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Technology Evaluation Report:

SITE Program Demonstration Test Horsehead Resource Development Company, Inc. Flame Reactor Technology Monaca, Pennsylvania

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Risk Reduction Engineering Laboratory Office of Research and Development U.S. Environmental Protection Agency Cincinnati, OH 45268

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A SITE demonstration of the Horsehead Resource Develop Flame Reactor Technology was conducted in March 1991 a Monaca, Pennsylvania. For this demonstration, seconda was treated to produce a potentially recyclable lead- product and a nonhazardous (based on the regulatory re Characteristic test) effluent slag. The lead and zinc concentrated about threefold from the feed concentrati determined to be nonhazardous based on extraction by t Leaching Procedure. Potential wastes that might be treated include i Conservation and Recovery Act wastes, Superfund wastes contaminated with metals and organic wastes.	ment (HRD) Company, Inc. t the HRD facility in ry lead smelter soda slag and zinc-enriched oxide quirements of the Toxicity in the oxide product were ons. The effluent slag was he Toxicity Characteristic ndustrial residues, Resource , and other wastes
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NOTICE

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FOREWORD

The Superfund Innovative Technology Evaluation (SITE) Program was authorized in the Superfund Amendments and Reauthorization Act of 1986 (SARA). The SITE Program is administered by the U.S. Environmental Protection Agency (EPA) Office of Research and Development (ORD). The purpose of the SITE Program is to accelerate the development and use of innovative cleanup technologies applicable to Superfund and other hazardous waste sites. This is accomplished through demonstrations designed to provide performance and cost data on selected technologies.

A field demonstration was conducted under the SITE Program to evaluate the Horsehead Resource Development Company, Inc., (HRD) Flame Reactor technology. The technology demonstration took place at HRD's facility in Monaca, Pennsylvania. The demonstration effort was directed to obtain information on the performance and cost of the technology regarding its utility for treating hazardous wastes. Documentation consists of two reports: (1) an Applications Analysis Report, which interprets the data and discusses the potential applicability of the technology, and (2) this Technology Evaluation Report, which describes the field activities and laboratory results.

Copies of this report can be purchased from the National Technical Information Service, Ravensworth Building, Springfield, Virginia 22161, 703/487-4600. Requests should include the document number found on the report's cover. Reference copies are available at EPA libraries in the Hazardous Waste Collection. Furthermore, the SITE Clearinghouse hotline at 800/424-9346 or 202/382-3000 in Washington, D.C., can supply information about the availability of all SITE reports.

E. Timothy Oppelt, Director Risk Reduction Engineering Laboratory

ABSTRACT

This report evaluates the Horsehead Resource Development Company, Inc., (HRD) Flame Reactor technology's ability to remove and recover volatile metals, such as lead and zinc, from waste while producing a vitrified slag that meets applicable disposal requirements.

The HRD Flame Reactor technology is a patented high-temperature thermal process designed to treat industrial residues and wastes containing metals. During processing, the waste material is introduced into the HRD Flame Reactor. After introduction to the Flame Reactor, the waste material is subjected to temperatures in excess of 2,000°C by exposure to reducing gases produced by the combustion of solid or gaseous hydrocarbon fuels in oxygen-enriched air. At these temperatures, volatile metals in the waste are fumed, and organic compounds should be destroyed. The waste materials react rapidly, producing a potentially nonhazardous vitrified slag and gases, including steam and metal vapors. Metal vapors further react in the combustion chamber and cooling system to produce metal-enriched oxide product that is collected in the baghouse portion of the oxide product recovery system. The resulting metal-enriched oxide product may be recycled to recover the metals. The amount of waste reduced to oxide and slag depends on the chemical and physical properties of the waste material.

The HRD Flame Reactor Demonstration was conducted under the SITE Program at HRD's facility in Monaca, Pennsylvania, in the spring of 1991. During the demonstration, secondary lead smelting slag was treated to produce a lead- and zinc-enriched metal oxide product and a slag that was determined to be nonhazardous based on current regulatory requirements (waste extraction by the Toxicity Characteristic Leaching Procedure [TCLP] and subsequent extract analysis). Greater than 75 percent of the 0.0411 weight percent cadmium, 5.41 weight percent lead, and 0.416 weight percent zinc in the waste was recovered in the potentially recyclable metal oxide product. In the metal oxide product, concentrations of cadmium, lead, and zinc were 0.128, 17.4 and 1.38 weight percent, respectively. The weight of the raw waste was reduced by 36.6 weight percent.

Based upon limited data, atmospheric emissions of metals from the Flame Reactor could be of concern. The planned addition of a modern emission control should reduce this concern.

The HRD thermodynamic model was found to be appropriate to establish preliminary operating conditions for the Flame Reactor, including waste feed and consumable flow rates.

During the SITE Demonstration, the HRD Flame Reactor experienced no major operational problems. Several auxiliary systems, such as the oxide product recovery system, cooling water system, and feed system experienced problems that did not affect operations of the Flame Reactor. As these auxiliary systems are to be upgraded, their problems were not considered to be significant.

The HRD Flame Reactor system processed waste from the National Smelting and Refining (NSR) site, under very rigorous testing conditions, at a cost of \$932 per ton. Data supplied by HRD for other studies show that the HRD Flame Reactor can process similar waste for as little as \$208 ton.

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LIST OF ABBREVIATIONS, ACRONYMS, AND SYMBOLS

ARAR	applicable or relevant and appropriate requirements		
ASTM	American Society for Testing and Materials		
BIF	Boiler and Industrial Furnace		
Btu	British thermal unit		
Btu/lb	Btu per pound		
°C	degrees Celsius		
CAR	corrective action recommendation		
Cd	cadmium		
CEM	continuous emission monitor		
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act		
CFR	Code of Federal Regulations		
CH4	methane or natural gas		
CI-	chlorine ion		
Cl ₂	chlorine		
СО	carbon monoxide		
CO ₂	carbon dioxide		
CV	cold vapor atomic absorption spectroscopy		
dscf	dry standard cubic feet		
EAF	electric arc furnace		
EPA	U. S. Environmental Protection Agency		
EP	extraction procedure		
°F	degrees Fahrenheit		
Fe	iron		
FeO	ferrous oxide		
Fe ₂ O ₃	ferric oxide		
FR	Federal Register		
g	gram		
GFAA	graphite furnace atomic absorption spectroscopy		
gr	grain		
H ₂	hydrogen		
H ₂ O	water		
H ₂ O ₂	hydrogen peroxide		

LIST OF ABBREVIATIONS, ACRONYMS, AND SYMBOLS (Continued)

hydrogen chloride gas or hydrochloric acid
hydrofluoric acid
nitric acid
high pressure liquid chromatography
hour
Horsehead Resource Development Company, Inc.
inductively coupled plasma atomic emission spectroscopy
kilogram
potassium permanganate
liter
pound
lb per hour
EPA Method 5
Methods for the Chemical Analysis of Water and Wastes (U.S. EPA, 1979)
milligram
milligram per kilogram
mg per liter
milliliter
minute
matrix spike
matrix spike duplicate
nitrogen
not applicable
sodium
sodium hydroxide
not calculable
not detected
National Emissions Standards for Hazardous Air Pollutants
nanogram
ng per kilogram
National Institute of Science and Technology

LIST OF ABBREVIATIONS, ACRONYMS, AND SYMBOLS (Continued)

formerly National Lead Company
nitrogen dioxide
nitrogen oxides
National Priorities List
new source performance standards
National Smelting and Refining Company, Inc.
oxygen
EPA Office of Research and Development
U.S. Occupational Safety and Health Administration
Pennsylvania Department of Environmental Resources
lead
parts per million
PRC Environmental Management, Inc.
particle size distribution
pounds per square inch
quality assurance
quality assurance project plan
quality control
Resource Conservation and Recovery Act
Research, Development, and Demonstration
U.S. EPA Risk Reduction Engineering Laboratory
request for proposal
relative percent difference
relative standard deviation
sulfur
Superfund Amendments and Reauthorization Act
standard cubic feet per minute
second
silicon dioxide (sand)
Superfund Innovative Technology Evaluation
secondary lead smelter
sulfur dioxide

LIST OF ABBREVIATIONS, ACRONYM5, AND SYMBOLS (Continued)

SO3	sulfur trioxide
SOP	standard operating procedure
SW-846	U.S. EPA Test Methods for Evaluating Solid Waste
TC	Toxicity Characteristic
TCLP	Toxicity Characteristic Leaching Procedure
THC	total hydrocarbons
TOC	total organic carbon
TSR	Technical Systems Review
tpy	tons per year
μg	microgram
Zn	zinc

CONVERSION FACTORS

	English (US)	x	Factor	z	Metric
Length:	l inch (in)	x	2.54	11	centimeter (cm)
	1 foot (ft)	x	0.305	=	meter (m)
	l mile (mi)	x	1.61	=	kilometer (km)
Агеа:	l square foot (ft ²)	x	0.0929	=	square meter (m ²)
Volume:	l gallon (gal)	x	3.78	=	liter (L)
	l cubic foot (ft ³)	x	0.0283	=	cubic meter (m ³)
Mass:	l grain (gr)	x	64.8	=	milligram (mg)
	l pound (lb)	x	0.454	=	kilogram (kg)
	l ton (t)	x	907	=	kilogram (kg)
Pressure:	l pound per square inch (psi)	x	0.0703	=	kilogram per square centimeter (kg/cm ²)
Energy:	l British Thermal Unit (Btu)	x	1.05	=	kilojoule (kJ)
	l kilowatt hour (kWh)	x	3.60	=	megajoule (MJ)
Temperature:	(°Fahrenheit - 32)	x	0.556	=	°Celsius

ACKNOWLEDGEMENTS

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The authors would like to acknowledge the help and support provided by the HRD Flame Reactor Division and its operations staff in the planning and preparing for the SITE Demonstration, the SITE Demonstration itself, and in preparing this report.

1.0 EXECUTIVE SUMMARY

In response to the Superfund Amendments and Reauthorization Act of 1986 (SARA), the U.S. Environmental Protection Agency (EPA) has established the Superfund Innovative Technology Evaluation (SITE) Program to accelerate the development, demonstration, and use of new or innovative technologies that offer permanent, long-term cleanup solutions at Superfund sites. The SITE Program is administered by the EPA Office of Research and Development (ORD) and has four primary goals:

- Identify and remove obstacles to the development and commercial use of alternate technologies.
- Structure a development program that nurtures emerging technologies.
- Demonstrate promising innovative technologies to establish reliable performance and cost information for site characterization and cleanup decision-making.
- Develop procedures and policies that encourage the selection of available alternative treatment remedies at Superfund sites, as well as other waste sites and commercial facilities.

As a part of the SITE Program, EPA solicits proposals from innovative waste treatment technology developers who have expressed an interest in participating in the SITE Program. Based on these proposals, EPA selects technologies for inclusion in the demonstration portion of the SITE Program. One of the selected technologies is the Horsehead Resource Development Company, Inc., (HRD) Flame Reactor.

The demonstration of the HRD Flame Reactor technology occurred at HRD's facility in Monaca, Pennsylvania, using secondary lead smelter (SLS) rotary kiln soda slag from the National Smelting and Refining Company, Inc., (NSR) Superfund site in Atlanta, Georgia. The goal of the HRD Flame Reactor technology is to produce a marketable metal oxide product and nonhazardous effluent slag.

The primary objectives of the HRD Flame Reactor SITE Demonstration include the following:

• Evaluate the technology's ability to treat waste materials to form a recyclable metal oxide product and a nonhazardous fused slag

- Evaluate the system's reliability
- Develop overall economic data on the technology

Secondary objectives were also defined. These are objectives that would be of interest to potential technology users but concern testing auxiliary systems rather than the actual Flame Reactor. Secondary objectives include the following:

- Assess the airborne emissions from the process
- Verify the predictions of the HRD thermodynamic process model so that the model can be used to predict costs for other projects

Due to their environmental concern (cadmium and lead), economic value (zinc), and concentration in the waste (lead and zinc); cadmium, lead, and zinc were the volatile metals of primary concern during the SITE Demonstration.

