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PREPARATIONS FOR HIGH-LEVEL DEFENSE WASTE IMMOBILIZATION AT SAVANNAH RIVER PLANT

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ABSTRACT

Methods are being developed to immobilize Savannah River Plant (SRP) wastes in high-integrity glass forms. The waste forms will be suitable for storage in an on-site facility or for shipment to an off-site repository. Alkaline wastes produced in SRP separations plants are currently stored in large, carbon-steel tanks. These wastes consist of a water-soluble fraction (salt cake and supernatant liquor) and an insoluble sludge. The water-soluble fraction contains most of the ^{137}Cs and the insoluble sludge contains most of the ^{90}Sr, waste actinides, and other fission products. ^{90}Sr and ^{137}Cs are the most hazardous radionuclides in aged waste.

A conceptual solidification process has been developed from laboratory tests with both actual and simulated waste. Engineering design studies are in progress. First, wastes are removed as a slurry from the waste tanks. The sludge is separated from the supernate, and then ^{137}Cs is removed from the clarified supernate by ion exchange. The resulting decontaminated supernate is evaporated to a salt for bulk storage.

* The information contained in this article was developed during the course of work under Contract No. AT(07-2)-1 with the U.S. Department of Energy.

In the second part of the process, ^{137}Cs is mixed with sludge and the mixture is calcined and then solidified in borosilicate glass. Off-gas from the calciner and glass melter is treated to ensure that no hazardous materials are released to the atmosphere.

INTRODUCTION

Savannah River Plant (SRP), operated by the Du Pont Company for the Department of Energy, occupies an area of 800 km^2 near Aiken, South Carolina, along the Savannah River and about 35 km downstream from Augusta, Georgia (Figure 1). The site contains a nuclear fuel fabrication plant, three operating reactors, two fuel reprocessing plants, and a facility for producing heavy water. The plant started producing nuclear materials for national defense programs in 1953 and has been in continuous operation since then.

Most radioactive waste at SRP originates in the two reprocessing plants. Wastes from the reprocessing operations are acidic, but are neutralized and made alkaline with NaOH before being transferred to carbon-steel storage tanks. The waste is held in cooled tanks for about two years until most of the short-lived fission-products have decayed, and then the liquid waste is concentrated to a salt cake for longer-term storage.[1]

Neutralizing the waste is necessary for storage in carbon-steel tanks. SRP currently has ∿35 waste tanks ranging in capacities from 750,000 to 1,300,000 gallons (2.8×10^6 to 4.9×10^6 liters) per tank. Figure 2 shows tank construction.

Neutralizing the waste causes insoluble oxides and hydroxides of fission products, waste actinides, and metals (e.g., iron, mercury, and manganese) to precipitate from the waste. Most radioactive isotopes are thereby confined to an insoluble sludge phase, Figure 3, which is ∿10% of the waste volume.

The supernatant solution of soluble salts, however, retains almost all the ^{137}Cs, about half the ^{106}Ru, and traces of ^{90}Sr. Aged supernates are evaporated and returned to cooled tanks where the salts crystallize as shown in Figure 4. This further reduces waste volume and helps immobilize the waste.

WASTE MANAGEMENT OPTIONS

Until 1971 the disposal process that was most actively considered among those shown in Figure 5 was to pump wastes from existing tanks into a bedrock cavern. The cavern would have been dug under the plant site, probably in an impermeable Triassic mudstone.[2] This alternative was extensively investigated and appears to be feasible. However, since 1971 work on this alternative has been deferred while waste solidification could be investigated. The main risk associated with bedrock storage is the possibility of waste entering the Tuscaloosa aquifer, which is above the Triassic mudstone. This could result from an earthquake or sabotage before the shaft connecting the cavern to the surface was sealed. There is also a small risk arising from the possibility of cracks forming to connect the cavern to the aquifer.

Another option is to continue storing in tanks and replace the tanks every 50 to 100 years as required by the condition of the tank.[2] This alternative is an indefinite extension of present practice and will continue until another alternative is selected and put into practice. This option costs less in the near term, but the costs continue indefinitely.

PRESENT CONCEPTUAL PROCESS FOR WASTE SOLIDIFICATION

Savannah River Laboratory (SRL) has developed methods to solidify radioactive SRP waste into high-integrity forms which can be either stored on the plant site or shipped to an off-site repository. These methods comprise the present conceptual process for long-term waste management. Key portions of this process are shown in Figure 6. Design studies for a Defense Waste Solidification Facility based on this conceptual process are being made by the Du Pont Engineering Department. According to this plan highly radioactive wastes amounting to 25 million gallons (95 million liters) of salt cake and 6 million gallons (22.7 million liters) of wet sludge are converted to 1.5 million gallons (5.7 million liters) of glass and 26 million gallons (98.7 million liters) of decontaminated salt cake. Processing will require a 20-year period beginning about 1990.

REMOVAL FROM PRESENT TANKS

Waste will be removed from each waste tank by re-dissolving the salt cake and hydraulically slurrying the salt solution and the sludge. Pumps like the one shown in Figure 7 will be arranged in risers on the waste tanks so that all parts of the tank bottom will be swept by the slurrying action. About 95% of the sludge in each tank can be removed by slurrying. Remaining sludge will be dissolved by treatment with oxalic acid.

SEPARATION OF SLUDGE AND SUPERNATE

Once removed from the waste tank, sludge and supernate are separated by a three-step procedure which includes centrifuging, agglomerating and gravity settling, and filtering through a bed of sand and anthracite coal. Figure 8 shows the effect of adding a small amount of starch to agglomerate fine sludge particles. The sludge is also washed to remove soluble salts. This separation procedure has been tested with liter quantities of actual waste and 100-liter quantities of simulated waste.

Ion Exchange Process

The clarified salt solution is sent through an ion exchange process to remove ^{137}Cs and ^{90}Sr.[3] Removing ^{106}Ru, the only other significantly hazardous isotope in the solution, is not necessary because its half-life is only one year. ^{106}Ru in the ion exchange product will have decayed to a very low level after the salt has been stored 12 years. Present plans are to return the decontaminated salt to cleaned waste tanks for indefinite storage.

The ion exchange process has several steps (Figure 9). ^{137}Cs is removed from solution by two beds of *Duolite* ARC-359 (Diamond Shamrock Chemical Co., Redwood City, California), an organic cation exchange resin. The process is controlled by an on-line γ-ray monitor located between the two beds. ^{106}Ru would interfere severely with ^{137}Cs analysis if the monitor were placed after the second *Duolite* column. ^{90}Sr is removed with a chelating resin, either *Chelex** 100 (Bio-Rad Labs, Richmond, California)

or *Amberlite* XE-318 (Rohm and Haas Co, Philadelphia, Pennsylvania).

In early 1976 about 775 liters of actual SRP waste supernate were decontaminated during 9 tests. Decontamination factors averaged ∿5 × 10^5 for ^{137}Cs and ∿1000 for ^{90}Sr. The combined residual activity of these two isotopes in decontaminated salt cake was <10 nCi/gram. Aside from ^{106}Ru, the only other measurable activities in the decontaminated waste were very low levels of ^{99}Tc, plutonium, and lanthanide isotopes.

