

IN-SITU THERMOELECTRIC STABILIZATION OF RADIOACTIVE WASTES

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INTRODUCTION

Prior to 1970 near-surface burial of transuranic (TRU) wastes was viewed as permanent disposal. Environmental studies are currently being conducted on a site-by-site basis to determine if additional treatment is required for some of these buried wastes. Due to the high cost and potential worker exposure associated with retrieval,¹ in-situ stabilization methods appear to be the most likely candidates for those wastes that require additional treatment.

Recognizing the need for cost effective in-situ stabilization techniques, Pacific Northwest Laboratory (PNL) developed a process for in-place solidification of buried wastes using electric melter technology developed for high-level waste immobilization.^{2,3} The process, in situ vitrification, converts buried wastes to a durable glass and crystalline material by melting the waste and surrounding soil in place.

Current analysis indicates that in situ vitrification is applicable to many wastes and soil types at a cost an order of magnitude less than exhumation, processing, and transportation to a deep geological disposal site. Once the waste materials have been solidified, future ground subsidence, wind erosion and plant or animal intrusion are virtually eliminated. Furthermore, the waste form is extremely durable.

Development to date has focused on buried radioactive wastes at Hanford; however, potential applications include both radioactive and nonradioactive hazardous material leaks and spills in addition to the intentionally buried wastes. A description of the process and a discussion of the development efforts are summarized in this report.

PROCESS DESCRIPTION

Solidification of buried waste and surrounding contaminated soil is achieved by inserting electrodes in the soil and establishing an electric current between the electrodes; Fig. 1 illustrates the process operating sequence. For startup, a small amount of specially prepared graphite is placed between the electrodes on the surface soil. Dissipation of power through the starter material creates temperatures high enough to melt a layer of soil, thereby establishing a molten, conductive path. This molten zone continues to grow in size as long as sufficient power is supplied to overcome heat losses. At the high temperatures created (>1700°C), organic materials decompose, and along with other noncombustible waste materials, dissolve or become encapsulated in the molten soil. Natural convective currents in the molten soil help distribute the waste materials uniformly and create a durable glass and crystalline waste

form. Off gas from the system is collected and treated in a portable off-gas system. Since subsidence may occur during processing, uncontaminated soil can then be backfilled over the site.

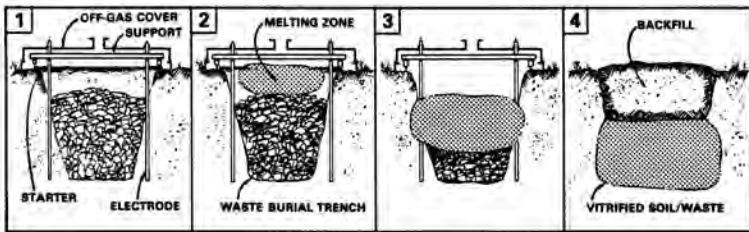


Fig. 1: In Situ Vitrification Operating Sequence

TEST EQUIPMENT DESCRIPTION

Three scales of test demonstrations are proposed for in situ vitrification: engineering (36-cm electrode separation), pilot (1.2-m electrode separation) and large (5-m electrode separation). Initial development and testing of the in situ vitrification process began in the engineering-scale test apparatus in which approximately 45 kg (30 liters) of soil were melted per test. The test apparatus illustrated in Fig. 2 and pictured in Fig. 3 consisted of a 1.2-m (4-ft)-dia x 0.6-m (2-ft)-deep insulated metal container filled with soil. A metal hood of the same dimensions covered the test apparatus to provide off-gas containment and electrode support. The hood was maintained under a slight vacuum during operation. Entrained or volatilized waste components in the off gas were isokinetically collected by the sampling system shown in Fig. 2. Combustion or pyrolysis gases were also periodically sampled and analyzed. Two electrodes positioned 36-cm (14-in.) apart extended 30-cm (12-in.) into the soil.

