

# IN SITU VITRIFICATION OF SOILS CONTAINING VARIOUS METALS

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## ABSTRACT

In situ vitrification (ISV) converts contaminated soil into a glass and crystalline product by melting it with electrical energy. Pacific Northwest Laboratory, the developer of ISV, is currently conducting research to extend the technology to buried wastes and underground tanks for the U.S. Department of Energy. Since these types of wastes are anticipated to contain high concentrations of metals, new processing techniques are being developed and tested. In addition, the effects of metals on melt shape and on the solubility of heavy metals are being studied and tested.

An electrode feeding technique has been developed and tested for processing high concentrations of metals. Instead of predrilling casings for electrode installation into the contaminated soil to be vitrified, electrode feeding allows the electrodes to be inserted as the vitrified soil melts downward. This concept has been successfully tested four times on engineering-scale equipment, which is 1/100th the capacity of large-scale equipment.

Preliminary information has been collected on the influence of metals on melt shape and on the solubility of heavy metals in the molten soil. Test results indicate that metals could be used to achieve greater depths with ISV. Also, even though the presence of metals may cause heavy metals to reduce and alloy with the molten metal pool at the bottom of the vitrified soil, the metallic phase passes all criteria for product durability. Additional and larger scale testing is needed to confirm these conclusions.

## INTRODUCTION

Pacific Northwest Laboratory (PNL) has been developing in situ vitrification (ISV) for the U.S. Department of Energy for various applications since 1980. ISV was originally developed and tested for radioactively contaminated soils. The process converts contaminated soils into a relatively stable glass and crystalline product that is similar to obsidian commingled with crystalline phases. PNL is currently extending the application of the technology to underground cribs, buried wastes, and underground tanks. Development of the technology to these new applications requires knowledge of the behavior of the process and development of new techniques for encountering various types of buried metals.

Figure 1 illustrates how the ISV process operates. A square array of four molybdenum electrodes is inserted into the ground to the desired treatment depth. Because soil is not electrically conductive when the moisture has been driven off, a conductive mixture of flaked graphite and glass frit is placed among the electrodes to act as a starter path. An electrical potential is applied to the electrodes to establish an electrical current in the starter path. The resultant power heats the starter path and surrounding soil to 1600°C to 2000°C, well above the initial soil-melting temperatures of 1100°C to 1400°C. The graphite starter path is eventually consumed by oxidation, and the current is transferred to the

molten soil, which is electrically conductive. As the molten or vitrified zone grows, it incorporates radionuclides and nonvolatile hazardous elements, such as heavy metals, and destroys organic components by pyrolysis. The pyrolyzed byproducts migrate to the surface of the vitrified zone, where they combust in the presence of oxygen. A hood placed over the area being vitrified directs the gaseous effluents to an off-gas treatment system.

Since PNL began developing the ISV technology, numerous experimental tests under a variety of conditions and waste types have been conducted. Table I describes the different scales of testing units that PNL used in developing ISV technology. The successful results of the bench-, engineering-, pilot-, and large-scale tests have proven the feasibility of the process.

This paper presents processing results from vitrifying through buried metals with a new self-feeding electrode technique. The effects of high metal concentrations on melt shape, an important consideration for applications concerned with achieving great depths and narrow widths, is also presented. Lastly, the influence of metals and their formation from the melt are discussed as they relate to the vitrification of arsenic, cadmium, and other heavy metals.

## SELF-FEEDING ELECTRODES

Prior to the development of electrode feeding, a limit of the amount of metals successfully tested in soils was