Waste Calcination and Solidification

Flowsheet Description and Selection

^{137}Cs and ^{90}Sr from ion exchange will be mixed with washed sludge and the mixture will be fed into a spray calciner that will produce a dry, free-flowing powder. The calciner is directly coupled to a continuous, ceramic melter. Glass-forming frit material is added to the melter along with calcined waste, and the mixture is melted to form a high-integrity glass product.

During initial process tests the following criteria for good radioactive waste forms were met by both glass and concrete.[4,5]

- High Waste Loading
- No Serious Chemical Compatibility Problems
- Low Leach Rates
- Good Mechanical Strength
- Good Radiation Stability

- Good Thermal Stability
- Compatible with Standard Container Materials

The costs of a concrete process and of a glass process were found to be about the same by the Du Pont Engineering Department. Glass, however, is the superior matrix because it has better resistance to water leaching than concrete. Container pressurization caused either by radiolysis or by heating in an accidental fire was also a potential problem for concrete that is not encountered with glass. Glass was therefore chosen as the solidification matrix for the present conceptual process.

Sludge Vitrification

SRP sludge composition varies greatly depending on the history of each individual waste tank (Table 1). An important part of the SRL work was to demonstrate that actual sludges could be made into good borosilicate glass waste forms.

Glass-forming mixtures (Table 2) used at SRL have a higher ratio of alkali metal oxides to silicon than usual borosilicate glasses. This allows the glass to melt at a lower temperature and thus reduces volatility of radioactive fission products. Lithium reduces melt viscosity so that the glass is easier to pour.

Washed, dried, powdered sludges (Figure 10) were mixed with the glass-forming frit in a weight ratio of 35% sludge to 65% frit. Mixtures were melted for 3 hours at 1150°C, poured into graphite molds, and annealed on hour at 500°C. Resulting buttons

were smooth, shiny, and homogeneous. Laboratory apparatus for glass making is shown in Figure 11.

Leach Testing

Resistance to leaching by water is a primary criterion for judging the quality of a radioactive waste form because accidental contact of the waste form by water can provide a direct path for radionuclides to enter the biosphere. Glass buttons containing actual SRP waste were leached in static distilled water according to a procedure similar to a proposed IAEA method.[6,7] The SRL method differed from the IAEA method in that at SRL, the entire glass button, rather than a single surface, was leached. Also the schedule for water changes differed from the IAEA method.

Leach rates are usually reported as the weight of glass that loses its share of radionuclides divided by the area exposed to water and the leaching time.

$$\text{Leach Rate } (g/cm^2\text{-day}) = \left(\frac{\text{Isotopic activity in water}}{\text{Isotopic activity in glass}}\right) \times \left(\frac{\text{Sample weight}}{\text{Surface area} \times \text{Time}}\right)$$

This expression is valid for homogeneous glass, but it should not be assumed to imply a particular leaching mechanism. Leach rates based on ^{90}Sr, ^{137}Cs, and plutonium analyses were found to be nearly equal in the SRL tests. Typical rates were 10^{-5} to 10^{-6} g/cm^2-day initially, 10^{-7} to 10^{-8} g/cm^2-day after two weeks, and 10^{-8} to 10^{-9} g/cm^2-day after 100 days (Table 3). These rates compare favorably with those of glasses and other candidate matrices that have been evaluated at other sites.[8]

Plant-Scale Melting

For plant-scale glass making, the continuous, joule-heated, ceramic melter is currently favored. In this melter, alternating electric current passes through the molten glass so that the glass acts as its own heating element. Molten glass pours out of the melter into the final container for the glass. Figure 12 shows electrodes in the SRL laboratory-scale melter, and Figure 13 shows the finished melter. This ∿3 kg/day melter is being tested with simulated wastes and a similar melter is being built to vitrify actual wastes. Engineering-scale tests are also being made with a melter at Battelle Pacific Northwest Laboratories (PNL).

A second vitrification method being considered for SRP wastes is the in-can method. Frit and calcined sludge are introduced directly into the final container. The container is then heated to melt its contents. A former disadvantage of this technique was the large number of melting stations necessary to produce the required 3,000 kg of glass/day using existing technology. Container corrosion during heating (Figure 14) is another problem with in-can melting. Recently, large in-can melters have been successfully operated and this option is becoming competitive with the continuous melter. Tests with simulated waste are in progress both on the laboratory-scale at SRL and on an engineering-scale at PNL.

Off-Gas Treatment

The off-gas system shown schematically in Figure 15 is

designed to ensure that no hazardous materials are released from the solidification plant. This system begins in the calciner where sintered metal filters remove particles and dust containing ^{144}Ce-^{144}Pr and ^{106}Ru. The off-gas stream is cooled in a quench column to remove alkali metal borates, about 95% of the mercury, and ^{137}Cs. Fine particulates that pass through the quench tower are removed in a cyclone separator. The stream is further cooled to $\sim$5°C to remove most of the remaining mercury. All of the mercury in the glass melt will volatilize. Although SRP sludge averages only $\sim$1% mercury, this amounts to about 200 tons (1.6×10^5 kg). This large quantity of mercury will be recovered and thoroughly cleaned for re-use.

Remaining traces of gaseous ^{106}Ru and mercury are removed by beds of silica gel and silver zeolite, respectively. Finally the off-gas passes through a series of high-efficiency particulate (HEPA) filters and a sand filter.

CONCLUSIONS

Figure 16 shows an artist's conception of the proposed waste solidification facility. The main building is about 700 meters long. Cost of building and operating the facility during its 20-year lifetime will be about six billion dollars.

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LIST OF FIGURES

TABLE 1

Composition of SRP Sludges

Component	*Unit*	*Average*	*Range*
Fe	Wt %	22.0	3.1 - 32.8
Al	Wt %	9.9	1.5 - 33.5
U	Wt %	6.7	0 - 15.4
Mn	Wt %	5.4	1.7 - 10.8
Ni	Wt %	2.8	0.3 - 6.3
Hg	Wt %	1.2	0.1 - 2.8
^{90}Sr	mCi/g	-	30 - 180
^{144}Ce	mCi/g	-	0.5 - 30
^{106}Ru	mCi/g	-	0.1 - 10
Alpha Act.	mCi/g	-	0.1 - 0.7

TABLE 2

Composition of Glass Frits

Component	*Wt %*	
	Mix 18	*Mix 21*
SiO_2	52.5	52.5
Na_2O	22.5	18.5
B_2O_3	10.0	10.0
TiO_2	10.0	10.0
CaO	5.0	5.0
Li_2O	-	4.0

TABLE 3

Glass Leach Rates Based on Pu Analysis

Glass Type	Leach Rates (g/cm^2-day) 1 (Day)	14 (Days)	100 (Days)
21-35-4,6[a]	2.2×10^{-8}	4.4×10^{-9}	1.9×10^{-9}
21-35-5	3.7×10^{-6}	9.7×10^{-8}	1.6×10^{-8}
21-35-13	6.4×10^{-7}	5.5×10^{-7}	4.8×10^{-8}
21-35-15	3.6×10^{-6}	7.8×10^{-7}	4.6×10^{-8}
21-35-16	1.2×10^{-6}	1.4×10^{-7}	1.2×10^{-8}
18-40-5[b]	1.1×10^{-6}	1.7×10^{-8}	3.6×10^{-9}
18-40-13	7.3×10^{-7}	1.5×10^{-7}	5.4×10^{-8}
18-45-5	1.7×10^{-5}	1.2×10^{-7}	2.3×10^{-8}

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a. 21 is the number of the glass mixture which contains lithium; 35 is wt % sludge; 4 refers to Tank 4 sludge, and 6 refers to Tank 6 sludge.

b. 18 is the number of the glass mixture which contains no lithium; 40 is wt % sludge; 5 refers to Tank 5 sludge.

