed volumes.

The initial concentration of pertechnetate in the load solution for resin FC-54-026-B was 6.99 mM, and 100% breakthrough was reached at 17 bed volumes (0.729 mL/BV) of load solution (Figure 18). Greater than 95% of the technetium was stripped in the first 8 bed volumes. The technetium loading capacity based on the total amount of technetium stripped from the resin was $81 \mu\text{mol/mL}$ (8.0 g technetium per liter of resin). The capacity values for both resins are of the same order of magnitude as typical rhenium saturation capacities measured for the ABEC resins discussed in previous sections.

Figure 18. Column loading and elution of TcO_4^- in BNFL Capenhurst waste simulant with resin FC-54-026-B.

V. Scale-Up

The formula summarized from the laboratory synthesis was scaled-up initially (synthesis of substrate), 5-liter (addition of PEG), and 110-liter (both synthesis of substrate and addition of PEG) reactors. The complete production flowsheets for the process used in the 110-liter reactor are presented in Appendix C. The processes and results of each step of scale-up are discussed in the following sections.

Synthesis of Substrate (Copolymerization): The quantity of monomers used for each size of reactor and the yield of copolymerization from each size of reactor are summarized in Table 12. The chlorine contents of the substrates (representative of the VBC incorporation into the polymer) prepared in both 2-liter and 110-liter reactors were determined (Table 12) and the values are very close to the theoretically calculated chlorine content of 0.65 meq/g. The stirring speed chosen for the 110-liter reactor was 150 rpm which gave a product containing 85% of the copolymer beads within the expected particle size range (30 to 60 mesh). The reaction showed a very minor exothermic phenomenon (Figure 19 and Appendix B) but the exotherm was well controlled by the reactor's cooling system. This exotherm could be avoided or minimized by decreasing the rate at which the temperature is raised from 67°C to 74°C.

Table 12. Reactant Quantities and Synthesis Yields for Scale-Up of Copolymer Synthesis

Lot #	FC-54-055	JW-53-152
Reactor Size	2-Liter	110-Liter
Styrene	616.25 g	18.486 Kg
VBC (10%)	71.65 g	2.148 Kg
DVB(2%)	26.03 g	0.781 Kg
BPO(0.3%)	2.15 g	64.5 g
Yield	93.0%	92.7%
Chlorine content	0.63 meq/g	0.61 meq/g
-30+60 Mesh	86.20%	84.1%

Addition of PEG-2000: The PEG addition reaction was scaled-up in 5-liter and 110-liter reactors. The quantity of chemicals used for both size reactors and the yields of functionalizations are summarized in Table 13A. The rhenium and technetium uptake performance of these ABEC-2000 resins prepared from different size reactors are compared in Table 13B, and technetium D profiles in NaOH solution are shown in Figure 20. These data indicate that the products are comparable, with JW-53-151-A and JW-53-155 exhibiting slightly higher affinity for rhenium and technetium than JW-53-140-C. This difference may be due to a slight modification of the process for JW-53-155.

Figure 19. Temperature record of copolymerization reaction in 110-liter reactor.

Table 13. Comparison of ABEC-2000 Resins from Different Size Reactors**Part A.** Synthesis Parameters and Yields

Lot #	Reactor Size	Copolymer	Diglyme	CH ₃ -PEG-2000-OH	NaH(60%)	Yield, Buchner dried	Yield, Volume
JW-53-140-C	500-mL	30 g	200 mL	39.00 g	1.56 g	53.2 g	80 mL
JW-54-151-A	5-liter	300 g	2000 mL	390 g	15.6 g	622.0 g	905 mL
JW-53-155	110-liter	6.60 kg	44 L	8.58 kg	343.2 g	14.7 kg	19.9 L

Part B. Characterization and Uptake Property

Lot #	Bed Density in H ₂ O (g/mL)	Bed Density in 4 M NaOH (g/mL)	% Solid	% Swelling During Stripping	Re Capacity μ mol of Re per mL of wet resin	Re Affinity μ mol of Re per mL of wet resin	TcO ₄ ⁻ D _w in 4 M NaOH	TcO ₄ ⁻ D _v in 4 M NaOH
JW-53-140-C	0.416	0.454	58.0%	8.3%	127	13.1	122	55.4
JW-54-151-A	0.359	0.370	52.1%	2.9%	158	13.7	176	65.1
JW-53-155	0.382	0.428	53.0%	10.7%	166	15.3	192	82.2

Figure 20. $\text{TcO}_4^- D_w$ vs. $[\text{NaOH}]$ for ABEC-2000 resins produced from larger scale reactions.

Because the PEG addition reaction step involves hydrogen evolution, the synthesis in the 110-liter reactor was processed with a nitrogen flow to dilute the concentration of hydrogen produced during the reaction and sweep it from the reactor headspace. Also, the sodium hydride was added over a longer, 8 hour period in order to control the rate of hydrogen gas evolution.

The column loading and elution behavior of ReO_4^- with resin JW-53-155 was investigated in two different experiments. In the first experiment (Figure 21) 26.4 BV's (161 mL) of load solution, consisting of 1.1 mg/mL rhenium ($6 \times 10^{-3} \text{ M}$) in 4 M $(\text{NH}_4)_2\text{SO}_4$ solution, was passed through the column at a rate of 1.4 mL/min. The column was rinsed with approximately 14.0 BV's (85.1 mL) of 4 M $(\text{NH}_4)_2\text{SO}_4$ solution and then stripped with 11.4 BV's (71.3 mL) of DI water. Greater than 95% of the rhenium was stripped in the first 3 BV's (mL) resulting in a concentration factor from load to strip of 10.2. The resin capacity for rhenium determined from this study was 1.1 $\mu\text{mol/mL}$ resin (24 g rhenium per liter of resin).

In the second experiment (Figure 22) 256 BV's (1557 mL) of load solution, consisting of 0.10 mg/mL rhenium (5.8×10^{-4} M) in 4 M $(\text{NH}_4)_2\text{SO}_4$ solution, were passed through the column at a flow rate of 5.6 mL/min. The column was rinsed with 4.1 BV's (25 mL) of 4 M $(\text{NH}_4)_2\text{SO}_4$ solution and then stripped with 18.4 BV's (115 mL) of DI water at a flow rate of 3.4 mL/min. A total of 101 mg of rhenium was removed from the column for a capacity of $87 \mu\text{mol}$ rhenium per mL of resin bed in water (16 g rhenium per liter of resin). Approximately 95% of the rhenium was stripped in the first 6.0 BV's (38 mL) for a final concentration factor from load to strip of approximately 25. Given that the concentration of rhenium used in this experiment was approximately 10 times greater than the expected average concentration of technetium in actual wastes, it is reasonable to assume that concentration factors of at least 100 can be attained for technetium from tank waste streams.

Figure 21. Column loading/elution curve for 1.1 g/L rhenium as NaReO_4 in 4 M $(\text{NH}_4)_2\text{SO}_4$ with resin JW-53-155.

Figure 22. Column loading/elution curve for 0.10 g/L rhenium as NaReO_4 in 4 M $(\text{NH}_4)_2\text{SO}_4$ with resin JW-53-155.

A column study with $^{95\text{m}}\text{TcO}_4^-/0.01 \text{ M } \text{NH}_4\text{ReO}_4$ was also conducted and the loading/elution curve is shown in Figure 23. The capacity measured in this study was 76 $\mu\text{mol/mL}$ resin bed in water (7.5 g technetium per liter of resin) based on loading to 10% breakthrough. The Tc/Re uptake performance and resin capacity of the 110-liter reactor product are comparable to those observed for resin produced in smaller reactors, therefore indicating a successful reaction scale-up.

VI. Economic Evaluation

The economic evaluation of ABEC-2000 resin is based upon the data collected from running the synthesis in Eichrom's 110-liter reactor. The detailed cost calculations for ABEC resin synthesis presented in Table 14 provide an approximate breakdown of costs between labor and materials. In general, all of the chemicals were purchased in

Figure 23. Column loading/elution curve for $^{95m}\text{TcO}_4^-/0.01\text{ M ReO}_4^-$ in 4 M NaOH with resin JW-53-155.

1-liter bottle to 5-gallon drum sizes. Further scale up will allow for dramatic cost reductions when it is possible to obtain certain chemicals in 55-gallon drum, or larger, quantities. For example, both diglyme and PEG-2000 can be directly purchased from the original manufactures, Grant Chemicals and Union Carbide, respectively, at much lower prices. Other components such as styrene and vinylbenzyl chloride can also be purchased at reduced costs, further lowering the overall cost, when the synthesis is scaled to a production reactor. Based upon previous scale up experience, the price summarized in Table 14 for ABEC resin is comparable with the cost for making other specialty resins at the 110-liter scale.

Table 14: Manufacturing Costs for ABEC Resin in 110-Liter Reactor Using Actual Quantities Purchased.

