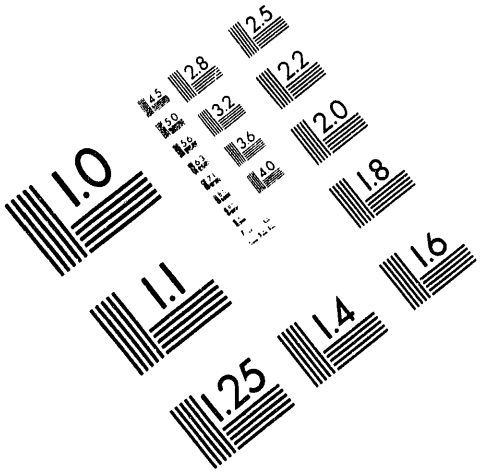

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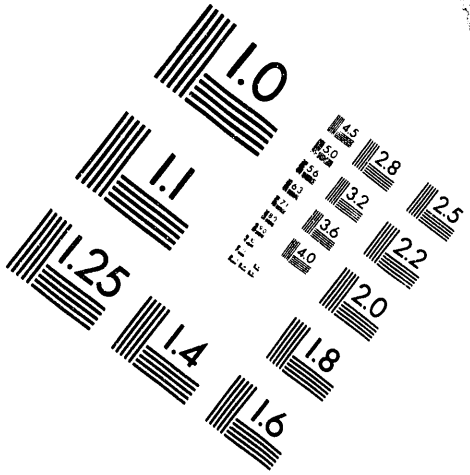

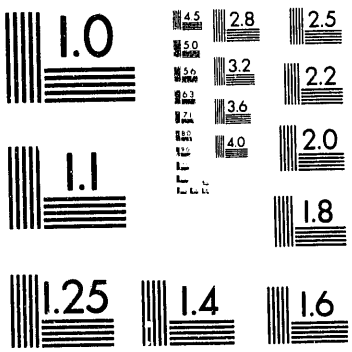

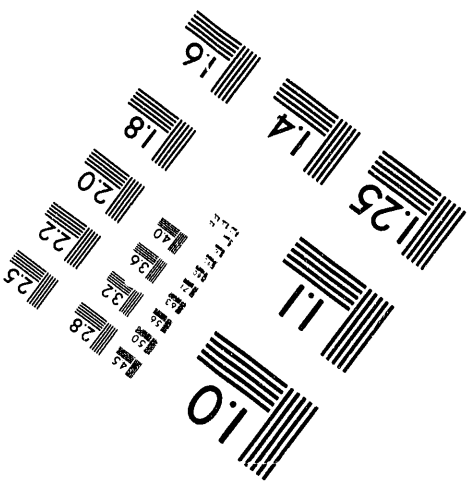

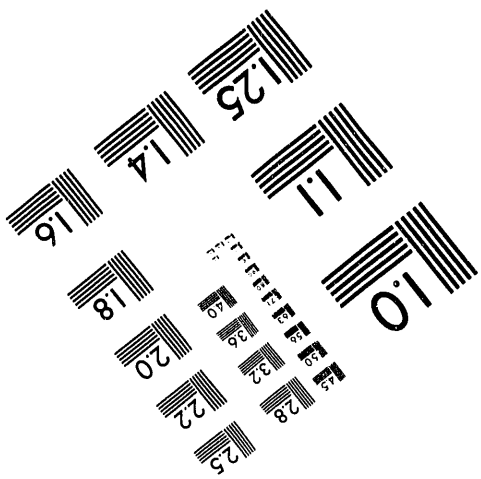

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CESIUM REMOVAL FROM HANFORD TANK WASTE

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Richland, Washington 99352

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Extended Abstract FYI
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CESIUM REMOVAL FROM HANFORD TANK WASTE

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Researchers at PNL are developing ion exchange processes to remove cesium from high salt, alkaline tank wastes at the Hanford site. The separated cesium will be concentrated and vitrified for disposal in the High-Level Waste Repository. The low-level waste fraction containing the majority of the waste constituents will be solidified in a grout waste form for disposal in underground concrete vaults. While the treatment and disposal requirements are still being defined, one goal is to remove enough cesium so that the low-level waste will meet the class A limits for Cs-137 (1 Ci/m^3).

An integrated laboratory testing and design effort is being used to speed the deployment of the ion exchange processes. The three main areas of laboratory investigation are equilibrium behavior, column performance, and material stability in the radioactive and chemical environment encountered during waste processing. Materials being investigated include a phenolic-carboxylic acid based resin, a resorcinol-formaldehyde resin, and the inorganic ion exchangers zeolite and silco-titanates. Concurrent with the laboratory work, a field deployable, modular compact ion-exchange unit is being designed to provide a means for rapid deployment of the technology. This distributed processing concept appears to offer several advantages relative to the traditional centralized fixed canyon facility. These include accelerating the start of tank waste pretreatment, flexibility to incorporate process improvements, flexibility to tailor a process to a particular waste type, and a reduced risk in deploying new processes.

1) Pacific Northwest Laboratory is operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-ACO6-76RLO 1830

FY93 PACIFIC NORTHWEST LABORATORY CESIUM REMOVAL FROM HANFORD TANK WASTE

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W. G. Richmond
L. A. Bray
B. C. Bunker
E. O. Jones

March 30, 1993

OUTLINE

- INTRODUCTION
- WASTE DESCRIPTION
- PRETREATMENT/DISPOSAL
- STRATEGY
- EXPERIMENTAL
- PROCESS SELECTION
- DEPLOYMENT
- SUMMARY

