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Feasibility Study and Concepts for Use of Compact Process Units To Treat Hanford Tank Wastes

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CHEMICAL TECHNOLOGY DIVISION

FEASIBILITY STUDY AND CONCEPTS FOR USE OF COMPACT PROCESS UNITS TO TREAT HANFORD TANK WASTES

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June 1994

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OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831
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for the
U.S. DEPARTMENT OF ENERGY
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1. INTRODUCTION

A team of experienced radiochemical design engineers and chemists (qualifications listed in Appendix A) was assembled at Oak Ridge National Laboratory (ORNL) at the request of the Underground Storage Tank Integrated Demonstration (USTID) Program to evaluate the feasibility and perform a conceptual study of options for the use of compact processing units (CPUs), located at the Hanford, Washington, waste tank sites, to accomplish extensive pretreatment of the tank wastes using the "clean-option" concept.[1] This concept includes chemical separation process steps that would minimize (1) the volume of the high-level wastes and (2) the toxicity of the low-level wastes.

The concept of using CPUs for pretreatment of Hanford tank wastes is currently receiving consideration. The term "CPU" is generally considered to mean a relatively small, transportable unit that can be used to perform one or more of the processing steps needed to achieve waste pretreatment goals; use of several CPUs together would be required to meet all of the goals. Reasons for considering the use of CPUs for waste pretreatment as an alternative to a large, central facility include the following:

1. Early progress in waste pretreatment will be easier to achieve with CPUs because of the long lead-time involved in construction of a large, central facility. The high cost of a large, central facility can lead to funding delays caused by the massive up-front funding requirement.
2. Potential safety problems that currently exist in some of the Hanford waste tanks can be remediated by processing to reduce the content of radioactive materials and hazardous chemicals. Early processing may prevent accidents that could cause harm to people and the environment.
3. Less technical certainty will be required to proceed with the design and operation of each particular CPU because of the lower initial investment required.
4. Initially, CPUs can function as a demonstration tool to facilitate technology development, while providing early progress in waste pretreatment. This will be valuable especially for Hanford tank wastes because of the different waste compositions that must be treated and the possibility that different processes may be required for different wastes.

The scope of the ORNL study included an evaluation of the constraints of the various chemical process operations that may be employed and the constraints of necessary supporting operations. The

latter include (1) equipment maintenance and replacement, (2) process control methods, (3) product and by-product storage, and (4) waste disposal.

2. "CLEAN-OPTION" PROCESS STEPS[2]

All of the Hanford waste storage tanks contain materials that have been made alkaline to minimize corrosion of the tanks. These materials contain varying concentrations of radioactive materials in the form of alkaline supernatant liquids, solidified salts, and insoluble sludges. Some of the single-shell tanks have suspected leaks, and thus the free liquid phase has been transferred to nonleaking tanks.

The "clean-option" process steps (Fig. 1) have been designed to retrieve, separate, and treat the liquid supernates and alkaline-soluble salts separately from the alkaline-insoluble sludge constituents. The initial step is to retrieve wastes from the tanks. Supernatant liquid and dissolved salt cake will likely be retrieved by means of hydraulic methods. These methods may also be used to sluice a slurry of alkaline-insoluble sludges. Thus a solids/liquid separation step will be required. A step is potentially included to destroy organic materials in the waste liquids if necessary to enable subsequent removal of the radioactive contaminants.

The alkaline supernate decontamination process steps include (1) removal of radiocesium (the dominant gamma emitter in Hanford tank wastes), (2) organic complexant destruction, if necessary, (3) polishing decontamination to remove the minor radioactive constituents, such as ^{90}Sr and ^{99}Tc, if required, (4) evaporation to remove water and concentrate the decontaminated salts, (5) denitration, if necessary, and (6) solidification of the low-level waste for interim storage. An inherent part of the alkaline supernate decontamination is the sludge washing process steps, which are intended to remove soluble constituents, such as sodium, aluminum, cesium, phosphates, and possibly uranium and chromium, from the alkaline-insoluble sludges. Solutions produced by water washing (to remove sodium) and caustic washing to dissolve and remove aluminum and to metathesize phosphates would be processed through the same steps as the original liquid supernate. Solutions produced by carbonate washing would be processed separately to recover uranium stock.

Processing of the sludges to separate the radioactive components requires dissolution in acid (possibly two stages), followed by a series of separation steps. The number of separation steps and the complexity of these steps depends, in general, upon the extent of separation necessary for the radioactive constituents. The extent of separation is dependent on acceptance criteria for final solid

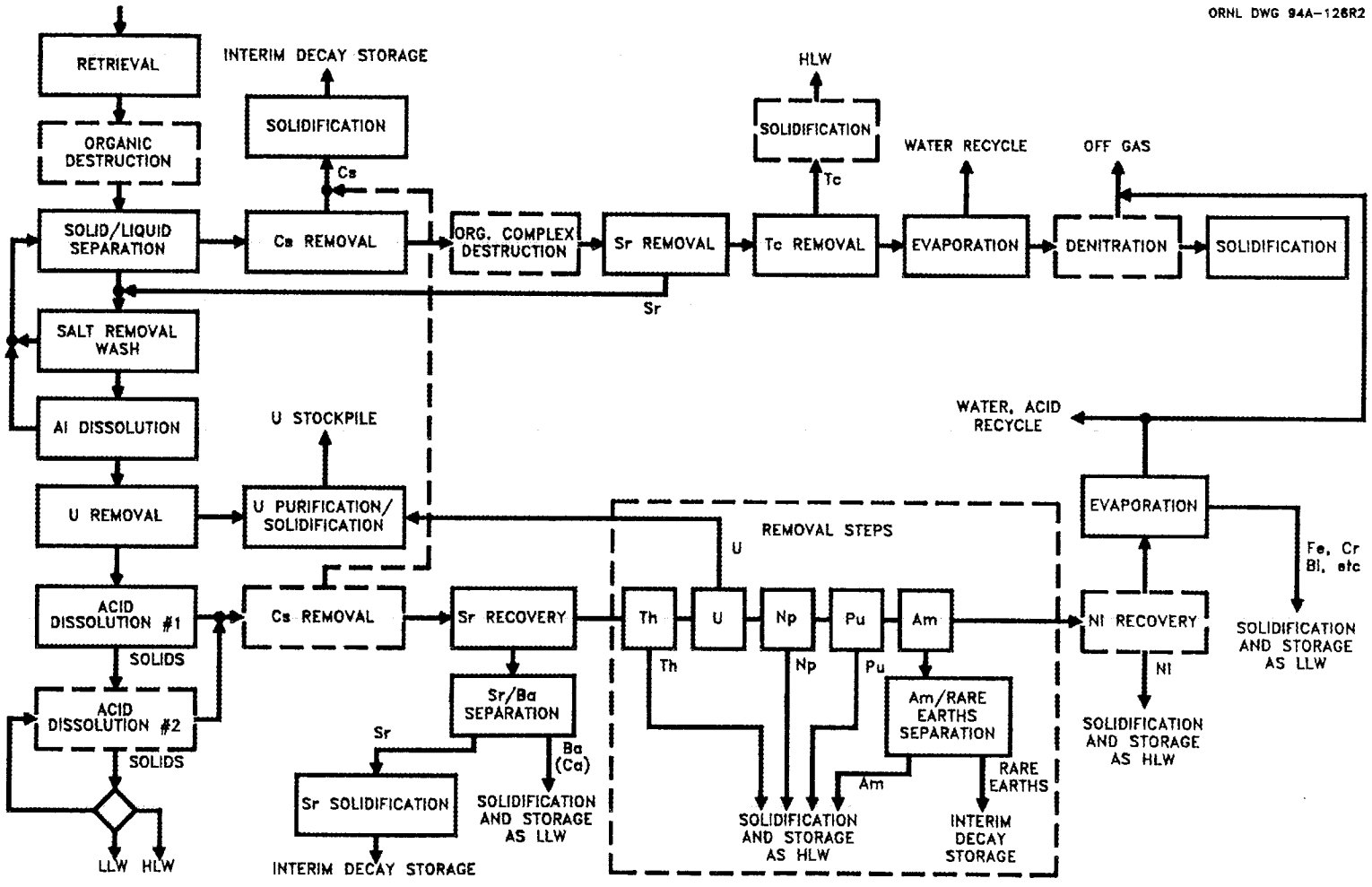

Fig. 1. Functional "clean-option" process steps.

waste forms. Clearly, the low-level waste must be "nontransuranic" ("non-TRU"), and the transuranic waste volume must be minimized. The "clean-option" process includes acidic separation steps to remove (1) residual radiocesium, (2) radiostrontium, (3) residual uranium, (4) thorium, (5) neptunium, (6) plutonium, and (7) americium. The nonradioactive components, such as iron, chromium, bismuth, etc., are intended to be solidified and disposed of as solid low-level waste.

3. CHARACTERISTICS OF A FEASIBLE COMPACT PROCESSING UNIT

3.1 CONFIGURATION

The CPU will be a transportable steel containment box that will house the chemical process equipment needed to treat the wastes. The exact dimensions of a CPU will be determined by the specific chemical equipment required to perform the waste treatment; however, for purposes of this study, a 10-ft-wide by 12-ft-high by 20-ft-long box, illustrated in Fig. 2, is used to describe the concept. The concept includes several containment boxes (CPUs) to provide a modular configuration, sufficient to hold all the necessary equipment.

Each CPU will need up to three roof access ports, which will be the pathway for adding or removing equipment or remote maintenance tools. The access ports would be designed to interface with other devices (such as the Mobile Maintenance Facility described below) via double-door arrangements or glove box bagging methods. This would maintain containment of the CPU and the interfacing device while they are connected and would provide sealing of both units when separated, with minimal transfer of contamination outside the containment boxes.

The chemical processing equipment in the CPU would be considered as the primary containment for the hazardous materials being treated in the CPU. The CPU box would be considered as the secondary containment; it would be connected to the waste tank by a separable trunk, as illustrated in Fig. 3. The trunk would serve as containment for the pipes from the tank to the CPU and also as an off-gas duct from the CPU to the tank. Standard connections would be used at the CPU end, but the tank end would be equipped to match the existing tank connections. The connection of the trunk at the tank, if not amenable to contact methods, would be performed remotely, as is presently conducted on the Hanford site.

