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TREATMENT OF MIXED RADIOACTIVE AND
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THE HYBRID TREATMENT PROCESS FOR TREATMENT OF MIXED RADIOACTIVE AND HAZARDOUS WASTES

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I. BACKGROUND

This paper describes a new process for treating mixed hazardous and radioactive waste, commonly called mixed waste. The process is called the Hybrid Treatment Process (HTP), so named because it is built on the 20 years of experience with vitrification of wastes in melters, and the 12 years of experience with treatment of wastes by the in situ vitrification (ISV) process.

Mixed wastes are being generated by both the U.S. Department of Energy (DOE) and by commercial sources. The wastes are those that contain both a hazardous waste regulated under the U.S. Environmental Protection Agency's (EPA) RCRA regulations and a radioactive waste with source, special nuclear, or byproduct materials. The dual regulation of the wastes increases the complexity of the treatment, handling, and storage of the waste. Current EPA regulations[1] require that DOE begin treating the mixed waste as a third-third waste by May of this year; however, DOE does not have treatment systems available to meet this deadline, and Congress is now considering various alternatives to extending the deadline for treatment. The DOE is the largest holder and generator of mixed waste. Its mixed wastes are classified as either high-level, transuranic (TRU), or low-level waste. High-level mixed wastes will be treated in vitrification plants. Transuranic wastes may be disposed of without treatment by obtaining a no-migration variance from the EPA. Low-level wastes, however, will require treatment, but treatment systems with sufficient capacity are not yet available to DOE. Various facilities are being proposed for the treatment of low-level waste. The concept described in this paper represents one option for establishing that treatment capacity.

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II. TYPES OF DOE MIXED WASTES

Information on the characteristics and volumes of mixed wastes was recently presented and published.[2] There is a need for treatment of about 70,000 m^3 of existing waste and 7700 m^3/yr of current generation waste. Four major waste streams have been omitted from these numbers. Two of these streams are at the Hanford Site, where much of waste from the single-shell and double-shell tanks is classified as mixed waste. These two streams are the largest DOE mixed-waste streams and amount to about 218,000 m^3 of existing inventory and 13,000 m^3/yr of annual generation waste. A Grout Treatment Facility has been established at Hanford to treat these wastes and prepare them for disposal. The third waste stream is partially cemented and uncemented sludge from a waste pond at the Oak Ridge K-25 site. This stream, with a volume of about 28,000 m^3, is also large enough to be treated in a dedicated facility, although such a facility has yet to be defined. The fourth waste stream is the "pondcrete" at the Rocky Flats site. This stream is currently being treated.

The 12 sites with the most significant processing needs are Fernald, Hanford, K-25 (Oak Ridge), Idaho National Engineering Laboratory (INEL), Lawrence Livermore National Laboratory (LLNL), Los Alamos National Laboratory (LANL), Oak Ridge National Laboratory (ORNL), Paducah Gaseous Diffusion Plant, Portsmouth Gaseous Diffusion Plant, Rocky Flats Plant (RFP), Savannah River Site (SRS), and Y-12 (Oak Ridge). These 12 sites account for about 98% of the mixed waste volumes. The relative current inventory and generation rate for the largest sites are shown in Figure 1.

As can be noted, INEL currently has the largest inventory of waste. The waste, however, will be from reclassification of currently stored TRU wastes that were shipped from the RFP. Y-12, SRS, and K-25 are the other sites with significant current inventories. INEL also has the largest generation rate, which can be attributed to one large aqueous waste stream that they currently plan to evaporate and treat with their intermediate-level waste. Without that stream, INEL's generation rate is only 31 m^3/yr and they are one of the smaller waste generation sites. Likewise, the high generation rate at SRS is from aqueous waste streams. It is not expected that these streams will continue to be stored as high-volume aqueous streams, but that they will be treated and appear as concentrates or sludges in the future.

To develop additional information about the wastes, each stream has been assigned a waste matrix category. The relative quantities of major categories of waste are shown in Figure 2. The seven major treatment categories are aqueous liquids, organic liquids, inorganic solids, metal wastes, organic solids, heterogenous wastes, and potential problem wastes. The division between aqueous and organic liquids is the 1% organic level in accordance with the RCRA requirements. The inorganic solids leave a high residue following thermal treatment. The metal wastes represent nearly pure metal streams that may require specific treatment technologies. The organic solids are generally those that would produce less residue from incineration or other thermal processes. The heterogeneous wastes are the most difficult to treat and contain mixtures of inorganic solids, metals, and organic solids. The last category is the potential problem wastes. These wastes need further evaluation to allow their incorporation into another category or to determine if specific processes are needed for their treatment. As can be noted, the inorganic solids are the largest current inventory, with nearly equal amounts of metal wastes, organic solids, and heterogeneous wastes. It is interesting to note the small volume of organic liquids, which have been a primary focus of much of the previous technology development activities for treatment of mixed wastes. Figure 3 shows a further breakdown of the major categories. At the level of detail shown by this figure, the needs for specific treatment can be assessed.