1.1 OVERVIEW OF THE HRD SITE DEMONSTRATION

The HRD Flame Reactor was demonstrated in February and March 1991. Seventy-two tons of waste material from the NSR site in Atlanta, Georgia, were treated during all phases of testing. This waste material was granular, SLS slag containing carbon, iron, sodium, sulfur, lead, silicon, chlorine, zinc, arsenic, cadmium, and many other metals and inorganic chemical compounds, including water. This waste material was considered a Resource Conservation and Recovery Act (RCRA) characteristic waste because of high cadmium and lead concentrations in the Toxicity Characteristic Leaching Procedure (TCLP) extracts of the waste. This waste was chosen as it was readily available, it contained high concentrations of several recoverable metals (lead and zinc), it contained no organic compounds (waste containing organic compounds could not be handled under HRD's state permits), and it was representative of a waste type available in large quantities throughout the country.

Once at the HRD facility, the waste material was dried and passed through a hammermill prior to treatment in the HRD Flame Reactor. The demonstration test runs included a series of shakedown runs to establish optimal operating conditions, a blank run with no waste treatment, four test runs (including one that was not used for interpretation of results due to sampling problems), and a series of additional runs to produce effluent slag with improved durability and to process remaining waste.

Extensive process operating data and numerous analytical samples were collected. The operating data include raw waste feed rate, processed oxide product and effluent slag production rates, natural gas and oxygen consumption rates, electrical consumption, and temperatures throughout the system. Laboratory analyses of the waste feed include metals, moisture, sulfur, chloride, fluoride, carbon, total organic carbon, and energy and ash content. Effluent samples (oxide product from the oxide product recovery system and processed effluent slag) were analyzed for metals. The waste feed and effluent slag were also extracted by the TCLP test and the extract was analyzed for metals. Concentrations of carbon monoxide (CO), carbon dioxide (CO₂), oxygen (O₂), nitrogen oxides (NO_x), sulfur dioxide (SO₂), and total hydrocarbons (THC), as well as hydrogen chloride gas (HCl), metals, and particulate in the stack gases were also measured.

1.2 TECHNOLOGY DESCRIPTION

According to the developer, the HRD Flame Reactor is designed to thermally treat granular solids, soil, flue dust, slag, and sludge containing metals. The goal of the treatment process is to yields two products: (1) a heavy metal oxide product that can potentially be recycled by metal producers, and (2) a vitrified slag that, if tested and shown to be nonhazardous, can be used as aggregate. The high-temperature reactor processes wastes with a hot reducing gas produced by the combustion of solid or gaseous hydrocarbon fuels in oxygen-enriched air. In the reactor, feed materials react in less than 0.5 second, allowing high waste throughput (HRD, 1989a).

Volatile metals in the waste material, including cadmium, lead, and zinc, are vaporized and oxidized, then captured downstream in a oxide product recovery system. Nonvolatile metals are predominantly encapsulated in the slag product. According to HRD, for optimum reaction conditions, the waste feed should contain less than 5 percent total moisture, and at least 80 percent of the feed should be sized less than 200 mesh. Waste material might require pretreatment by drying and by physical size reduction. In order to produce a fluid slag, the fusion temperature of the nonvolatile feed materials should not exceed 1,400°C. Deviations from these specifications, such as total moisture content up to 15 percent, higher fusion temperatures, or particle sizes up to 20 mesh, are acceptable but tend to decrease throughput and reduce the recovery of metals in the oxide product (HRD, 1989a).

3

After drying and size reduction, if required to meet the above specifications, pretreated waste material is transferred to temporary storage bins. From the temporary storage bins, the waste feed is transferred to the day bins, where it is metered by a screw feeder to a surge hopper and then pneumatically injected into the HRD Flame Reactor. In the Flame Reactor, the waste feed is heated to a high temperature (greater than 2,000°C) by the fuel-rich combustion of natural gas or coal and oxygen-enriched air. The high temperature forces water, volatile metals, and volatile inorganic compounds into the gas phase. Organic compounds and carbon in the waste are believed to be totally destroyed or removed. Nonvolatile and noncombustible materials are fused by the high temperatures and fall through the reactor into the horizontal slag separator. The effluent slag exits through the slag tap and then cools. Gaseous matter is drawn by reduced pressure into a combustion chamber, where air is introduced and oxidation occurs. The oxidized gases are cooled in a heat exchanger, and the enriched-metal oxide product is collected and recovered in a baghouse. The oxide product from this collection system is discharged through a screw conveyor into bulk storage bags for potential recycling (HRD, 1989a).

1.3 ANALYTICAL RESULTS

During the HRD Flame Reactor SITE Demonstration, a comprehensive sampling and analysis program was undertaken to characterize the SLS slag waste feed, the oxide product, the effluent slag, and stack gas emissions.

The analytical results of the SLS slag waste feed show that iron, lead, silicon, and sodium account for 28.9 percent of the slag. In addition, seven other metals (aluminum, calcium, copper, magnesium, potassium, tin, and zinc) are present at concentrations greater than 0.1 percent. The remainder of the slag is composed mainly of carbon, various inorganic compounds (such as compounds containing chloride and sulfur), water, and chemically bound oxygen.

The results of the TCLP extraction and analysis show that the SLS slag waste feed is a hazardous waste, as defined by RCRA, because both lead and cadmium leach at levels above the allowable RCRA limits.

The data show that metals are concentrated in the oxide product. The major metal constituents of the oxide product are lead (17.4 percent), sodium (15.7 percent), iron (3.22 percent), and zinc (1.38 percent). Seven other metals (antimony, arsenic, cadmium, calcium, copper, potassium, and tin) plus silicon are present at concentrations of greater than 0.1 percent.

Notably, over 75 percent of the three target metals (cadmium, lead, and zinc) in the waste feed was captured in the oxide product.

The effluent slag TCLP data show that, although the leachability of some metals (such as arsenic and barium) increased as compared to the SLS slag waste feed, the effluent slag is not a RCRA hazardous waste. In addition, data show that the predominant metals in the effluent slag are aluminum, calcium, iron, silicon, and sodium accounting for 38.7 percent of the effluent slag mass.

The total effluent slag and oxide product from the demonstration weighed 36.6 percent less than the total weight of the waste feed. This weight reduction of 36.6 percent is due to the essentially complete conversion of carbon to CO_2 , of moisture to steam, of chloride to HCl gas, and of sulfur to SO_2 .

The stack gas was sampled for NO_x , SO_2 , HCl, metals, and particulate. The results show that emission rates for arsenic, chromium, and lead exceed the proposed Tier II screening limits contained in the EPA document *Guidance on Metal and Hydrogen Chloride Controls for Hazardous Waste Incinerators* (EPA, 1989b). In addition, HCl emissions exceed the current limits for incinerators [40 Code of Federal Regulations (CFR) 264.343(6)] (CFR, 1988).

The only permit limitation currently placed on the HRD Flame Reactor is for 500 parts per million (ppm) for SO₂. Although the unit operated below this limit most of the time (averaging less than 300 ppm), the limit was briefly exceeded once during a test resumption.

Information was also collected on the reliability of the HRD Flame Reactor. The HRD Flame Reactor itself had no major operational problems affecting its performance during the demonstration. However, according to HRD staff, the reactor's oxide product collection system was undersized for the feed rate used during the demonstration. This caused the first sampling run to be scrapped, because isokinetic sampling conditions could not be maintained. Additionally, the heat exchanger and associated cooling water system developed several leaks.

1.4 QUALITY ASSURANCE PROCEDURES

The main quality assurance (QA) objective of all SITE Demonstrations is to produce well-documented sampling and analytical data of known quality. To accomplish this goal, a detailed and comprehensive Quality Assurance Project Plan (QAPP) was developed before the demonstration. The QAPP contains specific QA targets for precision, accuracy, representativeness, completeness, and comparability. It also specifies (1) the analytical methods to be used, (2) data for holding times, (3) number and types of blanks, (4) matrix spikes and matrix spike duplicates, (5) laboratory duplicates, (6) reference standards, and (7) method detection limits.

The waste feed and effluent slag from the reactor are nonhomogeneous and, because of their physical and mineralogical properties, difficult to digest and analyze for metals. Therefore, a method selection study was undertaken to select the best analytical method for digesting the samples to determine metal concentration. Based on this study, a slightly modified version (reduced sample size) of EPA SW-846 Method 3050 was chosen. However, the results of using EPA Method 3050 digestion of chromium in a high-silicon content matrix and silicon are known to be poor; consequently, results obtained for chromium and silicon from a digestion method developed by HRD are also presented in this report.

1.5 CONCLUSIONS

Based on the results of the HRD SITE Demonstration, the following conclusions were drawn concerning the performance of the HRD Flame Reactor technology.

- The HRD Flame Reactor technology processed SLS slag and produced both a potentially recyclable metal oxide product and an effluent slag meeting RCRA TCLP standards.
- The HRD Flame Reactor achieved a net weight reduction of 36.6 percent when the waste feed was processed into oxide product and effluent slag.
- During the demonstration, the HRD Flame Reactor had no major operational problems; however, auxiliary systems such as the oxide product collection system, cooling water system, and feed system experienced problems that did not affect the operation of the Flame Reactor.

- The HRD the modynamic model can be used to set preliminary operating conditions and to determine order of magnitude estimates for parameters used in a cost estimate, such as fuel and oxygen flow rates.
- The HRD Flame Reactor system processed SLS slag from the NSR site at a cost of \$932 per ton. Data supplied by HRD for other studies show that the HRD Flame Reactor can process similar waste for as little as \$208 ton.
- A site-specific risk analysis is required to assess the impact of the HRD Flame Reactor stack emissions. Based on limited data, the atmospheric emissions of metals could be a concern, however, due to data limitations, no conclusions could be reached on metal emissions.

1.6 COMMENTS

Based on the SITE Demonstration, the following comments were noted. These comments should be taken into account when the HRD Flame Reactor technology is considered for use to process waste material.

- HRD recommends that 80 percent of the feed be smaller than 200 mesh (0.0029 inch or 75 microns) for optimal recovery of volatile metals. Coarser feed material would decrease smelting efficiency and impede slag fusion, both of which decrease the recovery of volatile metals. Pretreatment can be performed by HRD to meet these specifications.
- The recommended total moisture content is less than 5 percent (free and chemically bound) as moisture consumes energy in the Flame Reactor. HRD operates a drier for feed pretreatment and desiccation.
- The HRD Flame Reactor oxide product collection system was designed to handle the gases generated while treating electric arc furnace (EAF) dust. During this demonstration, SLS slag was processed under conditions which generated larger volumes of off-gases. In addition, the heat exchanger used at the facility is old and could operate only at about 80 percent of capacity. Therefore, a larger volume of ambient cooling air was needed to maintain the temperature of the inlet gas to the oxide product collection system baghouse. As this system heated up during operation, the introduction of even larger volumes of air were necessary to control the baghouse temperature. Eventually, a larger volume of cooling air was required than could be drawn through the system by the induced draft baghouse blower, resulting in a positive pressure in the reactor. Under positive pressure, the reactor emits CO and metal vapors through the slag tap hole and must be shut down. Positive pressure typically shut down the reactor after approximately 4 hours of operation. For a full-scale Superfund remediation, the gas handling capacity of the oxide product collection system should be increased to allow continuous operation.

- There may be a cost involved in recycling the lead oxide dust. This cost depends on the current lead market (supply and demand for lead), the concentration of lead as well as impurities or contaminants in the material to be recycled, the amount of oxide product, and the cost of handling the oxide product. It should be noted that the amount of oxide produced during the demonstration was approximately 25 weight percent of the total dried waste feed.
- The cost and time estimates to perform Tier III metal emission assessments are considerable. These calculations are both waste and site specific and must done on a case by case base. Future HRD Flame Reactor work might not be done at Monaca, Pennsylvania - and the calculations would have to be redone. While this calculation is definitely desirable, its cost is prohibitive and beyond the scope of this SITE project. If the reader of this report is very interested in the HRD technology, he can contact HRD and discuss concerns before selecting this technology.
- Potential HRD technology users should be aware of, and make sure that they satisfy the requirements of, all applicable local, state, and federal regulations, such as RCRA revisions, the revised Clean Air Act, and state hazardous waste regulations.

2.0 INTRODUCTION

The purpose of this Technology Evaluation Report is to provide a comprehensive description of the HRD Flame Reactor SITE Demonstration and its results. It is intended for engineers and others making a detailed evaluation of the technology for a specific site and waste situation. These technical evaluators can use this report to understand, in detail, the performance of the technology during the demonstration and the advantages, risks, and costs of the technology for a specific application. This information can be used to produce conceptual designs in sufficient detail to make preliminary cost estimates for the demonstrated technology. For a discussion of advantages, disadvantages, and limitations of the technology, refer to the Applications Analysis Report for the HRD Flame Reactor.