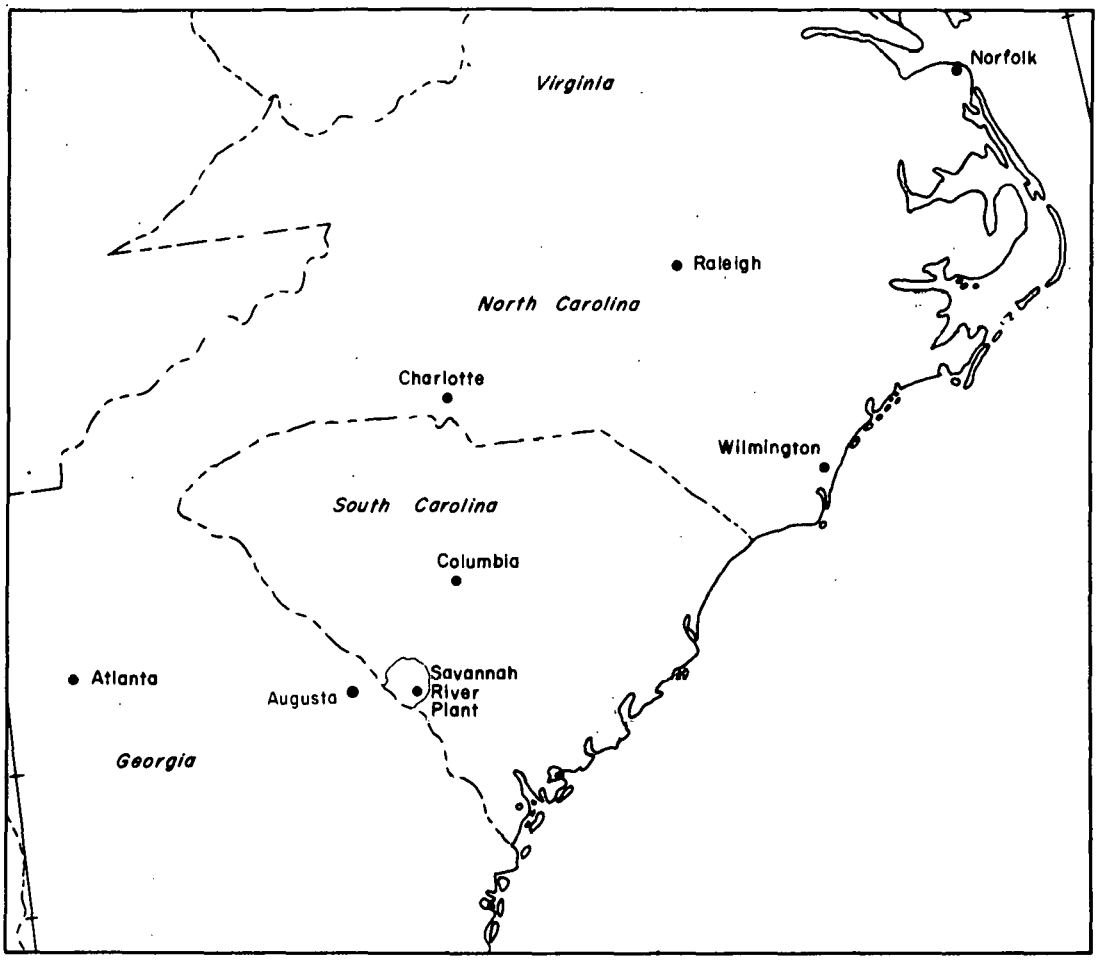


FIGURE 1. Location of Savannah River Plant

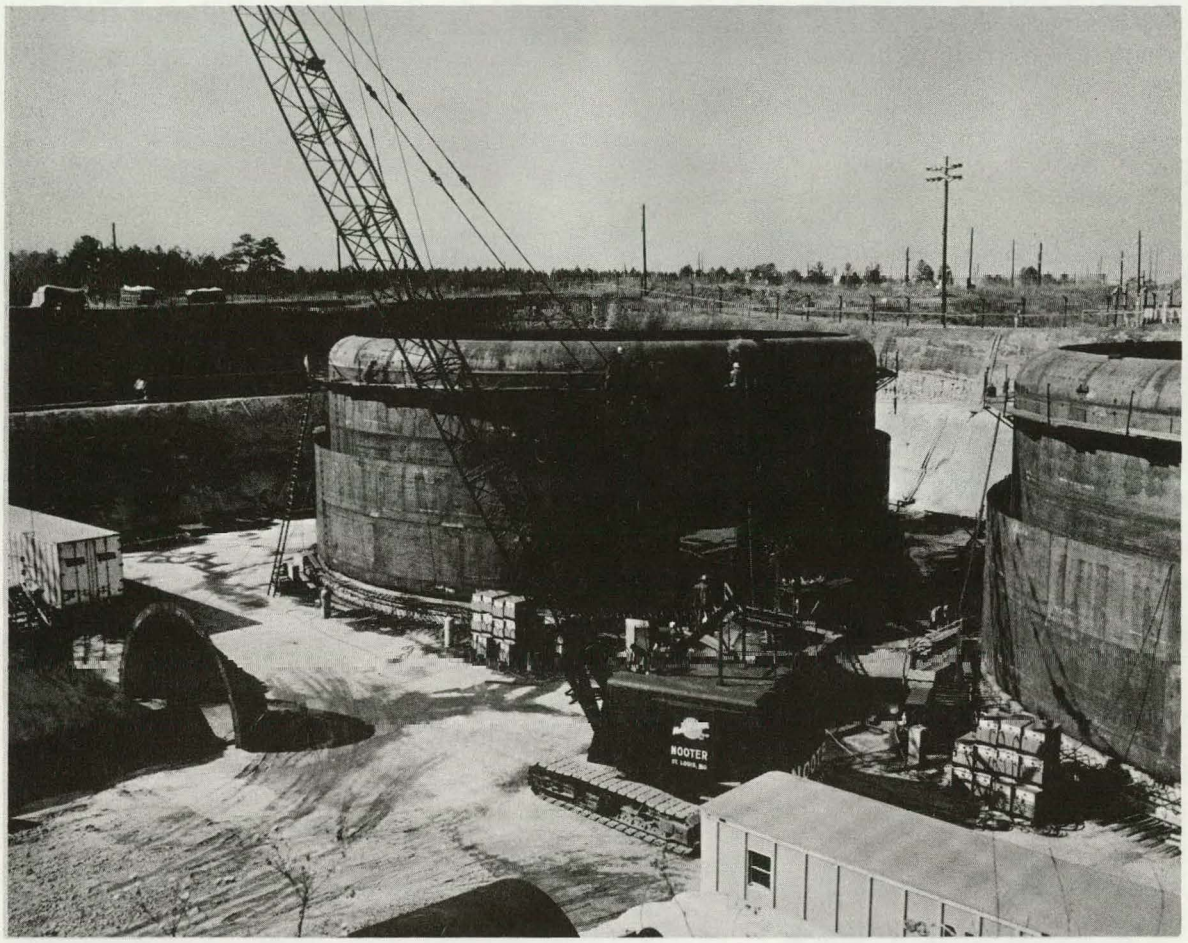


FIGURE 2. Photographs of Waste Tanks During Construction

FIGURE 3. Sludge Sample