ABEC Resin Cost per batch FP				batch size =	13.1 kg	UPDATED 1/6/98					
RAW MATERIALS					LABOR		O'hd rate	2			
	amount/ batch FP	\$/amount	\$/batch FP	\$/kg FP	hours	direct rate		\$/60 kg FP		\$/kg FP	
Copolymer, 2XL	6.6 kg	\$49.53	\$326.92				DL	OH	Total		
Diglyme	44 li	\$13.42	\$590.33		Preclean	2.5	\$17.79	\$44.48	\$88.95	\$133.43	LR11
PEG-2000-CH ₃	8.6 kg	\$59.30	\$508.79		Swelling	2	\$17.79	\$35.58	\$71.16	\$106.74	LR11
Nitrogen	610 cuft	\$0.17	\$102.00		Functionalization	4	\$17.79	\$71.16	\$142.32	\$213.48	LR11
NaH (60%)	0.343 kg	\$104.90	\$36.00		Quench	1	\$17.79	\$17.79	\$35.58	\$53.37	LR11
					Washing	2	\$17.79	\$35.58	\$71.16	\$106.74	LR11
					Clean-up	1	\$17.79	\$17.79	\$35.58	\$53.37	LR11
TOTAL RAW MATERIALS			\$1,564.05	\$119.30				\$177.90	\$355.80	\$533.70	\$40.71
FINISHING CHEMICALS											
IPA	33.0 li	\$1.56	\$51.58		Conditioning	4	\$17.79	\$71.16	\$142.32	\$213.48	LR11
DI Water	133.0 li	\$0.05	\$5.99								
TOTAL FINISHING			\$57.56	\$4.39				\$71.16	\$142.32	\$213.48	\$16.28
WASTE DISPOSAL					QC						
	Organic waste		\$67.34		Labor	1.5	\$16.35	\$24.53	\$49.05	\$73.58	LR21
	Aqueous waste		\$49.16								
			\$116.50	\$8.89							
COST		per batch FP	\$2,558.86					\$24.53	\$49.05	\$73.58	\$5.61
		per kg FP	\$195.18								
		per lb FP	\$88.72								
					Notes:						
	\$/kg	\$/cuft	% total	Waste disposal included (Wilpen)							
Materials	\$123.69	\$2,412.01	63%	Use Eichrom's 110-liter reactor							
Direct Labor	\$20.87	\$406.93	11%	Assume apparent density ~0.69 kg/L (19.5 kg/cuft)							
Overhead	\$41.74	\$813.87	21%	Diglyme from Aldrich (18 liters)							
Other	\$8.89	\$173.28	5%	PEG-2000-CH3 from Fluka (1 kg)							
total		\$195.18	\$3,806.09	100%							

VII. Sorption of Technetium Onto Silica-Based Anion Exchange Resin

Step two in the flowsheet for the separation, concentration and immobilization of Tc/I from alkaline supernate wastes involves stripping Tc/I from ABEC resin with water followed by loading onto a commercial silica-based anion exchange resin (NUCLEOSIL) from the strip solution. We have established (see Figures 18 and 21-23 above) that the ABEC-2000 resins are readily stripped with water. The pH of the water strip solution is expected to be near neutral or slightly basic. Experiments were conducted to determine the D_w values for technetium sorption by NUCLEOSIL in the pH range of 1 to 12 (Figure 24). Aniline was used to buffer the solution pH from 3 to 6 and ethylenediamine was used to buffer the solution pH from 7 to 12. The measured D_w values increased from about

Figure 24. Technetium uptake by NUCLEOSIL as a function of solution pH.

350 at pH 1 to almost 1300 at pH 5 and then decreased to less than 50 at pH 12. Due to inconsistencies in some of the D_w values measured using the buffered solutions, it was decided to measure the technetium uptake from unbuffered DI water at pH 6.5 for comparison (Table 15). The D_w values obtained were from 10 to 100 times greater than for the buffered solutions. The concentration of pertechnetate in the NUCLEOSIL uptake experiments was approximately 2×10^{-4} M, and all measurements were made in the same manner as technetium D_w measurements with ABEC resins. The average D_w was 1.0×10^4 at the 95% confidence level, with greater than 99.5% uptake of technetium by NUCLEOSIL resin under these conditions. This represents an additional concentration

factor for technetium of approximately 70; a factor of 20-25 concentration is already demonstrated for the first flowsheet step ABEC treatment of the original waste.

Table 15. Uptake of Technetium by NUCLEOSIL from DI Water

	DI Water (mL)	NUCLEOSIL (g)	Tc Added (mg)	% Loaded	D _w (mL/g)	Tc Loaded (μ mol/g)
1	1.00	0.0269	0.0215	99.5	8232	8.03
2		0.0271	0.0224	99.5	7496	8.31
3		0.0285	0.0224	99.7	10710	7.92
4		0.0235	0.0220	99.6	10591	9.42
5		0.0294	0.0214	99.7	11652	7.33
6		0.0242	0.0224	99.7	12437	9.32

Additional NUCLEOSIL loading data was gathered in preparation for encapsulation studies designed to demonstrate the third step in the flowsheet. In these experiments technetium was loaded onto three separate samples of NUCLEOSIL resin from DI water solution (Table 16). In preparations 1 and 2 the NUCLEOSIL resin alone was contacted for 48 h with DI water (pH 4 to 5) containing ⁹⁹Tc traced with ^{95m}Tc. In preparation 3 the NUCLEOSIL resin was encapsulated within the hydrous titanium oxide microspheres (40% resin/60% HTiO) prior to contacting the wet microspheres with the technetium solution for 48 h. The data in Table 16 indicate that technetium was strongly sorbed by NUCLEOSIL under both of these conditions. The maximum amount of technetium loaded per g of resin in these studies was approximately 70% of the stated resin capacity of 1 mmol/g and at least 99% of technetium in the load solution was sorbed on the resin in two out of the three experiments.

Table 16. Uptake of Technetium by NUCLEOSIL from DI Water Under Conditions Approaching Resin Loading Capacity

Preparation	DI Water (mL)	NUCLEOSIL (g)	Tc Added (mg)	% Loaded	D _(48h) (mL/g)	Tc Loaded (mmol/g)
A	8.57	1.161	77.8	94.1	117	0.64
B	19.19	3.1037	214	99.6	1360	0.693
C	26.3	1.05	47.5	99.0	958	0.452

VIII. Encapsulation of Silica-Based Anion Exchange Resin

Step three in the flowsheet for the separation, concentration and immobilization of Tc/I from alkaline supernate waste involves the encapsulation of Tc/I-loaded, silica-based anion exchange resin in hydrous titanium oxide (HTiO) microspheres. To demonstrate

this portion of the process, microspheres were prepared by suspending either Tc-loaded or non-loaded NUCLEOSIL resin in a predetermined formulation of broth containing hexamethylene-tetramine (HMTA), urea, and titanium salt. The exact composition of the broth was varied to yield air-dried microspheres with a composition of either 20% NUCLEOSIL resin/80% HTiO (Preparation A) or 40% NUCLEOSIL resin/60% HTiO (Preparation B) by weight. After forming and aging the microspheres in hot silicone oil (90°C) in the Internal Gelation Process apparatus, the microspheres were washed four times with trichloroethylene (TCE) to remove the silicone oil from the surface. To remove the reaction products (HMTA, urea, and ammonium chloride), the microspheres were washed four times with 0.05 M NH_4OH and once with DI water. All rinse fractions from preparations A and B made using Tc-loaded NUCLEOSIL resin beads were gamma counted to determine the amount of technetium desorbed by each rinse fraction. The data in Table 17 show that a total of approximately 5% of the loaded technetium was removed by all washes and rinses combined. The majority of technetium released was found in the first two NH_4OH wash fractions. Removal of a small amount of technetium at this stage

Table 17. Technetium Desorbed During Microsphere Preparations and Washing Steps.

⁹⁹ Tc Removed				
	Preparation A ^b		Preparation B ^c	
Component	μCi	%	μCi	%
TCE	BDL	BDL	BDL	BDL
Silicone Oil	BDL	BDL	BDL	BDL
(1) NH_4OH Wash ^a	42	3.33	91	2.52
(2) NH_4OH Wash ^a	10	0.79	40	1.12
(3) NH_4OH Wash ^a	7	0.55	16	0.45
(4) NH_4OH Wash ^a	7	0.55	17	0.46
H ₂ O Rinse	2	0.16	7	0.19
Total Removed	68	5.38	171	4.73

a. 0.05 M NH_4OH washes

b. 20% Nucleosil resin/80% HTiO microspheres⁹⁹Tc sorbed on resin at start of preparation = 1244 mCi)

c. 40% Nucleosil resin/60% HTiO microspheres⁹⁹Tc sorbed on resin at start of preparation = 3619 mCi)

does not present a problem because the aqueous wash solutions can be fed back into alkaline waste supernate solution where technetium will be removed by passing through the Tc/I selective resin. Following the washing steps the microspheres were placed in a drying container and dried at ambient temperature for 3 days. The microspheres were then divided into three fairly equal portions, and two of the portions were dried at higher temperatures, one at 105°C for 5.3 h and the other at 170°C for 5.3 h. Drying of the

microspheres was not attempted at higher temperatures because previous thermogravimetric studies with NUCLEOSIL resin indicated that the organic functional groups began to decompose at temperatures of 190 to 200°C.