Fig. 2: Engineering-Scale Testing Apparatus Schematic

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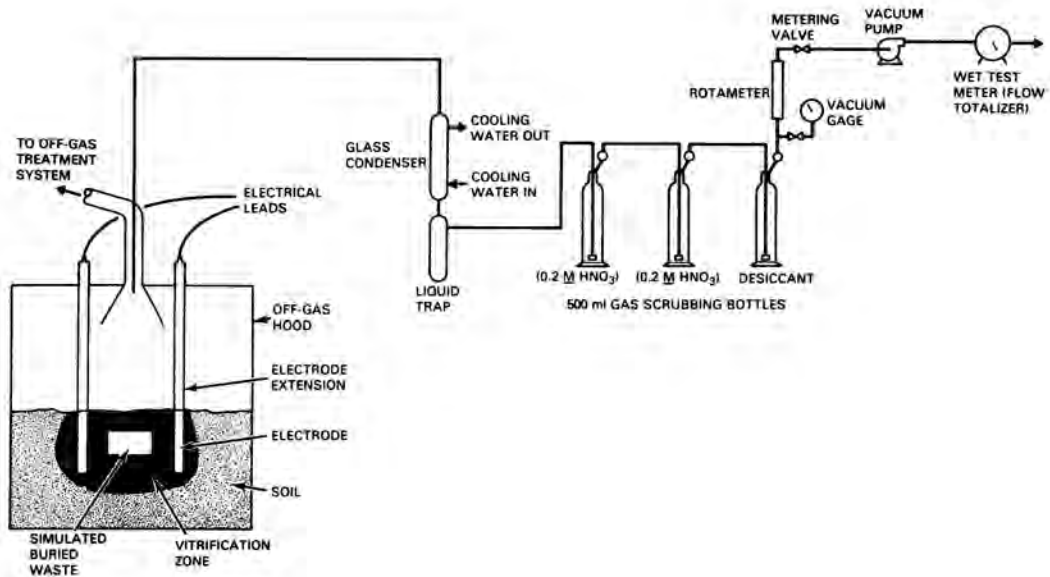




Fig. 3: Engineering-Scale Testing Apparatus

For most tests, simulated waste materials identified in Table I were buried between the electrodes. Soil for the tests was a non-radioactive sand and rock mixture obtained from a Hanford burial trench during excavation. Due to the small scale of the tests, rocks larger than approximately 8-cm (3-in.)-dia were removed from the soil.

TABLE I. Typical Simulated Waste Mixture For Engineering-Scale Tests

Material	Quantity Wt%
Rubber	5
Plastic	5
Glass	5
Concrete	5
Cardboard, paper & cloth	10
Refractory materials	15
Chemical waste analogs	15
Metal	40
TOTAL	100

TEST RESULTS

Engineering-scale tests were conducted for process verification and to develop reliable materials, electrical systems, startup techniques, operating sequences, and scale-up correlations for design of pilot-scale and large-scale testing facilities. The tests also investigated process characteristics, such as waste decomposition, off-gas behavior, radionuclide migration and waste-form quality.

Electrode Performance

After an evaluation of candidate electrode materials, molybdenum and graphite were selected for actual testing. Due to the relatively high cost of molybdenum electrodes (approximately \$28/lb), a reusable design was concluded to be necessary for actual large-scale operation. Initial tests with molybdenum verified that oxidation of the electrode near the soil-to-air interface would be unacceptably high. A thin protective coating of flame-sprayed metal, however, proved successful in reducing oxidation of the exposed molybdenum. At temperatures approaching the melting point of the coating, the surrounding soil was sufficiently molten to continue to provide protection. When the molten soil subsided, the layer of glass remaining on the electrode surface provided oxidation protection. Nominal corrosion rates for the molybdenum electrodes were not measurable over the 8-h to 12-h run periods; however, some minor pitting of the electrode surface was detected. Also when molten stainless steel contacted the electrode in one test, noticeable dissolution or alloying occurred.

Graphite electrodes were also selected for testing due to their significantly lower cost (25 times less costly than molybdenum electrodes). Test results indicated that corrosion rates were slightly higher than molybdenum, but still acceptable. Higher corrosion

rates can be tolerated with the relatively inexpensive graphite and reuse, although feasible, is not required.