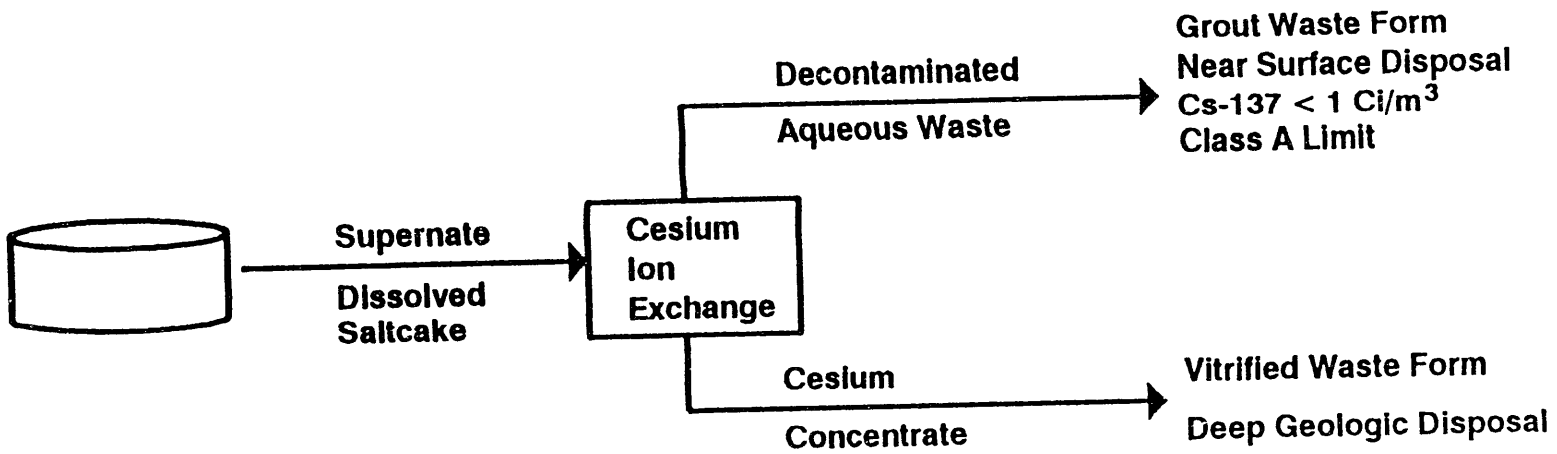
GENERAL WASTE TYPES

- LIQUID: SUPERNATANT AND INTERSTITIAL
  - High Salt (5 - 15 M Sodium)
- SALTCAKE: WATER SOLUBLE SODIUM SALTS
  - Generated by Extensive Evaporation
- SLUDGE: MIXTURES OF HYDRATED METAL OXIDES, HYDROXIDES, AND PHOSPHATES
  - Generally Insoluble

TYPICAL SUPERNATE COMPOSITION

$[Na^+]$	11.0
$[K^+]$	1.0
$[Al^{3+}]$	1.0
$[OH^-]$	5.0
$[NO_2^-]$	2.2
$[NO_3^-]$	3.5
Cs^+, Ci/L	0.5
Sr^{2+}, Ci/L	0.001
Total Volume (gallons)	1.0×10^6

Waste Pretreatment/Disposal



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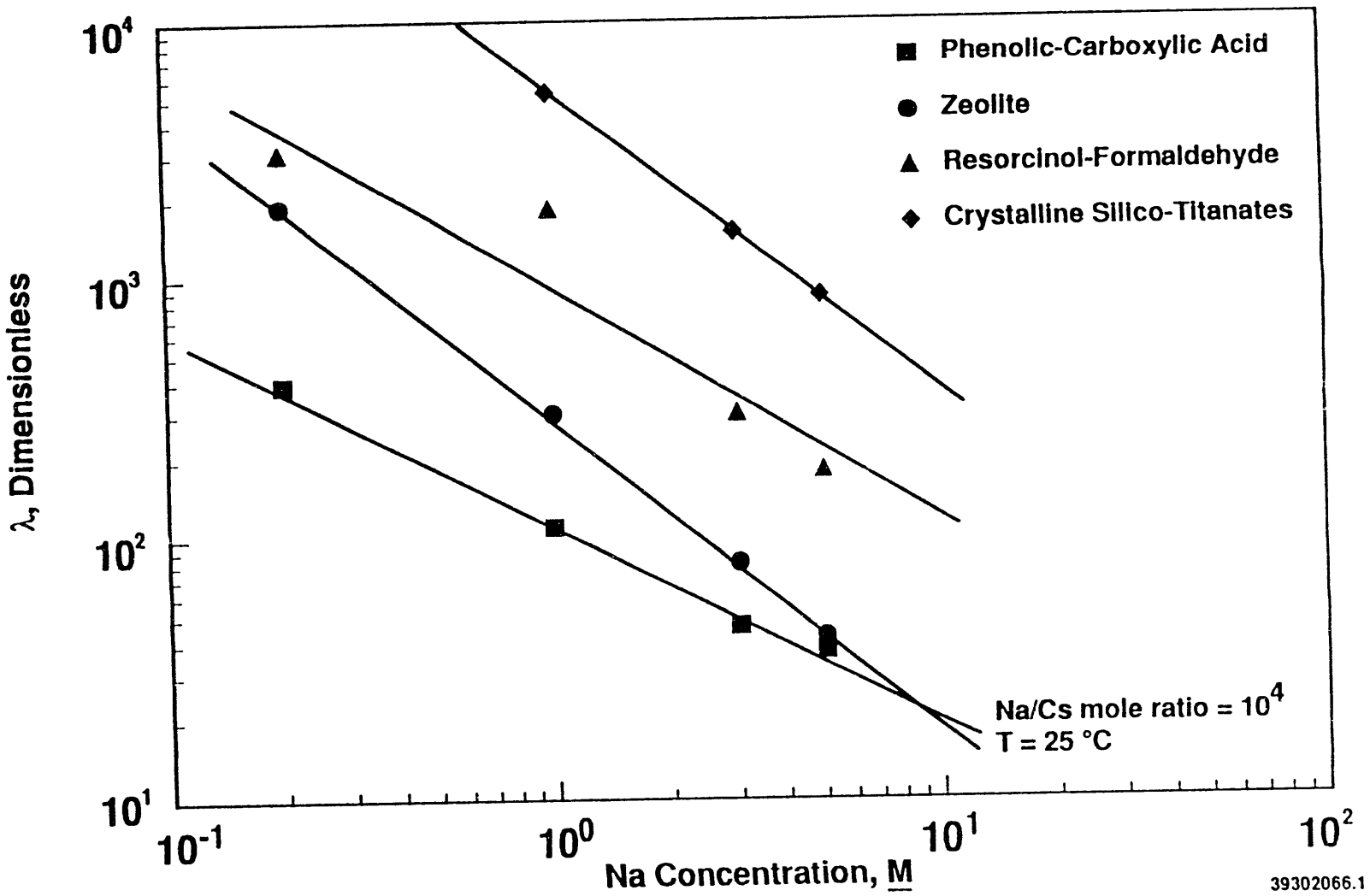
STRATEGY-CONCURRENT DEVELOPMENT

- EXPERIMENTAL
- PROCESS DEVELOPMENT AND SELECTION
- DEPLOYMENT

EXPERIMENTAL

- EQUILIBRIUM BEHAVIOR
  - Batch Contacts
  - Temperature (10° - 40°)
  - Total Ionic Strength
  - Competing Ions (Na, K)
  - pH
- COLUMN LOADING/ELUTION
  - 200 mL Columns
  - Loading - Vary Flow Rate (3-9 CV/hr)
  - Elution - Nitric/Formic Acid - Vary Concentration and Flowrate
- RADIATION TESTING
  - Waste Stimulants - Flow Through Testing
  - Cobalt 60 Source - 5 E + 8 Rads