This study included three different HTiO microsphere preparations of encapsulated NUCLEOSIL resin. The original test plan called for the encapsulation of Tc-loaded NUCLEOSIL resin beads within the HTiO microspheres. Therefore, the first two preparations contained 20% Tc-loaded NUCLEOSIL resin/80% HTiO and 40% Tc-loaded NUCLEOSIL resin/60% HTiO, respectively. These correspond to Preparations A and B in Tables 16 and 17 above. Drying the microspheres from Preparation A at 105° C and 170° C resulted in water losses of 17.4 and 35.9%, respectively while drying the microspheres of Preparation B resulted in water losses of 4.7 and 22.8%, respectively.

During the course of this work it was suggested by researchers at Oak Ridge National Laboratory that the process could be simplified greatly if the NUCLEOSIL resin could be encapsulated prior to loading with technetium. This approach has the added advantage of avoiding radioactive contamination of the Internal Gelation Apparatus and eliminating exposure hazards during the encapsulation process. Therefore, in the third experiment microspheres containing 40% NUCLEOSIL resin/60% HTiO were prepared, and then the wet microspheres were loaded with technetium prior to drying to collapse the microspheres (Preparation C in Table 16). It can be seen from the data in Table 16 that technetium is sorbed just as well by microspheres prepared in this way as when the NUCLEOSIL resin is loaded prior to encapsulation. Drying of these microspheres at 170°C resulted in a water loss of about 25%. Successful encapsulation of the Tc-loaded NUCLEOSIL resin was achieved in all three instances.

IX. Stability Studies of the Encapsulated Waste Form

Leaching Tests The final task in testing the proposed flowsheet involved performing stability studies on the encapsulated waste form. Parallel leaching experiments were conducted with microsphere samples that were dried at ambient temperature, 105 and 170°C. One set of experiments was conducted with toxicity characteristic leaching procedure (TCLP) leachant (Table 18) and the other set with a simulated Waste Isolation Pilot Plant (WIPP) brine solution (Table 19). The TCLP leachant stock was prepared by adding 11.4 mL glacial acetic acid to 1 L of DI water, adding 128.6 mL of 1.0 M NaOH, and diluting to a volume of 2 L. The pH of the solution was about 4.9. Two liters of brine solution was prepared that contained 1.83 M NaCl, 0.77 M KCl, and 2.87 M MgCl. The pH of this solution was about 6.6.

The samples of microspheres were gently mixed with the indicated volumes of leachants, as given in Tables 18 and 19. Samples were removed and counted after 24 h, 96 h, and 168 h and the activity of ⁹⁹Tc removed with time and the percentages of the initial ⁹⁹Tc removed were determined (Tables 20 and 21). Afterwards, these leachants

Table 18. Test Conditions at the Start of the TCLP Leaching Tests.

Type Microspheres	Sample Wt. (g)	NUCLEOSIL resin (g)	Sorbed ⁹⁹ Tc at the start (μCi)	Amount of Leachant (g)
20% (air-dried) ^f	0.7377	0.148	155	250
20% (105°C) ^a	0.5401	0.135	141	250
20% (170°C) ^a	0.5465	0.169	176	250
40% (air-dried) ^b	0.6425	0.257	285	250
40% (105°C) ^b	0.7104	0.298	331	250
40% (170°C) ^b	0.5458	0.283	313	250
40% (air-dried) ^c	0.6273	0.251	191	125
40% (170°C) ^c	0.5169	0.275	209	125

a. 20% NUCLEOSIL/80% HTiO microspheres (resin loaded with ⁹⁹Tc before preparation of beads)

b. 40% NUCLEOSIL/60% HTiO microspheres (resin loaded with ⁹⁹Tc before preparation of beads)

c. 40% NUCLEOSIL/60% HTiO microspheres (resin loaded with ⁹⁹Tc after preparation of beads)

Table 19. Test Conditions at the Start of the Brine Leaching Tests.

Type Microspheres	Sample Wt. (g)	NUCLEOSIL resin (g)	Sorbed ⁹⁹ Tc at the start (μCi)	Amount of Leachant (g)
20% (air-dried) ^f	0.5820	0.116	122	250
20% (105°C) ^a	0.4331	0.114	114	250
20% (170°C) ^a	0.6224	0.194	203	250
40% (air-dried) ^b	0.3885	0.115	172	250
40% (105°C) ^b	0.5649	0.237	263	250
40% (170°C) ^b	0.5746	0.298	330	250
40% (air-dried) ^c	0.6753	0.270	205	125
40% (170°C) ^c	0.4897	0.261	198	125

a. 20% NUCLEOSIL/80% HTiO microspheres (resin loaded with ⁹⁹Tc before preparation of beads)

b. 40% NUCLEOSIL/60% HTiO microspheres (resin loaded with ⁹⁹Tc before preparation of beads)

c. 40% NUCLEOSIL/60% HTiO microspheres (resin loaded with ⁹⁹Tc after preparation of beads)

were decanted from the microspheres and replaced with fresh solutions of leachants of equal volumes.

For both the TCLP and brine leaching tests, very little difference was observed for microsphere preparations dried at different temperatures. In the TCLP leaching study, the least amount of ^{99}Tc leaching was observed for the resin loaded with ^{99}Tc after preparation of the beads (preparation C). In the brine leaching study the maximum amount of ^{99}Tc leaching was observed for the 40% NUCLEOSIL/60% HTiO microspheres, which had been loaded with ^{99}Tc prior to bead preparation (preparation B). Approximately one third the amount of ^{99}Tc leaching was observed for the other two preparations. In both studies, significantly less ^{99}Tc was released upon contact with the second portion of leachant. In all cases, the maximum, cumulative amount of ^{99}Tc leached by either leachant was less than 1% of the initial amount of ^{99}Tc contained in the encapsulated waste form. Furthermore, with few exceptions, the majority of the technetium was leached in the first 24 hour period, indicating the technetium was primarily removed from the surface of the microspheres. This further suggests that washing the microspheres prior to long-term storage would eliminate any potential leaching problem. The minor amount of technetium in any rinse solution could be retreated.

The results of these leaching studies indicate that the encapsulated waste form from all three preparations is very stable with regard to leaching by prolonged contact with solutions of this nature. If the HTiO microspheres are further incorporated into a type of ceramic grout as a final waste form, it may be possible to eliminate leaching of technetium from the encapsulated waste altogether.

Heating and Shielding Calculations Calculations were performed to estimate the shielding properties for ^{99}Tc -loaded silica-based resin beads (5 μm diameter) when encapsulated in HTiO microspheres (1 mm diameter) at a volumetric loading of 20% silica beads. Calculations were performed for Tc-99 loadings of 1 nCi, μCi , and 1 mCi per bead. A Monte Carlo N-Particle (MCNP) code was used for this analysis. Analyses were performed to calculate a dose rate at the surface of a spherical silica-based resin bead both with and without encapsulation in HTiO. Gross estimates of heat generation in the different cases were also evaluated. The results of these analyses are given in Table 22.

Results of the shielding calculations for unencapsulated beads show that the dose rate at the surface of the bead increases with increasing ^{99}Tc loading. This dose rate is due almost entirely to bremsstrahlung-produced photons leaving the surface of the resin bead. Most of this is due to the interaction of electrons with technetium atoms ($Z = 43$) within the resin bead. These interactions increase dramatically as loading increases because the technetium atoms are much closer together. Heating produced by the radioactive decay of ^{99}Tc also increases with increasing loading.

Table 20. Results of the TCLP Leaching Tests.

	Tc-99 Removed by the First Leachant						Tc-99 Removed by the Second Leachant			
	24 h		96 h		168 h		24 h		96 h	
Microspheres	(μ Ci)	(%)	(μ Ci)	(%)	(μ Ci)	(%)	(μ Ci)	(%)	(μ Ci)	(%)
20% (air-dried) ^g	0.274	0.18	0.271	0.17	0.431	0.28	0.068	0.04	0.063	0.04
20% (105°C) ^a	0.101	0.07	0.104	0.07	0.358	0.25	0.090	0.06	0.106	0.07
20% (170°C) ^a	0.326	0.19	0.326	0.19	0.334	0.19	0.126	0.07	0.127	0.07
40% (air-dried) ^b	0.465	0.16	0.476	0.17	0.700	0.25	0.108	0.04	0.127	0.05
40% (105°C) ^b	0.516	0.16	0.522	0.16	0.749	0.23	0.257	0.08	0.235	0.07
40% (170°C) ^b	0.674	0.22	0.669	0.21	0.695	0.22	0.195	0.06	0.208	0.07
40% (air-dried) ^c	0.112	0.06	0.105	0.05	0.135	0.07	0.034	0.02	0.045	0.02
40% (170°C) ^c	0.095	0.05	0.108	0.06	0.154	0.07	0.048	0.02	0.062	0.03

- a. 20% NUCLEOSIL/80% HTiO microspheres (resin loaded with ⁹⁹Tc before preparation of beads)
b. 40% NUCLEOSIL/60% HTiO microspheres (resin loaded with ⁹⁹Tc before preparation of beads)
c. 40% NUCLEOSIL/60% HTiO microspheres (resin loaded with ⁹⁹Tc after preparation of beads)

Table 21. Results of the Brine Leaching Tests.