The trunks would also be of a modular configuration to permit connection interchangeability between CPUs and other facilities. The trunks would provide containment of contaminated piping as well as physical support and protection to other interconnections. Piping contained within the

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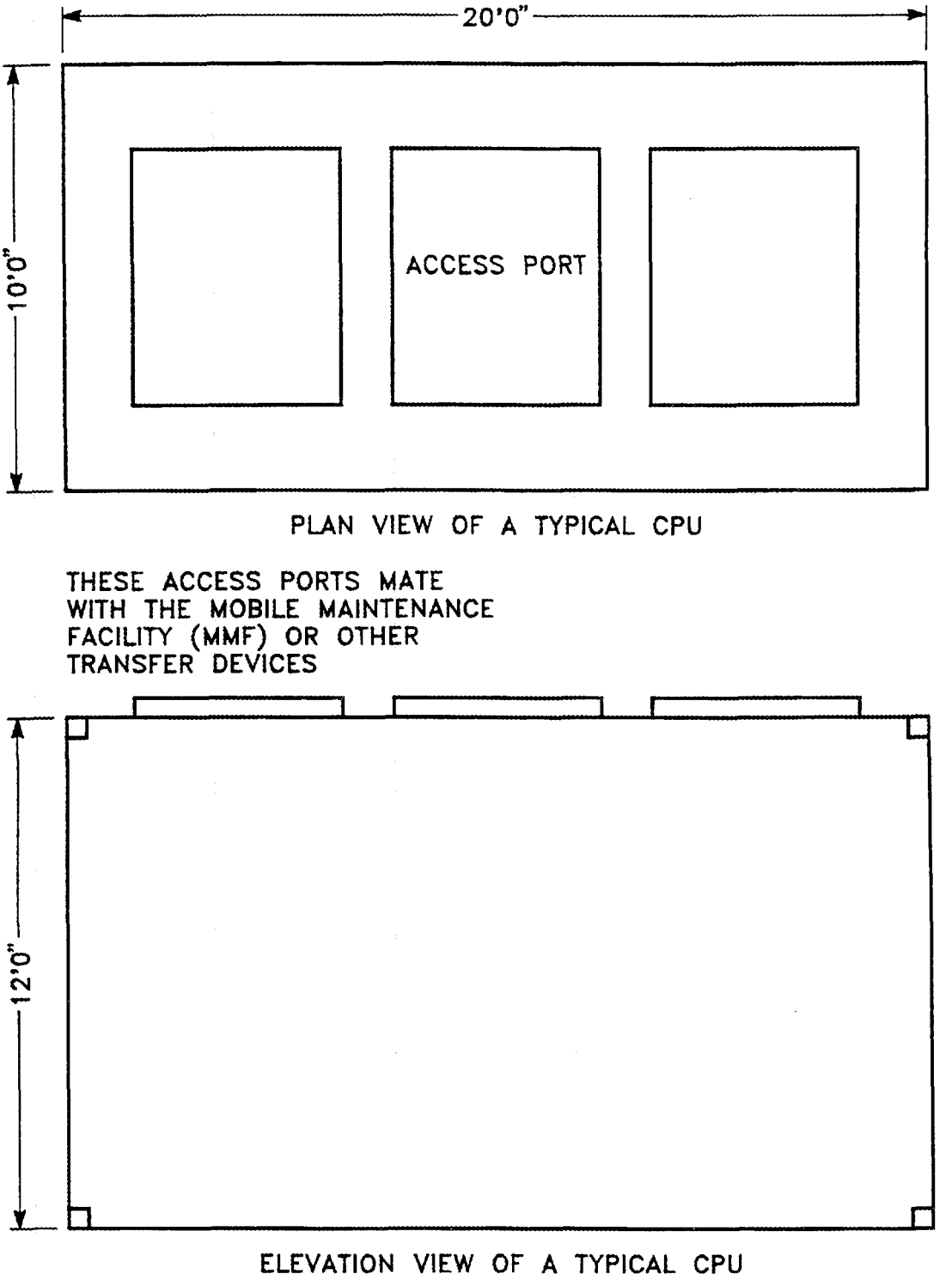

Fig. 2. Schematic arrangement of a typical CPU.

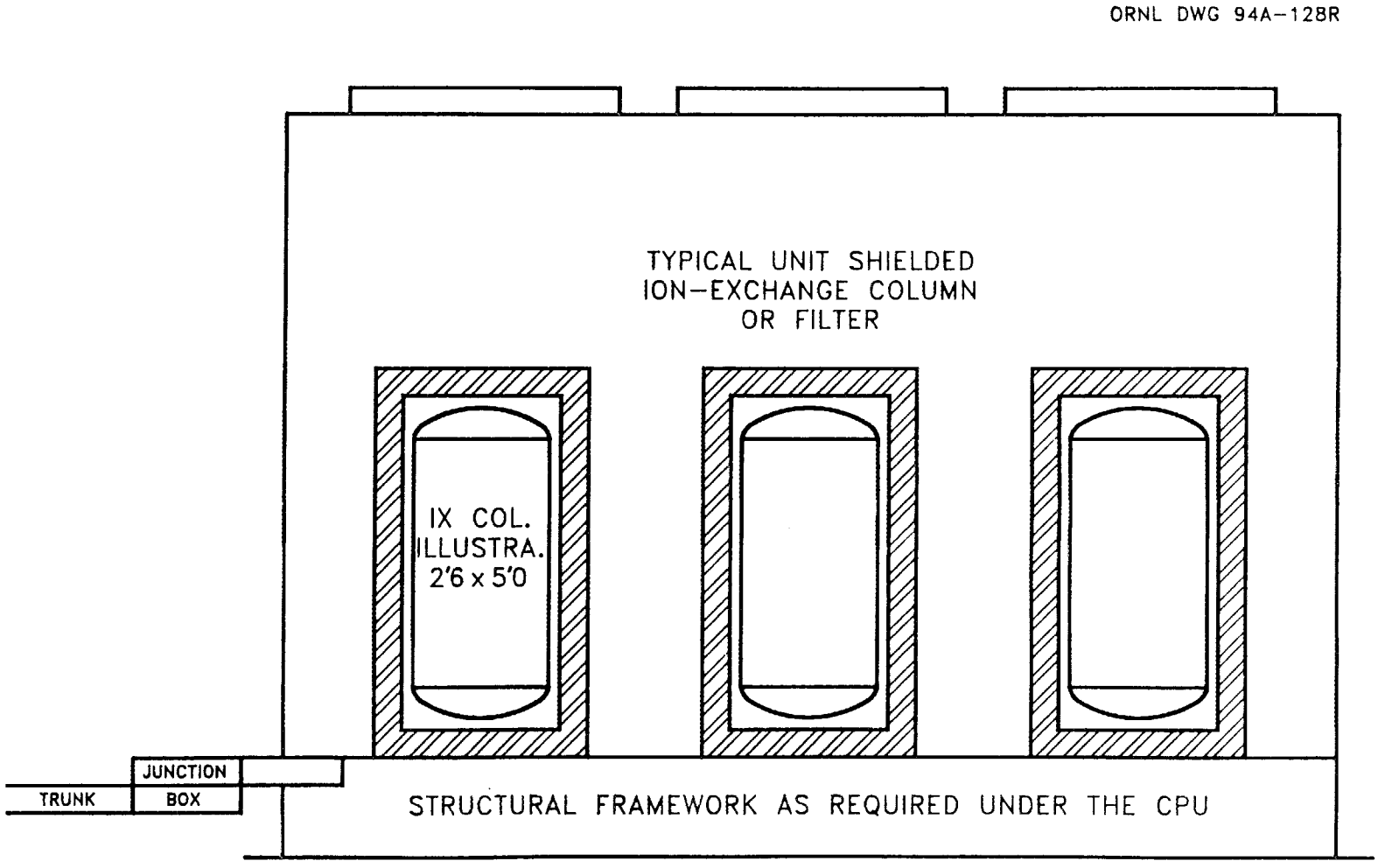

Fig. 3. Illustration of CPU equipment shielded for radioactivity.

trunks would include (1) connections between adjacent CPUs that house other waste treatment equipment, (2) inlets for cold chemical and routing for other service piping, and (3) routing for instrument and power wiring.

3.2 OPERATIONS CONTROL

Operation of equipment in the CPUs would be supervised from a control room connected to the enclosures by an umbilical cable or similar system. The control room would be portable and located near the CPUs or at a more distant site.

3.3 SHIELDING FOR RADIOACTIVITY

The thickness of shielding walls surrounding a CPU could be minimized by using unit shielding around the equipment as the primary shielding for radioactive materials in the CPU, that is, enclosing the equipment item with lead or other shielding material. The sludge filters/accumulator tanks and cesium ion-exchange (IX) columns are examples of such equipment.

This concept is illustrated in Fig. 3. In some cases, this approach may permit the CPU enclosure to serve only as a means of containment and would be particularly advantageous to operations that concentrate gamma activity within a small volume. This would enable (1) more "hands-on" operation and maintenance (when necessary); (2) easier replacement of equipment; (3) the use of "positive connectors" (jumpers) instead of valves, which are likely to leak; and (4) the disconnection and transportation of cesium-loaded ion-exchange columns to a better location for cesium product handling.

3.4 MAINTENANCE OF EQUIPMENT

During operation, the equipment in the CPUs would be maintained, as necessary, by means of remotely operated tools. This method of maintenance would avoid lengthy shutdowns for decontamination operations that would be necessary to permit contact maintenance. However, provision of an airsuit port in the wall of the CPU for manned-entry maintenance following proper decontamination should be provided.