Effective Capacity of IX Materials with Hanford Waste Simulants



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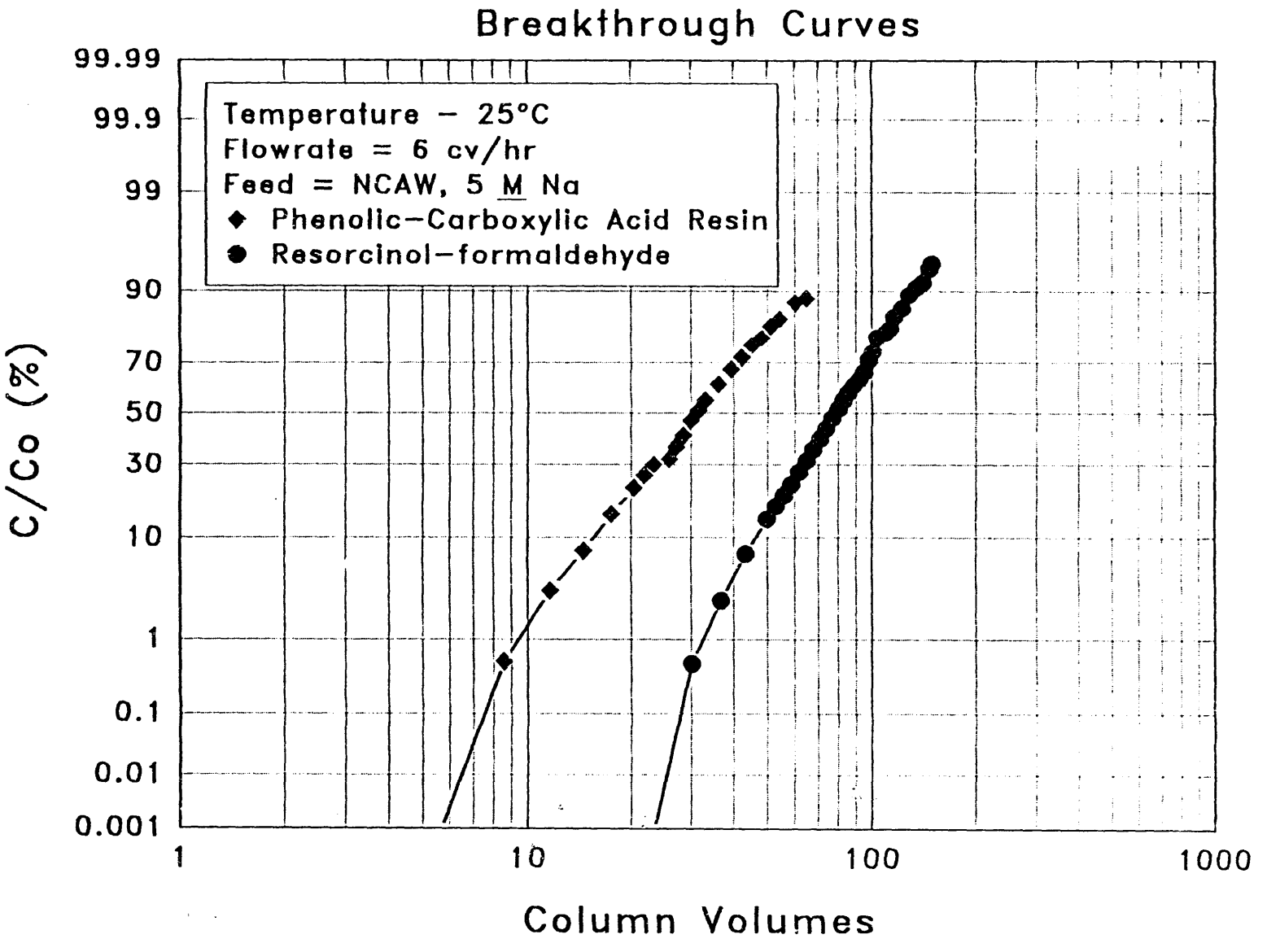