2.1 **REPORT ORGANIZATION**

This report is organized in eight sections. Section 1.0 is an executive summary. Section 2.0 presents introduction and background information on the SITE Program in general, the HRD Flame Reactor technology, and the HRD SITE Demonstration. Section 3.0 describes the hazardous waste site and the HRD facility. Section 4.0 provides a detailed description of the HRD Flame Reactor technology. Section 5.0 describes the demonstration operations, including demonstration preparation and the sampling program, and provides a summary of the demonstration. Section 6.0 discusses the analytical results and performance data in relation to the objectives of the HRD SITE Demonstration. Section 7.0 presents the quality assurance and quality control objectives and results for the HRD SITE Demonstration. A list of references is provided at the end of this report.

This report also includes seven appendices. Appendix A is a tabulation of analytical results from Versar, Inc. Appendix B is the Engineering-Science, Inc. emissions test results. Appendix C is HRD's analytical results. Appendix D is the mineralogical characterization report prepared by Pittsburgh Mineral and Environmental Technology, Inc. for HRD. Appendix E contains the field and laboratory Technical Systems Reviews performed as a part of the HRD Demonstration. Appendices F and G are the analytical methods employed for total carbon and total organic carbon analyses as well as the hydrofluoric acid digestion procedure.

2.2 BACKGROUND

Past hazardous waste disposal practices and the environmental and human health impacts of those practices caused Congress to enact the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) of 1980 [reference: Public Law (PL) 96-510]. The original act established a Hazardous Substance Response Trust Fund to handle emergencies at uncontrolled hazardous waste sites and to clean up the sites; this fund has become known as Superfund. EPA has investigated hazardous waste sites and established national priorities for site cleanups. The ultimate objective of these investigations is to develop plans for permanent site cleanups, although EPA does initiate short-term removal actions when necessary. The National Priorities List (NPL) is EPA's list of the Nation's top-priority hazardous waste sites that are eligible to receive federal cleanup assistance under the Superfund Program.

Congress recently expressed concern over the use of land-based disposal and containment technologies to address problems caused by releases of hazardous substances at hazardous waste sites. Because of this concern, the 1986 reauthorization of CERCLA, SARA, mandates that EPA select, to the maximum extent practicable, remedial actions at Superfund sites that create permanent solutions to the sites' effects on human health or the environment. In doing so, EPA is directed to consider use of alternative or resource recovery technologies.

2.2.1 SITE Program

EPA has established the SITE Program to accelerate the development, demonstration, and use of new or innovative technologies that offer permanent site cleanup. The program is administered by ORD.

Each year EPA solicits proposals to demonstrate innovative technologies. The most promising technologies are chosen for participation in the SITE Demonstration Program. ORD and EPA regional personnel match these technologies with a list of potentially appropriate sites.

The Demonstration Program is designed to develop detailed and reliable performance and cost data on the innovative alternative technologies so that potential users have sufficient information to make sound judgments about the applicability of the technology to a specific site and to compare it to other currently available technology alternatives. The program also identifies

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the governmental policy and regulatory requirements applicable to the technology and the hazardous substances being treated or destroyed.

2.2.2 Technology Demonstration Program Objectives

The SITE Program mandate is to seek cost-effective alternatives to the traditional practice of using land disposal and containment for the remediation of hazardous waste sites. To address this mandate, the following general objectives were developed for the SITE Demonstration Program:

- Determine the effectiveness of the process from an assessment of analytical results
- Identify the potential need for pre- and posttreatment processing of raw and treated materials
- Identify the types of wastes and media to which the process can be applied
- Identify the hazardous substances being treated or destroyed by the process
- Identify any potential process system operating problems and their possible resolutions
- Determine the approximate capital, operating, and maintenance costs
- Determine the projected long-term operating and maintenance costs
- Identify governmental policy and regulatory requirements applicable to the process

2.2.3 HRD Flame Reactor Technology

The HRD Flame Reactor technology is a patented, hydrocarbon-fueled, flash-smelting system that treats residues and wastes containing metals. The reactor processes wastes with a hot (greater than 2,000°C in the gas injection chamber) reducing gas produced by the fuel-rich combustion of solid or gaseous hydrocarbon fuels in oxygen-enriched air. Within the reactor, the feed materials react rapidly, allowing a high waste throughput. The end products are a potentially recyclable metal-enriched oxide product and a potentially nonhazardous, fused slag (a glass-like solid when cooled). The weight and volume reduction achieved (of waste feed to both the oxide product and effluent slag) depends on the chemical and physical properties of the waste but typically ranges from 10 to 40 percent (HRD, 1989a).

According to HRD, the Flame Reactor technology can be applied to granular solids, soil, flue dust, slag, and sludge containing heavy metals. The volatile metals in the waste material, such as cadmium, lead, and zinc, are vaporized, then oxidized and captured downstream in a oxide product recovery system. Nonvolatile metals are encapsulated in the slag product. At the elevated temperature of the process, organic compounds, if present, should be destroyed (HRD, 1989a).

Under most conditions, waste pretreatment is required. For high metals recovery, the process requires that waste feeds be dry enough (less than 5 percent total moisture) to be pneumatically conveyed and fine enough (80 percent less than 200 mesh) to react rapidly. Waste containing larger-sized particles (up to 20 mesh) can be processed; however, the efficiency of metals recovery is usually reduced (HRD, 1989a).

A more detailed process description is provided in Section 4.

2.2.4 Technology Evaluation Criteria

A Demonstration Plan was prepared before the HRD SITE Demonstration (EPA, 1990). The plan includes a Sampling and Analysis Plan designed to address the general demonstration program objectives. The Demonstration Plan outlined the following primary objectives:

- Evaluate the technology's ability to treat waste materials to form a potentially recyclable metal oxide product and a nonhazardous fused slag
- Evaluate the system's reliability
- Develop overall economic data on the technology

The Demonstration Plan also outlined secondary objectives. These are objectives that would be of interest to potential technology users but concerned testing auxiliary systems rather than the actual Flame Reactor. Secondary objectives include the following:

- Assess the airborne emissions from the process
- Verify the predictions of the HRD thermodynamic process model so that the model can be used to predict costs for other projects

Evaluation of the HRD Flame Reactor technology was based on its ability to treat waste material containing cadmium, iron, lead, zinc, and other metals at the HRD facility and produce a potentially recyclable oxide product containing the more volatile metals and an effluent slag with minimal leaching potential containing the less volatile metals.

2.2.5 Demonstration Preparation

HRD conducted startup testing to check the HRD Flame Reactor system for problems that would prevent smooth operation, such as the viscosity of the slag and clumping of the waste feed. It was determined that on-site pretreatment (drying and crushing) would be adequate.

The next phase of the demonstration was the shakedown period. The shakedown period was used to set the feed rates, reactor temperatures, oxygen content of the combustion air, and other operating parameters. The developer's thermodynamic process model was used to precalculate operating set points. These set points were then adjusted during shakedown by evaluating the condition of the slag generated.

About 4 weeks after the startup procedures and shakedown were completed, one background run was conducted to establish a process baseline. During this run, only natural gas was fired into the reactor without waste feed. Following the completion of the background run, four replicate test runs were conducted.

2.2.6 **Project Organization and Responsibilities**

For the SITE Demonstration, EPA and HRD cooperated to collect data of known quality to evaluate the performance of the HRD Flame Reactor technology. EPA had overall responsibility for the project: overseeing, reviewing, auditing, and approving technical and quality assurance aspects. HRD was responsible for providing and operating all of the demonstration equipment.

3.0 SITE BACKGROUND

This section describes background information for the NSR site, which is the source of the waste treated during the demonstration, and the HRD facility where the demonstration was performed.

3.1 NSR SITE

The waste treated during the HRD SITE Demonstration was transported to the demonstration site from the NSR Superfund site. The NSR site is located at 430 Bishop Street in the northwest portion of Atlanta, Georgia, in an industrialized area that is intermixed with residential communities. Approximately 1 acre of the 4-acre site is owned by the Southern Railroad Company (which is owned by Norfolk Southern Corporation), and the remaining 3 acres are owned by Atlanta Forge and Foundry Company. The waste treated is located on the property belonging to Atlanta Forge and Foundry Company (NL Industries, 1989; 1990).

The facility has been operated by various owners for approximately 80 years. During a portion of this time, lead smelting and refining activities were performed at the site. The most recent operations at the facility involved the recovery of lead from storage batteries and other lead-bearing scrap and secondary lead smelting activities. NSR purchased the facility from NL Industries on June 30, 1981, and operated the facility until March 1984, at which time NSR filed for bankruptcy. Since 1984, the facility has been inactive (EPA, 1989a; NL Industries, 1990).

During the 3 years that NSR operated the facility, approximately 350 tons of processed rotary-kiln SLS slag from the NL Industries' Superfund site in Pedricktown, New Jersey, were shipped to the NSR facility in Atlanta for possible recycling. This waste material was stored in two bunkers at the NSR site. Seventy-two tons of this material were collected, loaded in bulk storage bags in closed trailers, and manifested for shipment to the HRD facility for treatment during the SITE Demonstration.

3.2 HRD FACILITY

The HRD Flame Reactor pilot plant is located in Monaca, Pennsylvania, and is operated by HRD, a division of Horsehead Industries, Inc. The HRD Flame Reactor plant and associated facilities occupy about 3 acres on a 5-acre site. The plant and facilities include the main building that houses the reactor; an auxiliary storage building; liquid oxygen (O_2) and nitrogen (N_2) storage facilities; an oxide product or off-gas handling and collection system employing a baghouse; a cooling tower for the closed-loop, noncontact cooling water system; and a pretreatment facility containing a waste feed dryer and a hammermill. The facility is presently operating under authority of an EPA RD&D permit (U.S. EPA I.D. No. PAD 98 111 0570) and a Pennsylvania Department of Environmental Resources (PaDER) hazardous waste storage and treatment permit for research testing of EAF dust (RCRA code K061 hazardous waste), and certain characteristic wastes. These operating permits have allowed extensive testing of the HRD Flame Reactor.

The main building, measuring 40 by 80 feet and 60 feet high, presently contains the feed handling and storage equipment, the reactor and slag separator, the effluent slag cooling and conveying table, the control room connected to a computer in the main office building, and the motor control center. It also includes maintenance and spare parts storage. The auxiliary storage building, liquid O_2 storage facilities, baghouse, cooling tower, and pretreatment facility are located in the area outside the main reactor building. Adjacent to the Flame Reactor building is an office building housing administrative and engineering offices and the computer center.

4.0 HRD FLAME REACTOR PROCESS DESCRIPTION

The HRD Flame Reactor technology is designed to thermally treat granular solids, soil, flue dust, slag, and sludge containing metals. The treatment process yields two products: a heavy metal, metal-enriched oxide product that can potentially be sold to metal producers and a potentially nonhazardous effluent slag that can be used as aggregate. The high-temperature reactor processes wastes with a very hot reducing gas produced from the fuel-rich combustion of solid or gaseous hydrocarbon fuels in oxygen-enriched air. After entering the reactor, the waste feed reacts in less than 0.5 second, allowing high waste throughput (HRD, 1989a).

Metals in the waste feed, such as cadmium, lead, and zinc, are vaporized in the Flame Reactor and oxidized in the combustion chamber. These volatile metal oxides are subsequently captured downstream in a oxide product recovery system. Nonvolatile metals are generally encapsulated in the effluent slag product. For optimum reaction conditions, the waste feed should contain less than 5 percent total moisture, and at least 80 percent of the feed should be sized finer than 200 mesh. Waste material might require pretreatment by drying and physical size reduction. In order to produce a fluid slag, the fusion temperature of the nonvolatile feed materials should not exceed 1400°C. Fluxing agents (such as sand) can be added to improve effluent slag fluidity. Variations from these specifications are acceptable but tend to decrease throughput and reduce the recovery of metals in the oxide product.

Figure 1 presents a schematic of the HRD Flame Reactor process. The process consists of five sections (HRD, 1989a):

- Waste Feed System
- Flame Reactor
- Slag Separator
- Combustion Chamber
- Oxide Product Recovery System

FIGURE 1 HRD FLAME REACTOR PROCESS FLOW SCHEMATIC



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4.1 WASTE FEED SYSTEM

Waste feed system operations include (1) waste feed and solid fuel storage and handling, (2) metering and injection of waste feed and fuel into the reactor, and (3) metering and injection of O_2 and compressed air.