All of the CPUs located at a particular waste tank site would be designed in a modular configuration, as described previously. This would permit using a common maintenance device. The device, shown schematically in Fig. 4, could be called the "Mobile Maintenance Facility (MMF)" and

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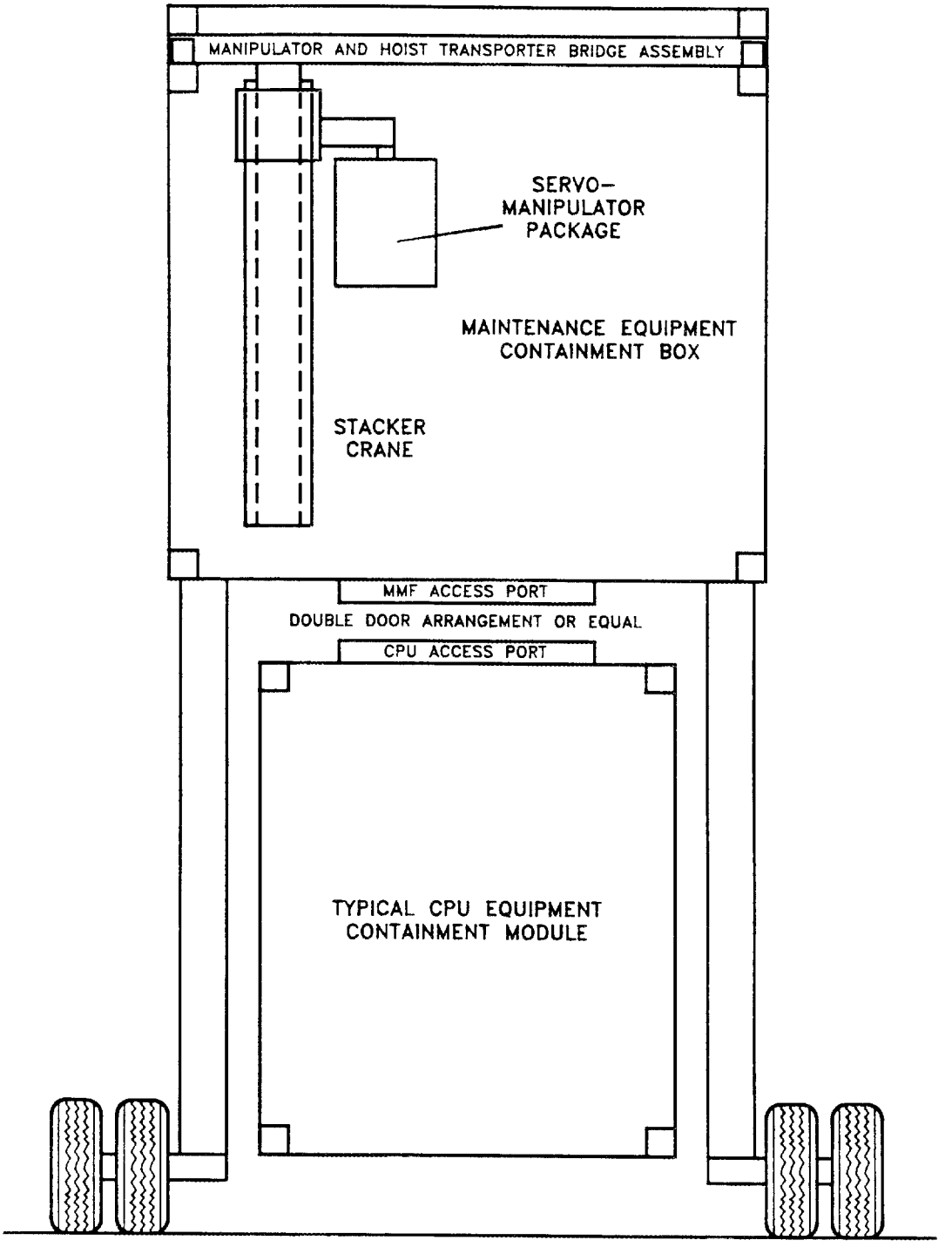

Fig. 4. Schematic arrangement of the Mobile Maintenance Facility for CPU maintenance.

would facilitate repair or replacement of equipment in any of the CPUs. The MMF could also be used as a means to transport equipment between the CPU and other facilities, such as a central facility provided for repair or disposal of equipment. The MMF would be a mobile, self-sufficient, maintenance equipment containment box.

The containment box would be positioned by the MMF transport system to mate with one of the ports on top of the CPU. The MMF enclosure box would be equipped with the necessary remote tools to reach down into the CPU to perform maintenance.

The components of the MMF would include (1) the containment box for the maintenance tools, (2) the stacker crane that would provide the ability to deploy a servomanipulator and television viewing into the CPU, (3) a double-door or equal interface arrangement to maintain containment of the MMF and the CPU independently or while connected, and (4) a transport vehicle that moves the box. The structure supporting the box would straddle the CPU and facilitate mating the box to one of the ports on top of a CPU by raising or lowering the box.

The MMF enclosure would be equipped with a remotely operable crane, either mounted on a separate bridge or on the same bridge that supports the stacker crane. The stacker crane would (1) support and deploy the servomanipulators, (2) provide mounting for a small auxiliary hoist to be used in concert with the manipulator, and (3) support television cameras for viewing the necessary remote manipulations. Remote operations would be supervised from a portable control room connected to the enclosure by an umbilical cable or by wireless signals from a distant permanent control facility. An airsuit port for manned-entry maintenance following proper decontamination would be provided for the MMF enclosure.

The MMF would be equipped with a small off-gas system to maintain a negative pressure and any other services needed during transport between destinations. When the MMF is connected to a CPU or other facility, it would be provided with off-gas and other necessary services provided by the interfaced destination.

The use of the MMF for servicing the CPUs would dictate site arrangement to provide access for the common maintenance device. Arrangement of the process equipment in the CPU with respect to the access port and maintenance tools would be necessary.

3.5 ARRANGEMENT OF A GROUP OF INTERCONNECTING CPUs

Placement of CPUs directly over the existing pumping pits located above a waste storage tank was examined and considered as undesirable. The pump pits should remain accessible for

maintenance of the contents in the pit. The CPU would require a large floor opening, require handling large remote tools, or have to be removed, possibly during a processing campaign if maintenance of the pump is required.

One configuration of a group of CPUs is shown in Fig. 5. This arrangement, located on the circumference of a waste tank, will provide shorter connections between adjacent or other CPUs and provide access for the MMF from a perimeter roadway.

4. FEASIBILITY OF CHEMICAL PROCESS OPERATIONS WITHIN CPUs

Considering the constraints of process equipment contained within CPUs as described above, the team evaluated the feasibility of chemical processes that might be employed to perform certain "clean-option" steps. The overall conclusion was that relatively small-scale, simple operations, such as fixed-bed ion exchange and precipitation/filtration processes, would be the most feasible for employment in CPUs. In contrast, processes such as continuous solvent extraction would not be sufficiently compact and would be too complicated and difficult to operate within CPUs. Such processes demand the simultaneous management of multiple inlet and outlet streams and their associated feed and collection tanks, evaporators, storage tanks, and solvent cleanup systems.

4.1 ALKALINE PROCESS STEPS

The consensus of the evaluation team was that the "alkaline" "clean-option" processing steps (those that would precede sludge dissolution in acid) could be successfully carried out in modular equipment within CPUs but that the limitation of relatively small-scale processing rates would likely apply. Initial application would be developmental and might evolve into larger scale operations.

The feasibility of successful application of CPUs for the "alkaline" process steps would be dependent on several characteristics of the wastes and the required treatment processes. In the opinion of the ORNL evaluation team, the presence of dissolved organic compounds in the Hanford tank wastes is unlikely to significantly interfere with the sorption of radiocesium onto an ion-exchange material; thus, organic destruction prior to cesium removal is not likely to be necessary. Since ^{137}Cs is the predominant source of gamma radiation in the Hanford tank wastes, heavily shielded and

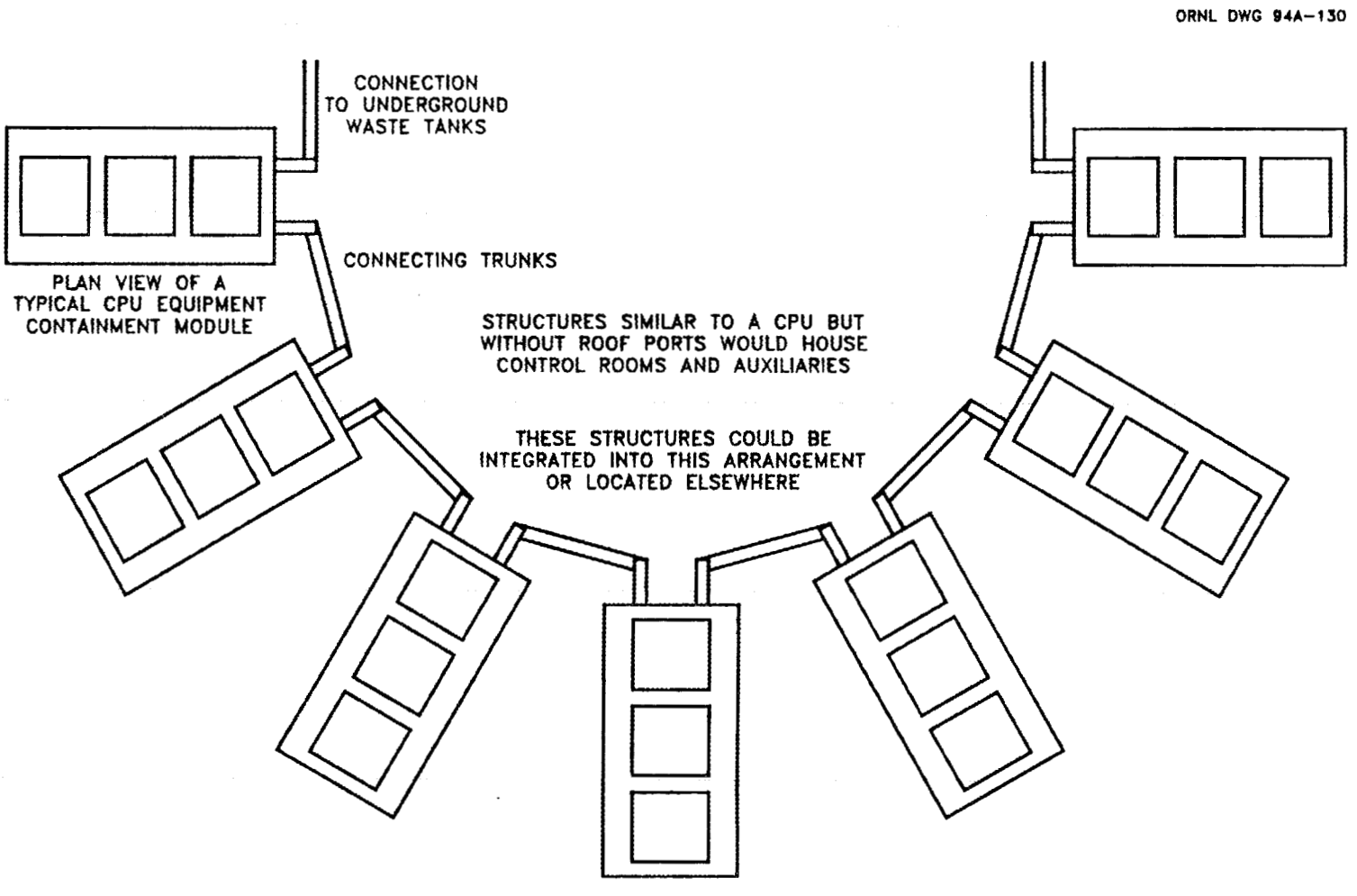

Fig. 5. Schematic arrangement of CPUs at a tank site.

contained equipment must be used for the process steps preceding and including ^{137}Cs sorption, elution, and solidification. The preceding steps would include retrieval and solids–liquid separation.