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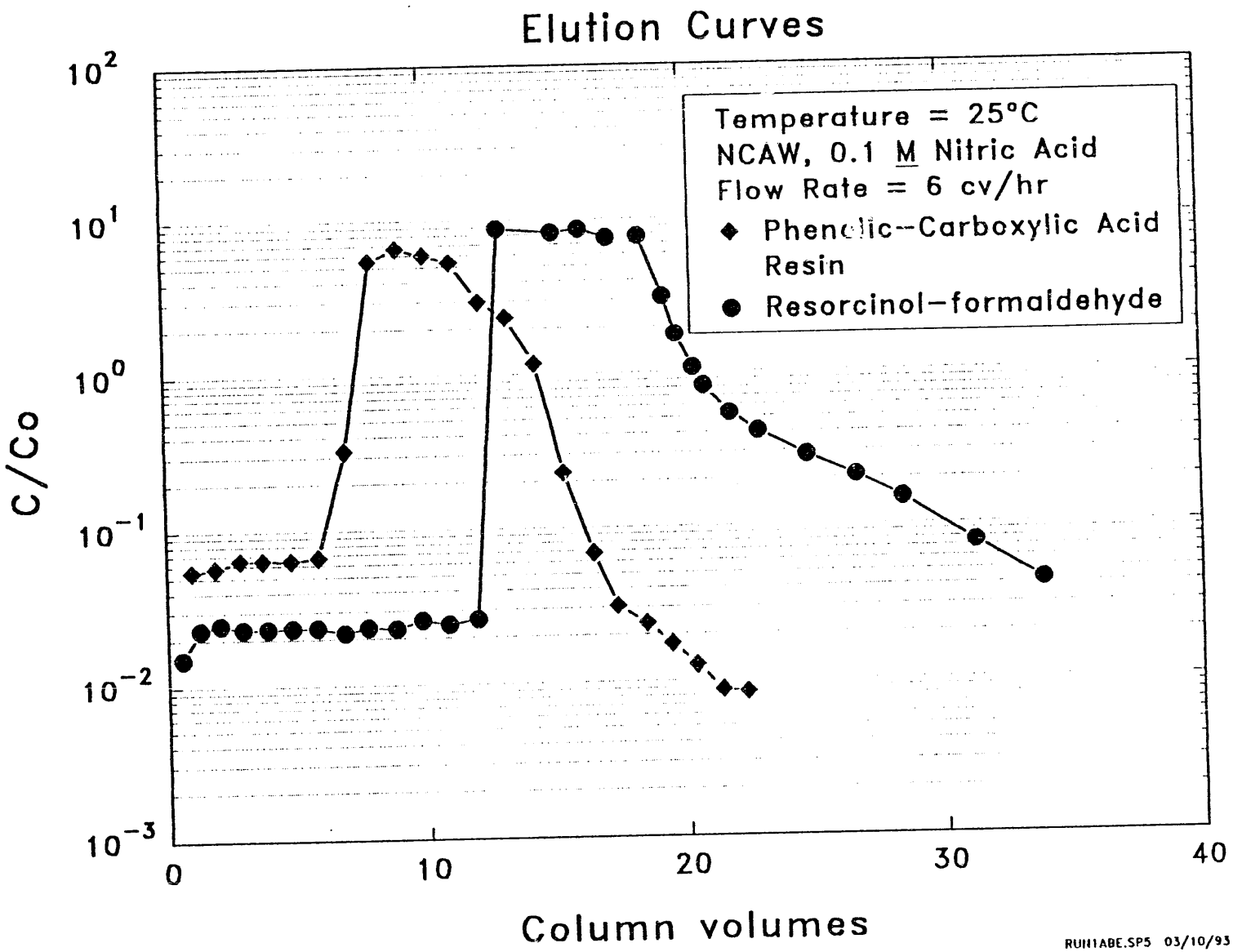
Elution Curves
Temperature = 25°C
NCAW, 0.1 M Nitric Acid
Flow Rate = 6 cv/hr
Phenolic-Carboxylic Acid Resin
Resorcinol-formaldehyde
C/Co
10^2
10^1
10^0
10^{-1}
10^{-2}
10^{-3}
0
10
20
30
40
Column volumes
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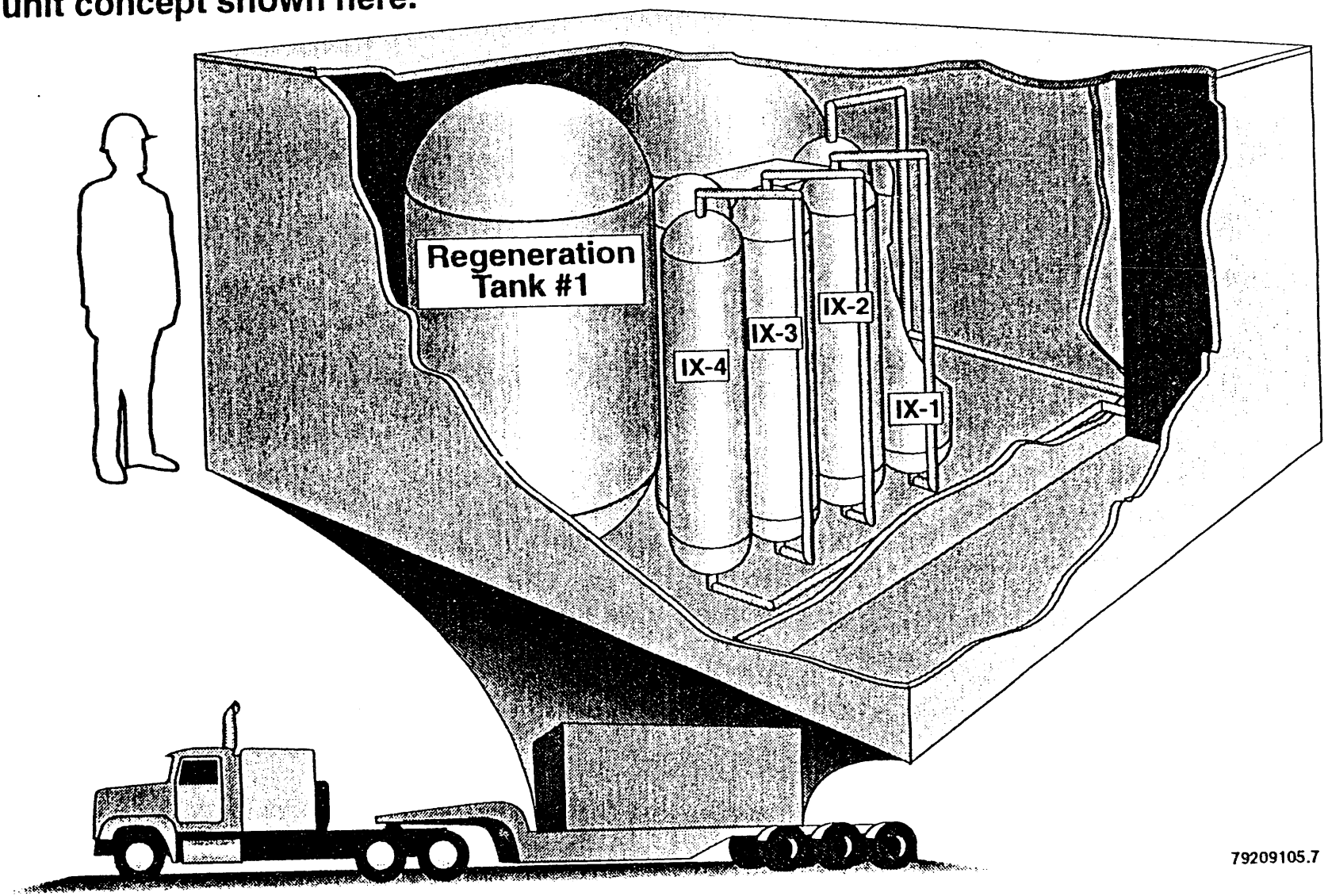
PROCESS SELECTION

Option	Decision	Reasoning
Resin	Formaldehyde Resorcinol	High Capacity; Selectivity
Elute versus Once-Through	Elute Column	Minimize Waste
Number of Columns	3 in Series / 1 Eluting	Attain High DF / Continuous Operation
Recycle or Recover HNO_3	Recycle Low [Cs] Eluant	Minimize Waste
Upward versus Downward Elution	Upward Elution	Higher Efficiency & DF
Dilution	None	Minimize Waste
Elute and Reload Onto Zeolite	Do not Reload onto Zeolite	Too much added Complexity; WFQ, Transport Issues

Compact Processing Unit

Selectively processes tank waste using mobile compact unit; different units may be combined depending on mission for a given tank. Cesium Ion-exchange unit concept shown here.



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CPU: FOUR MAJOR SUBSYSTEMS

- ION EXCHANGE PROCESS
- PROCESS CONTROL SYSTEM
- CONTAINMENT SYSTEM
- TANK FARM INTERFACE

CPU ADVANTAGES VERSUS CENTRALIZED FACILITY

- REDUCED COST
  - Initial Capital: $300-500 Million vs $1 Billion
  - Saves $2-7 Billion
- ACCELERATED SCHEDULE
  - 4-6 Years vs 7-15 Years
- REDUCED TECHNICAL UNCERTAINTY
  - Modular Facility Allows for Continuous Process Improvement
- REDUCED RISKS
  - Modular Concept; Allows for Lower Risk Development of New Processes

SUMMARY

- CESIUM REMOVAL AND CONCENTRATION REQUIRED FOR ENVIRONMENTAL AND ECONOMIC REASONS
- INTEGRATED LABORATORY TESTING AND DESIGN EFFORT TO SPEED DEPLOYMENT
- EXPERIMENTAL TESTING TO DEFINE EQUILIBRIUM BEHAVIOR, COLUMN DYNAMICS AND RADIATION STABILITY
- PROCESS SELECTION - FOUR COLUMN REGENERABLE SYSTEM USING A RESORCINOL-FORMALDEHYDE RESIN
- DEPLOYMENT IN COMPACT PROCESSING UNITS
  - Reduced cost
  - Accelerated pretreatment schedule
  - Reduced technical uncertainty
  - Reduced risk in new processes

INTRODUCTION

Waste Description

The Hanford Site in Washington State manages 177 underground storage tanks containing approximately 250,000 m^3 of waste generated during past defense reprocessing and waste management operations. These tanks contain a mixture of sludge, salt cake and supernatant liquids. The insoluble sludge fraction of the waste consists of metal oxides and hydroxides and contains the bulk of many radionuclides such as the transuranic components and Sr-90. The salt cake, generated by extensive evaporation of aqueous solutions, consists primarily of dried sodium salts. The supernates consist of concentrated (5-15 M) aqueous solutions of sodium and potassium salts. The bulk of the water-soluble radionuclides such as Cs-137 are contained in the salt cake and supernate.