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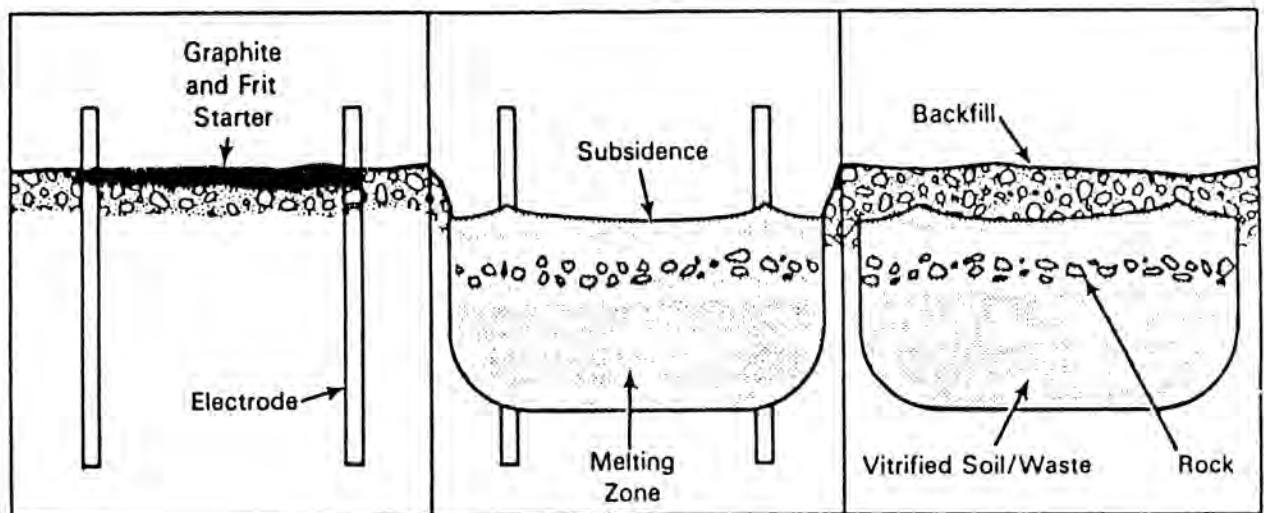


Fig. 1. The Process of In Situ Vitrification.

TABLE I  
Testing Units for Developing ISV Technology

| Equipment Size    | Electrodes Separation | Block Size    | Tests Completed(a) |
|-------------------|-----------------------|---------------|--------------------|
| Bench Scale       | 10 cm                 | 1 to 10 kg    | 19                 |
| Engineering Scale | 0.23 to 0.36 m        | 0.05 to 1.0 t | 33                 |
| Pilot Scale       | 1.2 m                 | 10 to 50 t    | 17                 |
| Large Scale       | 3.5 to 5.5 m          | 400 to 800 t  | 5                  |

(a)As of 1/26/90

established at 5 wt% (1). Concentrations in excess of 5 wt% would pool at the bottom of the molten soil and create an electrical short circuit between electrodes. Such an electrical short would prevent the ISV power supply from delivering adequate electrical power to the melt because the current would be diverted through the more conductive metal pool. The electrical current would reach the maximum limit of the ISV power system at low voltage, thereby creating insufficient power to continue melting operations. This behavior was proven during testing with stationary electrodes at a concentration of 16 wt% metals.

Another limit of metal concentrations was related to the linear separation of electrodes occupied by metal, such as a steel pipe or rod. The limit was established so that no more than 90% of the linear distance between any two electrodes could be occupied by metal. This limit was

established independent of the 5 wt% limit.

Application of ISV to buried wastes and underground tanks would likely exceed these concentration and linear separation limits. Consequently, engineering measures were investigated to determine how to extend the application of ISV to higher metal concentrations. The technique selected was electrode feeding.

Electrode feeding is accomplished by allowing the electrodes to rest on the bottom of the molten soil, letting them protrude into the contaminated soil or buried waste as the vitrified mass grows downward. Thus as high concentrations of metals are encountered, the electrodes can be held in place or raised off the bottom of the melt to avoid an electrical short with the metals that accumulate at the bottom of the molten soil.

The electrode feed system, depicted in Fig. 2, consists of a top stationary guide ring, a moving gripper/guide ring (for operator-controlled electrode feeding), and a bottom guide ring with electrical contact shoes for each electrode. The electrical contact shoes grip each electrode in a manner that allows for continuous feeding of the electrode while maintaining full power to the vitrified melt. The electrode feed system is operated using both gravity feeding and operator-controlled feeding of the electrodes. In operator-controlled feeding, the air-operated drive motor and gripper are used to raise and lower each electrode. Operator-controlled feeding is needed in ISV melts where a potential for electrical shorting exists. Air regulators on