Following radiocesium removal from the alkaline supernates and dissolved salts, more complicated CPU-type equipment could be used within a lightly shielded containment structure to process the decontaminated liquid. This processing would include (1) destruction of organic complexants, if necessary; (2) further decontamination from additional radionuclides; (3) concentration, probably by means of evaporation; (4) denitration, if necessary; and (5) solidification of the decontaminated salts.

Hanford tank farm personnel are currently retrieving supernates from suspected leaking single-shell tanks. Their technique utilizes submersible pumps or jet-pumps, submerged within a 12-in.-diam salt well in the center of the tank. The consensus of the ORNL evaluation team is that this type of pump system could be used effectively to provide feed to a series of shielded and portable filter and ion-exchange units. When used with a downstream evaporator for concentration of the decontaminated salt solution, the evaporator condensate could be recycled to the waste tank to dissolve additional salt cake and to provide a continuous liquid feed to the ion-exchange system. This would reduce the requirement for water addition and increased total volume of low-level wastes.

Feed adjustment by means of water addition to dilute the salt concentration or by means of caustic addition to increase the pH may be necessary. These additions could be made via in-line mixers with downstream sampling or process fluid monitoring, perhaps with closed-loop instrumentation for process control.

Solids–liquid separation will be a key step. Several methods may be applicable within CPUs. A backflushable cartridge filter may be acceptable to well-settled sludge, but a backflushable cross-flow filter system would be needed in most cases to operate satisfactorily when removing entrained solids from the pump discharge.

Salt-cake dissolution and sludge washing operations could be carried out more feasibly within the waste storage tanks rather than "mining" the cake and sludge and washing the sludge in external equipment. Submerged pumps similar to those used at the Savannah River Site (SRS) could be used to provide mixing within the tanks. This in-tank washing technique is planned for use at the SRS. The sludge washing steps would include caustic washing to remove aluminum salts, water washing to remove soluble sodium salts, and possibly carbonate washing to remove uranium salts.

Ion exchange is the preferred method for cesium sorption, and the SRS-developed resorcinol-formaldehyde resin[3] is the currently preferred sorbent since it can be used at sufficiently high pH levels to prevent precipitation of the dissolved aluminum that is present in most Hanford waste tanks

while providing a higher selectivity for cesium than other organic resins. However, the effectiveness of this resin in high-activity solutions and during reuse in multiple cycles of sorption and elution is as yet unproven. The current database indicates that this method will meet the objectives, but it does not adequately define the performance of this resin for design purposes. In any case, methods for resin replacement and spent resin disposal must be planned.

The shielded, portable ion-exchange columns loaded with radiocesium could be eluted into an existing double-shell tank or they could be transferred into a shielded central facility, such as the existing Waste Encapsulation and Solidification Facility, where the radiocesium would be eluted and converted to a concentrated, stable, solid form for interim storage. The latter method appears to be more favorable. The ion-exchange columns could receive the necessary maintenance and resin replacement within this central facility. This substantially simplifies the CPU operational requirements.

The initial alkaline pretreatment steps, applied in relatively small-scale, modular equipment, would serve as an opportunity to develop the pretreatment process on a pilot scale using real waste feeds. CPU equipment would be tested after processes and equipment are developed that give (1) satisfactory performance and decontamination of the tank liquids from soluble nuclides and TRU sludges and (2) adequate operability in regard to the organic complexant destruction step and the denitration step, should these be required.

4.2 ACIDIC PROCESS STEPS

The acidic process steps, beginning with sludge dissolution, require more complicated process and support equipment. Also, the acidic process steps will probably require shielded and remotely maintainable equipment because the solutions are likely to contain residual cesium and will definitely contain substantial bremsstrahlung emissions from ^{90}Sr and some gamma radiation from ^{154}Eu.

The acidic process steps are much more feasibly used in central processing facilities such as the existing Purex Plant. However, some very simplified acid process steps such as batch dissolution and precipitation/filtration may be feasibly employed in CPUs at relatively slow process rates.

5. A SIMPLIFIED ALTERNATIVE FLOWSHEET TO "CLEAN OPTION" AND THE EQUIPMENT FOR ITS IMPLEMENTATION IN CPUs

The simplified process steps that would be feasible for operation in CPU equipment are shown in Fig. 6. The process steps to be used for retrieval, solids-liquid separation, and treatment of the liquid supernates and alkaline-soluble salts are similar to those shown in Fig. 1 for the "clean-option" type flowsheet. However, the process steps following acid dissolution of the sludges include only relatively simple precipitation-filtration, fixed-bed ion-exchange, evaporation, and solidification operations. The acidic low-level waste liquid resulting from these steps will contain a variety of metal ions (Cr, Fe, Bi, Zr, etc.), including residual sodium and aluminum that were not removed in the preceding sludge washing steps.

6. CONCEPTUAL PRETREATMENT OF TANK 101AW WASTES

As a demonstration of feasibility, the process steps shown in Fig. 6 were evaluated conceptually for the treatment of wastes now stored in Tank 101AW. The evaluation, described below, included (1) equipment flowsheets, (2) process solution flow rates and concentrations, and (3) conceptual equipment arrangements in CPUs. The conditions illustrated would permit the contents of Tank 101AW to be processed in ~1 year. Removal of alkaline-insoluble sludges from Tank 101AW would be relatively slow initially; thus the sludge dissolution and processing would not occur frequently until 101AW is nearly empty of liquid supernate. Alternately, the sludge could be returned to 101AW or routed to another tank and processed later when convenient.

6.1 PROCESSING OF ALKALINE SUPERNATE AND DISSOLVED SALTS

As indicated in Fig. 6, the process steps in this part of the flowsheet include (1) removal of liquid from the tank; (2) separation of entrained solids from the liquid by means of filtration; (3) sorption of cesium onto an ion-exchange resin contained in a series of modular, transportable, shielded columns; (4) sorption of strontium, technetium, and other minor ionic impurities onto specially selected ion-exchange resins or adsorbents in lightly shielded fixed-bed columns; and (5) evaporation of the salt solution to a semidry cake. This scenario assumes that destruction of organics prior to strontium and technetium removal is not required. Also, it is assumed that the loaded ion-exchange

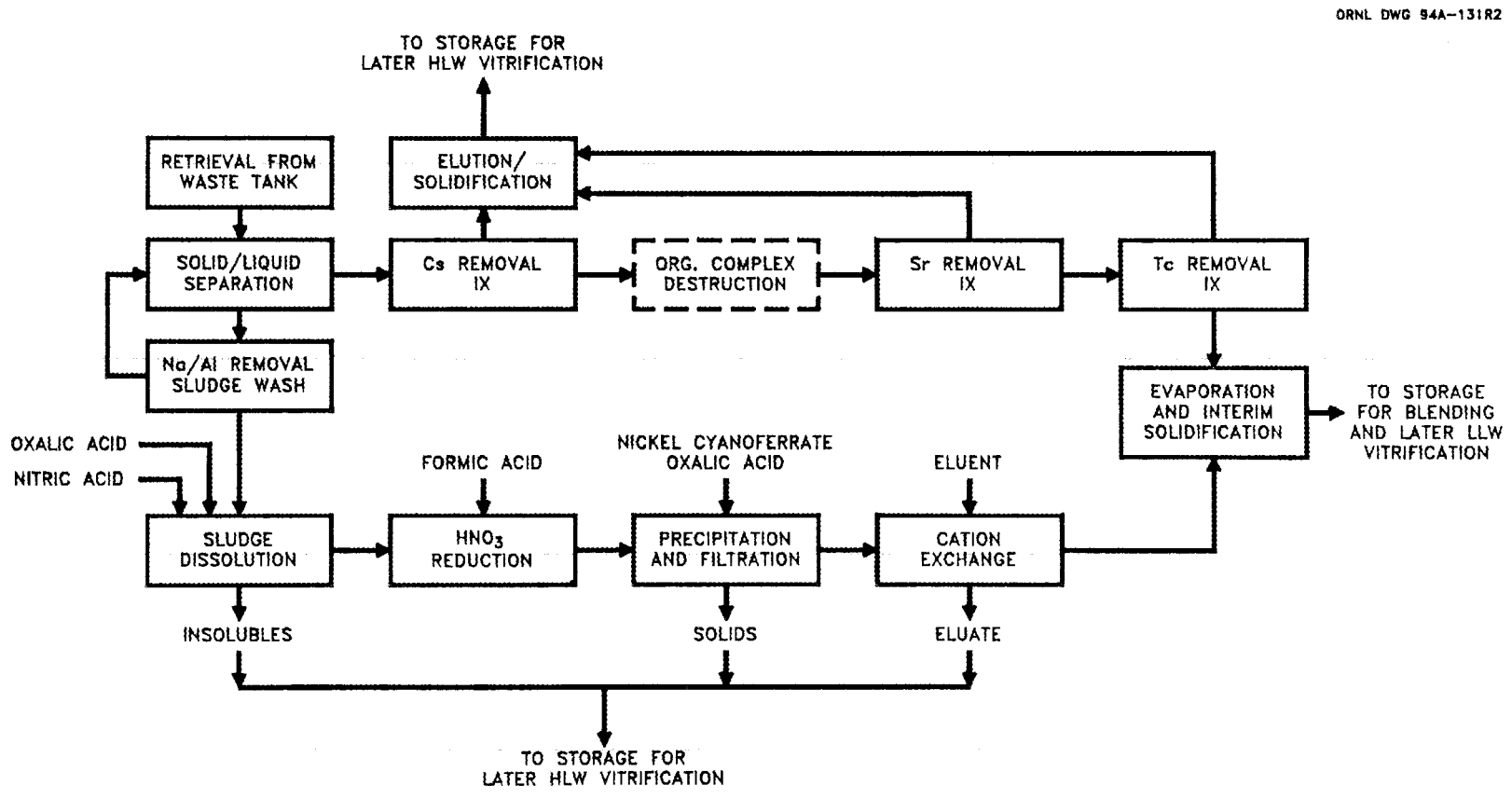

Fig. 6. Functional process steps simplified for use in CPU equipment.

columns are transported to a central facility for elution and solidification of the radionuclides and for replacement and disposal of the spent ion-exchange resin as necessary. The process chemistry options for radionuclides removed from alkaline supernate were previously discussed by Swanson.[2]

The equipment flowsheet is shown in Fig. 7, and the flow rate and stream composition data are listed in Table 1. Waste slurry from Tank 101AW would be pumped into a ~100-gal capacity, shielded mixing tank/solids-liquid filter system (Tank "T-1" and Filter "F-1"), taking filtrate as feed to the shielded, cesium removal ion-exchange columns.