Startup Technique

A startup technique using powdered or flaked graphite was selected for development because it was simple, relatively inexpensive, required little manpower and additional equipment to perform, and would achieve extremely high temperatures without vaporizing or oxidizing too rapidly. Four methods of graphite startup were tested:

1. a pure graphite path with soil cover
2. a pure graphite path without soil cover
3. a mixture of graphite and soil as a surface layer
4. a mixture of graphite and a low-melting (approximately 500°C) glass frit as a surface layer.

All four methods were successful in achieving startup; however, the last two methods were superior. In Methods 1 and 2, the electrical conductivity of the graphite was highly dependent on the packing of the graphite layer. Packing varied considerably and was difficult to reproduce. Also with the first two methods, some arcing within the startup path occurred. Method 2 was least effective because much of the graphite was oxidized before a molten path was created.

Due to improved heat transfer, the last two methods provided an earlier conductive path. Adding soil or frit to the graphite mixture also reduced the sensitivity to packing. Due to the low melting point and high conductivity of the frit, Method 4 provided the most stable and reproducible startup technique.

Hazardous Species Entrainment and Volatility

To evaluate the behavior of potentially hazardous species during in situ vitrification, nonradioactive isotopes of Cs, Sr, Ru, Cd and Pb were mixed with soil and placed in the engineering-scale test apparatus in several configurations: 1) contaminated soil was placed at an average depth of 7 cm (2.8 in.) below the surface of the soil with no combustible wastes in the soil; 2) contaminated soil was placed at an average depth of 24 cm (9.5 in.) below the surface in the waste burial box with the combustible and other noncombustible wastes; and 3) contaminated soil was placed in a layer directly below the simulated waste burial box, approximately 28-cm (11-in.) below the surface.

Figures 4 and 5 summarize the average isotope retention during melting as a function of burial depth for selected hazardous species. In general, the data show high retention. Ruthenium, strontium and lead had very high average retention (> 99.95%) for all three burial configurations as seen in Fig. 4. The nonvolatile behavior of ruthenium was attributed to the reducing conditions in the soil during melting.