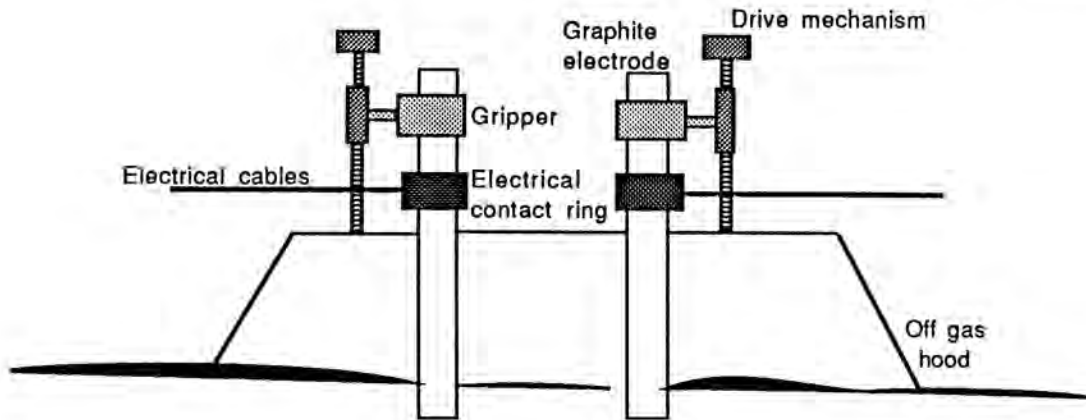


Fig. 2. The Electrode Feed System.

the air motor and gripper supply lines permit a wide range of operating speeds and gripping forces.

Another feature of the electrode feed system is that pure graphite is being used for the electrodes. The reference large-scale design for fixed, predrilled electrodes, shown in Fig. 3, consists of a 5-cm-diameter molybdenum core encased by a 30-cm-diameter graphite collar (1). Electrical continuity is maintained by a complex mixture of electrically conductive and oxidation-resistant powders and coatings in the annulus between the two components. As the vitrified mass grows downward, the graphite collars oxidize. The protected molybdenum, now exposed to air, continues to carry electrical current to the glass melt. Protective coatings cannot be used to help protect the graphite because, as the vitreous mass subsides, the coatings are corroded by the molten glass before being exposed to air. Consequently, the more complex design is necessary.

With electrode feeding, the use of pure graphite electrodes without the molybdenum core, powders, and coatings is possible due to the following reasons:

- Oxidation-resistant coatings such as silicon carbide on the graphite are more effective because the electrode is fed into the molten glass as the vitreous zone subsides. Molten soil cannot dissolve the coating at the surface of the molten glass, where oxidation protection is needed.
- Failure of an electrode has a greatly reduced effect on the operation of the process. The relatively inexpensive graphite material can be fed to the bottom of the molten soil after an electrode failure. The air-operated drive motor and gripper make the electrode recovery process much simpler. The principle of feeding electrodes to the melt as they oxidize is a common practice in the commercial glass-producing industry (2).

The electrode feed system has been tested four times with the engineering-scale ISV unit with great success.

These included two tests with buried metals, a test with an underground metallic tank (3), and a test on a dolomite-filled trench. Each electrode consisted of four 56- to 61-cm-long, 5.1-cm-diameter graphite sections that were joined by thread connections, for a total electrode length of 235 cm. The electrodes were initially inserted into the cover soil to a 15 cm depth to promote startup. They were spaced in a 30.5-cm x 30.5-cm square array. Many of the electrodes were coated with a silicon carbide coating that was applied to the graphite by paint brush or with a chemical vapor deposition (CVD) coating. After the engineering-scale tests were completed, the silicon carbide-coated electrodes were compared with the uncoated electrodes to determine if silicon carbide coatings inhibited electrode corrosion.

Table II summarizes the performance of the two different types of coating in retarding electrode oxidation for the first three engineering-scale tests. (Data from the fourth test are unavailable at this time). Both coatings were effective at significantly reducing the amount of oxidation. The major detriment of the coatings was that glass wets silicon carbide more than graphite, which causes the glass to bond to the electrode creating resistance to electrode feeding. The pilot-scale electrode feed system, although not yet tested, has been designed with greater force to overcome this resistance. Based on the results of the engineering-scale tests, the first pilot-scale test will be performed using paint-on silicon carbide coatings. (Based on the same rate of oxidation, greater than 100 h of continuous operation is expected with the 15-cm-diameter, coated, pilot-scale electrodes.) If the pilot-scale test is successful, as expected, a large-scale electrode-feeding concept will be tested.