When the accumulated solids content in Tank "T-1" reaches ~50 kg (actual amount must be determined by process tests), the transfer of waste slurry from 101AW would be stopped temporarily while the accumulated solids are washed to remove soluble sodium, aluminum, etc., and the washed sludge is dissolved and processed as described below. The batch sludge washing, dissolution, and processing steps would require approximately 1 day to accomplish. Thus the alkaline solution pretreatment would be suspended during this time. As an alternative, a second mixing tank/filter system could be added to enable uninterrupted pretreatment of the alkaline solutions while simultaneously performing the acid dissolution/processing steps in the other mixing tank/filter system.

The alkaline solution pretreatment ion-exchange system includes three shielded, cesium removal columns in series to maximize removal of ionic cesium. The series of cesium removal column is loaded until cesium breakthrough is detected from the second column. At this point, loading is stopped, and the first column is removed for transport to elution facilities. The second column is placed in the first position, and an eluted column is deployed at the second position. The third column is a polishing column and is changed very infrequently as required. Also, the strontium and technetium columns should require replacement only infrequently.

The effluent from the ion-exchange system is concentrated in a two-stage evaporator system to produce a semidry (15% water content) salt cake for interim storage and subsequent feed to a low-level vitrification system. The first stage evaporator is a conventional thermosyphon unit that concentrates the salt to ~13 *M*. The second stage evaporator is a wiped-film unit that produces the salt cake with minimum water content. Overheads from both evaporators are routed to a collection tank and are recycled to the mixing tank for dilution and to 101AW for salt cake dissolution.

Equipment arrangement in CPUs is illustrated in Figs. 8 and 9. As indicated, all of the ion-exchange columns have attached shielding, and the shielded columns can be removed from their containment CPU after disconnection of pipe lines. The cross-flow filter unit and each of the

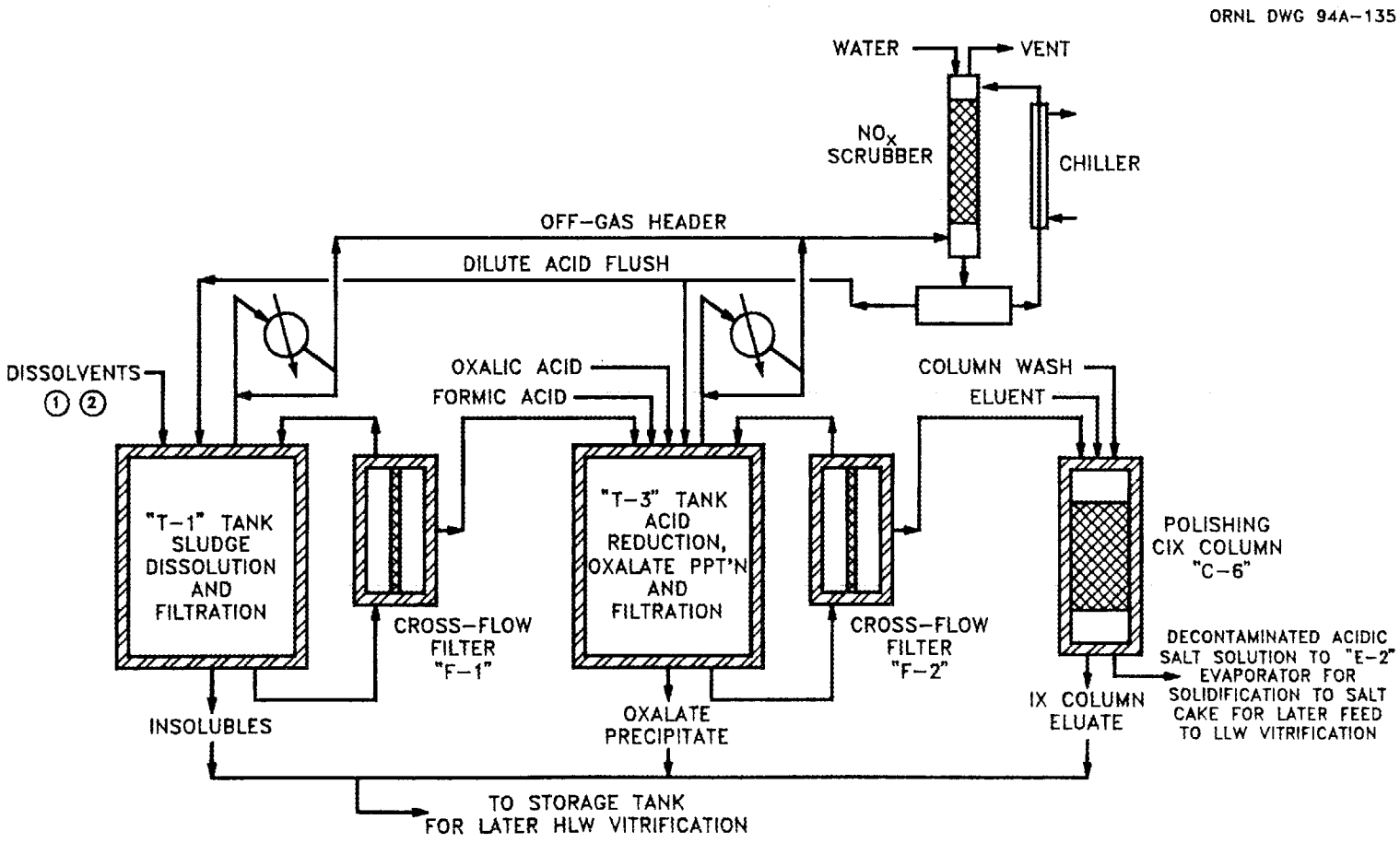

Fig. 7. Processing of alkaline supernate and dissolved salts.

Table 1. Flow and composition of streams for alkaline supernate in dissolved salt processing

Stream		Flow (L/min)	Na (*M*)	Salt (g/L)	Cs (*M*)
1	Liquid waste from 101AW	10.0	11.0	990	0.00016
2	Water for Na adjustment	11.8	0.0	0	0.0
3	Feed to filter	60.0	5.0	450	0.000073
3a	Return from filter	40.0	5.0	450	0.000073
4	Feed to Cs removal	20.0	5.0	450	0.000073
5	Clean salt from IX columns	20.0	5.0	450	0.00000007[a]
6	First evaporator salt concentrate	7.8	12.8	1167	0.00000019
7	First evaporator overheads	12.2	0.0	0	0.0
8	Clean salt product cake	5.5	18.2	1654	0.00000026
9	Second evaporator overheads	2.3	0.0	0	0.0
10	Recycle water to 101AW	2.7	0.0	0	0.0
11	Water for IX column flush	20.0	2.0	80	0.0

[a]Assumes that the decontamination factor is 1000.

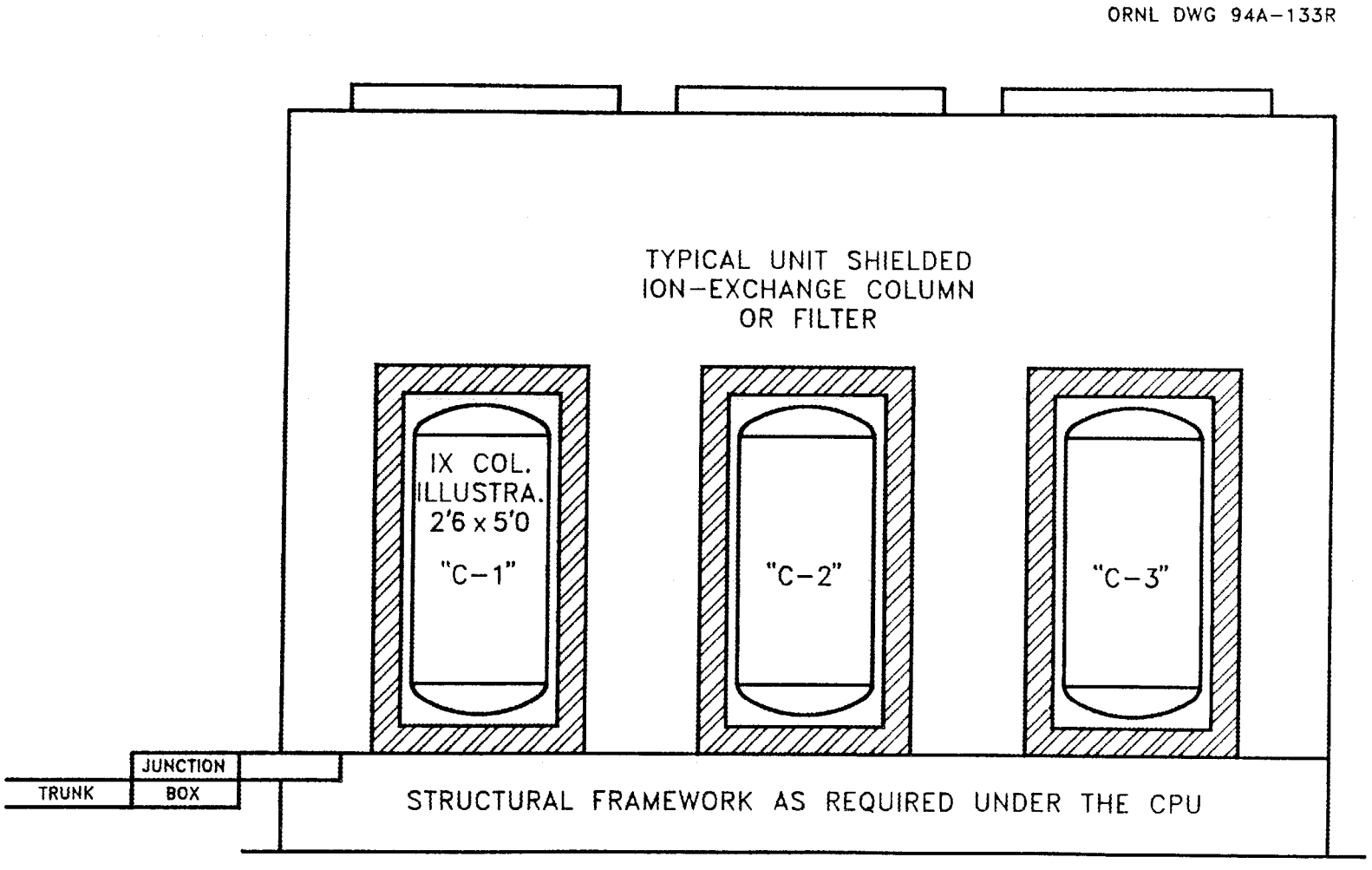

Fig. 8. CPU arrangement for filtration and cesium removal IX.