III. NEED FOR TREATMENT

The EPA Land-Ban regulations require that the mixed wastes be treated according to specific treatment processes corresponding to their hazardous materials content. The treatment technologies specified in the regulations are based on the Best Demonstrated Available Technologies (BDATs). The treatment needs, however, generally can be of three types. The first is organic destruction. It is applicable to all of the wastes that contain hazardous organic materials. The second is for the immobilization of hazardous metals, which cannot be destroyed by oxidization, but require incorporation into a matrix that provides leach resistance. The third is for recovery and recycle of materials. This alternative is not currently possible for the mixed wastes since it is DOE's policy not to release potentially contaminated materials into general commerce.

Several methods and approaches have been generated for the treatment of mixed wastes. The most comprehensive approach has been developed by the Mixed Waste Treatment Project (MWTP).[3] For this project an initial flowsheet was prepared that shows the various treatment options needed for each major waste category. Figure 4 illustrates the flowsheet, showing the various major waste streams and the various treatment steps required for the streams. For the process to operate each of the X's requires a process step and process equipment, some of which may be combined. However, the complexity of the whole process can be noted by the large number of separate operations. The overall process requires at least six different types of thermal treatment units, with a major effort required to sort and separate the various wastes into streams that can be treated by the specific thermal unit. This flowsheet is expected to be simplified with further evaluation and testing; however, it is still expected to represent a major DOE prototype facility for demonstrating mixed waste treatment technology.

IV. THE HYBRID TREATMENT PROCESS CONCEPT

To simplify the treatment facility and greatly reduce the costs of mixed waste treatment, the Hybrid Treatment Process (HTP) has been conceived. This concept, illustrated in Figure 5, draws on many different technologies. The process as currently envisioned begins at the disposal site, where a hole is excavated. The containment vessel for the process, a mild steel metal tank, is brought onto the site and assembled so that air flows around all its sides to keep it from melting during the high-temperature processing period. This batch-type processing is similar to that used with the in-can melting technology developed in the 1970s at PNL[4] and elsewhere. The inside of the vessel also may be lined with refractory materials to reduce the vessel's external surface temperatures. Waste drums or boxes would be prescreened to remove any unacceptable materials, then loaded into the vessel. Soil or other glass-former materials would be added around the drum and at the top and bottom of the waste to act as a particulate filter and a source of glass former. Valved piping would be placed so liquid wastes could be pumped into the waste materials either as a preparatory step or during processing. Additional solid materials also may be fed to the top of the melt; however, the process could be operated initially as a batch operation to simplify and expedite its establishment. The process vessel would be of sufficient size to accommodate even the largest waste items. For the concept described here, the vessel typically would be of the order of 35 ft in diameter and about 20 ft in depth, but the dimensions are not considered critical and could be varied to suit specific needs. After the wastes are emplaced and additional materials are added, the vessel would be heated slowly using in situ heating or another method to remove the liquids at low process temperatures. This step could vary, depending on the type of wastes within the process batch. If evaporation is desired for particular wastes, then the waste drums could be perforated either by mechanical methods or by internal pressurization and rupture of the drum seals. It is possible to fail sealed drums with low-temperature heating since pressures of less than 35 psi are all that are required to fail the drum seals. Mixed wastes drums currently in use are designed to fail at 7.5 psi. Pressures of 35 psi are obtained at a temperature of about 140°C. After heating the vessel to several hundred degrees and removing all of the highly volatile materials, the temperatures could be further increased by in situ vitrification (ISV)-type heating. As the waste is heated, organic and combustible materials are pyrolyzed and destroyed and vapors are collected by the off-gas hood and sent to an off-gas treatment system. The progress of the melting and thermal destruction activities would be monitored by thermocouples placed into the wastes when the waste is loaded into the process vessel. The process would be controlled from a mobile process control center located in a trailer. The high-temperature heating would form a homogenous melt because of the naturally occurring thermal convection currents in the process vessel. It is anticipated that about 7 to 10 days would be required to totally dry and melt each batch of waste.