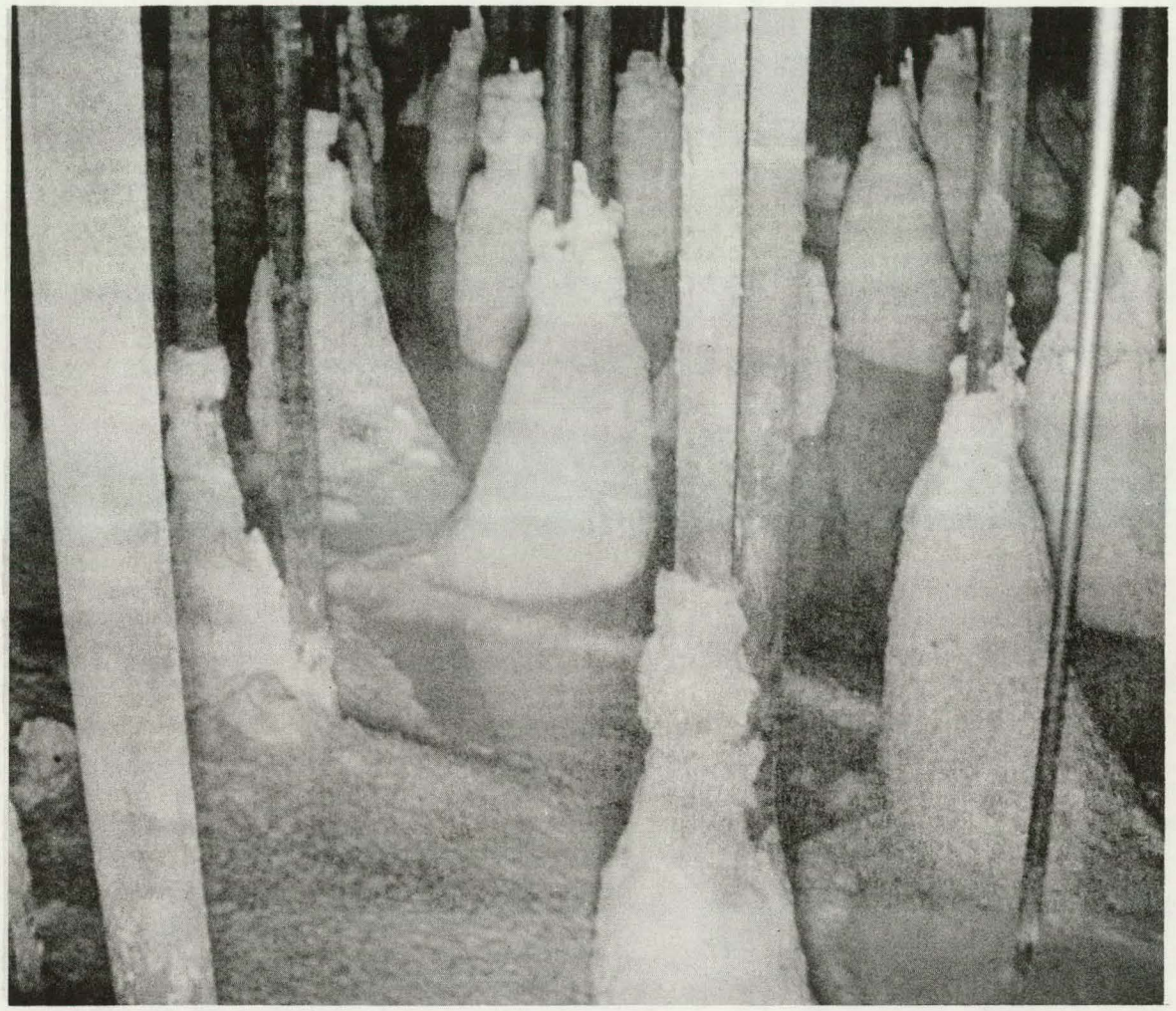


FIGURE 4. Photograph of Salt Crystals in Waste Tank

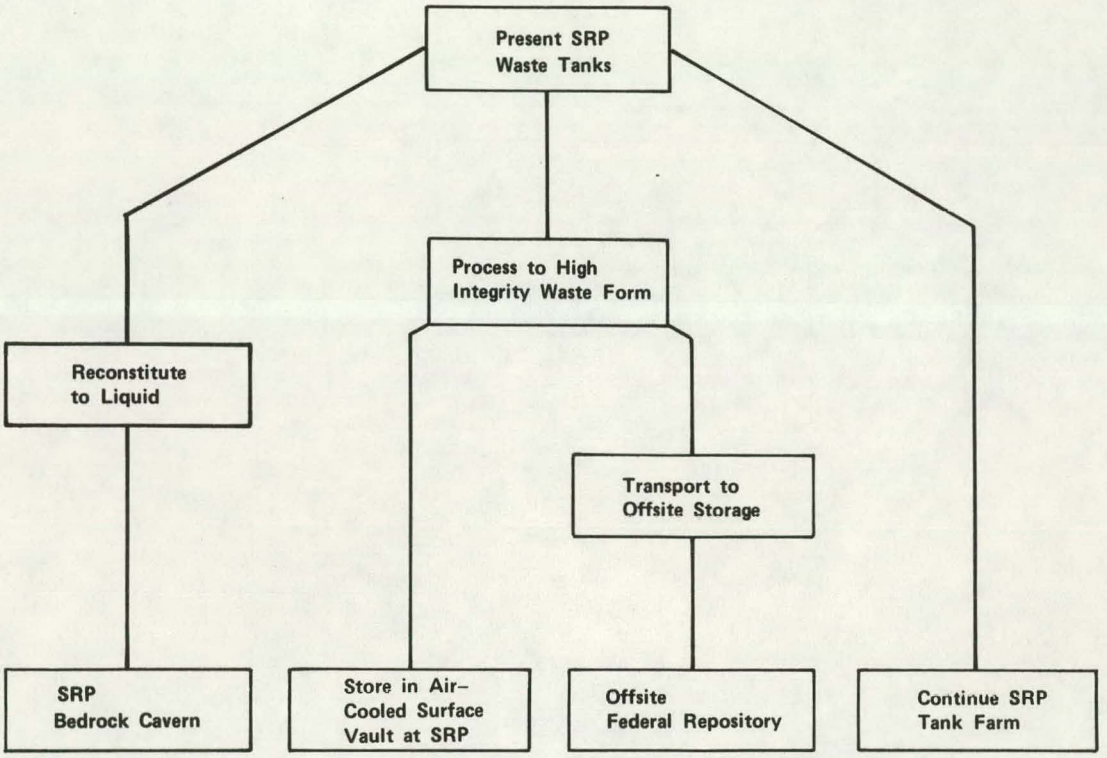


FIGURE 5. Major Alternative Plans

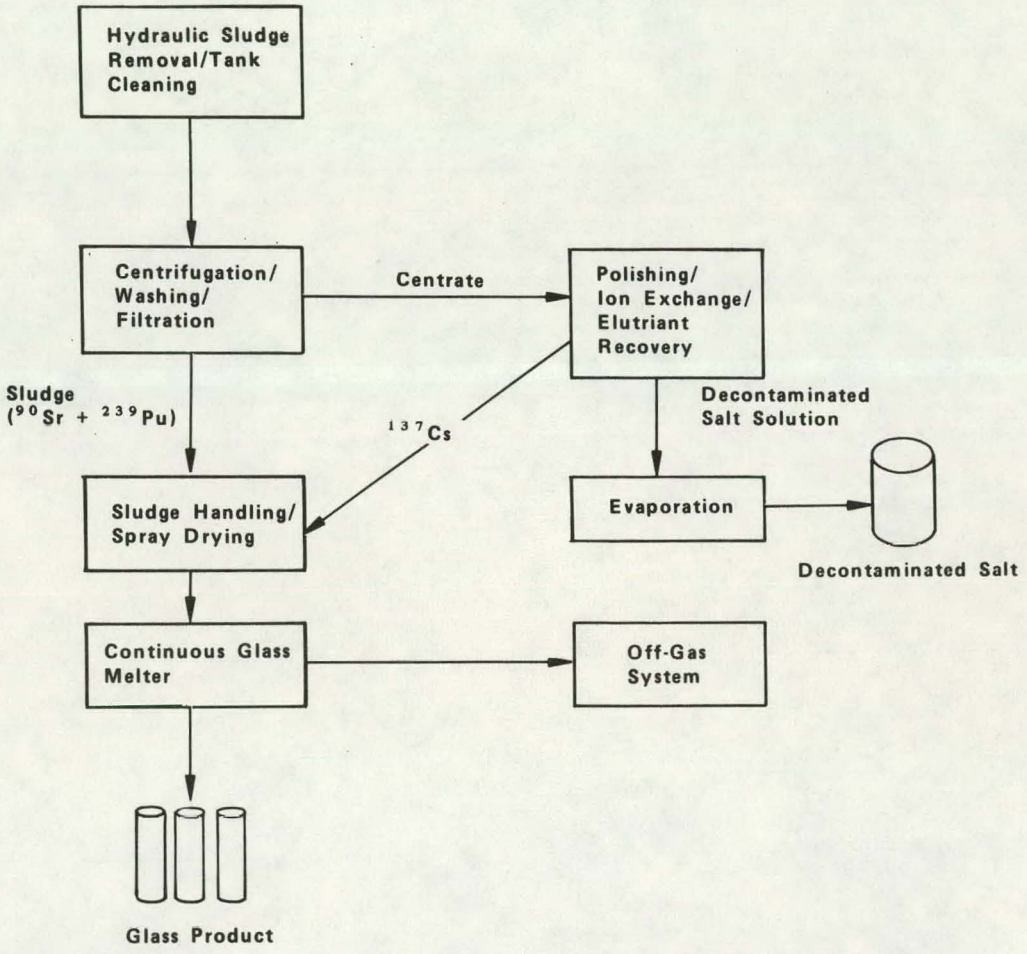