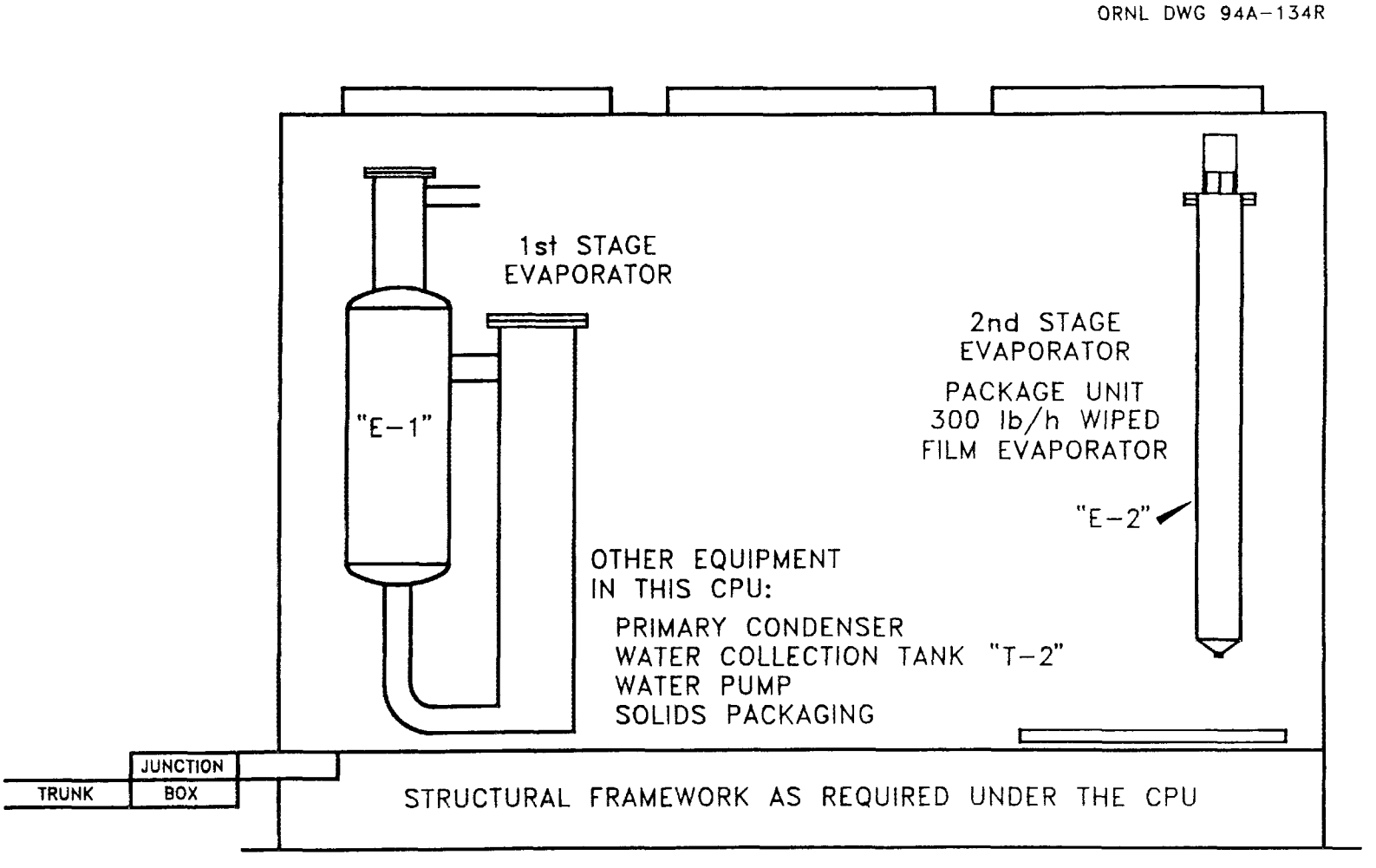

Fig. 9. CPU arrangement for basic flowsheet—first and second stage evaporators.

evaporator units are also modular and can be removed from the CPU for maintenance or replacement.

6.2 WASHED SLUDGE DISSOLUTION AND ACID PROCESSING

As indicated in Fig. 6, the process steps in this part of the flowsheet include (1) dissolution of soluble material in nitric and oxalic acids (the oxalic acid is added to complex and dissolve iron and other metals), (2) filtration by means of a cross-flow filter unit to remove acid-insoluble materials, (3) reduction of the nitric acid concentration of the filtrate by means of reaction of the nitric acid with formic acid at elevated temperature, (4) coprecipitation of cesium, strontium, transuranic elements, and rare earth fission products by means of a reaction of the cesium with nickel ferrocyanide and a reaction of the other nuclides with oxalic acid, (5) separation of the precipitated solids by means of a cross-flow filter unit, and (6) a polishing decontamination of the filtrate by means of sorption in a cation-exchange column.

Concentrated nitric acid would be added to the dissolver tank, and the solids would be digested at $\sim 100°C$ to dissolve the soluble components. Oxalic acid would be added to complex and dissolve iron and other metals. The dissolver solution would be filtered to remove insoluble material, which would be transferred to a high-level waste storage tank. The dissolver liquid filtrate would be transferred to another CPU containing an evaporator/precipitation tank, a cross-flow filter unit, and a cation-exchange column.

The evaporator would be heated to $\sim 80°C$, and formic acid would be added to the solution to initiate the formic acid/nitric acid reaction and reduce the acidity to ≤ 1 M HNO_3. Nickel cyanoferrate and oxalic acid would then be added to precipitate cesium, strontium, transuranic elements, and rare earth fission products. The resulting slurry would be filtered by means of the cross-flow unit, and the filtrate would be pumped through the cation-exchange column.

The cation-exchange column effluent, containing predominantly nonradioactive metals such as iron, chromium, nickel, and zirconium, would be evaporated to a semidry cake for interim storage and subsequent feed to a low-level vitrification system. The loaded cation-exchange resin would be eluted, and the eluate would be combined with the oxalate precipitate and acid-insoluble solids to await subsequent processing in a high-level waste vitrification system. The high-level waste material would be transported via shielded tanker to a centralized storage tank for the high-level waste vitrification system feed.

The equipment flowsheet is shown in Fig. 10. The sludge dissolution and processing would be carried out in a series of successive batch operations. Several of the process steps would be carried out in the same equipment, thus minimizing the number of CPUs required for these operations.

Primary equipment for these steps would be contained in two CPUs, as illustrated in Figs. 11 and 12. A third CPU would be required for off-gas treatment, as illustrated in Fig. 13. All of the equipment units would be modular and could be removed for maintenance or replacement.

Several process simplifications may be possible. One simplification is that, since the process steps are sequential, the operations carried out in Tanks T-1 and T-3 and Filters F-1 and F-2 (Fig. 10) can likely be done with only one tank and filter, thus reducing the equipment and CPU space required. Another possible simplification would be to dissolve the sludge using predominantly oxalic acid, with very little nitric acid; this would eliminate the need for a nitric acid destruction step following the dissolution.

7. CONCLUSIONS

The conceptual CPU system and the chemical/equipment flowsheets presented here are judged feasible on the basis of available information and of our broad and long experience in the field of radiochemical processing. That is not to say, however, that there is not considerable work yet to be done in terms of detailed design of CPUs and associated equipment, equipment testing, and experimental chemical flowsheet development to reduce process uncertainties (see Sect. 8). The following general conclusions can also be made in regard to the CPU concept:

- CPUs will make it possible to demonstrate early progress by avoiding the long lead time and expense associated with building a large, new central facility. This is particularly important for tanks that Hanford has placed on the safety concerns watch list. The initial CPU units could be modest in size and serve as pilot plants for more refined (and perhaps larger) follow-on units.
- Relatively small-scale, simple operations, such as fixed-bed ion-exchange and precipitation/filtration processes, are the most feasible for deployment in CPUs.
- The alkaline side processing portion of the "clean-option" concept is amenable to CPU processing because it involves relatively uncomplicated process steps in treating the alkaline supernates after initial separation and washing of the sludge.

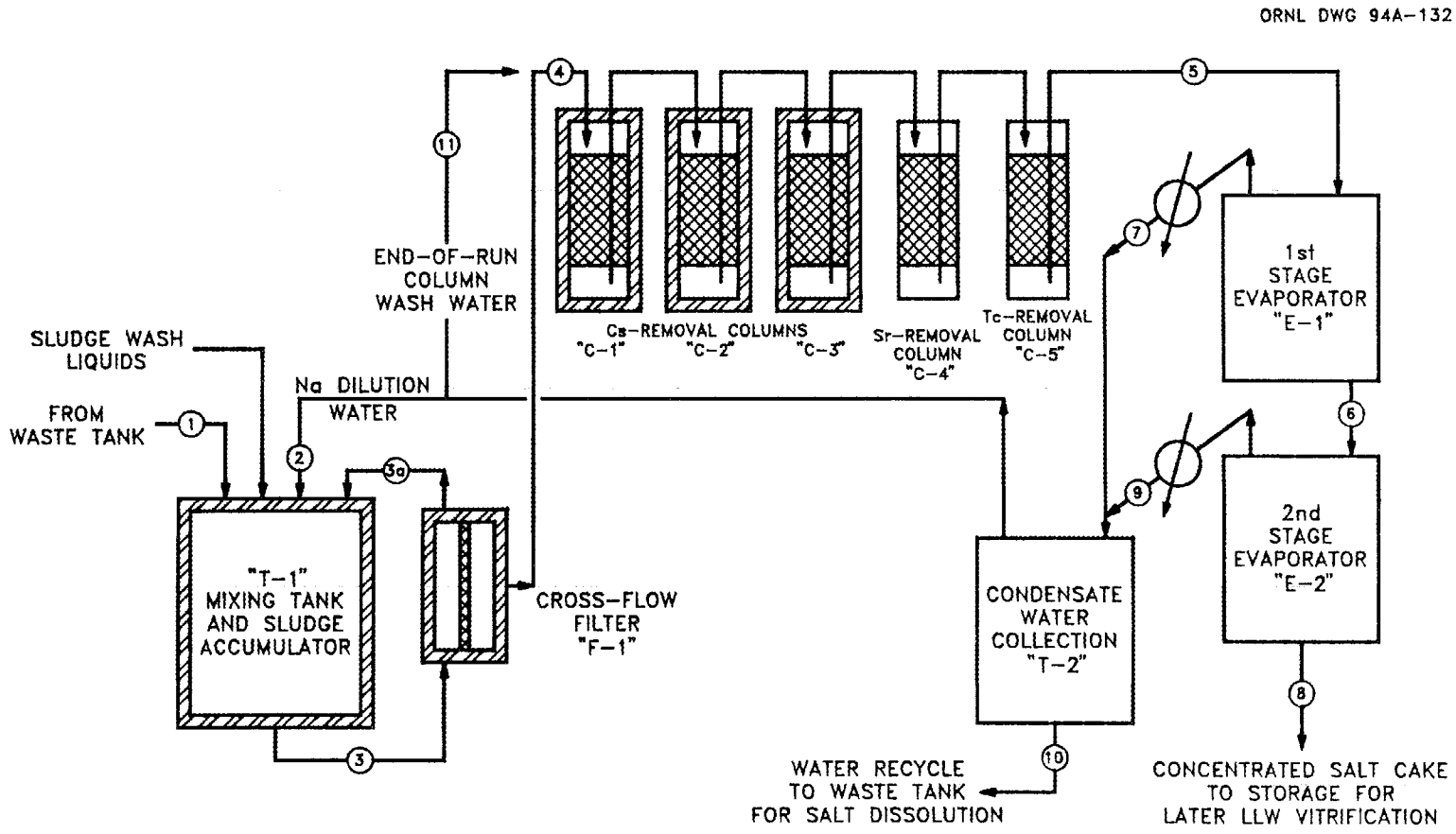

Fig. 10. Sludge dissolution and acid processing.