The waste feed storage and handling system consists of storage facilities, portable bins, day bins, and several conveying systems. The waste material to be fed into the reactor can be delivered to the site by rail or by truck. The waste material is stored in a storage building next to the main building prior to processing. If pretreatment of the waste (drying and crushing) is necessary, the waste is transferred to another building that contains the pretreatment equipment. After pretreatment, a loader empties the feed material into portable bins, which are moved to the Flame Reactor building. From the portable bins, waste is transferred to the day bins. The portable bins are placed on a discharge stand and the bottom discharge slide-gate is opened. Dusting is controlled by a seal located between the gasketed opening of the stand and the flange of the portable bin slide-gate. The waste is fed into a screw conveyor that empties into the tubular, day bin filling system.

Of the three day bins, two are used for waste, and one is used for solid fuel. Normally, solid fuel such as coal fines can be used to reduce costs; however, natural gas was chosen for the HRD SITE Demonstration because (1) it is more likely to be used in a site remediation and (2) it has a uniform composition. Each day bin has a capacity of 150 cubic feet and is mounted on a set of three, shear-beam, load cells that measure the day bin weight for inventory and process control. Material from each day bin is metered and pneumatically injected into surge hoppers prior to entering the reactor.

To calculate waste feed rate, the process control system records the loss of weight over time. The system uses a 10-minute average waste feed rate to control the feed system. Material is discharged from a day bin, through a live-bottom feeder, into a surge hopper set above a variable speed screw feeder with a rated capacity of 60 pounds per minute. The feeder accurately controls the flow of material into the reactor via a 2-inch, pneumatic injection line.

The gases used in the demonstration were O_2 , ambient air, and natural gas. O_2 is stored on-site as a cryogenic liquid in a 9,000-gallon storage tank. It is used to enrich the ambient air for combustion. Compressed air produced by a compressor, operating at 1,000 standard cubic feet

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per minute (scfm) at 40 pounds per square inch (psi), is used to combust the fuel. A second compressor, operating at 100 psi provides air for process controllers and for injecting solids into the reactor. Natural gas, supplied by pipeline from the local utility company, was used as the fuel during this demonstration. A 6,000-gallon liquid N₂ tank is also on-site, but it was not used in the demonstration. The N₂ is used to blanket coal fines as an added safety feature when coal is used as the fuel source.

4.2 FLAME REACTOR

The HRD Flame Reactor, shown on Figure 2, is a two-stage system consisting of a fuel burner system (first stage) and the metallurgical reactor (second stage). Carbon-based combustion and gasification reactions occur in the burner system, followed by metal smelting reactions in the metallurgical reactor. The reactor is 15 feet tall, positioned vertically, with an internal diameter of 23 inches (HRD, 1989b).

The fuel burner system consists of a mixing head, upper pilot, lower pilot, and gas injection chamber. In the mixing head, fuel and O_2 -enriched air (typically 50 percent to 80 percent O_2 by volume) are mixed. This fuel-rich mixture then ignites in the upper pilot and is stabilized by expansion into the lower pilot. Injecting O_2 -enriched air in the gas injection chamber helps control the reducing conditions, adjust the stoichiometry (CO:CO₂ ratio), and further stabilize the flame in the Flame Reactor. Because highly O_2 -enriched air is used, flame temperatures greater than 2,000°C are realized in the Flame Reactor. A different burner design is employed when solid fuel is used as the energy source.

Fine, dry, waste feeds containing metals are metered with a screw feeder and pneumatically injected into the reactor (second stage) at a location just below the exit of the burner (see Figure 2). The waste feed reacts in the high-temperature, reducing gas stream. CO from the incomplete combustion of the fuel reduces the metal compounds in the waste feed by the following reactions:

Combustion of natural gas (CH₄)

 $\begin{array}{l} CH_4 + 3/2O_2 \rightarrow CO + 2H_2O \\ CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \\ CH_4 + CO_2 + O_2 \rightarrow 2CO + 2H_2O \\ CH_4 + 1/2O_2 \rightarrow CO + 2H_2 \end{array}$
FIGURE 2 FLAME REACTOR TWO-STAGE SYSTEM



Reduction/Smelting of Volatile Metals

Iron:	$Fe_3O_4 + CO \rightarrow 3FeO + CO_2$
Zinc:	$ZnO + CO - Zn (vapor) + CO_2$
Cadmium:	$CdO + CO \rightarrow Cd (vapor) + CO_2$
Zinc-Iron:	$ZnFe_2O_4 + 2CO - Zn (vapor) + 2FeO + 2CO_2$
Lead:	$PbSO_4 + 2CO \rightarrow Pb (vapor) + SO_2 + 2CO_2$
Lead:	$PbSO_4 + CO - PbO + SO_2 + CO_2$

The nonvolatile components of the waste feed fuse, forming the effluent slag.

The energy required for fusion and reduction lowers the temperature to between 1,500°C and 1,700°C. In this temperature range, several elemental metals are above their boiling point, shown in Table 1, and volatilize into the gas stream. Recovery of cadmium, lead, and zinc is of particular interest because of their economic value.

The reactor vessel is water-cooled to assure that a layer of the molten slag solidifies on the inner reactor walls. The slag layer protects the reactor walls from intense heat and reduces the reactor heat loss. Molten material is conveyed down the reactor walls by gravity and by the combustion gases. At the end of the reactor, the molten metal is accelerated through a tapered transition section into the horizontal slag separator (HRD, 1989a).

4.3 SLAG SEPARATOR

The reactor continuously discharges material into a refractory-lined, water-cooled cyclonic separator that separates molten slag from reactor off-gases. Off-gases contain mainly CO, hydrogen (H_2) , and any metal vapors recovered from the waste feed. The effluent slag contains 35 to 75 percent of the mass of metals from the waste feed.

The slag separator is positioned horizontally between the flame reactor and the combustion chamber (see Figure 1). The gases, particulate, and metal vapors flow toward the combustion chamber, countercurrent to the slag. The molten slag runs out through a tap hole on the discharge end of the unit. Occasionally a small amount of effluent slag is carried over to the combustion chamber.

BOILING POINTS OF VARIOUS METALS

Metal	Boiling Point (*C)
Aluminum	150 ¹
Antimony	1,380
Arsenic	613 ²
Barium	1,640
Cadmium	765
Calcium	1,490
Chromium	2,670
Copper	2,600
Iron	2,750
Lead	1,740
Magnesium	1,110
Mercury	357
Nickel	2,730
Potassium	774
Selenium	685
Silver	2,210
Sodium	883
Thallium	1,460
Tin	2,260
Zinc	907

Note:

- ¹ Decomposes
- ² Sublimes
- °C = degrees Celsius

Source:

CRC Handbook of Chemistry and Physics. 71st Edition, 1990-1991.

4.4 COMBUSTION CHAMBER

The slag-free reactor off-gases are combusted again with air in a refractory-lined combustion chamber. The metal vapors oxidize and condense as solids, while combustible gases such as CO and H₂ are burned. The gas stream from the combustion chamber includes metallic oxides, CO₂, water (H₂O), sulfur trioxide (SO₃), and NO_x. For the SITE Demonstration, the temperature of the off-gases after the combustion chamber was typically between 700 and 1,000°C (HRD, 1989b). Reactions in the combustion chamber include:

 $CO + 1/2O_2 - CO_2$ $H_2 + 1/2O_2 - H_2O$ Metal (vapor) + 1/2O_2 - MetalO $SO_2 + 1/2O_2 - SO_3$ MetalO + SO_3 - MetalSO_4 $N_2 + xO_2 - 2NO_x$

4.5 OXIDE PRODUCT RECOVERY SYSTEM

The metal oxide product (MetalO) recovery system is designed to cool the gas stream and capture the metal oxides formed in the combustion chamber. The system consists of a heat exchanger, a tempering air inlet damper, and a baghouse for dust collection. A fan, located between the baghouse and the stack, provides the induced draft to power the system.

The gas is cooled by a shell-and-tube heat exchanger and by the addition of ambient air. The heat exchanger has water on the shell side and hot gases on the tube side. The addition of ambient air is controlled by a damper. The damper is located just before the baghouse and is used to maintain the baghouse temperature below 200°C. Because of the typically high particulate level in the gas stream, the heat exchanger tubes require frequent cleaning (HRD, 1989a).

The main component of the oxide product recovery system is a jet-pulsed baghouse designed to recover metal oxide product from the gas stream. The recovery system emits off-gases through the plant stack and discharges metal oxide product into enclosed bulk storage bags for recovery. A rotary air lock, screw conveyors, and a sealed boot connection reduce the possibility of fugitive emissions. The baghouse collects the oxide product dust on 8,900 square feet of cloth. The bag cleaning procedure consists of short, high-pressure pulses of air through the bags to dislodge the particles trapped on the surface. The pulses are initiated on a timed cycle based on typical gas flow rates and dust loadings. The particles fall by gravity into a screw conveyor below the baghouse bags. The screw conveyor transports the oxide product in one of two enclosed bulk storage bags. While one storage bag is filling, the other can be removed and replaced with an empty storage bag.

According to HRD the oxide product from the baghouse contains approximately 25 to 65 percent of the mass of the waste feed. This percentage is highly dependent upon the amount of volatile metals in the waste feed. Specific recoveries for volatile metals are generally very high. Based on past testing, the baghouse oxide product accounts for greater than 90 percent of the volatile metals in the waste feed. The remainder is encapsulated in the effluent slag, with a minimal fraction lost to the atmosphere as stack emissions (HRD, 1989a).

5.0 DEMONSTRATION PROCEDURES

This section contains a discussion of the demonstration preparation, operations, and sampling program.

5.1 DEMONSTRATION PREPARATION

Prior to the demonstration, a Demonstration Plan for the HRD Flame Reactor was prepared (EPA, 1990). The plan consists of four sections. The first section provides background information for the SITE Program and the HRD Flame Reactor technology. The second section contains the operating plan for the demonstration. The third section is a QAPP that presents testing and quality assurance objectives, a detailed sampling plan, and quality control measures. The fourth section contains a Health and Safety Plan. The Demonstration Plan was approved by RREL's quality assurance officer.

5.2 DEMONSTRATION OPERATIONS

Upon arrival at the demonstration site, the SLS slag waste, obtained from the NSR site, was transferred to the feed preparation equipment. The feed preparation equipment is designed to dry and crush the material, and a dryer and a hammermill are used. Once the SLS slag was adequately dried and crushed for use as waste feed, it was loaded into portable bins and transported to a storage facility adjacent to the Flame Reactor building.

Startup testing of the demonstration equipment began after the feed preparation equipment had processed a sufficient quantity of SLS slag to produce 5 to 10 tons of dry, crushed waste feed material. Prior to initial system startup, EPA and the SITE Team reviewed the Demonstration Plan with HRD personnel. During startup, the HRD Flame Reactor system was checked for any problems that would prevent smooth operation of the equipment, such as the viscosity of the slag and clumping of the waste feed. No problems were found.

The next phase was the shakedown period. The feed rates, reactor temperatures, oxygen content of the combustion air, and other operating parameters were set. A thermal chemical process model was used to precalculate operating set points. The set points were then adjusted during these runs by evaluating the condition of the effluent slag generated. The production of a free-flowing, low-lead content effluent slag indicates the attainment of the proper values for the

set points. The actual demonstration was performed with the values set during the shakedown runs.

Approximately 4 weeks after the startup procedures and shakedown were completed, the demonstration began. The first run was a background run to establish a process baseline. During the background test, only natural gas was fired in the Flame Reactor; no waste feed was admitted to the system. Only stack gas samples were collected during the background run.

Waste feed processing commenced following the completion of the background testing. Four test runs were conducted. The results first run were invalid due to fluctuations in the stack gas temperature, pressure, and flow rate. During all test runs, solid samples were collected for 6 hours while the stack samples were collected for approximately 2-1/2 hours during the middle of each sampling day. During all three runs, the Flame Reactor had to be shut down to allow the oxide product collection system to cool.

During the four test runs, samples were collected as they entered or exited the system at various points. These samples included waste feed, effluent slag, oxide product, and stack gas emissions. The number of samples collected at each location, the frequency, and the rationale for sampling and analysis parameters are discussed in Section 3.4 of the Demonstration Plan and in Section 5.3 of this report.

After the demonstration was complete, the remaining waste feed was processed through the HRD Flame Reactor system. Although detailed chemical analyses were not performed on the samples from these runs, the effluent slag was analyzed and found to be a nonhazardous waste and, therefore, could be disposed of in a nonhazardous waste landfill. The oxide product was analyzed and found to be enriched in the volatile metals. Several potential recycling opportunities are being explored for this lead-rich product.