	Tc-99 Removed by the First Leachant						Tc-99 Removed by the Second Leachant			
	24 h		96 h		168 h		24 h		96 h	
Microspheres	(μ Ci)	(%)	(μ Ci)	(%)	(μ Ci)	(%)	(μ Ci)	(%)	(μ Ci)	(%)
20% (air-dried) ^g	0.068	0.06	0.068	0.06	0.077	0.06	0.047	0.04	0.063	0.06
20% (105°C) ^a	0.126	0.11	0.123	0.11	0.161	0.14	0.054	0.05	0.073	0.07
20% (170°C) ^a	0.285	0.14	0.286	0.14	0.275	0.14	0.094	0.05	0.123	0.07
40% (air-dried) ^b	0.885	0.51	0.875	0.51	0.976	0.57	0.319	0.19	0.378	0.22
40% (105°C) ^b	1.470	0.56	1.490	0.57	1.490	0.57	0.401	0.15	0.457	0.14
40% (170°C) ^b	1.740	0.53	1.730	0.53	1.790	0.54	0.283	0.09	0.319	0.09
40% (air-dried) ^c	0.314	0.15	0.312	0.15	0.322	0.16	0.112	0.05	0.125	0.06
40% (170°C) ^c	0.345	0.17	0.344	0.16	0.356	0.18	0.079	0.04	0.096	0.05

- a. 20% NUCLEOSIL/80% HTiO microspheres (resin loaded with ⁹⁹Tc before preparation of beads)
b. 40% NUCLEOSIL/60% HTiO microspheres (resin loaded with ⁹⁹Tc before preparation of beads)
c. 40% NUCLEOSIL/60% HTiO microspheres (resin loaded with ⁹⁹Tc after preparation of beads)

Table 22. Dose Rate and Heating Calculations for Unencapsulated vs. Encapsulated Beads

Tc-99 Loading	Unencapsulated Bead Surface Dose ($\mu\text{rem/hr}$)	Encapsulated Bead Surface Dose ($\mu\text{rem/hr}$)	Fractional Change in Dose Rate Due to Encapsulation	Heating Per Unencapsulated Bead (Joules)	Heating Per Encapsulated Bead (Joules)
1 nCi	7.740E-03	1.594E-01	20.59	5.050E-19	1.632E-16
1 μCi	2.142E-01	1.670E-01	0.78	2.543E-17	4.068E-16
1 mCi	3.915E+00	5.941E-02	0.15	5.211E-16	9.148E-16

In the case of the encapsulated beads the calculated dose rate is higher at the 1 nCi loading level than it is for the unencapsulated bead. At this low level ^{99}Tc loading, the technetium atoms are farther apart on average than the range of an electron within the bead. Therefore, there is very little bremsstrahlung production in the unencapsulated bead. When the bead is encapsulated, however, ^{99}Tc decay near the surface of the bead results in increased bremsstrahlung production due to some interaction of electrons with the titanium atoms ($Z = 22$). At the higher levels of ^{99}Tc loading, where there is already significant production of bremsstrahlung photons, there is actually a reduction in surface dose rate on going from the unencapsulated bead to the encapsulated bead due to some shielding from the HTiO. Additional production of bremsstrahlung radiation due to interaction of electrons with titanium atoms is not very significant relative to the amount already produced in the unencapsulated beads. Again, heating due to decay ^{99}Tc increases with increasing loading.

Using simplifying assumptions shielding properties were also estimated for the case where the encapsulated beads were loaded in a 55-gallon drum. A spherical geometry was assumed for the 55-gallon drum and the inner volume was assumed to consist of a homogeneous mixture of air, HTiO, SiO₂ and ^{99}Tc . The dose rate at the inner surface of this mixture was estimated to be $1.48 \times 10^{-8} \mu\text{rem/hr}$. The dose rate at the outer surface of the drum was approximately zero. Decay heat calculations showed a heating of $5.83 \times 10^{-7} \text{ J}$ over the inner volume of the barrel.

In summary, the dose rate in any given case is a function of the degree of loading, the resulting bead density, bremsstrahlung production, and scattering and self-absorption of photons. At higher loadings (μCi to 1 mCi) the HTiO encapsulation is effective in reducing the dose rate compared to the unencapsulated case. At lower loadings (1 nCi), the HTiO encapsulation can result in a higher surface dose rate. Calculations show there is no dose rate at the outside surface of the steel 55-gallon drum. The dose rate at the inner surface of the mixture of air, HTiO, SiO₂ and ^{99}Tc was much lower than for the individual beads, indicating less bremsstrahlung production. This was attributed to the fact that technetium was spread out over a larger volume, thus reducing the probability for bremsstrahlung conversion to occur. All of the radiation emitted by ^{99}Tc is absorbed inside the drum, and heat generated from the decay of encapsulated ^{99}Tc is inconsequential.

for all geometries and levels of loading examined. Therefore, storage of drums containing the encapsulated waste form does not present a radiation or heat generation hazard.

X. Conclusion

An improved version of the Tc/I selective resin that resolves many of the outstanding performance issues of the original ABEC-5000 resin has been developed. The new resin is made by attaching PEG-2000 to a polystyrene substrate containing 2% DVB and 10% VBC. Due to the higher level of crosslinking the new resin exhibits much less swelling on crossover from load to strip and has a greater bed density than the original ABEC-5000 resin while still exhibiting the desired technetium uptake performance and loading capacity. The original solvent, THF, was successfully replaced by diglyme, a much safer solvent to handle on the production scale. Additional synthetic parameters were optimized in order to maximize the amount of product obtained and minimize production costs while maintaining desirable performance characteristics.

The production of the improved ABEC resin has been successfully scaled up in 5-liter and 110-liter reactors. The resins obtained from the scale-up reactions were found to have comparable physical properties and Tc/Re uptake performance to those prepared at the bench-top scale. A detailed cost evaluation was performed based upon the data collected from running the synthesis in Eichrom's 110-liter reactor. The cost projections are similar to other specialty resins and waste treatment of technetium bearing streams will not be prohibitively expensive.

Batch uptake properties and column load/strip behavior of technetium and rhenium have been determined for the resin produced in the 110-liter reactor (JW-053-155) as well as for resins produced on a smaller scale. The pertechnetate D_F for this resin from 4 M NaOH solution was 192 mL/g and the D_F was 82 mL/mL. The technetium capacity at 10% column breakthrough was 7.5 μ mol/mL of resin bed in water (7.5 g Tc/L of resin bed in water). Based on this loading capacity and a technetium concentration of 5×10^{-5} M in tank wastes, concentration factors of approximately 150 should be obtainable when technetium is loaded onto ABEC resin and stripped with water.

The loading of technetium onto NUCLEOSIL silica-based anion exchange resin was demonstrated over a pH range of 1 to 12. A maximum D_F of approximately 10 was obtained in DI water at pH 6.5, corresponding to a concentration factor in this instance of approximately 70. D_F values of greater than 10 were measured for uptake of technetium from DI water at pH 4 to 4.5, even at technetium loading equal to approximately 70% of maximum capacity. Given these very high D_F values, concentration factors of at least several hundred should be achievable for this step.

The Tc-loaded NUCLEOSIL resin was successfully encapsulated in HTiO microspheres by the technique of internal gelation. More importantly, it was demonstrated that NUCLEOSIL resin could be encapsulated in HTiO prior to loading technetium, and

the wet microspheres could then be loaded with technetium before drying to collapse the microspheres. This was a very significant finding in that it eliminates any radiation hazard during microsphere preparation, and the encapsulation process can be carried out without concern for radioactive contamination of the Internal Gelation Apparatus or associated chemical waste streams. This will both simplify and shorten the process as well as reduce associated costs.

Parallel leaching studies were performed on the different encapsulated waste forms using TCLP and abbreviated WIPP brine leachants. The maximum, cumulative amount of technetium released after contact with either leachant was less than 1% of the amount loaded and encapsulated. Heating and shielding calculations performed for encapsulated and unencapsulated beads showed that at higher levels of technetium loading (1 Ci to 1 mCi) encapsulation resulted in a lower surface dose rate than for the unencapsulated resin. Also, calculations for the case in which the Tc-loaded HTiO₂ microspheres were stored in a 55-gallon steel drum showed all of the radiation emitted by encapsulated ⁹⁹Tc was absorbed inside the drum. Heat generated from the decay of encapsulated ⁹⁹Tc was inconsequential for all geometries and levels of loading examined.

A summary of the results of the current effort compared with the success criteria originally required is given in Table 23.

Table 23. Comparison of Required Success Criteria vs. Success Achieved.

Task	Task Description	Required Success Criteria	Criteria Achieved
1.1	Synthesis		
1.1A	Study Alternate Substrates	Select Best Support Type Increase Bed Density Decrease % Swelling	Yes (gel) Yes Yes (<10%)
1.1B	Optimize PEG Addition Time	Determine Optimum Reaction Time	Yes (17 h)
1.1C	Alternative MW PEG's	Replace PEG-5000	Yes (PEG-2000)
1.1D	Alternatives to NaH	Find Safer Alternative	No - see p. 34 and Table 11
1.1E	Cost Evaluation	Estimate Manufacturing Costs	Yes (Acceptable Costs)
1.1F	110-Liter Scale-Up	Demonstrate Successful Scale-Up	Yes
1.2	Testing		
1.2A	Uptake Properties and Column Load/Strip Behavior	D _w > 100 Demonstrate Column Loading Demonstrate Water Elution	Yes Yes Yes
1.2B	Load Silica-Based Anion Exchange Resin	Demonstrate > 50% Loading	Yes
1.2C	Encapsulate Silica-Based Anion Exchange Resin	Demonstrate Successful Encapsulation	Yes
1.2D	Perform Stability Studies on Encapsulated Waste Form	Determine Percentage Tc Leached as a Function of Time	Maximum Percentage Tc Leached < 1%

XI. Recommendation for Future Work

The synthesis and scale up of ABEC-2000 resin have been accomplished as proposed. Several recommendations for further work are given below. These recommendations are aimed at making the production of ABEC resin more economical and the physical properties of these resins more suitable for various applications.