Off-gases from the process would be treated in a mobile treatment facility similar to the facility already developed for the ISV process. A secondary combustion capability would likely be needed to provide the high degree of organic destruction needed during the initial heatup period and possibly during the high-temperature melting and homogenization. Further engineering evaluation will be needed to decide if it is better to operate the vessel in an oxygen-deficient mode, thereby producing a metal slag and combustible gases, or in an oxygen-rich mode, thereby oxidizing all metals and avoiding pyrolysis gas accumulations in the vessel.

Figure 6 illustrates the disposal site following completion of the processing, cooling of the vessel, and backfilling, with the potential for incorporating an engineered barrier in conformance with RCRA requirements. It may be useful to incorporate an engineered barrier, such as a leachate collection system, into the system before setting up the tank. Other barriers could be installed after the processing has been completed.

It is anticipated that about one vessel a month could easily be processed by one crew, resulting in a processing capacity of about 6000 cubic meters per year per system. Assuming that there are processing units at several major sites, it is reasonable that DOE could be current in its waste processing within 5 years after the start of operations. It will require only about 200 batches to treat all of the current inventory and the inventory expected to be generated during the next 5 years.

MAJOR ADVANTAGES OF HTP

The major advantages of the HTP concept include very low relative costs, short development and deployment schedule, flexibility in waste acceptance, quality of the final waste product, reduced worker exposure to hazardous chemicals and radiation, treatment of reclassified TRU without plutonium concentration, and minor generation of secondary waste.

Preliminary costs of the system are estimated to be less than 10% of the cost of building and operating a large multi-process treatment facility. Table 1 lists the initial cost estimates. For comparison, it is assumed that both facilities process 25,000 m^3 of waste and that 30 people and 140 people are required to operate the HTP process and the full-scale plant, respectively. Neither option considers the transportation and disposal costs. The major savings occur in the costs for capital equipment, labor, process facility maintenance, and final D&D. The costs of both types of facilities will likely undergo significant changes as they are further developed and as they address additional regulatory and safety requirements.

The low capital costs facilitate a schedule advantage, since the HTP trailers and process equipment would not require line item authorization from Congress and the associated time required for that authorization. This advantage accelerates the potential application time by about 3 years, if the associated R&D can be completed. While several questions and uncertainties about the process need to be resolved, much of the R&D has been completed as part of other programs. It is anticipated that a prototype could be operational in about 5 years with an aggressive schedule, about 4 to 5 years ahead of a full-scale multifunctional plant. To meet this schedule it is necessary to begin the site disposal planning so that it is ready with the technology.

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Table 1. Preliminary Comparison of Treatment System Costs between the HTP and Full Treatment Facility

Cost Category	Hybrid Treatment Process	Mixed Waste Treatment Prototype
Capital Costs	$10,000,000	$300,000,000
Labor Costs	$15,000,000	$175,000,000
Process Vessels/55 gal Drums	$10,000,000	$5,000,000
Process Materials and Process Maintenance	$2,000,000	$70,000,000
Power	$2,000,000	$3,000,000
Total Operating	$29,000,000	$253,000,000
D&D Costs	$1,000,000	$30,000,000
Total Costs	**$40,000,000**	**$583,000,000**
Cost Per Cubic Meter	1,600	23,320

As noted above, the wastes to be treated vary greatly in composition and form. The HTP can accept widely varying waste forms since organics would be destroyed, the metals melted or incorporated into the matrix, organic and aqueous liquids volatilized and treated in a secondary combustion and their residue incorporated into the waste form matrix, and other inorganic solids melted and formed into a molten glass along with the residual from the other wastes types. Because of the ability to treat the wide variety of waste in one batch, the sorting, size reduction, and separation operations can be avoided. The soil and the wastes both provide silica to the melt. A detailed evaluation of the composition of mixed TRU wastes indicates that the resolved oxide composition of the waste alone would be about 45% SiO_2, 12% Al_2O_3, 24% CaO, 10% Fe_2O_3, and the balance other minor components. Mixed low-level waste should be similar with its high concentration of sludges and cemented sludges. The addition of contaminated soils provides additional silica in the melt and a method to dispose of contaminated soils, of which large volumes are expected from the site cleanup activities. Depending on the oxidization conditions during the melting period, much of the iron could remain as metal and form a separate ingot at the bottom of the vessel, thus reducing the content of iron in the glass. Mixing of the molten wastes for several days produces a nearly homogenous product[5] that makes sampling easier and makes verifying the quality of the final waste product practical and cost effective.