The electrode feed system was highly effective in overcoming electrical shorting when encountering high concentrations of metals. Table III is a comparison of three engineering-scale tests that demonstrate this point. The only significant difference among the three tests was in the type of electrodes, fixed or self-feeding. The results show that for high metal concentrations, electrode feeding en-



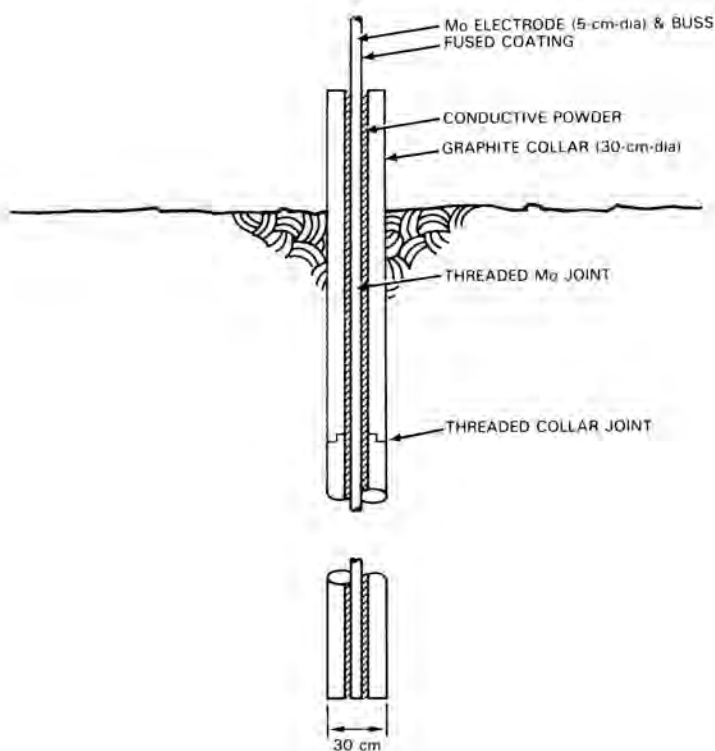


Fig. 3. Reference Design for Predrilled Electrodes.

hanced downward melting progress by 30%, increased power input to the melt by 30 to 80%, and increased the amount of soil vitrified by 150%.

During testing, the electrode depth was determined by the height of each electrode above the melt surface. The electrode depths were plotted against the depth of the vitrified melt, measured by thermocouples, to determine if melt depth could be monitored by electrode feeding. The plot of melt depth and measured electrode depth is shown in Fig. 4 for one test. The graphite electrodes effectively monitored melt depth during "gravity" feeding of the electrodes, until the electrode short required the electrodes to be raised. During the subsequent operator-controlled feeding stage, the electrodes provided an adequate measure of actual melt depth.

The results imply that melt depth could be continuously monitored by gravity feeding of electrodes on contaminated sites where metal pooling is not a consideration. This is based on assumptions that the amount of electrode corrosion experienced during electrode feeding would not compromise the electrode length. Melt depth could also be monitored for high metal concentrations using operator-controlled electrode feeding. However, it may be desirable to make melt depth measurements intermittently when the

ISV electrical system is not energized to avoid shorting through the molten metal pool during depth measurements.

#### INFLUENCE OF METALS ON MELT DEPTH

High concentrations of metals in the soil being vitrified are thought to influence the shape and depth of the vitreous material as it grows. As molten metal is formed in a pool at the bottom of the molten soil, a greater concentration of electrical current, and thus a higher power density, would be created near the bottom of the melt. Coupled with the higher thermal conductivity of the molten metal pool, a greater downward melting rate is expected, relative to the outward melting rate.

This point is illustrated by a comparison of three bench-scale tests conducted with varying concentrations of metals. Fig. 5 plots the melt depth versus energy input for each of the tests. The presence of the molten metal pool at the bottom of the melt focuses the power toward the bottom, thus creating a higher downward melt rate per unit of energy consumed. When significant concentrations of metals (> 10 wt%) are present, downward growth per unit energy was nearly twice that for low metal concentrations (< 5 wt%). These data indicate that the presence or introduction of metals into a melt could increase the achievable

**TABLE II**  
Effectiveness of Coatings on Graphite Electrodes

| Coating      | Number of Electrodes | Amount of Oxidation                         | Resistance to Feeding                        |
|--------------|----------------------|---|--|
| None         | 2                    | Significant (failure, 5.1 cm diameter loss) | Negligible                                   |
| Paint-on SiC | 8                    | Moderate (2 to 4 cm diameter loss)          | Moderate (2 of 8 electrodes frozen in place) |
| CVD SiC      | 2                    | Insignificant (0 to 2 cm diameter loss)     | Moderate                                     |