Further Study of Crosslinking of Copolymer The crosslinking level of the substrate used for making ABEC resin has significant influence on the quantity of ABEC resin yielded from the PEG addition reaction and on the swelling character of ABEC resin during stripping with water. Therefore, a fine tuning of crosslinking level between 1% and 2% should be further studied in order to enhance the yield of PEG addition reaction to an optimum level. Ideally, this study can give another significant cost reduction for making ABEC resin without sacrificing desirable swelling properties.

Further Study of Sodium Methoxide In the synthesis study using sodium methoxide for PEG addition reaction, the results of rhenium uptake experiments indicate that the products are not sufficiently functionalized with PEG. Changing the substrates to a lower level of crosslinking or changing the substrate matrix to possibly a VBC/acrylate copolymer may improve the yield of PEG addition associated with using sodium methoxide.

Further Study of Particle Size Since PEG-2000 is a relatively large molecule, each individual copolymer bead can probably be functionalized only to a certain depth from the surface. Using copolymer of slightly smaller particle size, such as 60 to 100 mesh, may yield product with a higher loading capacity simply due to the increased surface area.

Study of Substrate Matrix This effort focused on using styrene/VBC matrix as the substrate. Changing the hydrophobic section, styrene, to a more hydrophilic component such as acrylate may give a product with a totally different microenvironment with better metal ion uptake.

XII. Acknowledgments

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Appendix A

Flame AA Standard Operating Procedure

Introduction

Description

This document describes the operation of the FAAS, including preventive maintenance and calibration activities, at Eichrom Industries. It applies to all facilities that operate a FAAS.

Definitions

FAAS: Flame Atomic Absorption Spectrometer

HCL: Hollow Cathode Lamp

Reference Documents

Document #QA-0004 -- Control of Inspection and Test Equipment

Model 3110 Atomic Absorption Spectrometer Hardware Guide Perkin Elmer. Part Number 0993-8863, Release C, October 1995. Published in the USA.

Analytical Methods for Atomic Absorption Spectroscopy Perkin Elmer. Part Number 0303-0152, Release C, August 1994. Published in the USA.

Concepts, Instrumentation, and Techniques in Atomic Absorption Spectroscopy Perkin Elmer. Part Number 0993-9533, Release B, 1993. Published in the USA.

Appendices contain standard conditions and parameters for specific analytes.

Preparation

Read MSDS sheets for chemicals listed in 2.3.

Equipment

FAAS.

Burner Head (acetylene or NO)

Hollow Cathode Lamps (HCLs)

Class A volumetric flasks, if dilution required.

1 mL adjustable autopipettor (calibrated, record ID number in laboratory notebook) and pipet tips.

5 mL adjustable autopipettor (calibrated, record ID number in laboratory notebook) and pipet tips.

Chemicals

Metal standards for element(s) of interest.

Calibration Verification Standards for component(s) of interest. If using previously prepared standards, ensure that standards are less than 90

days old, and that enough standard exists for at least two runs. If not, prepare new standards. Newly prepared standards shall be compared with the standards which they are replacing, if available. The preparation of standards is recorded in the QC/Maintenance Log.

Samples

Distilled or Deionized water, ASTM Type I

Acetylene Gas, AA Grade

Nitrous Oxide Gas, AA Grade

KCl for controlling ionization interferences

Safety Equipment

Disposable gloves, with appropriate chemical resistance

Safety glasses

Lab jacket

Procedures

Safety Checks

General

Turn the vent on and ensure it is properly drawing before proceeding.

Close the flame door.

Ensure cylinders contain sufficient gas for the intended analysis.

Ensure a fire extinguisher is located near the equipment and ensure it is charged.

Burner Head

Ensure the proper burner head has been selected for the samples.

If changing the burner head, ensure the O-ring is in good condition. If the O-ring is damaged, replace it.

Ensure the burner head slot is clean.

Ensure the burner head is fully seated into the spray chamber, and secure the restraining cables and the interlock pin.

Drain System

Ensure the drain system has been properly installed.

If the level of waste in the drain vessel is high, properly dispose of the waste and reassemble the drain system. See section 7 for disposal guidelines.

Parameters

This section describes each of the parameters. The parameter settings for the elements are specified in the appendices to this procedure.

Lamp Current- Set this to the appropriate value, in mA, for the desired element to be tested.

Integration Time- The time the FAAS waits between sample replicates. Set to 1 second for quality procedures.

Replicates - The number of sample replicates. Set to 10 for quality control procedures.

Calibration Type- Linear, non-linear, or method of additions. Use the default value, non-linear, for quality procedures.

AA Technique- Flame, PK area, Peak height. The default is Flame, and this is the only option available on our 3110 model.

Standards 1-8- You have the option of using up to 8 standards. Three standards are the minimum. The decimal point is automatically set based on the first standard entered.

Reslope Standard- resets the calibration line based on the value entered. Do not use this option.

Read Delay Time- The spectrometer will delay reading the signal of the aspirated sample for the specified time. Use the default value, 0.

Print Calibration Curve- Default value is Yes. Set this parameter to No because the FAAS has no printer attached.

Calibration

Additional details and guidelines for calibration of the FAAS are on pages 119-121 of **Model 3110 Atomic Absorption Spectrometer Hardware Guide**

The calibration consists of a blank and at least three standards.

S1 should be equal to the high end of the linear range, S2 is three times S1, and S3 is six times S1. For additional explanation, refer to pages 16-23 of the **Analytical Methods for Atomic Absorption Spectrometry**

Standards should be matrix matched to the samples being run for best results.

The FAAS software automatically creates a calibration curve.

Re-analyze standards as samples during runs.

Igniting and optimizing the FAAS

Turn on the FAAS.

Dial the wavelength to the appropriate setting for the element to be analyzed. Use the first wavelength listed unless another is required. Record deviations in the QC/Maintenance Log.

Set the slit width to the correct setting for the element being analyzed, as specified in the appendices. Record deviations in the QC/Maintenance Log.

Install the applicable HCL into the lamp holder and set the lamp current to the correct mA for the element being tested. Record the HCL energy in the QC/Maintenance Log.

Align the lamp to achieve the maximum energy.

Turn on the gas supply at the tanks.

Adjust the burner height.

Ignite the flame.

Adjust the horizontal and rotational position of the burner.

Adjust the nebulizer.

Record the energy level in QC/Maintenance Log.

Autozero the instrument in the Continuous Mode using deionized water. Then check the characteristic concentration solution and record the absorbance value in the QC/Maintenance Log.

Record the date and analyst's initials next to the entries in the QC/Maintenance Log.

Running Samples

Samples must be bracketed by the standards. If the samples are beyond the range of the standards, dilute the samples or prepare a new set of standards bracketing the samples.

Prepare solutions.

Enter parameters. The parameters are specified in the appendix for the element.

Enter the data collection mode.

Run the standard blank.

Run the standards.

Analyze DI water between the standards and the samples. Also analyze DI water before and after each check standard.

Run the samples.

Re-analyze the standards after every set of 10 samples. If the standards deviate by more than 20%, recalibrate and rerun the last batch of samples.

Run one duplicate sample for every set of 10 samples run. If duplicate value deviates by more than 20%, recalibrate and rerun the batch of samples.

Powering Down the System

Aspirate de-ionized water for a few minutes to clean the burner head.
Turn the gas control switch on the pneumatics control panel to OFF.
Close all gas source valves.
Turn the gas control switch to Air to allow acetylene and oxidant to bleed.
Turn the gas control switch to OFF.
Turn the instrument OFF.
Turn the vent OFF.

Calculations

Calculate metal concentration in the sample using the following equation:

$$\text{ppm} = C \times D$$

Where: ppm = The actual concentration of metal in the sample. (ppm)
C = The reading from the FAAS. (ppm)
D = The dilution factor.

Maintenance

Burner Head

Clean burner head at least monthly. Record in QC/Maintenance Log.
If aspirating samples with high solids content, clean the burner daily. Record in QC/Maintenance Log.
Clean the slot in the burner with the thin metal strip provided with the instrument before each use. Record in QC/Maintenance Log.
The burner head can also be soaked overnight in a mild detergent and then rinsed with deionized water and blown dry.

Air compressor

Drain the air compressor of water monthly. Record in QC/Maintenance Log.

Sample Retention and Disposal

Retain samples for metal analyses one month (30 days). Retain samples longer when requested by the client. Identify each collection of samples so the contents of the samples can be identified. Mark disposal date on each collection of samples.

Segregate samples for disposal by matrix type. Collect waste in 5 gallon or smaller containers, as appropriate for the expected volume during a 180 day period.