Pretreatment/Disposal

The disposal options for these tank wastes are either vitrification to produce a waste form for disposal in the high-level waste repository or production of a low-level waste (LLW) grout for near-surface disposal. Systems engineering studies indicate that disposal of these wastes without futher treatment is precluded by economic and environmental considerations. Direct disposal of these wastes as a vitrified waste form in the high-level waste repository is prohibitively expensive due to a relatively large volume. Direct disposal of much of the waste as a LLW grout is unacceptable because of potential environmental impacts. Consequently, various pretreatment operations are under consideration for the separation and concentration of the radionuclides.

Although the pretreatment and disposal requirements are still being defined, one of the first steps in most pretreatment scenarios will be a sludge wash step followed by solid/liquid separation. Most of the cesium is expected to be in the aqueous liquids and it is these solutions that are the focus of the cesium removal process. This process is being designed with the goal of removing enough cesium so that the LLW will meet the NRC 10CFR61 class A limits for Cs-137 (1 Ci/m^3). The separated cesium will be concentrated and vitrified for disposal in the high-level Waste Repository.

The decontaminated aqueous liquid will be solidified as a LLW grout for near-surface disposal.

PNL Solution

An integrated laboratory testing and design effort is being implemented by the Pacific Northwest Laboratory (PNL) to speed the deployment of an ion exchange process for the removal of cesium from Hanford tank wastes. The three main areas of laboratory investigation are equilibrium behavior, column testing and performance, and material stability in the radioactive and chemical environment encountered during waste processing (see further discussion below). Materials being investigated include two organic materials and several inorganic ion exchangers. Concurrent with the laboratory work, a field deployable, modular compact ion-exchange unit is being designed to provide a means for rapid deployment of the selected process. This distributed processing concept appears to offer several advantages relative to the traditional centralized fixed canyon facility. These include accelerating the start of tank waste pretreatment, flexibility to incorporate process improvements, flexibility to tailor a process to a particular waste type, and a reduced risk in deploying new processes.

EXPERIMENTAL APPROACH

The three main areas of laboratory investigation are equilibrium behavior, column testing and performance, and material stability in the radioactive and chemical environment encountered during waste processing. Materials being investigated include a phenolic-carboxylic acid resin, a resorcinol-formaldehyde resin developed at Westinghouse Savannah River Co. (Bibler 1989; Bray 1990), a zeolite, and crystalline silico-titanates (CSTs) being developed at the Sandia National Laboratory and Texas A&M.

Equilibrium Behavior

The first step in assessing the ion exchange materials was to conduct a number of batch equilibrium tests using waste simulants. These experiments provide information on the capacity and selectivity of the exchangers. Performing these experiments at a defined set of conditions allowed for the rapid screening of new materials. Promising materials were tested over a wide range of conditions, allowing the selection of materials with superior performance. The parameters investigated included the temperature, total

ionic strength, concentration of competing ions (i.e. sodium), and the solution pH. Some of the test results are shown in Figure 1 where the distribution coefficient, λ, is shown as a function of the sodium concentration at a constant Na/Cs mole ratio. The distribution coefficient, λ, is defined as

$$\lambda = \frac{C_s}{C_l}$$

where C_s = the concentration of cesium on the exchanger, Ci/L
C_l = the concentration of cesium in the waste, Ci/L

The material with the largest effective capacity at these conditions is the CST with the resorcinol-formaldehyde resin next.

Column Testing

Column loading and elution testing has been initiated in laboratory-scale columns containing 200 ml of exchanger. A series of tests with waste simulants are planned at different flow rates to assess column kinetic behavior. The waste simulants contain Cs-137 in trace amounts to allow for rapid and accurate determination of the breakthrough curves by gamma counting. An example of the breakthrough curves for the phenolic-carboxylic acid and the resorcinol-formaldehyde resins is shown in Figure 2. The loaded columns will be eluted (Figure 3) at various conditions using nitric and formic acid to provide the data necessary to optimize the elution process and minimize the volume of high-level waste (HLW) produced. Column testing has been limited to the phenolic-carboxylic acid and resorcinol-formaldehyde resins. The CSTs have not been produced in sufficient quantities and fabricated into useable pellets to allow column testing. The zeolites have been dropped from further consideration because of their relatively low capacity and selectivity for cesium.

Radiation Testing

The impact of the radiation and chemical environment on the organic resins is being assessed. Small columns containing exchanger are being irradiated with a Co-60 source while waste simulants are passed through the bed of exchanger. Small amounts of exchanger sufficient for equilibrium testing will be withdrawn periodically for batch contacts to determine the