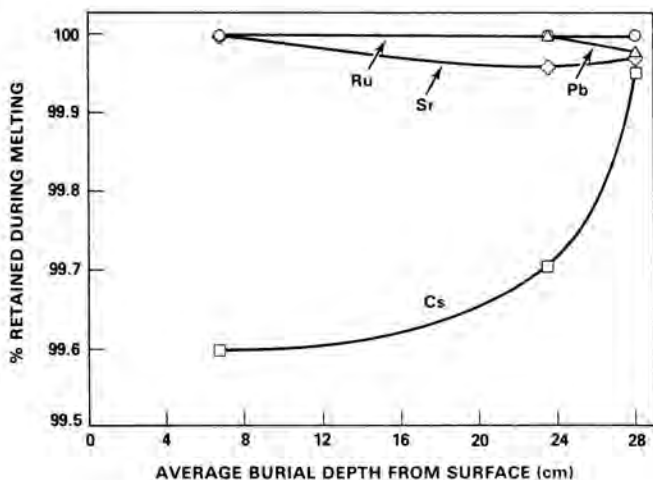


Fig. 4: Retention of Selected Species During Melting

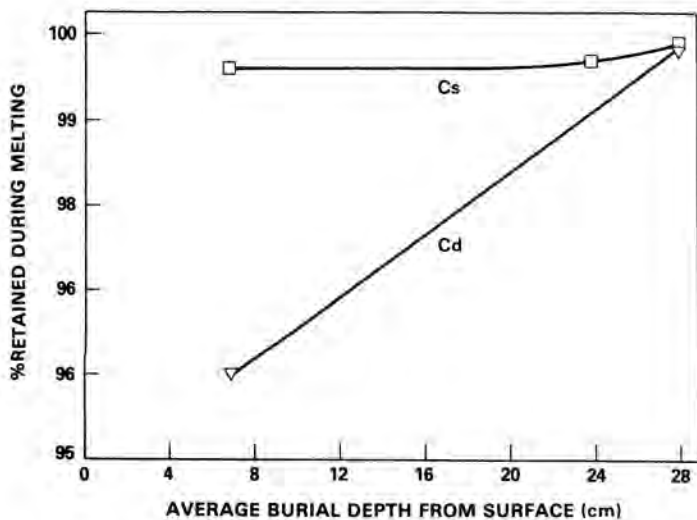


Fig. 5: Retention of Semivolatiles During Melting

Some cesium and cadmium volatility was observed and appeared to correlate with burial depth as shown in Fig. 5. Their volatility was highest when the contaminated soil was placed close to the surface. The higher losses were apparently due to the nearness of the melt surface and the semivolatile nature of these elements. When the wastes were close to the surface, the cesium and cadmium apparently volatilized while the surface was molten during startup. After startup, heat losses caused the surface to resolidify to form a cold cap. This cold cap appeared to effectively limit the diffusion of the volatilized species to the surface. For this reason, when the Cs and Cd were positioned deeper, losses approached the low values exhibited by the other hazardous species.

No detectable increase in the physical entrainment resulted when the wastes were mixed with combustible materials inside the burial box. The escaping gases from decomposition of the combustibles may have contributed to the higher Cs volatility, however, by providing low-resistance pathways for volatilized Cs to reach the surface. The strong reducing conditions in the vicinity of the burial box may have also contributed to the increased losses by increasing the decomposition of cesium oxide to the more volatile metallic cesium.

Waste Decomposition and Simulated Radionuclide Distribution

Tests were conducted with a mixture of waste materials typical of a radioactive waste burial ground. The high temperatures created caused the stainless and carbon steels to melt and collect on the bottom of the melt zone. Ceramic and glass materials, such as concrete, laboratory crucibles, and glassware, were either completely dissolved or encapsulated by the molten soil. Due to the deficiency of oxygen below the soil, pyrolysis of the organic materials occurred and resulted in the release of combustible gases. Some of the gases diffused through the viscous melt and spontaneously burned at the surface. Slightly elevated levels of carbon monoxide, hydrogen and methane in some of the tests indicated that a portion of the decomposition gases escaped without being completely oxidized.

To attain concentrations great enough for accurate analyses, nonradioactive cesium, strontium and ruthenium were mixed in the soil at concentrations up to a million times greater than would be expected in a typical Hanford waste site. Samples of the surrounding soil showed that none of these species were present above background levels beyond the vitrified block. Ruthenium migration within the block was minor, compared to cesium and strontium. The migration of cesium and strontium occurred in all directions, with a sharp decrease close to the edges of the vitrification zone. The movement of cesium in the vertical direction, however, was higher than strontium, possibly due to the volatile nature of cesium. The relatively uniform cesium and strontium concentrations throughout the molten soil confirm that a transport mechanism exists which will homogeneously distribute the waste materials. The anomaly of minor ruthenium migration cannot be explained without further testing and analysis. The minor ruthenium migration explains, however, why no loss of ruthenium to the off gas was detected for any of the tests.

The tests confirmed that although movement of radionuclides occurs within the vitreous zone, migration beyond the vitrified mass will not be a problem. Apparently the viscosity near the vitrification edge is high enough to prevent movement of radionuclides into the surrounding soil.

Waste Form Evaluation

The vitrified soil from each of the tests remained as a solid, nearly crack-free block. The blocks were removed from the test apparatus and sectioned for evaluation. In general, the interior of the block was a nonporous glass similar to natural obsidian. Leaching studies were conducted to determine the chemical durability of the vitrified Hanford soil. Samples were crushed and subjected to a continuous 72-h soxhlet test. Fig. 6 shows the resulting total weight loss during leaching. For comparison, published data on typical commercial glasses and some common minerals which have existed in nature for millions of years have been included.^{4,5} The leaching results show the vitrified soil has a bulk leach rate significantly better than granite, marble, or bottle glass and comparable to pyrex. Calculations based on the observed low leach rate of in situ vitrification glass and the expected large particle size indicate that the waste form can meet the criteria for repository disposal of transuranic waste as proposed in Nuclear Regulatory Commission (NRC) guidelines 10CFR60 ($<10^{-5}$ parts/yr of inventory released) if the criteria were applied to the waste form alone.