FIGURE 6. SRP Defense Waste Solidification Reference Process

FIGURE 7. Photograph of Slurry Pump Operating in TNX - 1/2 Tank Mockup

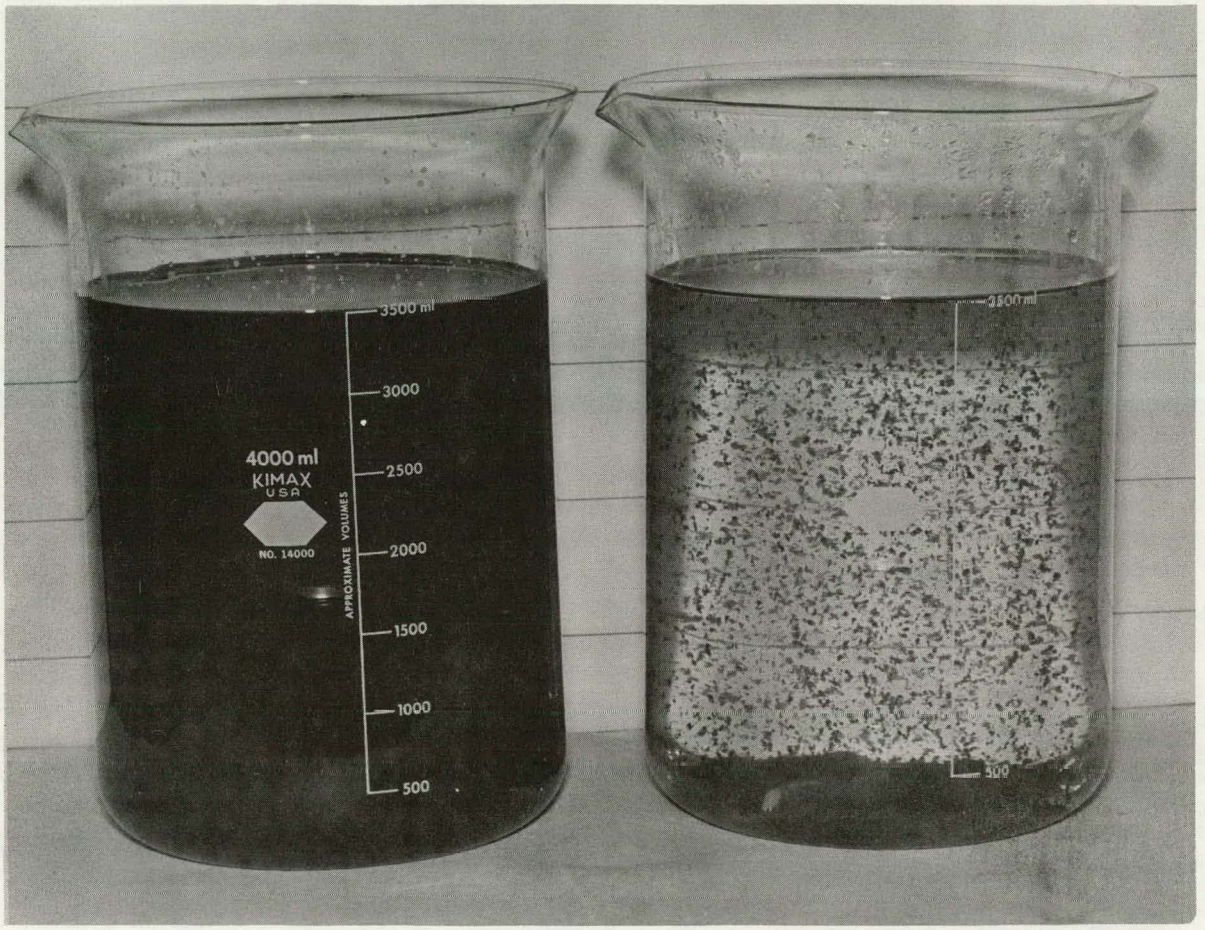


FIGURE 8. Photograph of Agglomeration - Gravity Settling Test