5.3 SAMPLING PROGRAM

The primary objective of the demonstration was to collect sufficient data so that the effectiveness of the HRD Flame Reactor could be evaluated for (1) removing volatile metals from high metal-bearing wastes to produce a potentially recyclable, metal-enriched oxide and (2) producing a nonhazardous fused slag. The following sections describe the specific sampling objectives and sample point locations.

5.3.1 Sampling Locations

To evaluate the effectiveness of the HRD Flame Reactor for treating waste from the NSR site, samples were collected from several points. Figure 3 is a block diagram of the HRD Flame Reactor, showing the locations where the following process operating parameters were monitored and recorded:

Monitoring	
Location	Description
1	Natural gas feed rate (scfm)
1	Oxygen feed rate (scfm)
1	Air feed rate (scfm)
1	Waste feed rate (lb/hr, lb/test)
1	Reactor heat loss (Btu/hr)
2	Effluent slag flowrate (lb/hr, lb/test)
3	Combustion chamber temperature (°C)
4	Temperature of cooling chamber exit gas (°C)
5	Oxide product flowrate (lb/hr, lb/test)
6	Stack temperature (°C)

Also shown on Figure 3 are the locations of each sample point:

Sampling Location	Sample
1	Waste feed
2	Effluent slag from slag separator
5	Oxide product
6	Stack gases to determine particulate and metal emissions
6	Stack gases to determine HCl emissions
6	Continuous emissions monitoring (CO ₂ , CO, O ₂ , NO _x , SO ₂ , THC)

Samples of the waste feed (Point 1, Figure 3) were collected from the surge hopper located above the screw feeder and below each feed bin. Samples of the effluent slag from the slag separator (Point 2, Figure 3) were collected from the shaker conveyer before the slag was discharged to a collection bin. Samples of the oxide product (Point 5, Figure 3) were collected at the discharge end of the screw conveyor located along the bottom of the baghouse.

FIGURE 3 SAMPLING AND MONITORING LOCATIONS



Samples of the fuel feed (natural gas) were not collected. Instead, copies of the vendor specifications for the natural gas supplied for this demonstration were obtained.

Samples of the gases (Point 6, Figure 3) exiting the baghouse were sampled in a 48-inch circular duct. The gas samples were obtained by traversing the duct using the two existing sampling ports (90° apart) on a 10-foot 2-inch straight piece of the duct. Twenty-four sampling points were used (12 per traverse).

Measurement of waste feed rates (Point 1, Figure 3) for inventory and process control was accomplished using load cells. The output of the load cell was recorded during testing. Effluent slag and oxide product weights were recorded using a floor scale in the Flame Reactor building. The floor scales and load cells were calibrated several times by adding known weights to the units.

Measurement of temperatures throughout the HRD Flame Reactor facility was performed by the HRD computerized process control system.

Equipment and impinger solution blank samples for quality assurance purposes were also collected. These included a system blank of an EPA modified Method 5 metals train that was assembled and leak-tested; blanks of the impinger solutions and filter and probe washes were collected also. Other quality assurance samples included reagent blanks of the test reagents, such as sodium hydroxide (NaOH), acetone, water, nitric acid (HNO₃), hydrogen peroxide (H₂O₂), and potassium permanganate (KMnO₄).

5.3.2 Sample Size, Sampling Frequency, and Analytical Parameters

A summary of the sampling program is presented in Table 2. Prior to collecting the samples shown in this table, the HRD Flame Reactor operated with no waste feed (only natural gas and air/oxygen were introduced into the reactor). During this period of time, a single background stack gas sample was collected. The background sample required approximately 2-1/2 hours to collect and consisted of 120 minutes of continuous emission monitoring for SO₂ and NO_x and stack gas sampling for metals, particulate, and HCl using two EPA Method 5 stack sampling trains. After the background sample was collected, four test runs, over 4 days, were conducted processing waste feed. The solid samples were collected over a period of 6 hours. About 2 hours after each run began, stack gas sampling was begun. Continuous emission monitors

HRD DEMONSTRATION SAMPLING FREQUENCY (sheet 1 of 2)

Sample description	Sample type	Sampling frequency	Number of samples per run	Number of runs	Total number of samples	Analysis
1. Waste feed	Composite ¹ (hourly)	One grab every 15 minutes	6	3	18	Total chloride, Btu content, metals ² , percent ash, water content (moisture), particle size distribution, leachable metals ³ , TOC ⁴ , total carbon, sulfur, chloride, fluoride
2. Effluent slag	Composite ¹ (hourly)	One grab every 15 minutes	6	3	18	Metals ² , leachable metals ³
3. Oxide product	Composite (daily)	One grab every 15 minutes	1	3	3	Metals ²
 4. Stack gas (M5-metals) a. Acetone probe wash b. HNO₃ probe wash c. Particulate filter d. Impingers 1-3 e. 50 mL from impingers 1-3 f. Impinger 4 	EPA Method 5 Liquid Liquid Solid Liquid Liquid Liquid	120 minutes ⁵	1 1 1 1 1 1	4 4 4 4 4	4 4 4 4 4	Particulate, metals ⁶ Metals ⁶ Particulate, metals ⁶ Metals ⁷ Mercury Mercury
5. Stack gas (HCl) a. Impingers	EPA Method 5 Liquid	120 minutes ⁵	1	4	4	Total chloride, moisture
 6. Blanks/Background a. Alkaline solution (NaOH) b. Acetone wash c. Water d. HPLC water⁸ e. HNO₃ f. H₂O₂ g. KMnO₄ 	Grab Grab Grab Grab Grab Grab Grab	Once before test Once before test Once before test Once before test Once before test Once before test Once before test	1 1 1 1 1 1 1	1 1 1 1 1 1	1 1 1 1 1 1	Metals ³ Metals ³ Metals ³ Metals ³ Metals ³ Metals ³

HRD DEMONSTRATION SAMPLING FREQUENCY (sheet 2 of 2)

Sample description	Sample type	Sampling frequency	Number of samples per run	Number of runs	Total number of samples	Analysis
 7. System blank (M5-metals) a. Acetone probe wash b. HNO₃ probe wash c. Particulate filter d. Impingers 1-3 e. 50 mL from impingers 1-3 f. Impinger 4 	EPA Method 5 Liquid Liquid Solid Liquid Liquid Liquid	Once after all runs Once after all runs	1 1 1 1 1 1	1 1 1 1 1	1 1 1 1 1	Particulate, metals ⁶ Metals ⁶ Particulate, metals ⁶ Metals ⁶ Metals ⁶ Metals ⁶
8. System blank (M5-HCl) a. Impingers	EPA Method 5 Solid	Once after all runs	1	1	1	Total chloride, moisture
 9. Duplicate samples a. Waste feed b. Effluent slag c. Oxide product 	Solid Solid Solid	One during Run 2 One during Run 2 One during Run 2	1 1 1	1 1 1	1 1 1	Archived Archived Archived
 Decontamination water Equipment rinsate blanks 	Liquid Liquid	Once after demonstration Once during each run	1	1	1	Metals ² Metals ²

Notes:

¹ Composite samples consisted of a grab sample taken every 15 minutes. Every four samples were homogenized and split into sample aliquots for each hour of sampling. Field duplicate samples were collected from individual grab samples.

² Metals included aluminum, antimony, arsenic, barium, beryllium, cadmium, calcium, chromium, copper, iron, lead, magnesium, manganese, mercury, potassium, selenium, silicon, silver, sodium, thallium, tin, and zinc.

³ Leachable metals as extracted by the TCLP included arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver.

⁴ Total organic carbon

⁵ All stack sampling was performed concurrently during each 120-minute sampling episode.

⁶ Metals analysis included antimony, arsenic, barium, beryllium, cadmium, chromium, lead, mercury, silver, and thallium.

Metals analysis included all metals listed in note (3) except mercury.
 High grangers liquid absorber production of the production

⁸ High pressure liquid chromatography grade (high purity) water

Source: EPA, 1990

(CEM) operated for all 6 hours of each run. Run 1 results were discarded because of fluctuations in the stack gas temperature, flowrate, and pressure.

As shown in Table 2, the waste feed and effluent slag from the slag separator were collected every 15 minutes. Sampling of the waste feed began at the start of each test run. Sampling of the effluent slag from the slag separator was initiated 15 minutes after each run began to account for the residence time of the molten slag in the Flame Reactor, in the slag separator, and on the water-cooled conveyor.

Hourly composite samples of the waste feed and effluent slag from the slag separator were made by compositing the four samples taken during each hour. Therefore, a total of six composite samples were collected for each test run.

A subsample of the oxide product was collected every 15 minutes. At the end of each run, a composite sample was made from the 24 subsamples.

Gas samples for metals, particulate, and HCl were collected at the outlet of the baghouse. CEM samples were collected at a location on the baghouse outlet duct near the point where the stack gas samples were collected.

5.3.3 Sampling Methods

The following sections describe the sampling collection procedures that were followed to collect the solid and gas samples.

5.3.3.1 Solids Sampling

(1) <u>Waste Feed</u>. Samples of the waste feed were collected from each of the two feed bins through one of several ports on the surge hoppers above the screw feeders. Every 15 minutes the port was opened, and a small sample scoop was used to collect a sample from the surge hopper. The sample was placed in a clean plastic container and temporarily sealed to prevent contamination. After four samples were collected, they were mixed thoroughly, and an hourly composite sample was prepared. Each run produced six composite samples.

(2) <u>Effluent Slag from the Slag Separator</u>. Samples of the effluent slag were collected

with a stainless steel sample scoop. Care was taken to collect the effluent slag from various locations and at regular intervals on the shaker conveyer so that representative samples were collected. A grab sample was taken every 15 minutes. Each sample was allowed to cool in a stainless steel bucket that was covered with clean aluminum foil to prevent contamination. After cooling, the sample was placed in a clean sample jar to achieve constant sample volume prior to compositing. Some size reduction was required to place the effluent slag in the sample jars. A small rubber mallet was employed to reduce pieces to no larger than 1/4-inch in size. Every effort was made to include all particles, including very fine particles, with the collected samples. Further size reduction was accomplished in the laboratory by a mortar and pestle prior to analysis. Hourly composite samples were taken from four consecutive grab samples, for a total of six composite samples per run.

(3) <u>Oxide Product</u>. Samples of the oxide product were obtained with a scoop from the discharge end of the screw conveyor located at the bottom of the baghouse. A grab sample was taken every 15 minutes. After all of the grab samples were collected, they were homogenized by manually mixing with a plastic trowel. A single composite sample was prepared from the grab samples. Therefore, one sample was collected and analyzed for each run.

5.3.3.2 Gas Sampling

(1) <u>Stack Gases to Determine Metals Emissions</u>. During all runs, two EPA Method 5 (M5) stack gas sampling trains were used. The first M5 train was modified and used to sample for metals. The second M5 train was used to sample for the stack HCl concentration. Total particulate loading was determined in the metals train. This section provides a description of the metals/particulate stack sampling train. Subsection (2) below provides a description of the HCl stack sampling train.

Sampling for metals was conducted using a modified version of the Method 5 (M5) sampling train. This method has been proposed for acceptance by the EPA and is currently being validated (EPA, 1991a). A schematic of the sampling train is shown on Figure 4. A detailed description of this method is contained in the Demonstration Plan (EPA, 1990).

The front half of the sample train was similar to a standard M5 train, except that all of the components that come into contact with the sampled gas were constructed of glass and Teflon[®] (with the exception of a stainless steel nozzle). The probe and filter holder were borosilicate glass.

FIGURE 4 SCHEMATIC DIAGRAM OF THE METALS SAMPLING TRAIN



A Teflon[•]-coated screen was used to support the filter. Both probe and filter holder were heated to $120^{\circ}C \pm 14^{\circ}C$ to prevent moisture condensation. A high-purity, high-efficiency (99.95 percent determined on 0.3-micron dioctyl phthalate particles) quartz fiber filter without organic binder was used.

This sampling train is designed to capture metals in both the solid and vapor phases. Solid samples were collected as particulate in the filter and probe rinse. The back half of the impinger train was modified to capture the metals in the vapor phase. The impingers were arranged as follows:

- 1. Empty knockout impinger (Modified Greenburg-Smith)
- 2. Greenburg-Smith impinger containing a 100 mL solution of 5 percent HNO₃ and 10 percent H_2O_2
- 3. Same as Number 2 above
- 4. Greenburg-Smith impinger containing a 100 mL solution of 4 percent KMnO₄ and 10 percent H₂SO₄
- 5. Modified Greenburg-Smith impinger containing about 200 grams of indicating silica gel

An ice bath was used to maintain an impinger exit temperature of less than or equal to 20°C. All connections were made with leak-tight, ground glass joints.