COMPARATIVE CHEMICAL DURABILITIES

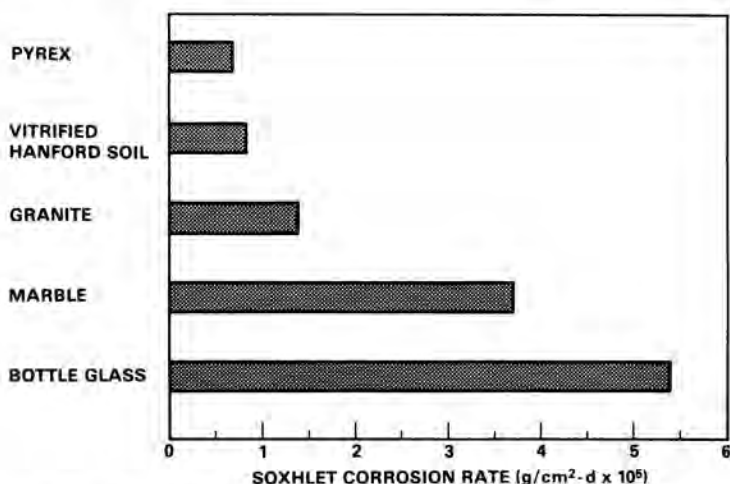


Fig. 6: Comparative Leach Resistance of Selected Materials

PROCESS EVALUATIONS

Waste and Soil Property Effects

Application of in situ vitrification requires that either the waste or surrounding media provide an electrical current path for joule heating. Since waste disposal sites frequently contain a large soil-to-waste weight ratio, the waste composition at these sites will have little effect on process operation or final waste form.

Although soil is normally an electrical insulator, at high temperatures it becomes an ionic conductor or electrolyte. This occurs when the viscosity of the soil is reduced enough to permit migration of the relatively free ions, primarily alkali metal ions, which carry the electric current. If the electrical resistivity of the soil is either too high or too low, the process becomes impractical due to difficulties in dissipating sufficient power. Also, if the melting temperature of the soil is too high, electrode corrosion and waste volatility become concerns.

A study of soil from eight selected radioactive waste burial sites located throughout the U.S. was conducted to determine the feasibility of stabilization by in situ vitrification at these sites. The sites are listed in Table II. The soil properties with the greatest influence on process feasibility are melting temperature and electrical resistivity.

In the soil tests, the approximate temperature at which fusion began was used for comparison. Since the chemical compositions of all the soil samples were very similar, i.e. high in silica and alumina, most of the soils began to fuse at about the same temperature as the Hanford soil. Fuquay soil from Barnwell, South Carolina, which began to fuse about 300°C above the Hanford soil, required the highest temperature. This temperature is well within in situ vitrification capabilities.

Molten soil conductivities were measured using a two-probe technique⁶ with an alternating current at a frequency of 1000 Hz to minimize polarization effects. Due to temperature limitations of the equipment, Na₂O flux was added to the soil for the actual measurements, and the data were then extrapolated to determine conductivity at the nominal soil composition. The data showed that even though the total alkali content of the soils varied significantly, from 0.5 to 7 wt%, the extrapolated electrical conductivities varied only between 3×10^{-2} to 5×10^{-2} (ohm-cm)⁻¹ at 1400°C. The variation was small because increases in the alkali oxide concentrations, which increase conductivity most significantly, were generally countered by increases in alkaline earths, which reduce electrical conductivity. The conductivity variations encountered are acceptable for stabilization by in situ vitrification.

TABLE II. Soil Types Investigated

Location	Soil Type
West Valley, New York	Churchville
Sheffield, Illinois	Fayette
Barnwell, South Carolina	Fuquay
Los Alamos, New Mexico	Puye
Los Alamos, New Mexico	Carjo
Maxey Flats, Kentucky	Tilsit
Nevada Test Site, Nevada	Beatty
Oak Ridge, Tennessee	--
Hanford, Washington	--

Scale-Up

Encouraging results from the engineering-scale tests led to the design and construction of a pilot-scale field test unit. The pilot-scale system, which uses four electrodes in a 1.2-m array, has successfully solidified up to 9000 kg of soil at a time, a scale-up of approximately 200 on a weight or volume basis.