Figure 1. Effective capacity of IX materials with Hanford waste simulants

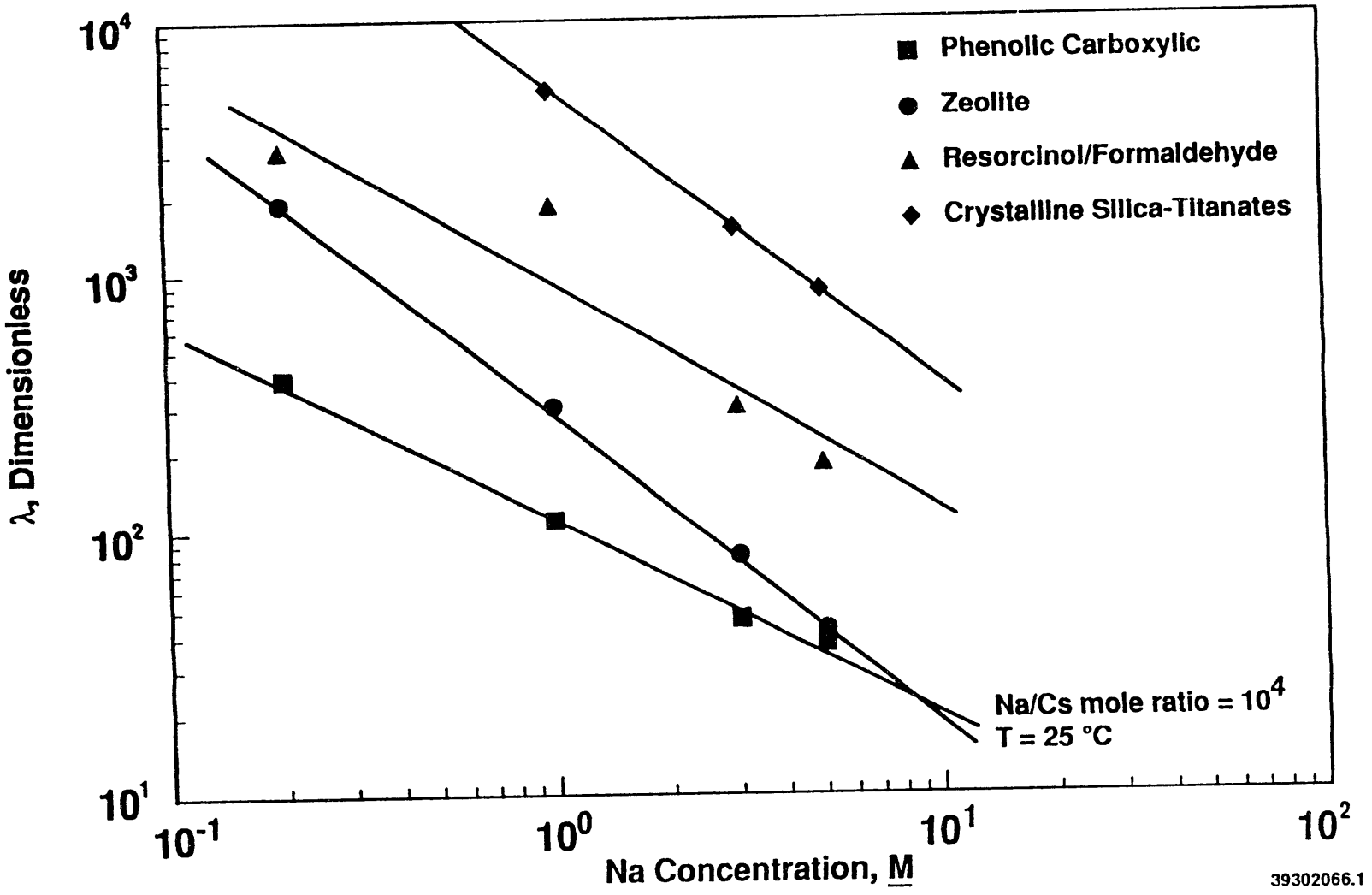

Figure 2, Breakthrough Curves

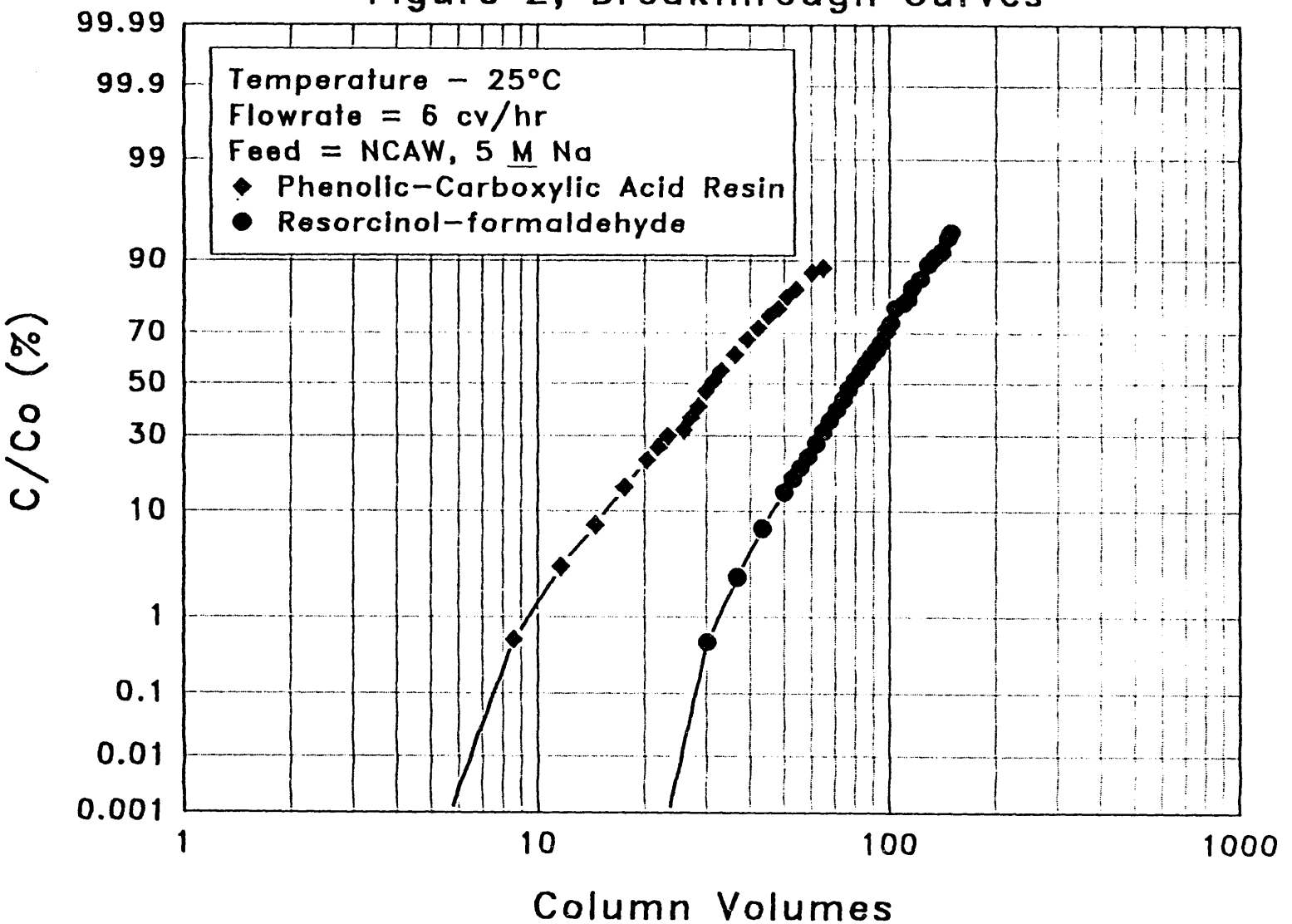

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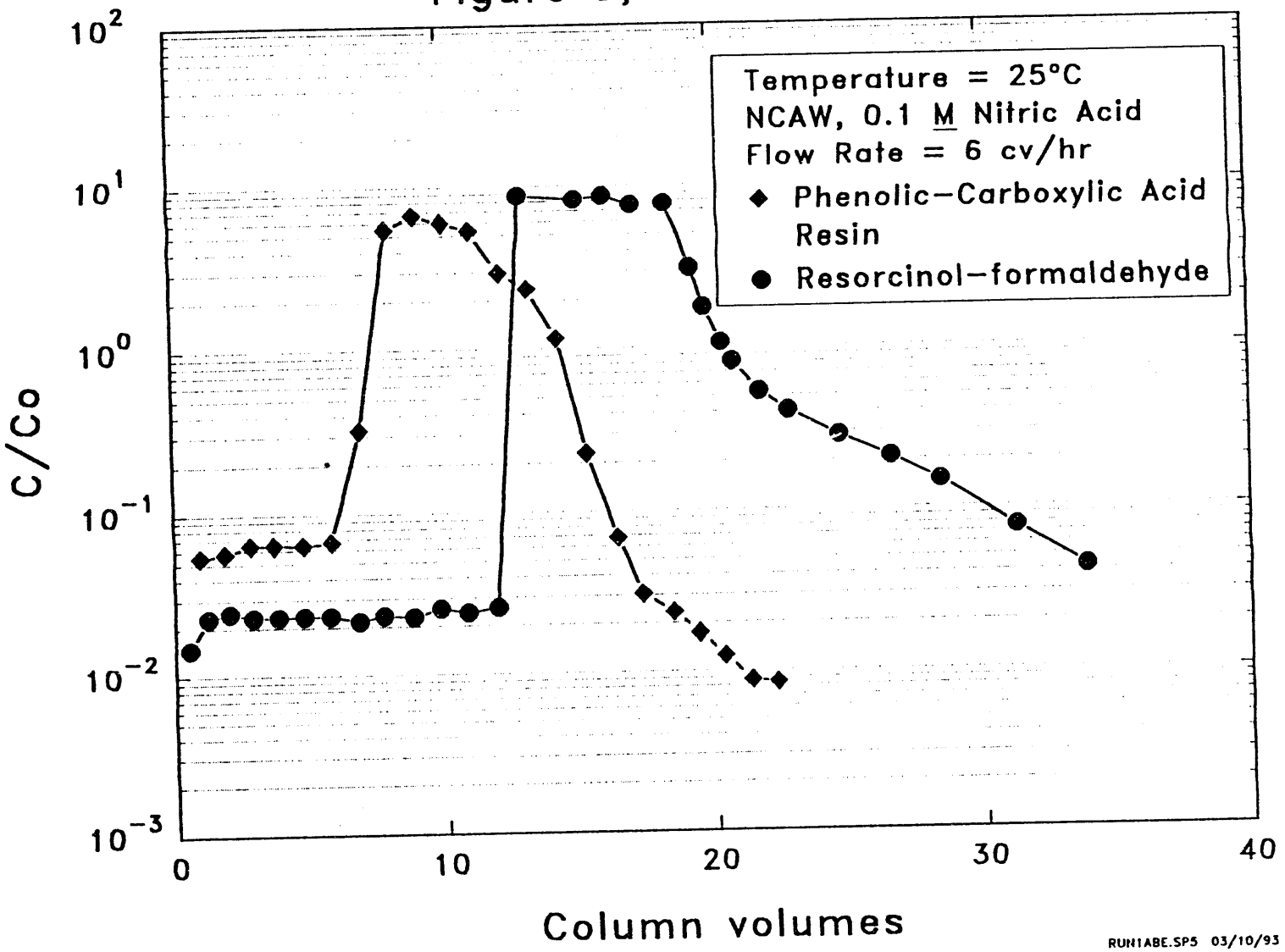
Figure 3, Elution Curves



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effect on capacity and selectivity. Exposure will be up to 5 E+8 Rads which represents several months of exposure if fully loaded at typical operating conditions.

PROCESS DEVELOPMENT AND SELECTION

Based on the experimental data collected to date and on available performance data in the literature, a four-column system has been selected to form the basis for the process design. At any given time, three of the columns will be in a loading cycle and one will be in the elution cycle allowing a continuous operation while maximizing the cesium decontamination factor. It is presently planned to process undiluted waste through the columns although dilution water could be easily added. While different eluants are being investigated in the laboratory, nitric acid has been chosen for the design. The columns will be eluted upflow, as this mode of operation has the potential to provide greater efficiency and higher DFs since the cleanest exchanger is now at the bottom of the column. The volume of cesium concentrate will be minimized by recycling the eluant that has a low cesium concentration.

The resorcinol-formaldehyde resin has been chosen for the column operation because of its high capacity and selectivity for cesium. The zeolites have been dropped from further consideration because of their relatively low capacity and selectivity for cesium and the lack of a suitable eluant. While CSTs have a higher capacity for cesium, these materials are still in the initial phases of development. Larger quantities need to be produced and fabricated into pellet form useable in a column operation. Commercial quantities of the resorcinol-formaldehyde resin have been produced by the Boulder Scientific Co. and the phenolic-carboxylic acid resin has been commercially available for several years.

DEPLOYMENT

PNL developed the concept of distributed processing for radioactive tank waste in fiscal year 1991. This development showed that processing of the tank waste in a distributed fashion was technically feasible and led to the conceptual development of a means to carry out this type of processing. The method developed was to use a series of unit process modules called Compact Processing Units (CPUs) to perform the processing required. The CPUs would be

deployed at or near the tank requiring the waste treatment and would be relocated following the processing of a tank of waste. The design concept for a CPU and the advantages of using CPUs as a deployment means for waste treatment technology are discussed below.