The flue gas was withdrawn from the stack isokinetically for 120 minutes collecting a gas sample of at least 50 dry standard cubic feet (dscf). Nominally, the expected stack flow rate was 13,000 dscf. At the end of the test run, the train was checked for leaks and then disassembled into three parts: (1) probe, (2) filter and connecting glassware, and (3) impingers. Each part of the sample train was sealed to prevent sample loss or contamination. These parts of the sample train were then transferred to the field laboratory for recovery.

(2) <u>Stack Gases to Determine HCl Emissions</u>. The HCl sampling method involved pulling an integrated gas sample from the stack through distilled water. Sampling of HCl was performed concurrently with stack sampling for metals. A schematic diagram of the EPA Method 5 sampling train that was used for HCl sampling is shown on Figure 5.

FIGURE 5 SCHEMATIC DIAGRAM OF THE HCI SAMPLING TRAIN



The sampling train was placed in a port located at the same height on the stack as the metals M5 train. The sample was introduced to the train through a heated borosilicate glass probe and a quartz fiber particulate filter before entering the impingers. Although a particulate filter was required in this sampling train, it was not used to measure total particulate. The sample was collected at a single point.

Four impingers were used to collect the HCl sample. The first impinger was empty. The second impinger contained 100 mL of distilled water, and the third impinger contained 100 mL of 0.1 normal (N) sodium hydroxide. The final impinger contained silica gel as a final water catch. The gas then proceeded through a vacuum pump, flow rate meter, and dry gas meter.

The HCl sample was collected for 120 minutes at a nominal flow rate of 1 cubic foot per minute. After each test was completed, the volume of liquid in each impinger was determined by pouring the contents into a graduated cylinder. The final impinger containing the silica gel was weighed. The total stack gas moisture was determined as the sum of the impinger contents (less the 100 mL of NaOH and 100 mL of distilled water) and the moisture in the silica gel. The first three impingers were then recovered into a leak-free sample bottle, followed by a water rinse of each of the impingers and the connecting glassware.

In the distilled water, the HCl gas was solubilized and formed chloride ions (Cl^{-}). The concentration of the chloride ions in the sample was then determined in the laboratory. Reagent blanks of the distilled water were collected for analysis with the flue gas samples.

(3) <u>Continuous Emission Monitoring</u>. CEMs were used to continuously monitor the concentration of SO_2 , NO_x , CO, CO_2 , O_2 , and THC in the flue gas. A detailed description of the CEMs is in the Engineering-Science report, Emissions Testing at Horsehead Resource Development Company (Appendix B of this report). The NO_x analyzer was calibrated by EPA Method 7E [40 CFR 60, Appendix A, July 1989]. The O_2 and CO_2 analyzers were calibrated using EPA Method 3A [40 CFR 60, Appendix A, July 1989]; the CO analyzer by Method 10 [40 CFR 60, Appendix A, July 1989]; the THC analyzer by Method 25A [40 CFR 60, Appendix A, July 1989]; and the SO₂ monitor by Method 6C [40 CFR 60, Appendix A, July 1989].

5.4 **DEVIATIONS FROM THE DEMONSTRATION PLAN**

During the demonstration, one major change to the HRD Demonstration Plan and two

minor changes to the air sampling procedures were made.

The demonstration plan specified that three background stack samples would be collected. However, before the demonstration began, the EPA Project Managers, with the approval of the EPA quality control manager and auditors, decided that only one blank run would be conducted. Although the auditors commented that one run would not be statistically significant (a minimum of three is required for statistical significance), the EPA Project Managers and the technology vendor agreed that, because the background run was not representative of background contamination, only one background run would be conducted and that the three treatment runs would not be corrected for background contamination.

The EPA Method 5 stack sampling procedures had to be modified in the field because the Flame Reactor off-gas temperature gradually increased during the first run. Because the increasing temperature led to increasing gas velocities, isokinetic sampling (required by EPA Method 5) could not be maintained. After Run 1 was discarded because of this problem, the required sample volume was decreased from 100 ft^8 to 50 ft^8 . This decision traded reduced detection limits for valid cu sampling. At this time, glass sampling probe nozzles were replaced with stainless steel nozzles.

The HCl stack gas sampling procedure was also modified. The QAPP specified that the HCl train would be operated at a nominal flow rate of 1 scfm for 120 minutes. After the second run, the pH in the final impinger was slightly acidic (pH 5.5), another impinger was added (100 mg of NaOH) for Run 3. After Run 3, the pH was checked again and found to be slightly acidic (pH 5). For Run 4, the additional impinger was used and the sampling time reduced to 60 minutes. The Run 4 final pH was 7. This should not be interpreted to mean that there may have been losses of HCl during sampling. HCl is a strong acid and is stable in solution up to 37 percent. (The new EPA-approved Method 26 protocol for sampling HCl and Cl₂ (chlorine gas) uses an acidic solution to trap HCl.) Therefore, even though acid conditions existed in the impingers, all the HCl was captured and results were not impacted.

6.0 PERFORMANCE DATA AND EVALUATION

To evaluate the technology's performance with respect to the demonstration objectives (see Section 2.2), detailed analytical and performance data were gathered and evaluated. This section discusses these analytical and performance data.

Subsections are as follows:

- Method Selection for Sample Digestion -- discussion of how the digestion procedure for the metal analysis was chosen
- Characterization of the Waste Feed -- presentation of the analyte concentrations in the waste feed, the TCLP results for the waste feed, and the results of particle size distribution, moisture, and chemical constituent analysis
- Characterization of the Metal Oxide Product -- presentation of the analyte concentrations for the oxide product and the percent recovery of the volatile metals
- Characterization of the Effluent Slag -- presentation of the TCLP and analyte concentrations for the effluent slag
- Mass Balance -- discussion of the mass balance performed on the system and the weight reduction of the oxide product and effluent slag, as compared to the waste feed
- HRD Flame Reactor Process Reliability -- discussion of the HRD Flame Reactor reliability
- Stack Monitoring and Emissions Sampling Results -- presentation of the airborne emissions from the HRD Flame Reactor, including metals, HCl, SO₂, NO_x, and particulate emissions
- HRD Flame Reactor Operating Parameters -- presentation of the ranges of operating parameters of the HRD Flame Reactor during the SITE Demonstration
- The HRD Thermodynamic Model -- discussion of the accuracy of the HRD model in predicting the operation of the HRD Flame Reactor while processing waste feed

6.1 METHOD SELECTION FOR SAMPLE DIGESTION

The Demonstration Plan (EPA, 1990) recommends that EPA Method 3050, from

SW-846 (EPA, 1986), be used to digest all of the solid samples from the HRD SITE Demonstration. EPA Method 3050 uses nitric and hydrochloric acids to digest the sample. The Demonstration Plan also presented two alternative digestion methods (American Society for Testing and Materials [ASTM] Method E886-A, Lithium Tetraborate Fusion and ASTM Method E886-B, Aqua Regia Dissolution) that could be used if EPA Method 3050 could not completely digest the samples.

Because of the potential analytical problems associated with digesting the waste feed, oxide product, and effluent slag, analyses were performed using various digestion methods. These analyses compared digestion methods using lithium tetraborate (ASTM Method E-886A), hydrofluoric acid (HF) (see to Appendix G), EPA Method 3050, and the HRD digestion method.

Although analytical digestion by the HRD method was also considered, this method is not yet validated by EPA. The HRD digestion method uses a two-stage microwave bomb digestion procedure. The first stage uses HF and perchloric acid, and the second stage uses nitric and hydrochloric acids.

Table 3 presents the analytical results obtained from analysis of split samples of waste feed, effluent slag, and oxide product after digestion by EPA Method 3050, HF, lithium tetraborate, and the HRD method. The choice of method is not obvious. Each digestion method has advantages and disadvantages when all of the metals are considered. For the HRD SITE Demonstration, the metals of primary concern were lead and zinc; therefore, selection of the digestion method that was used was based mainly on these two metals.

For the effluent slag, the lead and zinc concentrations were about the same for all four digestion methods. However, for the waste feed, the lead concentration obtained from both the HF and lithium tetraborate method was one-third that obtained from EPA Method 3050 and the HRD method. In addition, reported lead concentrations in the oxide product from using the HF Method were one order of magnitude below the other three digestion methods.

Based on the available data, a slightly modified EPA Method 3050 (using a sample size of 0.2 rather than 1.0 gram) was selected as the best method to digest all of the samples collected during the HRD SITE Demonstration. Appendix E contains a copy of the August 1, 1991, "Response to: Technical Systems Review (TSR) of Versar Laboratories, Inc., Springfield, Virginia," which contains the supporting data used to make the selection. However, the results of

COMPARISON OF METAL DIGESTION PROCEDURES USING EPA METHOD 3050, THE HYDROFLUORIC ACID METHOD, THE LITHIUM TETRABORATE FUSION METHOD, AND THE HRD METHOD (mg/kg)

	Waste Feed					
Metal	Method 3050	HF	Lithium Tetraborate	HRD		
Arsenic	425	546	<23	620		
Cadmium	389	452	<5	340		
Chromium	40	251	536	240		
Lead	59,000	16,600	17,500	71,100		
Selenium	108	55	<69	<10		
Thallium	<9.8	3	<95	60		
Zinc	3,380	5,010	3,220	5,600		

		Effluer	it Slag	
Metal	Method \$050	HF	Lithium Tetraborate	HRD
Arsenic	<12	757	251	2 90
Cadmium	8	7.5	<5	1,600
Chromium	99	68 6	1,760	1,880
Lead	5,740	7,740	6,460	6,590
Selenium	<7.1	43	<70	<10
Thallium	104	2	<96	130
Zinc	1,250	1,590	1,630	2,870

	Oxide Product					
Metal	Method 3050	HF	Lithium Tetraborate	HRD		
Arsenic	1,110	1,300	134	1,460		
Cadmium	1,380	1,710	<5	1,640		
Chromium	288	372	320	350		
Lead	128,000	13,2 00	143,000	197,000		
Selenium	74	47	347	<10		
Thallium	68	9	113	90		
Zinc	20,400	19,700	17,600	22,100		

Note:

< = less than; mg/kg = milligram per kilogram

the method selection project also indicate that the waste feed and effluent slag are nonhomogeneous and difficult to digest. Additionally, the analytical results of using EPA Method 3050 are known to be poor for chromium and silicon. Consequently, results from the HRD method, performed on samples by HRD, as well as EPA Method 3050, performed by the SITE Team, are reported for these two metals.

To determine whether complete digestion of the metals occurred, a sequential digestion using EPA Method 3050 was conducted on the three matrices. First, the samples were digested using EPA Method 3050. Then the digestate was filtered, and the liquid portion was then analyzed to produce the sample concentration. The solid portion was redigested using EPA Method 3050, filtered, and the new liquid portion was analyzed to determine the concentration, if any, of metals not digested by the previous extraction. For lead and zinc, the filtrate concentration was always less than 2.3 percent of the sample concentration. For chromium, the filtrate concentration was 12.3 percent of the sample concentration. Since chromium was not of primary concern, these results were considered acceptable. To improve the ability of EPA Method 3050 to digest all subsequent samples, the sample size was reduced to one-fifth that specified in the analytical method. Because almost 98 percent of the lead and zinc are extracted in the first digestion, it was determined that sequential digestion was not required.

6.2 CHARACTERIZATION OF THE WASTE FEED

The waste feed was digested by a slightly modified EPA Method 3050, which used only 20 percent of the normal sample size, and extracted by the Toxicity Characteristic Leaching Procedure (TCLP). The digestates and extracts were analyzed by appropriate SW-846 methods to determine metal content. Waste feed samples were also analyzed by various chemical methods to determine characteristics such as particle size distribution and moisture content.

6.2.1 Metal Content

The metals data for the waste feed are presented in Table 4. Sodium, iron, and lead account for the majority of the metals as well as the total mass of the waste feed. Seven other metals, aluminum, calcium, copper, magnesium, potassium, tin, and zinc, as well as silicon, are present in the waste feed at concentrations of greater than 0.1 percent. A significant percentage (2.89 to 23.8 percent according to HRD analyses) of the waste feed is silicon.