**TABLE III**  
Engineering-Scale System Performance Comparison

| Parameter            | Test 1<br>Electrode Feeding | Test 2<br>Fixed Electrodes (4) | Test 3<br>Fixed Electrodes (4) |
|----------------------|-----------------------------|--------------------------------|--------------------------------|
| Total run time       | 34.4 h                      | 18.9 h                         | 19.9 h                         |
| Vitrified glass wt   | 373 kg                      | 154 kg                         | 142 kg                         |
| Melt depth           | 0.89 m (35 in.)             | 0.69 m (27 in.)                | 0.66 m (26 in.)                |
| Melt width           | 0.77 m (30 in.)             | 0.51 m (20 in.)                | 0.46 m (18 in.)                |
| Average power        | 16.0 kW                     | 12.5 kW                        | 8.9 kW                         |
| Total energy         | 550 kWh                     | 202 kWh                        | 171 kWh                        |
| Energy-to-mass ratio | 1.3 kWh/kg                  | 1.3 kWh/kg                     | 1.2 kWh/kg                     |
| Metals content       | 12.4 wt%                    | 12.5 wt%                       | 15.9 wt%                       |

**TABLE IV**  
Half Reactions and Standard Reduction Potentials for Heavy Metals

| Half Reaction               | Standard Reduction Potential, V (7) |
|-----------------------------|-------------------------------------|
| $Ag^+ + e^- \rightarrow Ag$ | +0.7996                             |
| $As + 3 + 3e^- \rightarrow$ | not available                       |
| $Ba + 2 + 2e^- \rightarrow$ | -2.912                              |
| $Cd + 2 + 2e^- \rightarrow$ | -0.403                              |
| $Cr + 2 + 2e^- \rightarrow$ | -0.913                              |
| $Hg + 2 + 2e^- \rightarrow$ | +0.851                              |
| $Ni + 2 + 2e^- \rightarrow$ | -0.257                              |
| $Pb + 2 + 2e^- \rightarrow$ | -0.1262                             |

vitrification depth beyond the 5 m currently demonstrated (5) and even beyond the 10-m projected depth. Data at larger scales need to be collected to confirm this behavior, however. Engineering-scale tests performed to date have

not been performed with enough controlled parameters to verify this conclusion.

**INFLUENCE OF METALS ON VITRIFICATION OF HEAVY METALS**

A small sampling of ISV products indicated that the ISV molten soil is quite reducing, with measured ferrous/ferric molar ratios of more than 15 to 1 (6). (Typical ratios for high-level nuclear waste glasses are less than 1, which are much more oxidizing.) Even so, the presence of high concentrations of metals in the soil can enhance the reducing nature of ISV further. Thus, metals may have an impact on the solubility of certain heavy metals such as arsenic, silver, and cadmium. The solubility of any element in its oxidized state is generally quite high in molten soil (>10 wt%). However, if reduced to the metallic state, heavy metals will become relatively insoluble in glass and will settle and be alloyed with the molten metal pool at the bottom of the melt.

An indication of whether heavy metals reduce to the metallic phase can be provided by an examination of the standard reduction potentials compared with that of iron. Iron is a common element in most soils and metals. If the

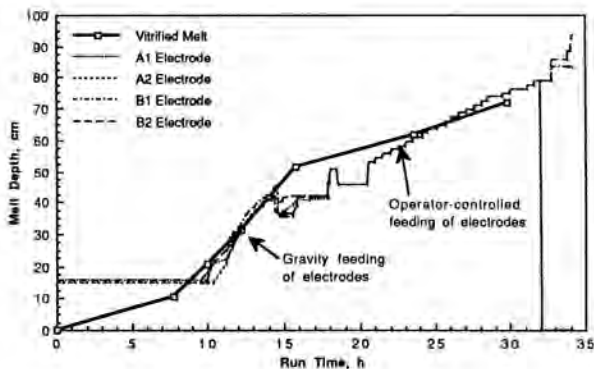


Fig. 4. Melt Depth Versus Measured Electrode Depths.