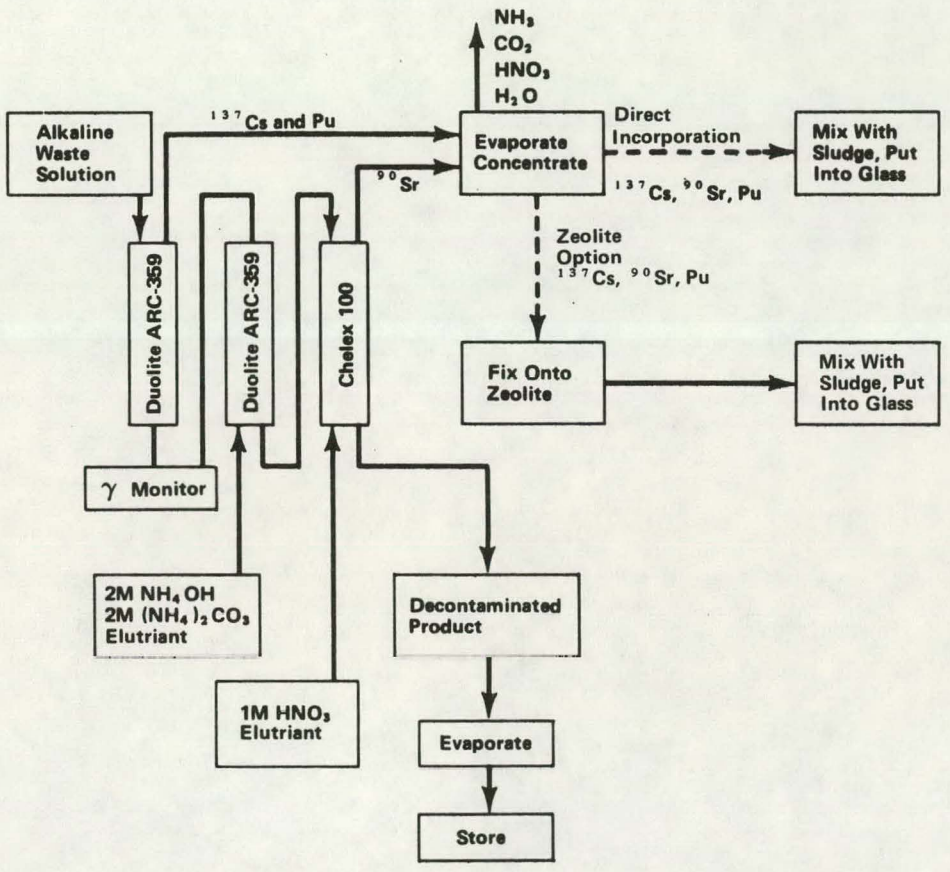


FIGURE 9. Ion Exchange Process

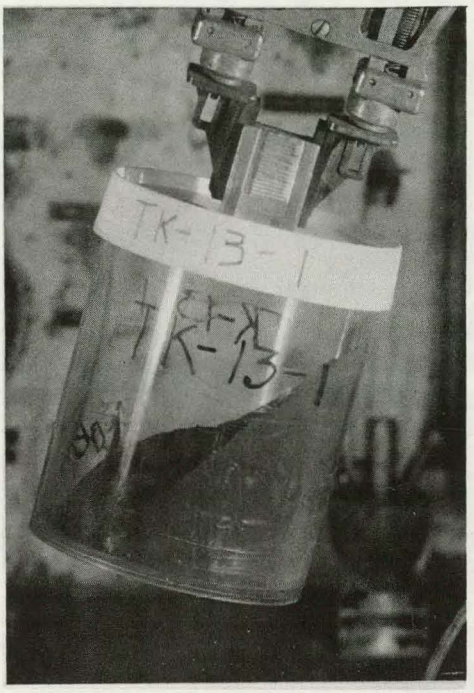


FIGURE 10. Powdered Sludge Product

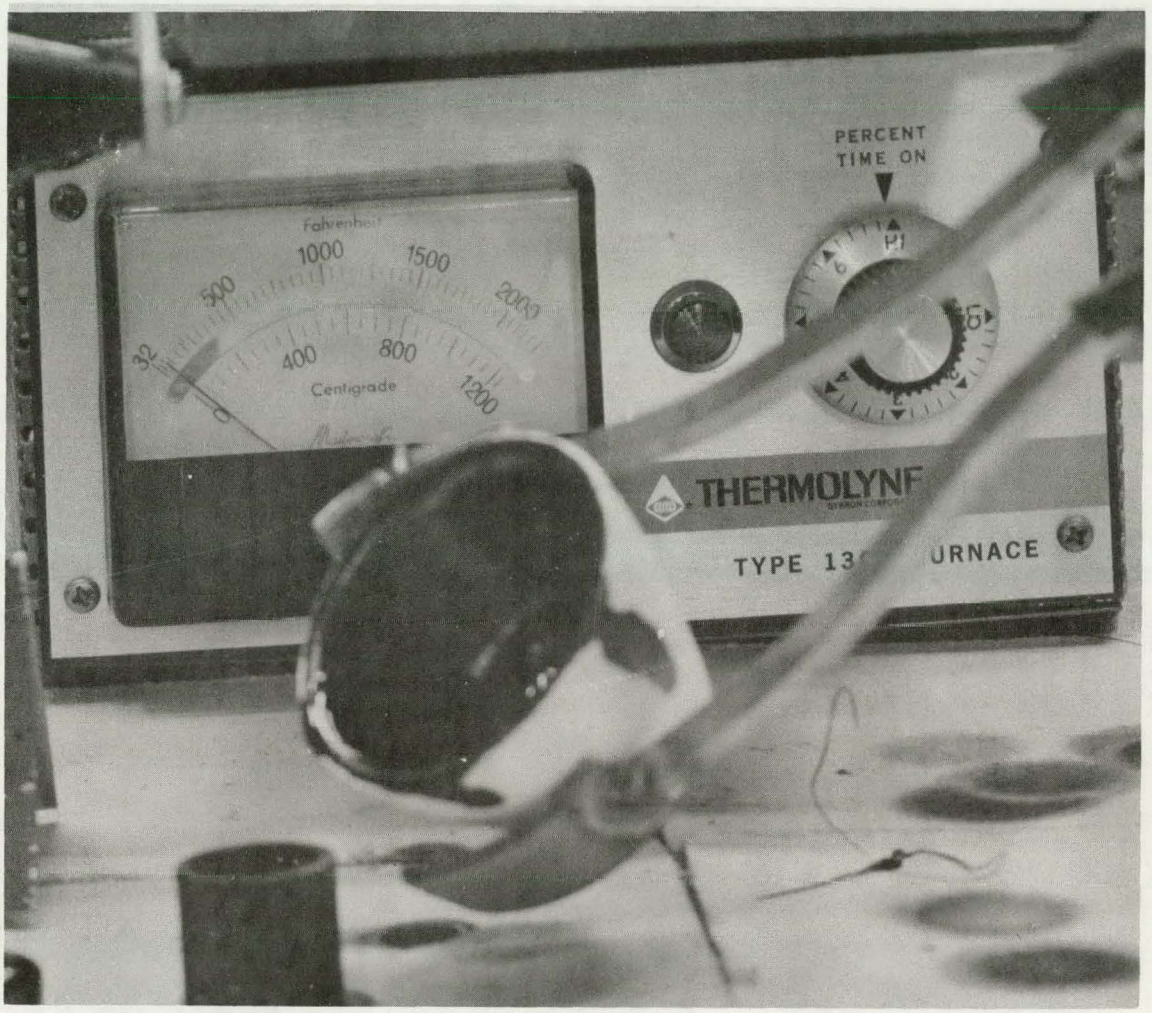