The operational exposure of the workers to hazardous chemicals and radiation will be reduced by avoiding the need to open drums, not sorting the waste, reducing the analytical needs, avoiding dusty size reduction operations, and reducing the need to handle and transport the waste. Fewer workers will be required, further reducing the likely operational exposures.

An anticipated benefit would be processing the reclassified TRU materials (10 to 100 nci/g) and homogenizing the TRU material into a durable waste form with other non-TRU wastes and soils, thus maintaining the concentrations of TRU in the below 100 nci/g limit in a durable waste form.

Without the separation of the wastes from the drums and the internal processing, secondary wastes in the HTP are also reduced. Typical processes will decontaminate drums for recycle, and will have significant volumes of failed equipment, filters, process trash, worker clothing, cleanup materials, and other potential wastes. The simple processing in the HTP avoids most of these waste generation activities. Both processes will generate some off-gas wastes that will need to be recycled into the process or companion processes.

TECHNOLOGY AND INSTITUTIONAL DEVELOPMENT NEEDS

Before the process can be operated at a large scale, there are design and operating questions that must be answered through analysis, testing, and development. Some of the questions are related to drum pressurization, pyrolysis gas oxidization, the potential need for dual containment of operations, the effects of high-temperature operations on the integrity of the tank, the influence of the oxidization state of the melt on process and product performance, and the effects of a cold wall on the process and hazardous constituents. Besides these technical issues, there are several institutional issues that need to be addressed. These issues are related to the use of alternative technologies rather than BDAT technologies; the need for engineered barriers for the RCRA disposal site; and typical issues of state and EPA acceptance, such as sampling requirements and configurations.

V. SUMMARY

The HTP has been conceptualized to provide a process for treating a wide variety of mixed low-level wastes. The process may have application to other wastes types, such as D&D wastes and buried wastes, as well. The major advantages of the process are

- costs that are less than 10% of the full facility alternatives
- fast deployment schedule, with waste processing in 3 to 5 years
- flexibility in waste acceptance
- production of a homogenous, high-quality waste form
- low worker exposure to hazardous chemicals and radioactive materials.

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The concept needs to be developed to resolve issues identified during the conceptualization activities, as well as potential institutional issues.

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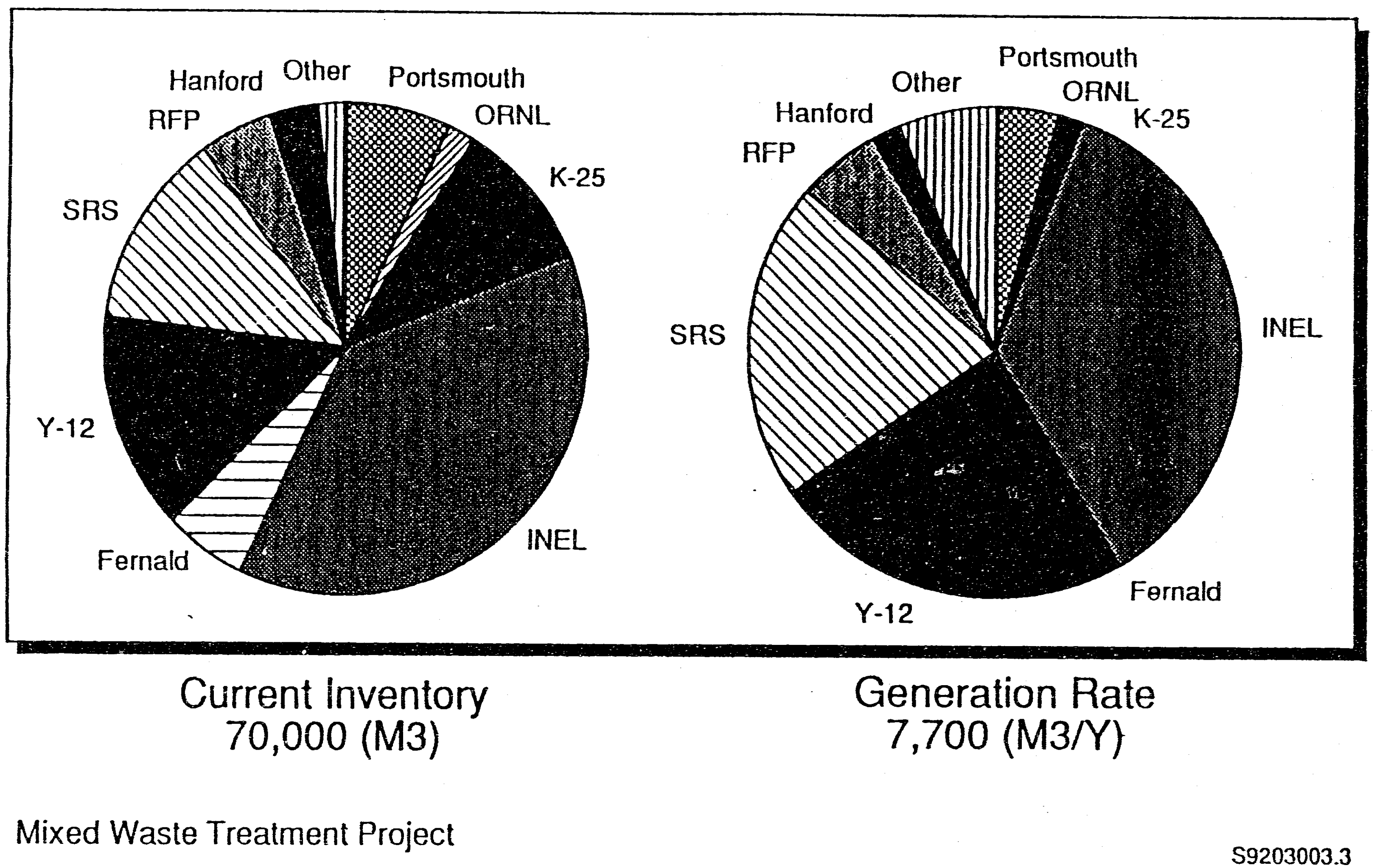