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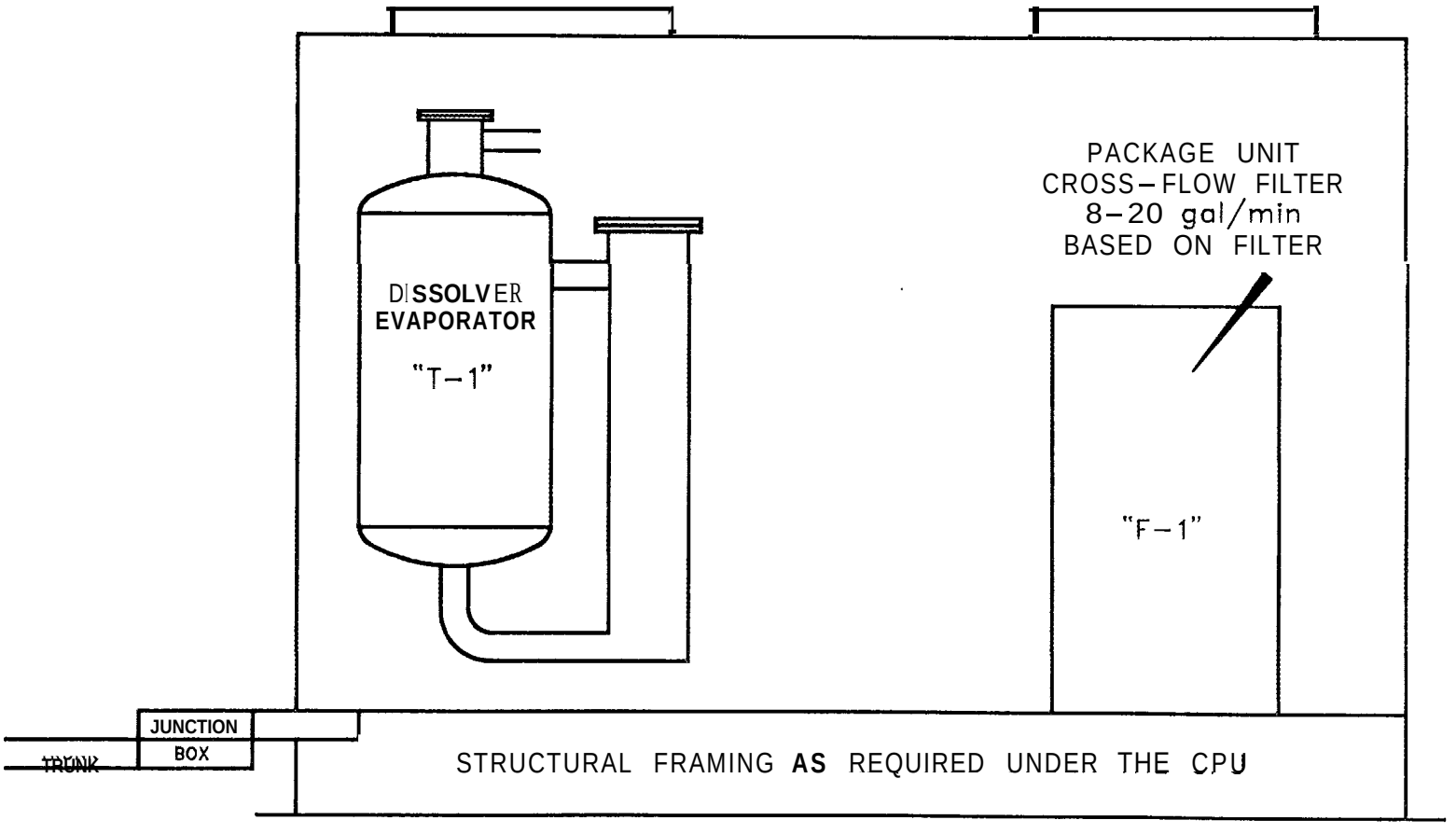

Fig. 11. CPU arrangement for first precipitator-evaporator for acid flowsheet.

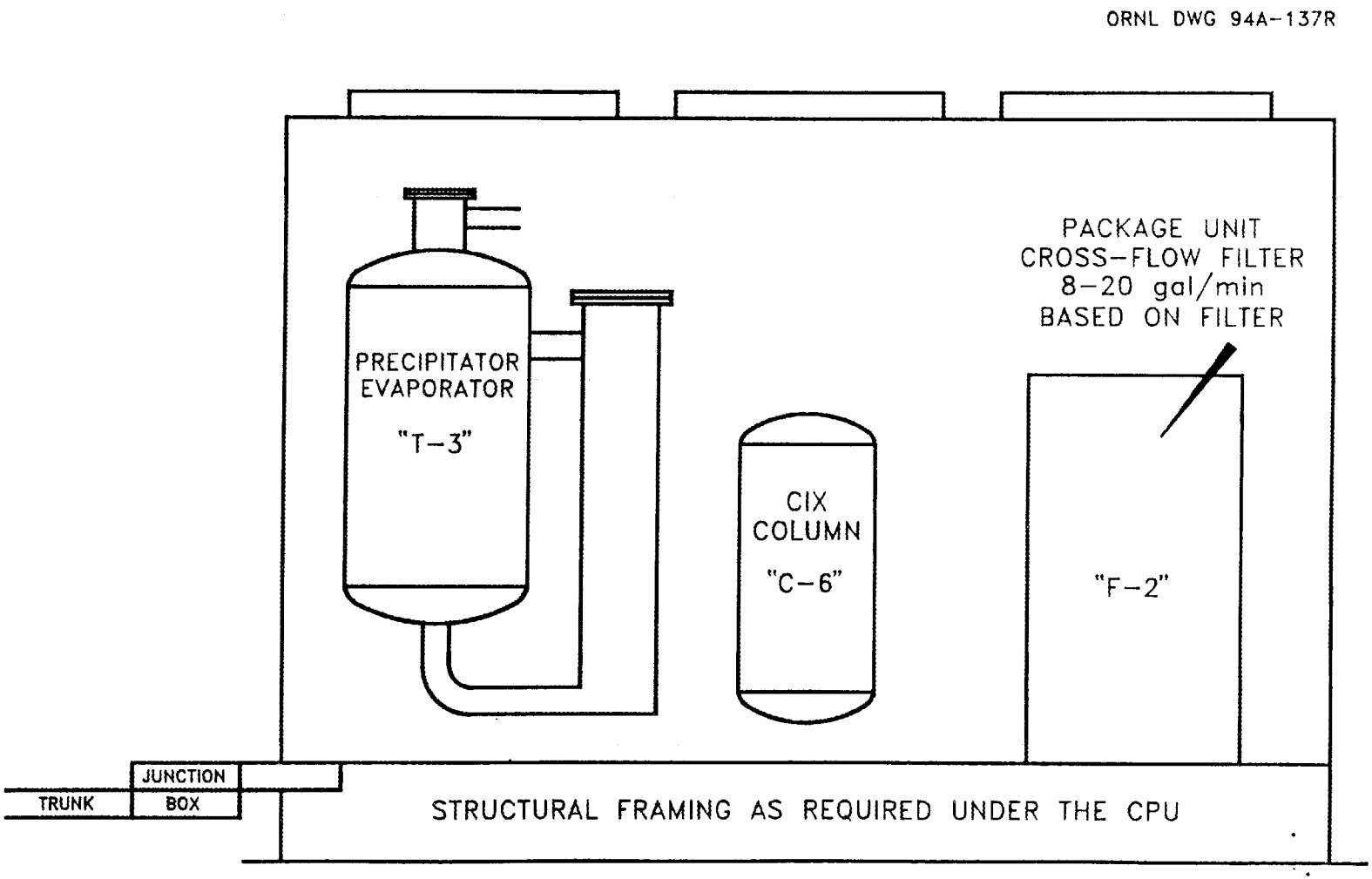

Fig. 12. CPU arrangement for second precipitator-evaporator and IX column for acid flowsheet.