Separate RCRA listed metals from the other metals.

Label each waste storage container with its contents and start date.

Records

Record all data in a lab notebook. Record Maintenance and HCL energy in QC/Maintenance Log.

Data should include the element tested, wavelength, slit width, and the energy of the HCL.

A copy of the data should accompany the quality report for the test performed.

Maintain laboratory notebooks as specified in document GEN-0010, Control of Quality Records.

List of Appendices

Appendix A - Europium

Appendix B - Strontium

Appendix C - Nickel

Appendix D - Lead

Appendix F - Rhenium

Standard Atomic Absorption Conditions for Rhenium

Wavelength	Slit	Relative Noise	Characteristic Concentration	Characteristic Concentration Check	Linear Range
(nm)	(nm)		(mg/L)	(mg/L)	(mg/L)
346.0	0.2	1.0	14.0	650.0	500.0

1. Use a nitrous oxide - acetylene flame.
2. Use calibration standards of 100, 300, and 500 ppm Re.

Parameters

Lamp Current	60mA
Integration time	1 sec.
Replicates	10
Calibration Type	linear
AA Technique	flame
Read Delay Time	0 sec.

Appendix B

110-Liter Reactor Temperature Profile

Time	Rxn Temp C	Heater Temp. C	Heat In C	Heat Out C	Comments
12/9/97 10:21 AM	18.8	22.3	21.6	20.6	
12/9/97 10:26 AM	19.2	26.6	26.1	23.7	
12/9/97 10:31 AM	19.7	30.4	29.5	27.1	
12/9/97 10:36 AM	21.2	33.7	32.9	30.5	
12/9/97 10:41 AM	23.0	36.9	36.1	33.8	
12/9/97 10:46 AM	25.0	39.7	38.9	36.7	
12/9/97 10:51 AM	26.8	42.6	41.6	39.3	
12/9/97 10:56 AM	29.1	45.4	44.5	42.4	
12/9/97 11:01 AM	31.5	41.8	41.5	41.9	
12/9/97 11:06 AM	33.2	40.9	40.4	40.9	
12/9/97 11:11 AM	34.3	40.2	39.8	40.4	
12/9/97 11:16 AM	34.9	39.4	39.1	39.6	
12/9/97 11:21 AM	35.4	39.1	38.6	39.2	
12/9/97 11:26 AM	35.8	38.8	38.6	39.1	
12/9/97 11:31 AM	35.7	38.6	38.3	38.9	
12/9/97 11:36 AM					Paper Jammed
12/9/97 12:58 PM	38.8	46.1	45.6	46.1	Ramp Set point slowly to 67
12/9/97 1:03 PM	39.5	48.3	46.8	44.9	
12/9/97 1:08 PM	40.1	51.8	50.5	48.6	
12/9/97 1:13 PM	41.4	54.7	53.5	51.6	
12/9/97 1:18 PM	42.9	57.3	56.1	54.2	
12/9/97 1:23 PM	44.7	59.8	58.4	56.8	
12/9/97 1:28 PM	46.6	59.3	59.9	59.1	
12/9/97 1:33 PM	48.3	61.5	60.1	58.6	
12/9/97 1:38 PM	50.1	64.4	62.9	61.3	
12/9/97 1:43 PM	51.9	66.9	65.3	63.9	
12/9/97 1:48 PM	54.1	69.1	67.7	66.2	
12/9/97 1:53 PM	56.1	71.1	69.7	68.4	
12/9/97 1:58 PM	57.9	66.0	65.2	66.3	
12/9/97 2:03 PM	59.4	68.2	66.4	65.2	
12/9/97 2:08 PM	60.4	71.8	70.1	68.8	
12/9/97 2:13 PM	61.8	74.1	72.6	71.2	
12/9/97 2:18 PM	63.7	76.4	74.8	73.6	Set point set to 67
12/9/97 2:23 PM	65.2	78.6	76.9	75.7	
12/9/97 2:28 PM	66.5	75.2	74.1	75.4	
12/9/97 2:33 PM	68.2	73.8	72.8	74.1	
12/9/97 2:38 PM	69.2	72.8	71.7	73.2	
12/9/97 2:43 PM	69.7	72.1	71.1	72.6	
12/9/97 2:48 PM	70.0	71.6	70.5	72.0	
12/9/97 2:53 PM	69.7	70.9	69.8	71.3	
12/9/97 2:58 PM	69.7	70.4	69.3	70.8	
12/9/97 3:03 PM	69.6	70.1	69.1	70.4	
12/9/97 3:08 PM	69.4	69.7	68.6	69.9	
12/9/97 3:13 PM	69.0	69.1	68.2	69.6	

12/9/97 3:18 PM	68.6	68.6	67.6	68.9	
12/9/97 3:23 PM	68.2	68.0	67.0	68.3	
12/9/97 3:28 PM	67.9	67.6	66.6	68.1	
12/9/97 3:33 PM	67.7	67.3	66.3	67.7	
12/9/97 3:38 PM	67.3	66.9	65.9	67.2	
12/9/97 3:43 PM	67.0	66.5	65.6	66.9	
12/9/97 3:48 PM	66.2	65.9	64.9	66.2	
12/9/97 3:53 PM	65.8	71.8	70.3	69.1	
12/9/97 3:58 PM	66.1	74.7	73.2	72.1	
12/9/97 4:03 PM	66.9	71.6	70.6	71.8	
12/9/97 4:08 PM	67.6	70.4	69.4	70.7	
12/9/97 4:13 PM	67.9	69.7	68.6	70.0	
12/9/97 4:18 PM	67.6	68.8	67.8	69.1	
12/9/97 4:23 PM	67.5	68.3	67.3	68.6	
12/9/97 4:28 PM	67.5	67.9	66.8	68.2	
12/9/97 4:33 PM	67.3	67.4	66.4	67.8	
12/9/97 4:38 PM	66.9	67.0	66.1	67.4	
12/9/97 4:43 PM	66.5	66.5	65.6	66.8	
12/9/97 4:48 PM	66.1	72.8	71.2	70.1	
12/9/97 4:53 PM	66.6	71.4	70.6	71.6	
12/9/97 4:58 PM	67.2	70.2	69.2	70.5	
12/9/97 5:03 PM	67.5	69.4	68.4	69.7	
12/9/97 5:08 PM	67.4	68.6	67.7	68.9	
12/9/97 5:13 PM	67.2	67.9	67.0	68.3	
12/9/97 5:18 PM	67.2	67.6	66.6	68.0	
12/9/97 5:23 PM	66.9	67.2	66.2	67.6	
12/9/97 5:28 PM	66.8	66.8	65.9	67.2	
12/9/97 5:33 PM	66.4	73.3	71.7	70.5	
12/9/97 5:38 PM	66.6	72.0	71.2	72.1	
12/9/97 5:43 PM	67.4	70.6	69.7	71.1	
12/9/97 5:48 PM	68.0	69.9	68.9	70.3	
12/9/97 5:53 PM	68.1	69.2	68.3	69.7	
12/9/97 5:58 PM	67.7	68.5	67.4	68.8	
12/9/97 6:03 PM	67.5	68.0	67.0	68.3	
12/9/97 6:08 PM	67.5	67.7	66.7	68.1	
12/9/97 6:13 PM	67.3	67.3	66.3	67.7	
12/9/97 6:18 PM	67.0	66.8	65.9	67.3	
12/9/97 6:23 PM	66.4	69.4	67.8	66.7	
12/9/97 6:28 PM	66.1	73.4	71.8	70.6	
12/9/97 6:33 PM	66.9	71.7	70.8	72.0	
12/9/97 6:38 PM	67.6	70.6	69.5	70.9	
12/9/97 6:43 PM	67.8	69.6	68.6	69.9	
12/9/97 6:48 PM	67.7	68.8	67.8	69.2	
12/9/97 6:53 PM	67.9	68.5	67.5	68.9	
12/9/97 6:58 PM	67.7	68.1	67.1	68.5	
12/9/97 7:03 PM	67.3	67.6	66.6	67.9	
12/9/97 7:08 PM	67.0	67.1	66.1	67.3	
12/9/97 7:13 PM	66.7	66.8	65.8	67.2	
12/9/97 7:18 PM	66.6	70.0	68.3	67.4	