FIGURE 1. Locations of Mixed Wastes

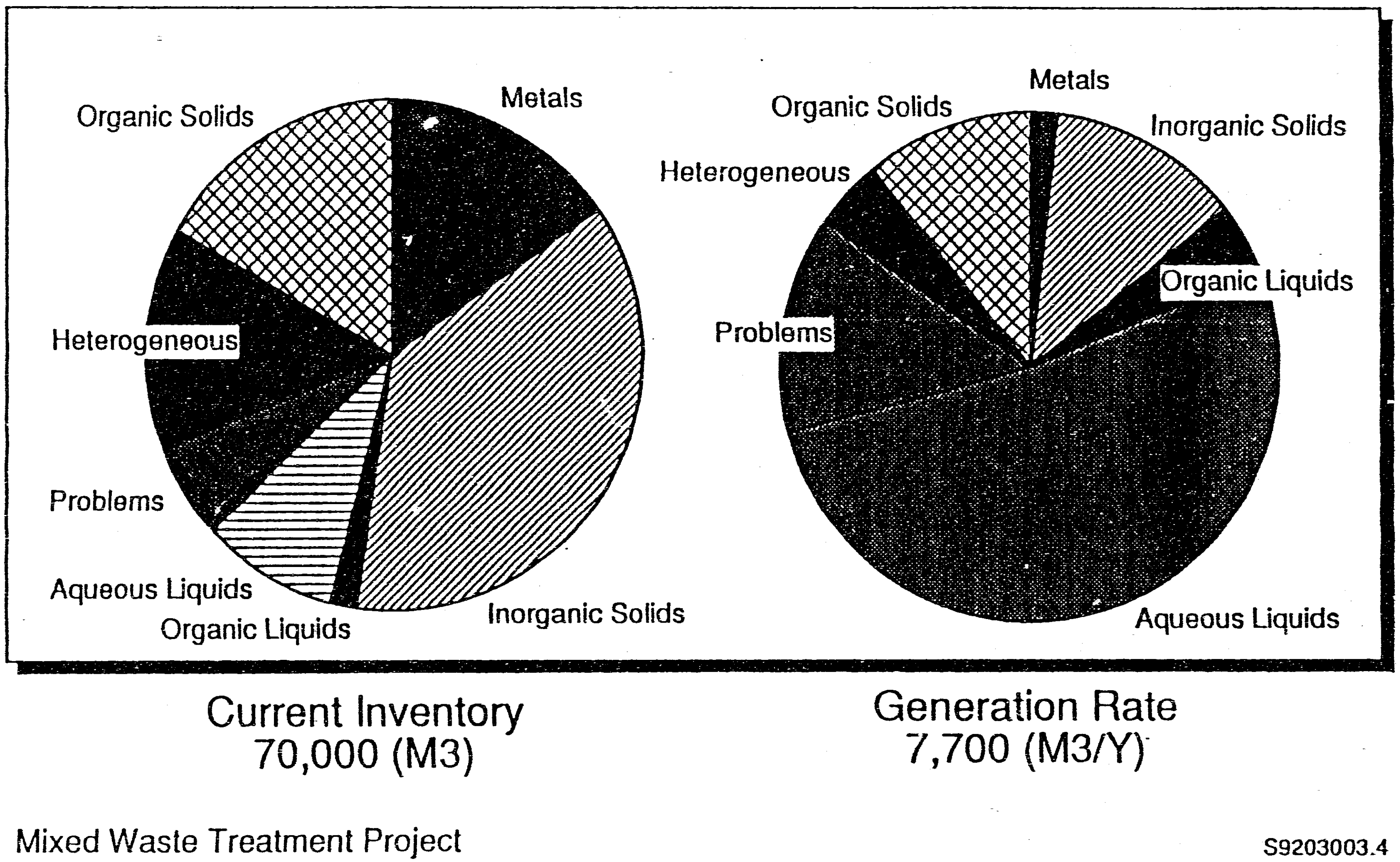

FIGURE 2. Major Categories of Wastes

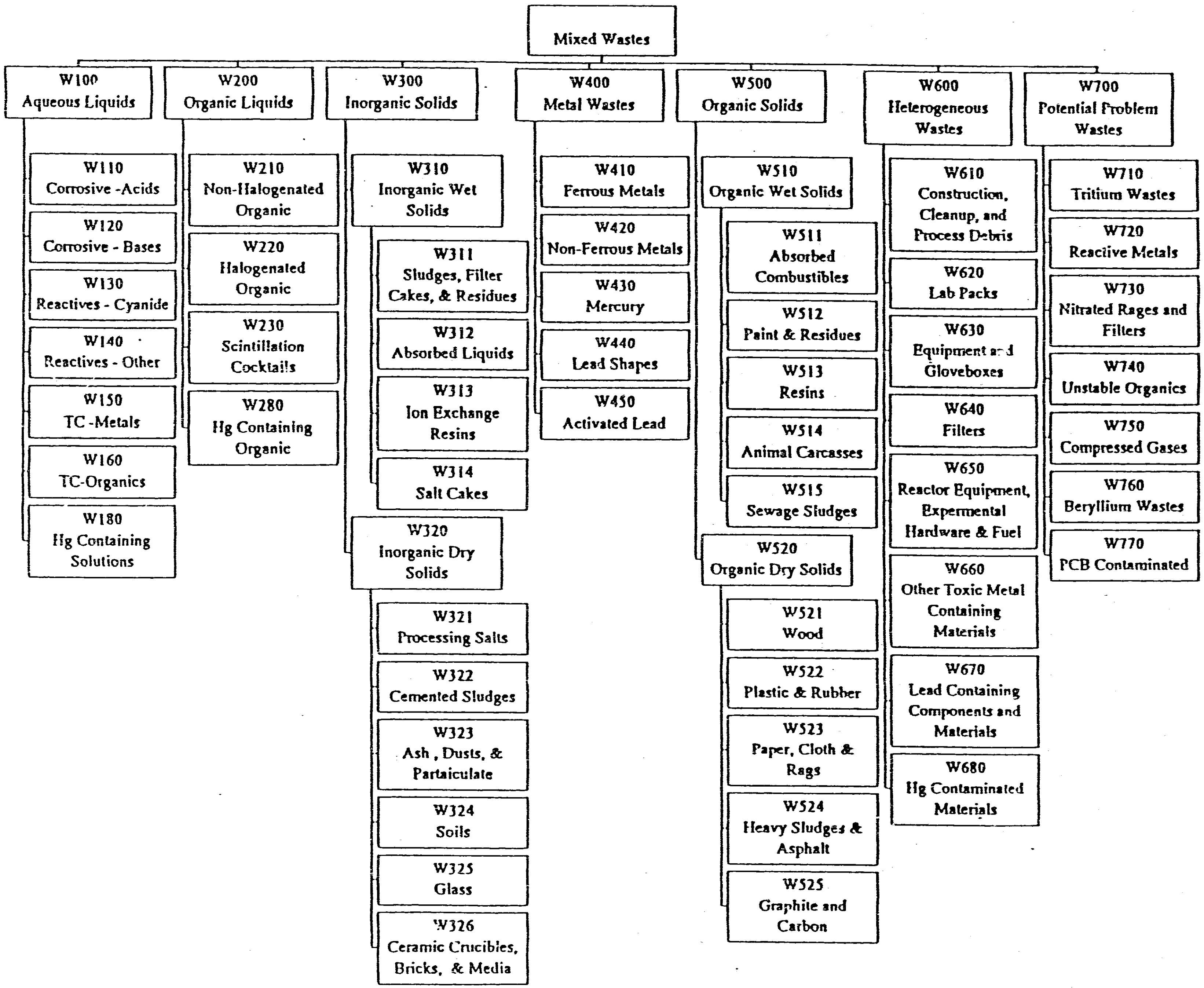

FIGURE 3. Mixed Waste Matrix Characterization Categories

		POTENTIAL TREATMENT PROCESS IN FULL SCALE FACILITY						
	Segregation to Major Lines	Opening and Removal	Sorting and Assignment	Feed Preparation and Size Reduction	Primary Treatment	Off-Gas Treatment	Final Waste Form Treatment	Characterization
Aqueous Wastes	X	X	X	X	X	X	X	X
Organic Wastes	X	X	X	X	X	X	X	X
Inorganic Solids	X	X	X	X	X	X	X	X
Metals	X	X	X	X	X	X	X	X
Organic Solids	X	X	X	X	X	X	X	X
Heterogenous Wastes	X	X	X	X	X	X	X	X