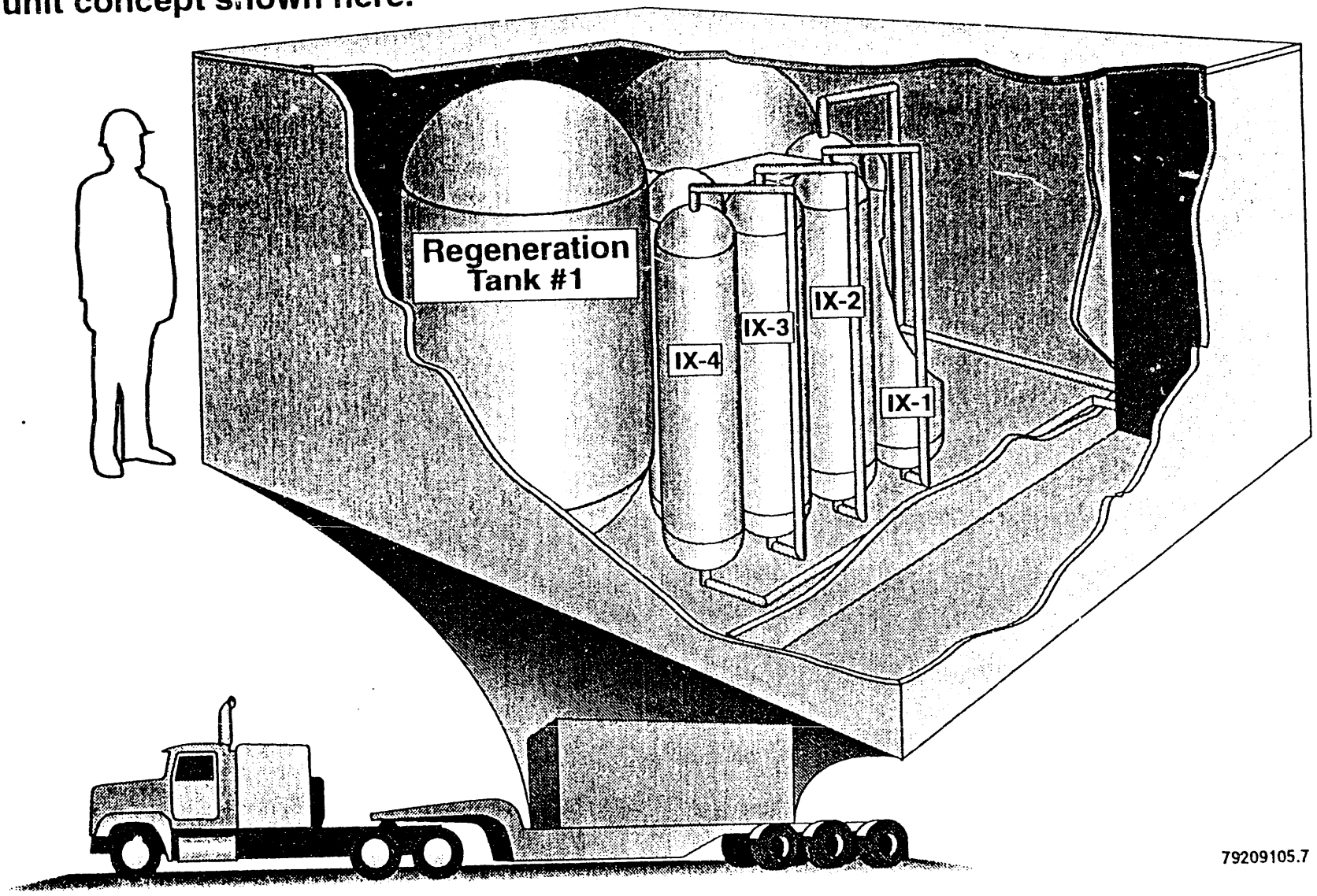
A CPU is a small relocatable process unit designed to treat tank waste at a rate of 2 to 5 gal/min (Figure 4). The CPU consists of four major subsystems: the containment system, the process system, the control system, and the process interface subsystem. This modular design concept will allow for off-site fabrication of the CPU components and reuse of the components for different process deployments.

The use of CPUs to process tank waste appears to have several advantages when compared to either in-tank processing or the use of centralized facilities. Compact processing appears to offer advantages relative to other processing alternative in four areas: cost, schedule, reduction of technical uncertainty, and reduction of new process deployment risk.

The overall cost of waste pretreatment is dominated by the cost of deploying the waste treatment processes. Large centralized facilities for supernate waste treatment are expected to cost approximately $1 billion. A comparable treatment facility using a CPU concept is estimated to cost approximately $300 to $500 million. The reduction in cost for a CPU alternative is believed to be due to several key differences in design concept between the facilities, as will be described in subsequent paragraphs in this paper. In addition to reducing total capital cost for deployment of waste treatment capability, the CPU concept allows waste treatment capacity to be deployed in a time-phased manner in accordance with capacity requirements. This type of deployment and capital spending profile is not possible with a centralized facility where the entire capital cost is incurred before any waste treatment begins. This advantage is significant relative to a centralized facility deployment scenario.

Compact Processing Unit

Selectively processes tank waste using mobile compact unit; different units may be combined depending on mission for a given tank. Cesium Ion-exchange unit concept shown here.



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The critical path for deployment of waste pretreatment processes involves four major activities: process development and selection, process design, facility design, and facility construction. The deployment of processes using a centralized facility carries out all of these activities serially primarily because of the interactions and impact of the process design on the facility design and the high costs associated with design changes. This schedule in effect requires that the process be selected and fully developed 7 to 10 years before it can be deployed. The smaller scale of the CPU allows the final development of the process to proceed in parallel with the design of the CPU. This development scheme, coupled with the smaller scale of the CPU, allows deployment of waste treatment processes in 4 to 6 years as compared to the 7 to 15 years required for a centralized facility. This rapid deployment schedule has the potential to reduce waste treatment costs by $2 to $7 billion based on the schedule acceleration.

One of the primary sources of technical and cost uncertainty for the waste treatment process is related to the type of facility used to deploy the processes. The high cost and lengthy schedule for process deployment in a centralized facility makes selection of the correct process a key decision for successful facility deployment. Because this selection must take place very early in the overall deployment schedule, a significant cost and schedule risk is associated with this decision. This risk is due to the large cost to design and build the facility before it is known that the process will work. The fact that this decision must be made early in the design process increases this risk. The CPU deployment allows for the modular deployment of waste treatment processes in small, relatively inexpensive units. This reduces the risk associated with the selection of the process to be deployed. The CPU deployment concept also allows the phased selection of waste treatment processes, further reducing the risk by allowing early process selection decisions to be made where the processes are at a mature state of development and deferral of process selection to allow further development for other processes. This type of phased process selection is not possible with a centralized facility.

The treatment of the tank waste requires the development of new waste separation and treatment processes. In some cases there is significant uncertainty as to which process will best meet the treatment requirements.

The inclusion of multiple processes for the same treatment is not desirable in a centralized facility because of the great impacts on facility cost. The reduced cost of process deployment using a compact processing concept will allow the cost-effective testing of several potential processes before selecting the best process. This lower cost reduces the risk for the deployment of new processes and allows for continuous process improvement as better treatment processes are developed.

Currently PNL is developing the first CPU for field deployment. This process unit will process tank waste to remove cesium using a regenerable ion-exchange system. The system design will be completed in October of 1993 and issued for construction as a firm fixed price procurement. When the system is received on site it will be subjected to extensive non-radioactive verification testing prior to deployment for a radioactive demonstration in 1997. The demonstration will last for a period of 1 year and will treat 1,000,000 gallons of radioactive tank waste. If the demonstration is successful, the CPU will remain deployed as part of the overall tank waste remediation process system.

SUMMARY

An integrated laboratory testing and design effort is being implemented by the PNL to speed the deployment of an ion exchange process for the removal of cesium from the Hanford tank wastes. The three main areas of laboratory investigation are equilibrium behavior, column performance, and material stability in the radioactive and chemical environment encountered during waste processing. The process design is based on a four column operation with three columns being loaded in series while the fourth column is eluted with dilute nitric acid. A resorcinol-formaldehyde resin that was developed at the Savannah River Site has been chosen as the ion exchange material. Concurrent with the laboratory work, a field deployable, modular compact ion-exchange unit is being designed to provide a means for rapid deployment of the technology. This distributed processing concept appears to offer several advantages relative to the traditional centralized fixed canyon facility. These include accelerating the start of tank waste pretreatment, flexibility to incorporate process improvements, flexibility to tailor a process to a particular waste type, and a reduced risk in deploying new processes.

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