12/9/97 7:23 PM	66.5	73.9	72.4	71.2	
12/9/97 7:28 PM	66.8	71.5	70.6	71.7	
12/9/97 7:33 PM	67.4	70.2	69.3	70.6	
12/9/97 7:38 PM	68.0	69.7	68.6	70.0	
12/9/97 7:43 PM	68.1	69.1	68.2	69.5	
12/9/97 7:48 PM	67.8	68.6	67.5	68.8	
12/9/97 7:53 PM	67.6	68.0	67.0	68.2	
12/9/97 7:58 PM	67.6	67.7	66.8	68.1	
12/9/97 8:03 PM	67.4	67.4	66.4	67.8	
12/9/97 8:08 PM	67.2	67.1	66.2	67.6	
12/9/97 8:13 PM	66.6	66.7	65.7	66.9	
12/9/97 8:18 PM	66.2	70.4	68.9	67.8	
12/9/97 8:23 PM	66.4	74.3	72.8	71.6	Set point at 74
12/9/97 8:28 PM	67.2	77.2	75.6	74.6	
12/9/97 8:33 PM	68.6	79.6	77.9	76.8	
12/9/97 8:38 PM	70.0	81.9	80.1	79.0	
12/9/97 8:43 PM	72.2	84.3	82.4	81.4	
12/9/97 8:48 PM	74.6	81.4	80.3	81.9	
12/9/97 8:53 PM	76.2	80.0	78.3	79.7	
12/9/97 8:58 PM	77.1	78.9	77.6	79.3	
12/9/97 9:03 PM	77.9	78.5	77.2	78.9	
12/9/97 9:08 PM	78.6	78.2	77.0	78.8	
12/9/97 9:13 PM	78.8	78.0	76.7	78.3	
12/9/97 9:18 PM	78.9	77.8	76.5	78.2	
12/9/97 9:23 PM	79.4	78.0	76.6	78.1	
12/9/97 9:28 PM	79.6	78.0	76.6	78.3	
12/9/97 9:33 PM	79.6	77.8	76.4	78.0	
12/9/97 9:38 PM	79.6	77.8	76.4	78.2	
12/9/97 9:43 PM	80.1	78.1	76.8	78.5	
12/9/97 9:48 PM	80.6	78.4	77.1	78.6	Cooling water turned on
12/9/97 9:53 PM	78.1	73.4	23.6	12.1	Cooling water turned off
12/9/97 9:58 PM	71.2	30.6	29.6	28.3	
12/9/97 10:03 PM	64.3	39.6	38.4	37.0	
12/9/97 10:08 PM	58.9	45.1	44.2	42.4	
12/9/97 10:13 PM	54.9	49.2	48.2	46.5	
12/9/97 10:18 PM	52.7	52.6	51.7	50.0	
12/9/97 10:23 PM	51.6	55.6	54.7	53.1	
12/9/97 10:28 PM	51.1	58.4	57.2	55.6	
12/9/97 10:33 PM	50.9	60.4	59.3	57.8	
12/9/97 10:38 PM	51.7	62.9	61.7	60.4	
12/9/97 10:43 PM	52.8	65.2	64.0	62.6	
12/9/97 10:48 PM	54.0	67.3	66.1	64.7	
12/9/97 10:53 PM	55.5	69.4	68.1	66.8	
12/9/97 10:58 PM	57.3	71.7	70.4	69.1	
12/9/97 11:03 PM	59.2	73.5	72.4	71.2	
12/9/97 11:08 PM	61.0	75.4	74.0	72.8	
12/9/97 11:13 PM	63.4	77.5	76.1	75.0	
12/9/97 11:18 PM	66.1	79.7	78.2	77.2	
12/9/97 11:23 PM	68.3	81.8	80.2	79.4	

12/9/97 11:28 PM	70.6	79.6	78.6	80.1	
12/9/97 11:33 PM	73.0	78.3	77.2	78.9	
12/9/97 11:38 PM	74.2	77.9	76.7	78.4	
12/9/97 11:43 PM	74.6	77.4	76.3	77.9	
12/9/97 11:48 PM	75.4	77.4	76.2	78.0	
12/9/97 11:53 PM	76.3	77.7	76.5	78.2	
12/9/97 11:58 PM	76.8	77.7	76.5	78.2	
12/10/97 12:03 AM	77.2	77.7	76.3	78.0	
12/10/97 12:08 AM	77.3	77.6	76.4	78.2	
12/10/97 12:13 AM	77.3	77.6	76.3	78.1	
12/10/97 12:18 AM	76.3	77.0	75.8	77.4	
12/10/97 12:23 AM	75.6	76.6	75.3	76.9	
12/10/97 12:28 AM	75.1	76.2	75.1	76.6	
12/10/97 12:33 AM	74.4	75.8	74.7	76.2	
12/10/97 12:38 AM	73.5	75.2	73.9	75.4	
12/10/97 12:43 AM	72.9	80.8	79.2	78.2	
12/10/97 12:48 AM	72.9	83.9	82.2	81.1	
12/10/97 12:53 AM	73.1	86.2	84.3	83.3	
12/10/97 12:58 AM	73.6	82.6	81.4	82.7	
12/10/97 1:03 AM	74.3	81.0	79.8	81.3	
12/10/97 1:08 AM	74.5	79.9	78.7	80.2	
12/10/97 1:13 AM	74.1	78.8	77.4	79.1	
12/10/97 1:18 AM	74.3	78.1	76.9	78.5	
12/10/97 1:23 AM	74.1	77.4	76.3	77.9	
12/10/97 1:28 AM	73.4	81.9	80.0	79.2	
12/10/97 1:33 AM	73.4	84.9	83.0	82.0	
12/10/97 1:38 AM	74.0	81.8	80.7	82.1	
12/10/97 1:43 AM	74.4	80.3	79.2	80.7	
12/10/97 1:48 AM	74.2	79.1	77.8	79.4	
12/10/97 1:53 AM	74.1	78.2	77.0	78.6	
12/10/97 1:58 AM	74.2	77.6	76.4	78.0	
12/10/97 2:03 AM	73.7	81.0	79.0	78.3	
12/10/97 2:08 AM	73.4	84.2	82.3	81.3	
12/10/97 2:13 AM	73.7	83.8	83.7	83.8	
12/10/97 2:18 AM	74.3	81.4	80.2	81.8	
12/10/97 2:23 AM	74.3	79.9	78.7	80.3	
12/10/97 2:28 AM	74.3	79.0	77.8	79.4	
12/10/97 2:33 AM	74.4	78.2	77.1	78.7	
12/10/97 2:38 AM	74.0	77.5	76.3	77.9	
12/10/97 2:43 AM	73.5	80.4	78.4	77.8	
12/10/97 2:48 AM	73.4	83.9	82.2	81.3	
12/10/97 2:53 AM	73.8	85.4	84.7	83.8	
12/10/97 2:58 AM	74.1	81.4	80.1	81.6	
12/10/97 3:03 AM	74.3	80.1	78.8	80.4	
12/10/97 3:08 AM	74.6	79.2	77.9	79.6	
12/10/97 3:13 AM	74.3	78.3	77.1	78.7	
12/10/97 3:18 AM	74.1	77.4	76.2	77.7	
12/10/97 3:23 AM	73.9	80.3	78.3	77.8	
12/10/97 3:28 AM	73.7	83.7	82.2	81.2	

12/10/97 3:33 AM	73.7	82.8	81.8	83.1	
12/10/97 3:38 AM	74.1	80.6	79.4	80.8	
12/10/97 3:43 AM	74.5	79.6	78.3	80.0	
12/10/97 3:48 AM	74.4	78.7	77.4	79.0	
12/10/97 3:53 AM	74.0	77.7	76.4	77.9	
12/10/97 3:58 AM	73.9	80.9	78.9	78.3	
12/10/97 4:03 AM	73.7	84.3	82.5	81.6	
12/10/97 4:08 AM	73.8	81.9	80.9	82.3	
12/10/97 4:13 AM	74.1	80.2	79.0	80.6	
12/10/97 4:18 AM	74.6	79.3	78.1	79.7	
12/10/97 4:23 AM	74.3	78.3	77.2	78.8	
12/10/97 4:28 AM	73.9	77.5	76.3	77.8	
12/10/97 4:33 AM	73.7	83.1	81.1	80.3	
12/10/97 4:38 AM	73.9	85.9	83.9	83.1	
12/10/97 4:43 AM	74.1	81.1	79.8	81.3	
12/10/97 4:48 AM	74.4	79.8	78.5	80.1	
12/10/97 4:53 AM	74.7	78.9	77.7	79.3	
12/10/97 4:58 AM	74.4	78.1	76.8	78.4	
12/10/97 5:03 AM	73.9	77.2	75.9	77.4	
12/10/97 5:08 AM	73.8	82.9	81.1	80.1	
12/10/97 5:13 AM	73.9	85.7	83.9	83.0	
12/10/97 5:18 AM	74.1	81.2	80.0	81.5	
12/10/97 5:23 AM	74.4	79.9	78.6	80.2	
12/10/97 5:28 AM	74.6	78.9	77.8	79.4	
12/10/97 5:33 AM	74.3	78.0	76.8	78.4	
12/10/97 5:38 AM	73.9	77.2	75.9	77.4	
12/10/97 5:43 AM	73.9	81.8	79.9	79.2	
12/10/97 5:48 AM	73.7	84.7	82.9	81.9	
12/10/97 5:53 AM	74.0	82.3	81.2	82.6	
12/10/97 5:58 AM	74.2	80.4	79.2	80.7	
12/10/97 6:03 AM	74.7	79.4	78.2	79.8	
12/10/97 6:08 AM	74.6	78.6	77.4	79.0	
12/10/97 6:13 AM	74.1	77.6	76.3	77.9	
12/10/97 6:18 AM	73.7	81.3	79.3	78.6	
12/10/97 6:23 AM	73.8	84.7	82.8	81.9	
12/10/97 6:28 AM	74.1	80.8	79.6	81.1	
12/10/97 6:33 AM	74.1	79.3	78.0	79.6	
12/10/97 6:38 AM	74.3	78.3	77.2	78.8	
12/10/97 6:43 AM	74.2	77.7	76.4	78.1	
12/10/97 6:48 AM	73.5	82.9	80.8	80.0	
12/10/97 6:53 AM	73.7	85.4	83.7	82.7	
12/10/97 6:58 AM	74.3	81.2	80.1	81.6	
12/10/97 7:03 AM	74.7	79.9	78.7	80.2	
12/10/97 7:08 AM	74.4	78.7	77.5	79.0	
12/10/97 7:13 AM	74.3	77.9	76.8	78.3	
12/10/97 7:18 AM	74.2	77.3	76.2	77.8	
12/10/97 7:23 AM	73.6	82.7	80.9	80.1	
12/10/97 7:28 AM	73.7	85.5	83.7	82.6	
12/10/97 7:33 AM	74.4	87.8	86.0	85.1	Set point ramp to 92 begins