Analyte	Mean Weight ¹	Standard Deviation	Range
Aluminum	0.596	0.0800	0.490-0.787
Antimony	0.0373	0.00503	0.0278-0.0455
Arsenic	0.0515	0.0132	0.0428-0.104
Barium	0.0861	0.00312	0.0804-0.0940
Beryllium	<0.00011	NA	<0.00011
Cadmium	0.0411	0.00345	0.0356-0.0512
Calcium	0.653	0.0702	0.552-0.835
Chromium ²	0.00877	0.00148	0.00631-0.0113
Copper	0.185	0.0239	0.146-0.259
Iron	10.3	0.753	9.56-13.0
Lead	5.41	0.414	4.82-6.17
Magnesium	0.228	0.0559	0.163-0.346
Manganese	0.0753	0.00706	0.0672-0.0903
Mercury	0.000068	0.000010	0.000054- 0.000087
Potassium	0.244	0.0255	0.204-0.284
Selenium	0.00727	0.00290	0.00400-0.0175
Silicon ²	0.276	0.0716	0.176-0.444
Silver	0.000339	0.000096	0.000160- 0.000540
Sodium	12.2	0.478	11.5-13.2
Thallium	0.0253	0.00424	0.0181-0.0317
Tin	0.282	0.0129	0.261-0.314
Zinc	0.416	0.0744	0.321-0.681

ANALYSIS OF THE WASTE FEED AFTER DIGESTION BY EPA METHOD 3050 (weight percent)

Notes:

¹ Average of 18 hourly composites, six each from Runs 2, 3, and 4

² Due to matrix interferences, analytical results are known to be lower than actual concentrations for chromium and silicon. The analytical data from the HRD method indicate that the values for chromium are as follows: mean - 0.024; standard deviation - 0.006; and range - 0.016 to 0.034. The values for silicon are as follows: mean - 8.10; standard deviation - 5.32; and range - 2.89 to 23.8.

NA = Not applicable; < = less than

6.2.2 TCLP Results

The results of the TCLP extraction and analysis, presented in Table 5, show that the waste feed is a hazardous waste, as defined in the RCRA Toxicity Characteristic (TC) Rule, because both lead and cadmium are leached at levels above the toxicity characteristic criteria [40 CFR 261.24]. The data also show that cadmium was present in a more leachable form than lead in the waste feed because, although the total cadmium concentration is one hundredth that of lead, the cadmium leached at 12.8 mg/L, compared to 5.75 mg/L for lead.

6.2.3 General Chemical Analyses for Waste Feed Characterization

The waste feed was also characterized by using a series of general chemical analyses. The analyses used to characterize the waste feed material included PSD, moisture content, total carbon, Btu content, ash content, chloride concentration, fluoride concentration, and sulfur concentration. Table 6 summarizes the PSD results, and Table 7 summarizes the remaining analyses.

HRD recommends that 80 percent of the feed be less than 200 mesh for optimal recovery of volatile metals, because a small particle is required for efficient heat and mass transfer in the reaction zone of the Flame Reactor.

As shown in Table 6, 66.6 percent of the waste feed used for this demonstration was less than 200 mesh, which approached HRD's recommended sizing. The complete distribution is shown in Table 6. The standard deviation shows that the waste feed PSD for all of the runs was relatively consistent.

As received from the NSR site, the waste feed had a moisture content of up to 30 percent. Before being treated during the demonstration, the waste feed was dried to an average total moisture content of 3.3 percent. The recommended moisture content is less than 5 percent total moisture (free and chemically bound), because elevated moisture content increases fuel consumption and adversely affects pneumatic conveying of the waste feed into the Flame Reactor.

Both total carbon and total organic carbon (TOC) analyses were performed. The average total carbon content of the waste feed was 15.0 percent. The average TOC content of the waste feed was 14.9 percent. The carbon in the waste feed was believed to contain unreacted coal particles from the secondary lead smelting process. The waste feed carbon content, which is

TCLP RESULTS FOR THE WASTE FEED (mg/L)

	E			
Analyte	Mean ¹	Standard Deviation	Range	RCRA TC Criteria ²
Arsenic	0.213	0.0124	<0.210-0.264	5.0
Barium	0.0347	0.0143	0.0177-0.0675	100.0
Cadmium	12.8	2.63	7.61-15.8	1.0
Chromium	0.184	0.0334	0.140-0.283	5.0
Lead	5.75	0.705	4.35-6.80	5.0
Mercury	<0.010	NA	<0.010	0.2
Selenium	0.0716	0.0480	<0.030-0.160	1.0
Silver	<0.050	NA	<0.050	5.0

Notes:

¹ Average of 18 values; when the analyte was not detected, the detection limit is reported and was used in the calculations.

² From 40 CFR 261.24

NA = Not applicable

< = less than

mg/L = milligrams per liter

Mesh Size	Sieve Opening (microns)	Mean ²	Standard Deviation	Range
30 < x	600	7.92	1.01	5.74-9.69
60 < x < 30	250	8.74	0.693	7.34-10.1
100 < x < 60	150	7.53	0.694	6.40-9.25
200 < x < 100	75	9.16	0.897	7.25-11.0
325 < x < 200	45	2.29	0.308	1.87-3.04
x < 325	< 45	64.3	1.54	61.6-67.8

PARTICLE SIZE DISTRIBUTION¹ OF THE WASTE FEED (percent by weight)

Notes:

¹ Particle size distribution was determined by ASTM Method D422.

² Average of 18 weight percent values, six each from Runs 2, 3, and 4 < = less than

SUMMARY OF OTHER CHEMICAL ANALYSES

Analyte	Method ¹	Mean	Units	Standard Deviation	Range
Moisture	ASTM D2216	3.35	percent	0.538	2.26-4.07
Total Carbon	Versar SOP	15.0	percent	2.26	9.56-19.4
Organic Carbon	Versar SOP	14.9	percent	2.01	11.3-19.6
Btu Content	ASTM D2015	1,670	Btu/pound	179	1,240-1,880
Ash Content	ASTM D3174	81.6	percent	0.549	80.6-82.4
Chloride	SW-846 9252	24,600	mg/kg	2,650	21,200- 28,900
Chlorine as Chloride	ASTM D3177 and MCAWW 300.0	16,600	mg/kg	2,080	13,200- 20,800
Fluorine as Fluoride	ASTM D3761	130	mg/kg	15.1	106-166
Sulfur as Sulfate	ASTM D4239 and MCAWW 300.0	15.7	percent	1.10	14.3-19.3
Sulfur	Calculated from Sulfate	5.25	percent	0.367	4.77~6.44

Notes:

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 ASTM = American Society for Testing and Materials, ASTM, 1991 MCAWW = Methods for the Chemical Analysis of Water and Wastes, EPA, 1979 SW-846 = Test Methods for Evaluating Solid Waste, EPA, 1986 The Versar SOP for total carbon and total organic carbon (TOC) is contained in Appendix F. mg/kg = milligram per kilogram Btu = British thermal unit consumed in the Flame Reactor, is not a feed characteristic that affects the recovery of volatile metals.

The average Btu content of the waste feed material was 1,660 Btu per pound (Btu/lb). Residues from high temperature processes such as secondary lead smelting are typically expected to have low heating values. However, almost all of this can be attributed to the 15.0 percent carbon, as the carbon content of the waste feed was believed to contain unreacted coal particles. If all of the Btu content of the waste feed was from the carbon, the heating value of the carbon would be 11,100 Btu/lb. (If the waste feed has a Btu content of 1,660 Btu/lb, which is attributable to 15 percent of its composition then that 15 percent composition [carbon] must have a heating value of 1,660/0.15 or 11,100 Btu/lb.) A poor grade of bituminous coal has a heating value of between 10,500 and 11,500 Btu/lb (Perry, 1985). Therefore, it is reasonable to assign all of the heating value of the waste feed to the 15.0 percent carbon content.

The waste feed averaged 81.6 percent inorganic residue or ash. This was not surprising considering the fact that the waste feed is residue from a high temperature process (secondary lead smelting). The remaining 18.4 percent is volatile material composed almost entirely of carbon (15.0 percent) and free moisture (3.3 percent).

The waste feed was analyzed for three chemical constituents: chloride, fluorine, and sulfur. The waste feed averaged 2.46 percent chloride by weight (24,600 mg/kg). Fluorine was present at an average concentration of 0.0130 percent by weight (130 mg/kg). The sulfur content of the waste feed averaged 5.25 percent by weight.

6.2.4 Summary of the Waste Feed Composition

The composition of the waste feed discussed in the previous sections is summarized as

follows:

Constituent	Percent		
Carbon	15.0		
Sodium	12.2		
Iron	10.3		
Silicon	8.10 (by HRD analysis)		
Lead	5.40		
Sulfur	5.25		
Moisture (H_2O)	3.35		
Chloride	2.46		
Miscellaneous metals	3.00 (includes HRD analysis for chromium)		
TOTAL	65.0 percent		

Of the above constituents, only moisture and carbon are present in the form presented above. The other constituents are present as various chemical compounds (such as oxides and sulfates). HRD provided laboratory analyses by X-ray diffraction analysis and scanning electron microscopy. These techniques can produce semiquantitative mineralogical data. The complete summary of analytical results are presented in Appendix C. Compounds with significant concentrations are presented below:

Compound	Concentration	<u>Chemical formula</u>
Thenardite	>10 percent	Na ₂ SO ₄
Hydrous Iron Oxides	>10 percent	Fe _x O _y
Halite	3-10 percent	NaCl
Caracolite	3-10 percent	$Na_3Pb_2(SO_4)_3Cl$

The analytical results presented above indicate that of the remaining 35 percent of the waste feed, a significant portion was oxygen bound as oxides and sulfates. Therefore, a methodology was developed to estimate the oxygen content of the waste feed. The estimated weight percent of oxygen in the waste feed was calculated using the following assumptions. An example calculation is shown for the first assumption.

• It was assumed all the lead in the waste feed (5.41 percent) was present as caracolite $(Na_3Pb_2(SO_4)_3Cl)$, which contains 2.50 percent O_2 .

The calculation for oxygen content is as follows:

- The waste feed is 5.40 percent lead. Assume a 100 gram basis. Therefore, there are 5.40 grams of lead in the waste feed. The molecular weight of lead is 207.19 grams/mole. The 5.40 grams of lead equals 0.0261 moles (5.40 grams/207.19 grams/mole = 0.0261 moles).
- (2) All lead is assumed to be present as caracolite $Na_3Pb_2(SO_4)_3Cl$. For every 2 moles of lead, there is 1 mole of caracolite. Therefore, there are 0.0130 moles of caracolite (0.0261/2).
- (3) Each mole of caracolite contains 12 moles of oxygen (six moles of O₂). Therefore, there are 0.156 moles of oxygen in the waste feed from caracolite.
- (4) The 0.156 moles of oxygen (molecular weight 15.99 g/mole) equals 2.50 grams. Because we are working on a 100 gram basis, the waste feed is 2.50 percent oxygen from caracolite.
- (5) Using the same procedure, the remaining number of moles of sodium (Na), sulfur (S), and chlorine (Cl) bound in other compounds, such as NaCl, Na₂SO₄, can be calculated.
- It was then assumed that all the remaining sulfur (the sulfur not bound in the caracolite) was present as thenardite (Na₂SO₄), which contains 8.0 percent O₂.
- All the remaining chloride (the chloride not bound in the caracolite) was assumed to be present as halite (NaCl), which contains no O_2 .
- It was assumed that all excess sodium (not bound in the caracolite, thenardite, or halite; about 4.26 weight percent) was present as sodium oxide (Na₂O), which contains 1.5 percent O₂.
- Further it was assumed that all the iron was present as ferric oxide (Fe_2O_3), which contains 4.4 percent O_2 .
- Finally, all the silicon was assumed to be present as silicon dioxide (SiO_2) , which contains 9.2 percent O_2 .

Using this methodology, the oxygen content of the waste feed is estimated at 25.6 percent. It should be noted that this is not exact. It is known that small quantities of lead are present as metallic lead and as sulfates, and that iron is present in several oxidation states (FeO, Fe_2O_3 , and others). However, using these assumptions, more than 90 percent of the waste feed has been characterized; 65 percent from constituent analysis and 25.6 percent from estimated oxygen content.