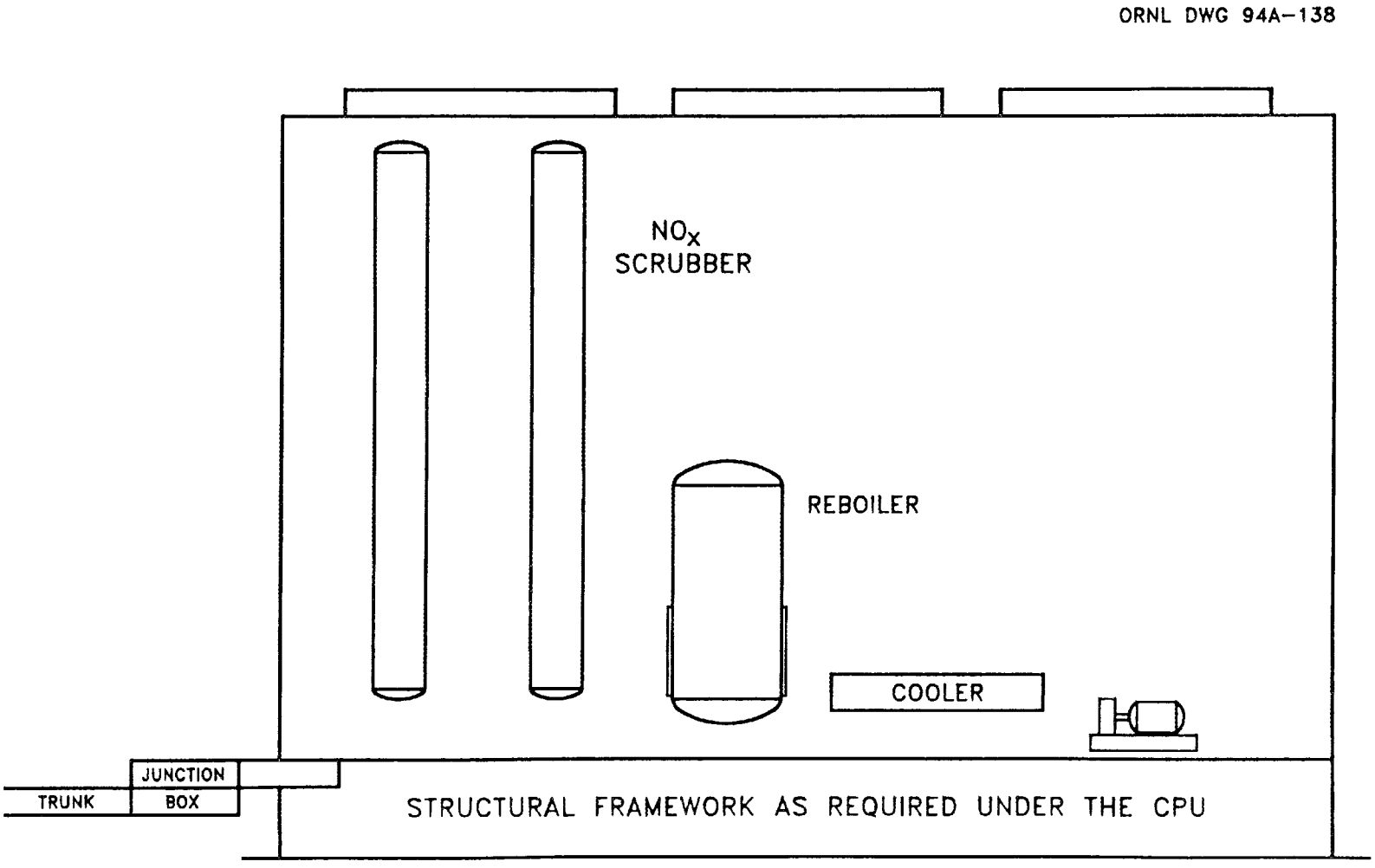

Fig. 13. CPU arrangement for NO_x scrubber, HEPA filters, and blowers.

- Cesium-loaded ion-exchange columns can be handled best by transporting the columns to a central facility, such as the existing Waste Solidification and Encapsulation Facility, for elution of the columns and solidification of the cesium. These operations are too complex for operation within CPUs.
- Following removal of ^{137}Cs from alkaline supernates and dissolved salts, more complicated equipment within lightly shielded CPUs can be used to further decontaminate the liquid (if necessary) and solidify the decontaminated salts for interim storage. Subsequently, the solidified low-level waste could be blended as necessary prior to conversion to the final low-level waste form.
- The acid side processing portion of the "clean-option" concept is more complex than the alkaline side. However, we judge it to be feasible provided it is carried out batchwise instead of continuously and if complex operations such as solvent extraction are avoided. We propose a precipitation/ion-exchange step to remove actinides rather than the solvent extraction processes[2] proposed for "clean option" at a central facility. We acknowledge that this proposed step has not been tested with Hanford wastes and needs verification.
- Unit shielding should be used around the CPU equipment that will contain high concentrations of gamma-emitting radionuclides, such as ^{137}Cs. Equipment such as sludge filters/accumulator tanks and cesium removal ion-exchange columns are examples of equipment that should be unit-shielded.
- All equipment in CPUs must have provision for remote operation, maintenance, and replacement.

8. RECOMMENDATIONS

A number of uncertainties exist with the chemical flowsheets posed here. The process steps of these flowsheets have been evaluated mainly in small laboratory-scale tests with nonradioactive simulants and with a limited number of actual waste samples. A significant amount of this type of work is already in progress throughout the Department of Energy sites in regard to sludge dissolution and washing and with respect to the removal of Cs, Sr, and Tc by sorption on ion exchangers, by precipitation, and by solvent extraction. However, the work has not progressed beyond small-scale experiments in the cold laboratory and in hot cells, except for cesium removal. Removal of cesium

from alkaline supernates by the resorcinol-formaldehyde resin has been conducted on the experimental engineering scale,[3,4] including hot tests at ORNL[4] at kilocurie loadings of ^{134}Cs-^{137}Cs.

Since the CPU concept of treating tank wastes appears to be technically feasible, we recommend:

1. Early design, fabrication, and deployment of small-scale units at various Hanford tank sites to determine the effects of uncertainties in the physical and chemical treatment processes with real wastes. Results from these efforts should be used to design larger scale units for production operations.
2. Laboratory work should be expanded to examine the precipitation/ion-exchange process[5-7] proposed here (Fig. 6) for removal of actinides, strontium, and cesium in acid processing of the sludge. Although the removal processes have been demonstrated for solutions of other compositions, they have not been tested with the range of compositions that is expected from dissolving Hanford sludges. Optimum oxalate/metal cation concentration ratio and solution acidity for precipitation and ion-exchange treatment must be determined for Hanford wastes. In addition, the volume of precipitates, their filterability, and factors that govern filterability need to be determined.

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APPENDIX A: TEAM BIOGRAPHY

Emory D. Collins

Mr. Collins has 28 years of experience in radiochemical engineering development at Oak Ridge National Laboratory. He has extensive experience in the development and application of radiochemical separations processes. This has included start-up and operation of the Transuranium Element Processing Facility and the Process Waste Treatment Plant at ORNL and development of the ion-exchange process used to decontaminate high-activity-level water at Three Mile Island, Unit 2. Mr. Collins graduated from Auburn University in 1958 with a B.S. in chemical engineering and did graduate studies at The University of Tennessee. He is currently head of the Isotope Technology Programs at ORNL.

Walter D. (Walt) Bond

Dr. Bond is a senior staff member at Oak Ridge National Laboratory and has a Ph.D. in physical chemistry from Vanderbilt University. He has been principally concerned with chemical research and process development in the nuclear field, with special emphasis on the nuclear fuel cycle, throughout his 36-year career at ORNL. In addition, he has performed significant research in the areas of actinide separations and the synthesis of high technology ceramic materials. Dr. Bond is a widely recognized national and international expert on the process chemistry of the nuclear fuel cycle—especially in fuel reprocessing, fuel fabrication, and waste treatment. He has made significant contributions to fuel cycle chemistry and technology. His work has led to important improvements in chemical process flowsheets for reprocessing, fuel fabrication, and waste treatment. He played a key role in the development of sol-gel processes for the remote fabrication of nuclear fuels and has helped extend that technology to an important area outside the nuclear field—high technology ceramic materials. Dr. Bond is a lifetime member of the American Chemical Society and is listed in *American Men of Science*, *Who's Who in the South and Southwest*, and *Frontier of Science and Technology*.

David O. Campbell

Dr. Campbell received the Ph.D. in physical chemistry from Illinois Institute of Technology in 1953. He was subsequently employed in research and development in the Chemical Technology Division at Oak Ridge National Laboratory until his retirement in 1991, except for military service in the Army Reactors Branch of the Atomic Energy Commission (1955–1957) and a one-year attachment to the Atomic Energy Research Establishment, Harwell, in the United Kingdom (1983–1984). His work has involved a wide range of problems in the areas of the nuclear fuel cycle and radiochemical processing, including equipment decontamination, americium recovery, protactinium chemistry, molten-salt reactor fuel processing, separations chemistry, ion exchange, solvent extraction, isolation of transplutonium elements, hot-cell studies of light-water reactor and light metal fast breeder reactor fuel dissolution and processing, flowsheet development, and waste treatment. He has been a consultant to the Nuclear Regulatory Commission and Department of Energy in regard to waste treatment and to General Public Utilities regarding recovery following the accident at Three Mile Island, Unit 2. He has many publications and five patents and has chaired sessions at several international meetings.

Frank E. Harrington

Mr. Harrington is currently a consulting engineer. He has a B.S. in chemical engineering from Northeastern University. He began work with Oak Ridge National Laboratory in 1946 in the Radiochemical Analysis Section and has participated in the pilot plant design and operations for Redox, PUREX, and Thorex processes; the design, construction, and start-up of the solvent exchange processes for the Idaho Chemical Processing Plant; Union Carbide's design, through start-up, of uranium ore processing plants; and troubleshooting in uranium ore mills. When he retired from ORNL in 1985, he was Group Leader for Chemical Technology Division Process Design. He holds two patents and two Industrial Research Awards (IRA-100's) and has coauthored numerous technical reports. His most recent work involved Atomic Vapor Laser Isotope Separation Product Conversion and the Nitrate to Ammonia process.

Dairin W. Malkemus

Mr. Malkemus graduated from Purdue University in 1988 with a B.S. in chemical engineering. He worked as an engineer in the semiconductor industry and has been at Oak Ridge National Laboratory since 1991. Mr. Malkemus is currently a member of the Chemical Technology Division at ORNL.

Frank L. Peishel

Mr. Peishel received his B.S. in mechanical engineering from The University of Tennessee in 1961 and has a retired Professional Engineer's license. He has 43 years of experience in the nuclear industry, with expertise in facility and equipment design, including interfacing with architectural engineering and plant operation engineering. His most recent experience has been with nuclear fuel reprocessing plant design, in collaboration with such groups as the Power Reactor and Nuclear Fuel Corporation of Japan, the United Kingdom Atomic Energy Authority, and Liquid Metal Reactors in concert with General Electric. Mr. Peishel was a principal author of *Design Guides for Radioactive Materials Handling Facilities and Equipment*, published by the American Nuclear Society, and has coauthored a number of papers presented at national and international meetings of the Remote Systems Technology Division and the Fuel Reprocessing and Waste Management Division of the American Nuclear Society. He is retired from ORNL and is currently serving as a consulting engineer.

Orlan O. Yarbro

Mr. Yarbro has a B.S. in chemical engineering from The University of Tennessee and graduated from the Oak Ridge School of Reactor Technology in 1955. He has 38 years of experience in the field of nuclear fuel reprocessing, including plant and equipment design, plant operation, and management of research and development. Mr. Yarbro is currently retired from ORNL; for the past 7 years, he has been a private consultant specializing in flowsheet development, process control and automation, and equipment design.

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