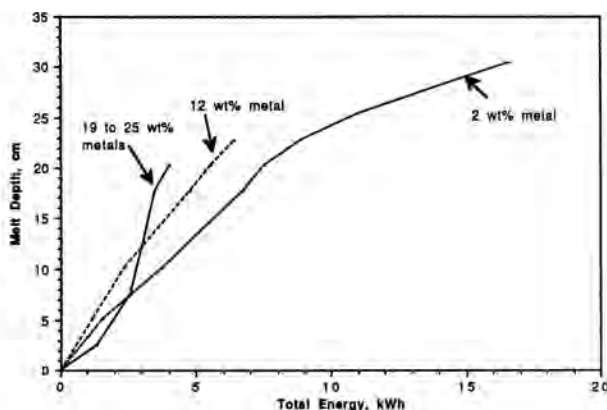
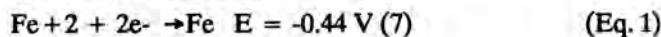


Fig. 5. Melt Depth Versus Energy Input for Three Bench-Scale ISV Tests.

standard reduction potential,  $E$ , is less than that of the following half-reaction,



the heavy metal is not likely to reduce to the metallic state. An examination of the half reactions and their standard reduction potentials in Table IV shows that mercury, silver, lead, and nickel have a significant potential to be reduced in the presence of high concentrations of iron-based metals. Cadmium is roughly equivalent to the reduction potential of iron and would also be expected to be reduced. Barium and chromium are not likely to be reduced from the molten soil because of their low reduction potential. They will remain in the vitrified product in their oxidized, soluble form.

Although the standard reduction potential is not available for arsenic, it is also thought to be significantly reduced to its metallic state in the presence of metals. Arsenious oxide ( $\text{As}_2\text{O}_3$ ) is commonly used in the glass industry to oxidize iron, sulfur, and carbon (8,9); consequently, it can be expected to reduce to the metallic form at the bottom of the melt. Two bench-scale tests with arsenic have confirmed this behavior by the detection of arsenic in the metallic phase by x-ray diffraction. In addition, a bench-scale test with silver, which has a relatively high reduction potential, showed significant concentrations of silver in the metallic phase.

Nevertheless, Toxic Characteristics Leach Procedure (TCLP) tests show that the metallic phase passed the maximum allowable concentrations for an unregulated waste for all heavy metals. Table V shows the measured and allowable heavy metal concentrations in the metallic phase leachate from two tests.

### SUMMARY AND CONCLUSIONS

Experience with ISV for soils containing high concentrations of various types of metals continues to expand. An electrode feeding technique for processing metals in the soils has been selected and tested. In addition, preliminary information has been gathered on the influence of metals on melt shape. Finally, the expected influence of iron-based metals on reducing certain heavy metals has been confirmed in bench-scale tests. Based on the results of these tests, the following conclusions can be made for soils containing high concentrations of metals:

- The electrode feeding concept is ready for pilot-scale testing. Although paint-on silicon carbide coatings should be tested first, additional tests should be performed with no coatings and with CVD coatings to select a satisfactory electrode design for large-scale testing.
- Pilot- and large-scale testing should be performed under controlled conditions to determine whether the presence or introduction of metals can be used in

**TABLE V**  
TCLP Concentrations for Metallic Phase from One Bench-Scale Test

| Contaminant | Initial Conc. in Soil, $\mu\text{g/g}$ | TCLP Conc., Metal, mg/L | Allowable Conc., mg/L |
|-------------|--|-------------------------|-----------------------|
| Arsenic     | 4400                                   | <5                      | 5                     |
| Barium      | 4400                                   | <1                      | 100                   |
| Cadmium     | 4400                                   | <1                      | 1                     |
| Chromium    | 270 to 4400                            | <0.2 to 2.7             | 5                     |
| Silver      | 4400                                   | <0.1                    | 5                     |
| Lead        | 50                                     | <0.1                    | 5                     |
| Mercury     | 46                                     | <0.0001                 | 0.2                   |

conjunction with electrode feeding to control the depth and shape of the molten soil.

- Even though certain heavy metals can be reduced from the vitreous phase into the metallic phase at the bottom of the molten soil, the iron-based metal makes a sufficiently durable waste form. Leachability tests performed to date show that heavy metal concentrations in the leachate are below allowable limits for unregulated waste. Future tests being conducted with metals should expand the data base and confirm the durability of the metallic phase.

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