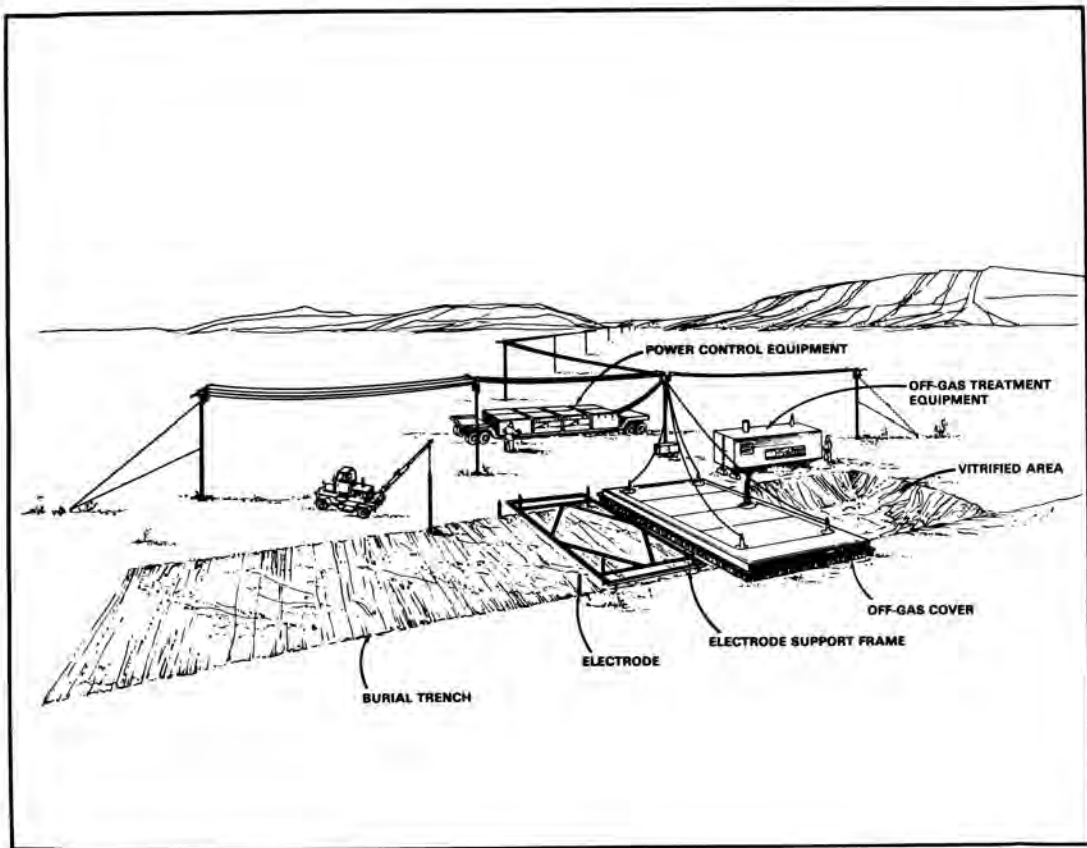
Close agreement between engineering-scale and pilot-scale tests verifies that the scale-up correlations are appropriate. These same correlations predict that for unmodified Hanford soil, electrode separations of 5 to 6 m are obtainable with a conventional 4160-V power system. Analysis shows that the power and off-gas equipment for this scale of system can readily be made portable. Portable generators in the required size are available for applications in remote areas where electric power is not readily accessible. For large areas, solidification might proceed in an incremental fashion throughout the length of the trench, as shown in Fig. 7, or all at the same time with multiple power units.