12/10/97 7:38 AM	75.5	89.8	87.9	87.0	
12/10/97 7:43 AM	76.4	91.7	89.7	88.7	
12/10/97 7:48 AM	78.0	93.6	91.6	90.8	
12/10/97 7:53 AM	79.3	95.2	93.3	92.6	
12/10/97 7:58 AM	80.8	97.3	95.1	94.3	
12/10/97 8:03 AM	82.1	98.7	96.6	96.0	
12/10/97 8:08 AM	83.4	100.2	98.1	97.5	
12/10/97 8:13 AM	84.7	102.0	99.5	98.9	
12/10/97 8:18 AM	86.3	103.6	101.3	100.8	
12/10/97 8:23 AM	87.9	105.3	102.9	102.6	Set point to 92
12/10/97 8:28 AM	93.8	103.6	102.3	103.9	
12/10/97 8:33 AM	98.4	100.7	99.0	101.1	
12/10/97 8:38 AM	95.8	99.1	97.4	99.6	
12/10/97 8:43 AM	96.3	97.8	96.1	98.3	
12/10/97 8:48 AM	95.6	96.5	94.9	97.0	
12/10/97 8:53 AM	94.6	95.3	93.7	95.8	
12/10/97 8:58 AM	93.3	94.2	92.6	94.6	
12/10/97 9:03 AM	92.5	93.3	91.7	93.7	
12/10/97 9:08 AM	91.5	97.9	95.7	95.3	
12/10/97 9:13 AM	91.3	100.6	98.4	97.8	
12/10/97 9:18 AM	91.8	102.5	100.3	99.7	
12/10/97 9:23 AM	92.3	98.7	97.1	98.9	
12/10/97 9:28 AM	92.4	96.6	94.9	96.9	
12/10/97 9:33 AM	92.6	95.3	93.7	95.7	
12/10/97 9:38 AM	92.4	94.2	92.5	94.6	
12/10/97 9:43 AM	91.9	100.3	98.0	97.4	
12/10/97 9:48 AM	91.9	102.2	100.0	99.4	
12/10/97 9:53 AM	92.6	97.7	96.0	98.0	
12/10/97 9:58 AM	92.8	96.0	94.4	96.4	
12/10/97 10:03 AM	92.6	94.7	93.1	95.1	
12/10/97 10:08 AM	92.1	99.4	97.2	96.7	
12/10/97 10:13 AM	91.9	101.7	99.4	98.9	
12/10/97 10:18 AM	92.4	98.9	97.3	99.1	
12/10/97 10:23 AM	92.8	96.9	95.3	97.3	
12/10/97 10:28 AM	92.9	95.4	93.8	95.9	
12/10/97 10:33 AM	92.6	94.3	92.7	94.6	
12/10/97 10:38 AM	92.1	100.2	98.0	97.4	
12/10/97 10:43 AM	92.3	102.5	100.2	99.6	
12/10/97 10:48 AM	92.6	97.9	96.2	98.1	
12/10/97 10:53 AM	92.6	96.0	94.4	96.4	
12/10/97 10:58 AM	92.6	94.7	93.1	95.2	
12/10/97 11:03 AM	92.2	98.8	96.6	96.2	
12/10/97 11:08 AM	91.9	101.4	99.2	98.6	
12/10/97 11:13 AM	92.6	98.9	97.4	99.2	
12/10/97 11:18 AM	92.5	96.6	94.9	96.8	
12/10/97 11:23 AM	92.6	95.2	93.5	95.6	Cooling water turned on.
12/10/97 11:28 AM	89.6	82.7	27.9	12.5	
12/10/97 11:33 AM	77.5	79.7	18.7	12.4	
12/10/97 11:38 AM	64.8	71.3	16.9	13.4	

12/10/97 11:43 AM	54.9	61.4	15.1	12.4	
12/10/97 11:48 AM	46.6	58.0	13.9	12.1	
12/10/97 11:53 AM	40.9	55.1	13.6	12.2	
12/10/97 11:58 AM	36.2	52.2	13.3	12.4	
12/10/97 12:03 PM	32.3	49.7	13.0	12.4	
12/10/97 12:08 PM	29.3	47.9	13.0	12.4	
12/10/97 12:13 PM	26.4	45.3	12.7	12.3	
12/10/97 12:18 PM	24.1	43.6	12.4	12.1	

Bold face indicates jacket is cooling.

Appendix C

ABEC^R Copolymer Flow Sheet

ABEC^(R) Resin Flow Sheet

ABEC^R Copolymer Equipment Table

**Styrene is a possible carcinogen

ABEC[®] Copolymer Equipment Table (continued)

Equipment

Reaction Vessel (Open)
Heater
Condenser

PPE / Mechanical Controls

Respirator (Organic)
Safety Goggles
Chemical resistant gloves
Protective Clothing

Chemical Fume Hood
Safety Shower
Eye Wash

Equipment

Reaction Vessel (Open)

Cooling Water

PPE / Mechanical Controls

Respirator (Organic)
Safety Goggles
Chemical resistant gloves
Protective Clothing

Chemical Fume Hood
Safety Shower
Eye Wash

Equipment

Reaction Vessel (Open)

PPE / Mechanical Controls

Respirator (Organic)
Safety Goggles
Chemical resistant gloves
Protective Clothing

Chemical Fume Hood
Safety Shower
Eye Wash

Equipment

Sieving Apparatus
Pump

PPE / Mechanical Controls

Respirator (Organic)
Safety Glasses
Chemical resistant gloves
Protective Clothing

Safety Shower
Eye Wash

ABEC^R Resin Equipment Table

Equipment	Equipment	Equipment	Equipment	Equipment	Equipment
Reaction Vessel	Reaction Vessel	Reaction Vessel	Reaction Vessel Heater Condenser Nitrogen Tank	Reaction Vessel Condenser Nitrogen Tank	Reaction Vessel Heater Condenser Nitrogen Tank
PPE / Mechanical Controls	PPE / Mechanical Controls	PPE / Mechanical Controls	PPE / Mechanical Controls	PPE / Mechanical Controls	PPE / Mechanical Controls
Safety Glasses	Respirator (Organic) Safety Goggles	Respirator (Organic) Safety Goggles	Respirator (Organic) Safety Goggles	Respirator (Organic) Safety Goggles	Respirator (Organic) Safety Goggles
Chemical resistant rubber gloves	Chemical resistant rubber gloves	Chemical resistant gloves	Chemical resistant gloves	Chemical resistant gloves	Chemical resistant gloves
Protective Clothing	Protective Clothing	Protective Clothing	Protective Clothing	Protective Clothing Full Face Mask	Protective Clothing
	Chemical Fume Hood	Chemical Fume Hood	Chemical Fume Hood	Chemical Fume Hood	Chemical Fume Hood
Safety Shower	Safety Shower	Safety Shower	Safety Shower	Safety Shower	Safety Shower
Eye Wash	Eye Wash	Eye Wash	Eye Wash	Eye Wash	Eye Wash

ABEC[®] Resin Equipment Table (continued)

*Hydrogen will evolve. Nitrogen purge needs to be sufficient to keep H₂ levels within safe operating conditions. For the first run this is 10 LPM minimum.

Equipment	Equipment	Equipment	Equipment	Equipment	Equipment
Reaction Vessel	Reaction Vessel	Reaction Vessel	Reaction Vessel	Reaction Vessel	Conditioning Column
Condenser		Condenser			Vacuum Pump
Nitrogen Tank					
PPE / Mechanical Controls	PPE / Mechanical Controls	PPE / Mechanical Controls	PPE / Mechanical Controls	PPE / Mechanical Controls	PPE / Mechanical Controls
Respirator (Organic)	Respirator (Organic)	Respirator (Organic)	Respirator (Organic)	Respirator (Organic)	
Safety Goggles	Safety Goggles	Safety Goggles	Safety Goggles	Safety Glasses	Safety Glasses
Chemical resistant gloves	Chemical resistant gloves	Chemical resistant gloves	Chemical resistant gloves	Chemical resistant gloves	Chemical resistant gloves
Protective Clothing	Protective Clothing	Protective Clothing	Protective Clothing	Protective Clothing	Protective Clothing
Chemical Fume Hood	Chemical Fume Hood	Chemical Fume Hood	Chemical Fume Hood	Chemical Fume Hood	
Safety Shower	Safety Shower	Safety Shower	Safety Shower	Safety Shower	Safety Shower
Eye Wash	Eye Wash	Eye Wash	Eye Wash	Eye Wash	Eye Wash