FIGURE 11. Laboratory Process for Making Glass Buttons

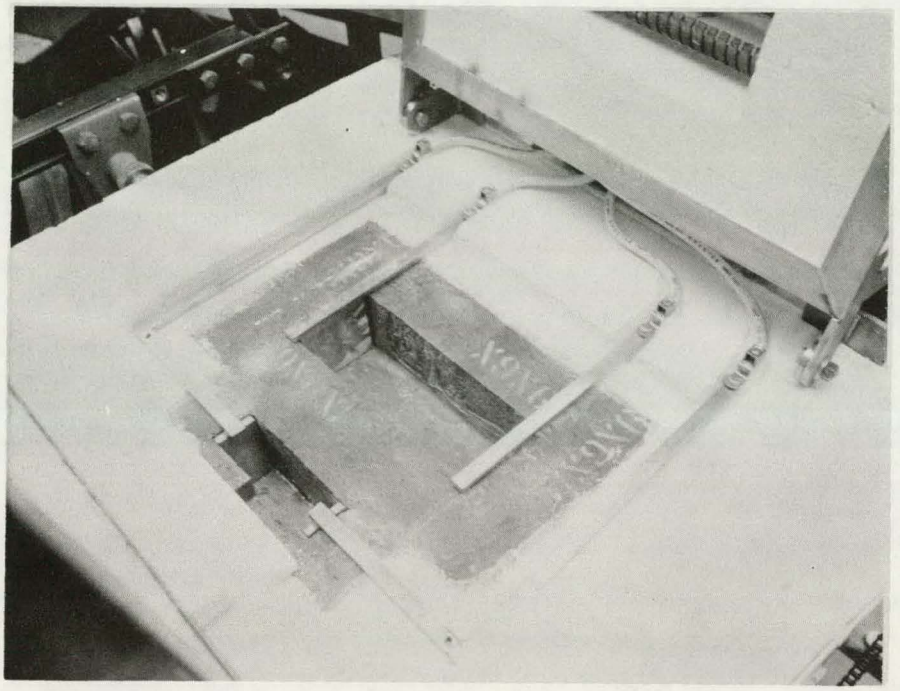


FIGURE 12. Photograph of Melting Cavity in Laboratory-Scale Melter

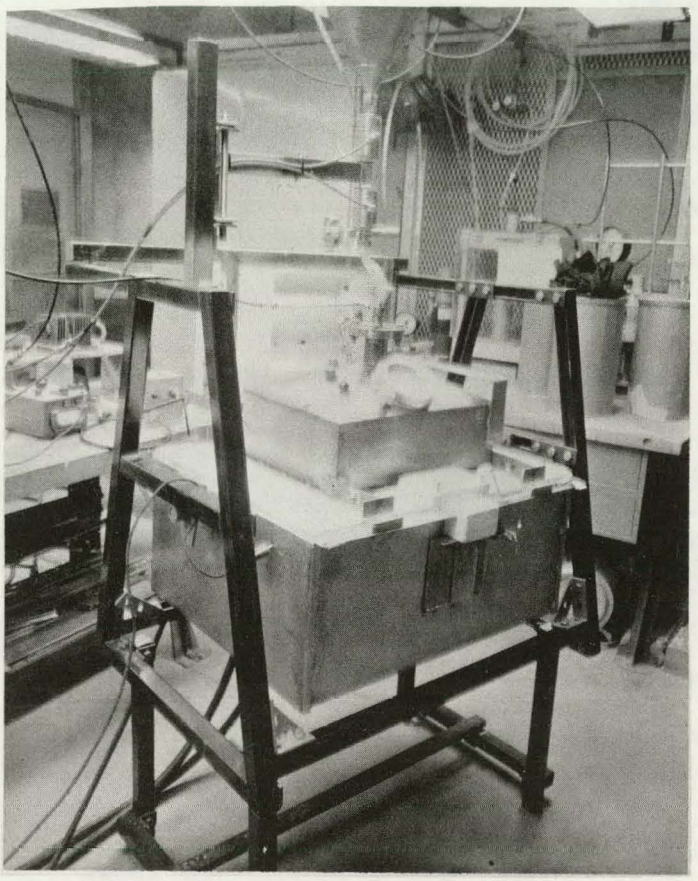
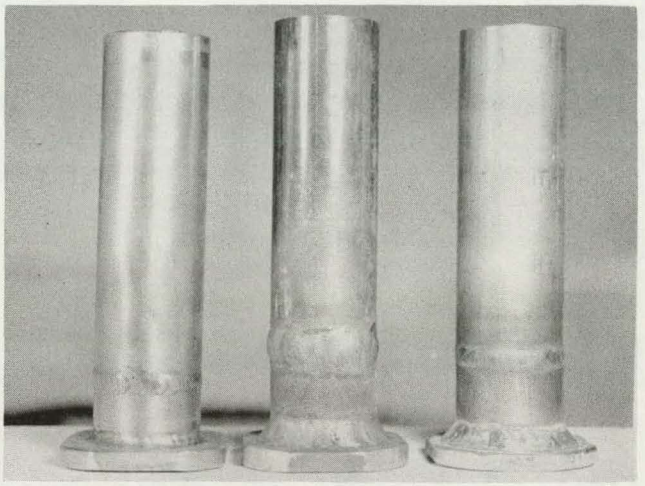