Economic Analysis

A cost of \$420/m³ of waste was estimated for application of in situ vitrification to radioactive wastes already buried in trenches. For the purpose of the estimations a 4500 m³ trench (5-m wide by 6-m deep by 150-m long) containing 3000 m³ of waste was assumed to be completely vitrified. Costs were based on a 10-yr equipment life and electrical energy costs of \$0.025 per kWh, which is currently conservatively high for Hanford. Table III summarizes the cost of the in situ vitrification process per cubic meter of waste. Labor is the most significant cost; however, this could be reduced by increasing the power input to the system and thus reducing the operating time. For this estimate an average power consumption of 2000 kW was selected.

A comparison of costs for in situ vitrification and several other proposed stabilization options is given in Fig. 8. Other in situ stabilization options considered involved injecting grouts, such as cement or self-hardening organic compounds, into the waste area. Costs for the three grouting options were obtained from Aroa et al. (1980) with escalation to 1981 dollars. Costs for the deep geological disposal option was obtained from Murphy and Holter

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Fig. 7: Artist's Conception of Full-Scale In Situ Vitrification



(1980). Costs for in situ vitrification are comparable to the cost of the chemical grouting methods and are at least an order of magnitude below the cost of exhumation followed by processing, transportation and deep geological disposal. Grouting methods of stabilization result in encapsulated waste formations that are expected to be reasonably durable between 25 and 100 yr.^{1,7} On the other hand, in situ vitrification is expected to remain relatively inert for thousands of years.

TABLE III. Estimated Unit Cost For In Situ Vitrification

Cost Category	\$/m ³ Waste
Equipment	38
Labor	275
Materials	40
Power and fuel	67
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TOTAL	420

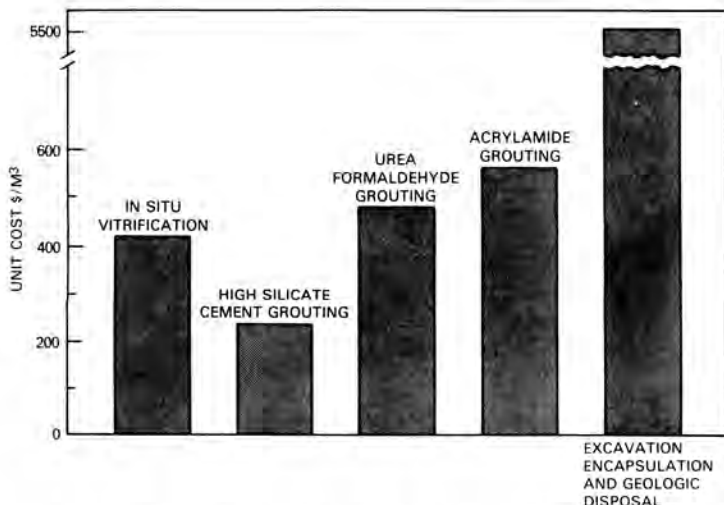


Fig. 8: Costs for Selected Stabilization Alternatives

CONCLUSIONS

Engineering-scale testing has demonstrated the technical/economic feasibility of in situ vitrification and led to important developments and improvements in the process. A startup technique using a graphite/glass frit mixture placed on the surface between the electrodes has proved to be very reliable. Corrosion rates of both molybdenum and graphite electrodes have been limited to acceptable levels by proper design. High process temperatures and the large quantity of soil in many burial grounds have combined to make the in situ vitrification process relatively insensitive to the waste type. Tests have shown that hazardous species losses to the off gas can be controlled to very low levels. The tests have also shown that the cool, viscous boundary layer at the leading edge of the vitrification zone prevents migration of hazardous species outside of this zone.

Current cost projections predict that in situ vitrification is competitive with other proposed in-place stabilization techniques, while providing a more durable waste form. Projections also indicate in situ vitrification costs are at least an order of magnitude below the cost of exhumation, processing, transportation and deep geological disposal. Leach studies indicate the vitrified soil is a very durable waste form that will remain inert for thousands of years. Most wastes treated with this process can be left in place and still meet proposed disposal criteria. Scale-up correlations based on tests vitrifying over 9000 kg of soil at a time predict electrode separations up to 6 m (20 ft) are practical. Analysis of various soils indicates the process is feasible in both eastern and western U.S. soils. Further studies including radioactive and larger-scale tests are planned to aid in further defining the limitations and potential applications of in situ vitrification.

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