FIGURE 4. Flowsheet for Various Treatment Options for Each Major Waste Category

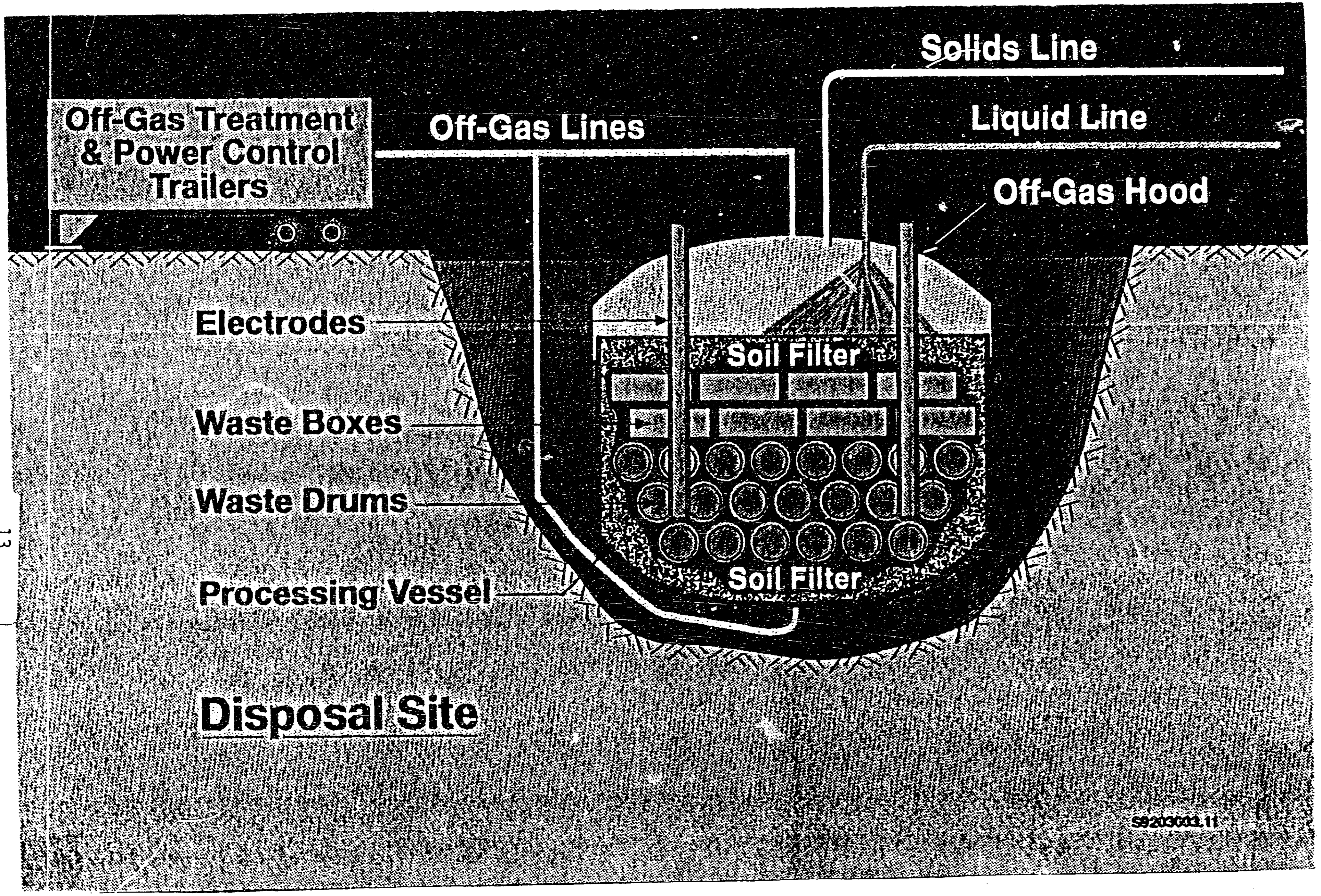

FIGURE 5. Hybrid Treatment Process: Disposal Site Processing