FIGURE 13. Photograph of Glass Pouring from Laboratory-Scale Melter



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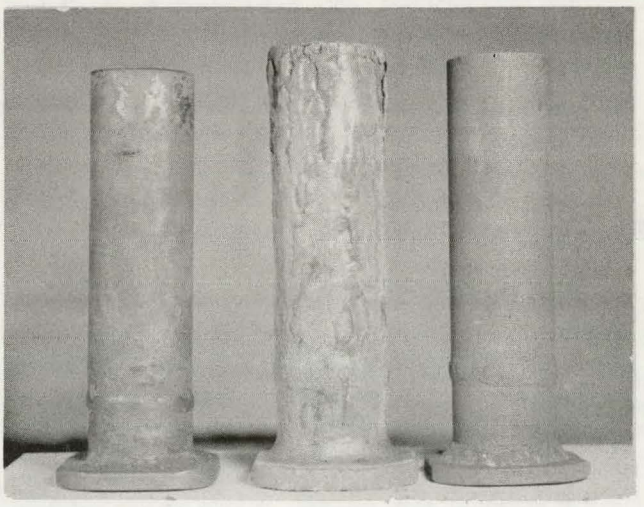

FIGURE 14. Metal Canisters for In-Can Melting

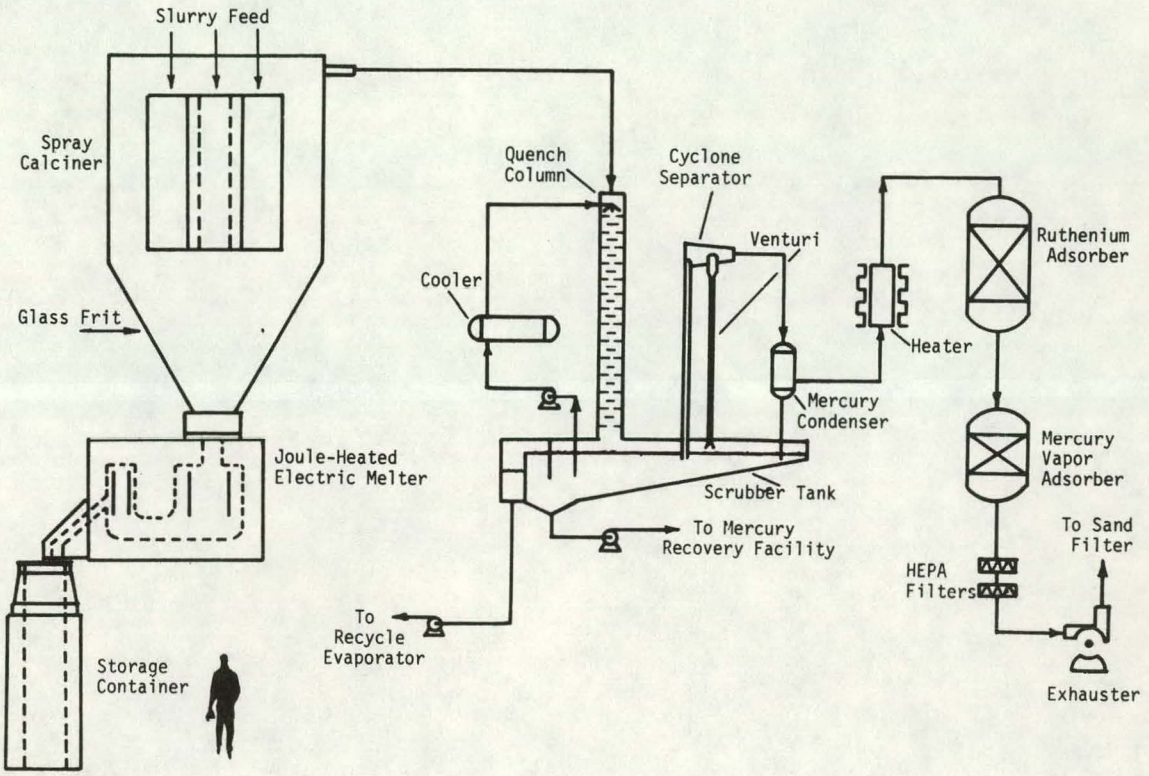

FIGURE 15. Spray Calciner/Melter/Off-Gas Defense Waste Solidification Facility

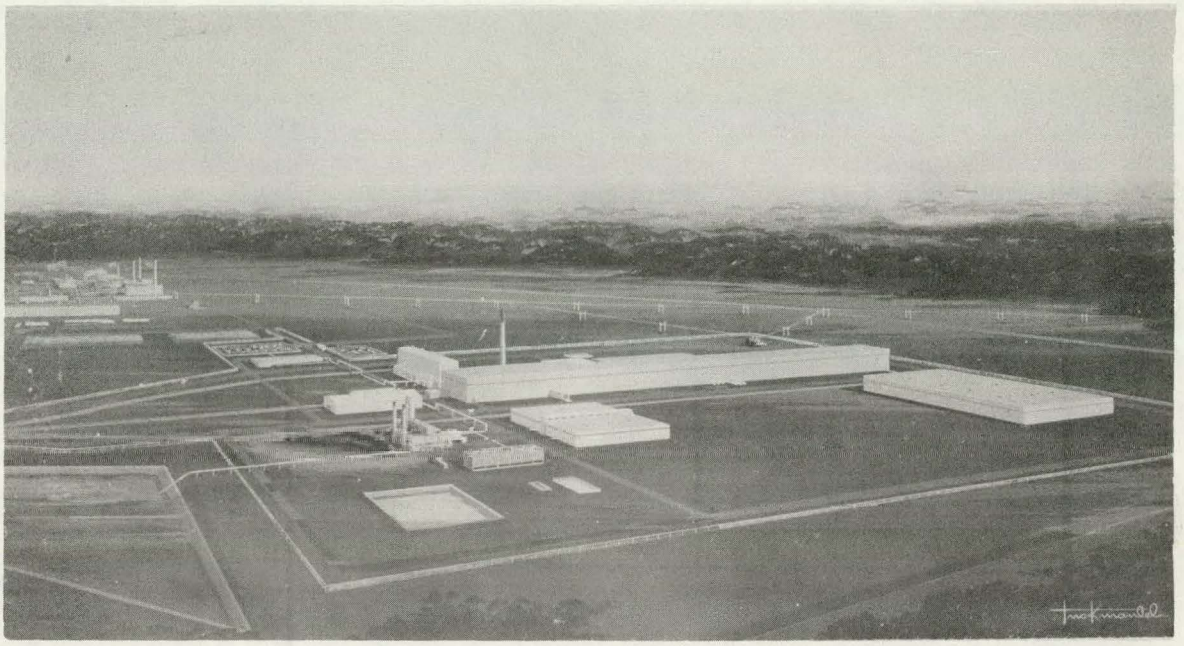

FIGURE 16. Artist's Concept of Defense Waste Solidification Facility