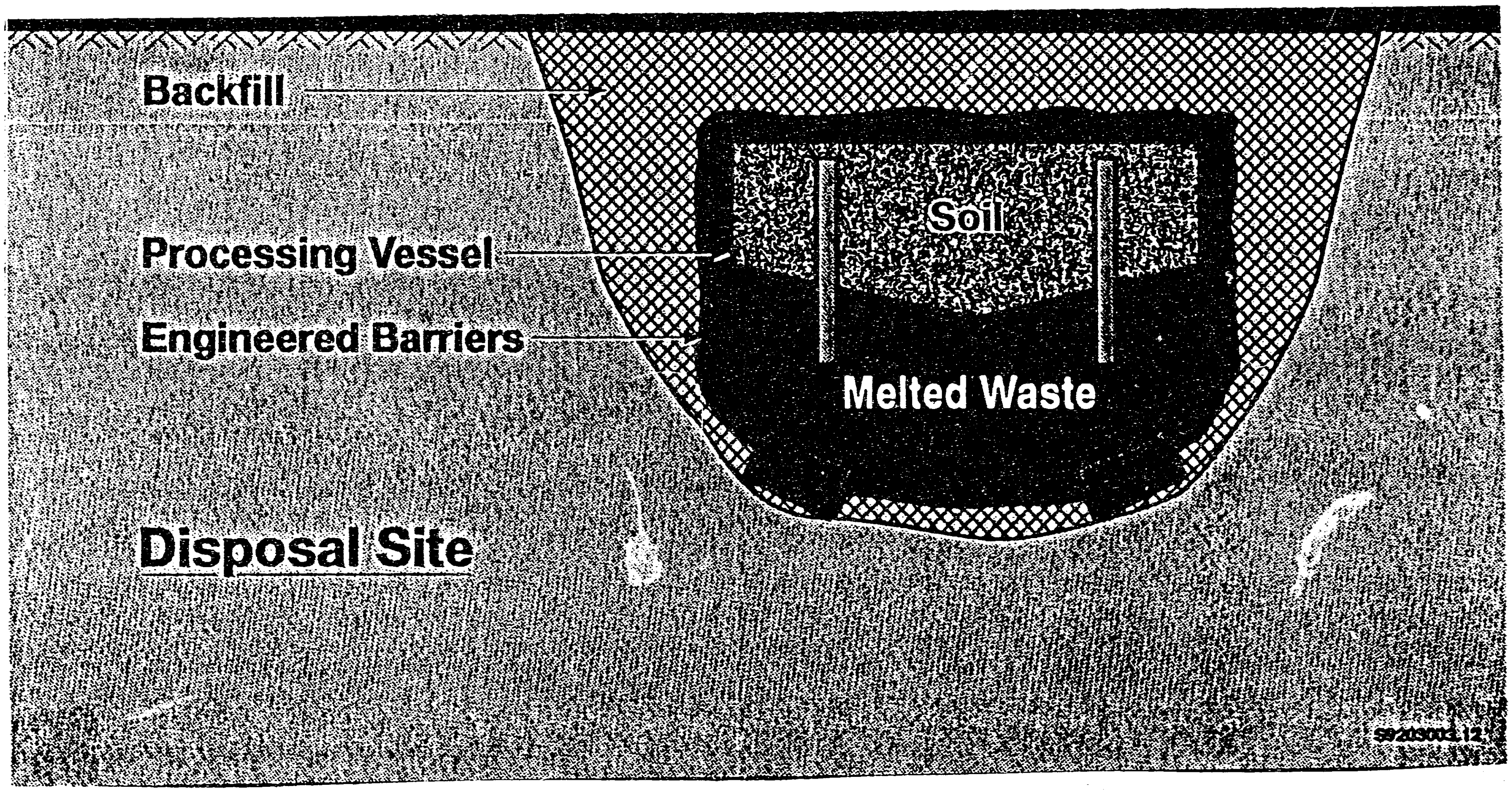

FIGURE 6. Hybrid Treatment Process: Disposal Site Post-Processing

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