6.3 CHARACTERIZATION OF THE METAL OXIDE PRODUCT

Table 8 presents the metal analysis data for the oxide product. A comparison of the oxide product data with the waste feed and effluent slag data clearly show that (1) the volatile metals (such as antimony, arsenic, cadmium, lead, potassium, sodium, and zinc) were concentrated in the oxide product, and (2) the nonvolatile metals (such as aluminum, calcium, and iron) were concentrated in the effluent slag. The major metal constituents of the oxide product were lead (17.4 percent), sodium (15.7 percent), iron (3.22 percent), and zinc (1.38 percent). Seven other metals (antimony, arsenic, cadmium, calcium, copper, potassium, and tin) plus silicon were present at concentrations of greater than 0.1 percent. According to HRD data, silicon was present in the oxide at 10.5 percent. The oxide product contained a small concentration of nonvolatile species because the horizontal slag separator is not 100 percent efficient. Some slag, including iron particles, was entrained with the off-gas stream.

Recovery of the volatile metals is a measure of the efficiency of the Flame Reactor process. Typically, the recovery of the volatile metals is the total mass of volatile metals in the oxide product compared with the total mass in the waste feed. EPA and HRD have no fully satisfactory explanation for the relatively low recoveries of arsenic, barium, or thallium in the oxide product. These metals do not behave as one would expect based solely on their boiling points. Arsenic is very volatile. Barium and thallium are less volatile, having boiling points similar to that of lead. The presence of metal species such as oxides or chlorides may explain the anomalous recoveries. The recoveries of these volatile metals warrant further study, which is outside the scope of this report.

One objective of this SITE Demonstration was to form a recyclable metal oxide product enriched in lead and zinc. The Flame Reactor was successfully optimized by HRD to do this. Arsenic and barium - and possibly thallium - have negative economic impact on oxide product recycling and were not desired in this product.

The HRD Flame Reactor oxide product was enriched in the volatile metals lead, zinc, and cadmium, demonstrating greater than 75 percent recovery for all three. Section 6.5.3 discusses the recovery of all metals in the oxide product. Recycling opportunities are currently being discussed with various consumers.

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Analyte	Mean Weight ¹	Standard Deviation	Range
Aluminum	0.0562	0.00734	0.0459-0.0623
Antimony	0.125	0.00403	0.122-0.131
Arsenic	0.110	0.00680	0.101-0.117
Barium	0.0282	0.00310	0.0248-0.0323
Beryllium	<0.0001	NA	<0.0001
Cadmium	0.128	0.0139	0.108-0.138
Calcium	0.202	0.0343	0.155-0.234
Chromium ²	0.0300	0.00154	0.0278-0.0313
Copper	0.161	0.0168	0.138-0.178
Iron	3.22	0.267	2.91-3.56
Lead	17.4	1.10	15.9-18.4
Magnesium	0.0327	0.00441	0.0266-0.0368
Manganese	0.0265	0.00370	0.0214-0.0300
Mercury	0.000013	0.000002	<0.000010- 0.00014
Potassium	0.707	0.0548	0.630-0.751
Selenium	0.00520	0.00102	0.00415-0.00659
Silicon ²	0.127	0.0102	0.113-0.137
Silver	0.00269	0.000622	0.00190-0.00342
Sodium	15.7	1.40	13.7-16.8
Thallium	0.00746	0.000243	0.00714-0.00773
Tin	0.660	0.0342	0.612-0.687
Zinc	1.38	0.272	1.00-1.62

ANALYTICAL DATA FOR OXIDE PRODUCT DIGESTION BY EPA METHOD 3050 (weight percent)

Notes:

¹ Average of three composite samples from Runs 2, 3, and 4; when an analyte was present below the detection limit, the detection limit was used to calculate the average.

² Due to matrix interferences, analytical results are known to be lower than actual concentration for chromium and silicon. The analytical data from the HRD method indicate that the values for chromium are as follows: mean - 0.034; standard deviation - 0.002; and range - 0.032 to 0.037. The values for silicon are as follows: mean - 10.5; standard deviation - 5.8; and range - 3.75 to 18.0.

NA = Not applicable; < = less than

6.4 CHARACTERIZATION OF THE EFFLUENT SLAG

Table 9 presents the mean, range, and standard deviation of the TCLP extraction and analysis results on the effluent slag, as well as the RCRA TC criteria. These results show that the effluent slag was nonhazardous for all eight characteristic metals. In fact, when compared to the waste feed, the leachable levels of cadmium, chromium, and lead were all reduced to nondetectable values, and the level of leachable selenium was reduced by half. The levels of leachable arsenic and barium both increased, although they were still below the TC criteria. Barium, a nonvolatile metal, was concentrated in the effluent slag by the technology, so increased leachability may be reasonable. However, the concentration of arsenic in the effluent slag was less than that in the waste feed, so a decrease in the TCLP value of arsenic is expected. Because the TCLP value of arsenic was higher in the effluent slag than in the feed, the technology may convert arsenic into a more leachable state.

The effluent slag was also digested by EPA Method 3050 and analyzed for metals. Table 10 presents these results, which show that the effluent slag was composed of more than 50 percent metals. The major components were iron, sodium, silicon, aluminum, and calcium, which accounted for more than 48 percent of the effluent slag mass and more than 95 percent of the metals. Seven metals (barium, copper, lead, magnesium, manganese, potassium, and zinc) were present in concentrations of greater than 0.1 percent. Based upon HRD results, the effluent slag contained 10.2 percent silicon.

Based upon the TCLP extraction procedure, the effluent slag from the HRD Flame Reactor did not leach any metals above the TC criteria; therefore, the effluent slag was considered to be nonhazardous.

6.5 MASS BALANCE

A mass balance was performed on the HRD Flame Reactor process using materials inventory data (total waste feed, oxide product, and effluent slag) and the metals concentration data for all three streams. Mass balance is an accounting of where chemicals in the waste feed are partitioned in the products after processing. Mass balance closure is a determination of the amount of each chemical present in the waste feed that can be accounted for in the products. Stack emissions are not included because they are small in relation to the other streams. For example, lead, the largest stack emission, totaled 0.2 pounds compared to approximately

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TCLP RESULTS FOR THE EFFLUENT SLAG (mg/L)

	Extract Concentration			
Analyte	Mean ¹	Standard Deviation	Range	RCRA TC criteria ²
Arsenic	0.474	0.188	<0.210-0.930	5.0
Barium	0.175	0.0420	0.109-0.281	100.0
Cadmium	<0.050	NA	<0.050	1.0
Chromium	<0.060	NA	<0.060	5.0
Lead	<0.330	NA	<0.330	5.0
Mercury	<0.010	NA	<0.010	0.2
Selenium	0.0326	0.010	<0.030-0.730	1.0
Silver	<0.050	NA	<0.050	5.0

Notes:

¹ Average of 18 values; for analytes that were not detected, the detection limit is reported and used in calculations.

² From 40 CFR 261.24

NA = Not applicable

mg/L = milligram per liter

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Analyte	Mean Weight ¹	Standard Deviation	Range
Aluminum	1.53	0.138	1.33-1.85
Antimony	0.0357	0.0412	0.0100-0.190
Arsenic	0.0262	0.0291	0.00921-0.134
Barium	0.165	0.0136	0.139-0.183
Beryllium	0.000101	0.00008	<0.00087- 0.000110
Cadmium	0.000373	0.000254	<0.00023-0.00135
Calcium	1.30	0.0973	1.06-1.45
Chromium ²	0.00890	0.00786	0.00339-0.0385
Copper	0.344	0.0324	0.273-0.389
Iron	20.4	1.60	16.7-22.8
Lead	0.552	0.252	0.156-1.14
Magnesium	0.543	0.0847	0.441-0.761
Manganese	0.175	0.0268	0.132-0.231
Mercury	<0.000010	NA	<0.000010
Potassium	0.238	0.0194	0.199-0.269
Selenium	0.00344	0.00345	<0.00226-0.0176
Silicon ²	0.327	0.0979	0.183-0.525
Silver	0.000394	0.000082	0.000250- 0.000510
Sodium	15.5	1.06	12.8-16.8
Thallium	0.0689	0.00862	0.0535-0.0852
Tin	0.0796	0.0150	0.0544-0.111
Zinc	0.113	0.0287	0.07110-0.168

ANALYTICAL DATA FOR EFFLUENT SLAG DIGESTION BY EPA METHOD 3050 (weight percent)

Notes:

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Average of 18 hourly composites, six each from Runs 2, 3, and 4; when an analyte was present below the detection limit, the detection limit was used to calculate the average. Due to matrix interferences, analytical results are known to be lower than actual concentrations for chromium and silicon. The analytical data from the HRD method indicate that the values for chromium are as follows: mean - 0.040; standard deviation -0.023; and range - 0.013 to 0.11. The values for silicon are as follows: mean - 10.2;

standard deviation - 4.7; and range - 7.77 to 28.4.

NA = Not applicable; < = less than
2,000 pounds of lead in the oxide product for the entire demonstration.

6.5.1 Materials Inventory Data

During the demonstration, the masses of the waste feed, oxide product, and effluent slag were determined by HRD. The materials inventory data were obtained from calibrated scales. The amount of waste feed used was calculated from the differences in the load cell readings of the day bin feed hoppers. The masses of oxide product and effluent slag were determined by weighing the full bulk storage bags of oxide product and full metal bins of effluent slag. Because the bags and bins were not always full at the end of a run, the materials inventory data are meaningful when data from all four demonstration runs are summed. Table 11 presents the materials inventory data.

Because the metals concentration from Run 1 samples are unknown (samples were not analyzed because of sampling problems), there is an element of uncertainty in applying the metals concentration data to the combined materials inventory data. Because the metal concentrations in samples from Runs 2, 3, and 4 were consistent, we assume the partitioning in Run 1 was similar, therefore the risk of error in the overall materials inventory data is believed to be small.

In addition, the materials inventory includes a line item referred to as cleanout. This material results from cleaning the oxide product recovery system and material deposited in the shell and tube heat exchanger and combustion chamber. The cleanout material contained oxide product mixed with slag that was entrained with the off-gas. Therefore, this material was a mixture of oxide product and effluent slag.

6.5.2 Weight Reduction

For all four test runs, a total of 47,300 pounds of waste feed were processed, generating 11,200 pounds of oxide product and 15,300 pounds of effluent slag. The total mass of oxide product and effluent slag only account for 56.1 percent of the waste feed mass. Therefore, the process has a net weight reduction of 43.9 percent. After the demonstration was complete, a total of 3,460 pounds of treated waste was cleaned out of the combustion chamber and heat exchanger. This is 7.32 percent of the total waste feed processed. Therefore, if the cleanout material is included, the weight reduction is 36.6 percent. This information is summarized in Table 11.

MATERIALS INVENTORY DATA FROM THE HRD SITE DEMONSTRATION (pounds)

	Run 1 ¹	Run 2	Run 3	Run 4	Total ²
Waste feed	14,700	11,100	10,300	11,100	47,300
Oxide Product	3,360	2,400	2,250	3,210	11,200
Effluent Slag	4,340	5,170	1,640	4,160	15,300
Cleanout	3	1,640	3	1,810	3,460

Notes:

¹ Although concentration data were not collected for this run because of fluctuations in stack gas temperature, the materials inventory data are reported.

² Due to rounding errors, the total weight does not equal the sum of the weights of the four runs.

³ No combustion chamber and heat exchanger cleanout material was weighed on these days.

The weight reduction was primarily the result of essentially complete conversion of carbon to carbon dioxide $(CO_2)(15.0 \text{ percent})$, moisture to steam (3.35 percent), and chloride to hydrogen chloride (HCl) gas (2.46 percent). In addition, sulfur was partially converted to sulfur dioxide $(SO_2)(2.26 \text{ percent})$. The remaining sulfur (2.99 percent) was trapped in either the oxide product or the effluent slag. These values are the average of data from Runs 2, 3, and 4.

The remaining 13.5 percent weight reduction is attributed to the strong reducing conditions of the Flame Reactor and analytical variations.

6.5.3 Percent Recovery

Because no metal concentration data are available for Run 1, only data from Runs 2, 3, and 4 were used to calculate percent recoveries. The materials inventory data for these runs include: 32,500 pounds of waste feed, 7,860 pounds of oxide product, and 11,000 pounds of effluent slag. Table 12 presents metal recovery data in two forms. The first form is the raw percent recovery when the oxide product is compared to the feed. Because mass balance closure is less than 100 percent, due mainly to build up of material in the combustion chamber and heat exchanger, the percent recoveries are low. For lead, zinc, and cadmium, the percent recoveries are 77.7, 80.0, and 75.0, respectively. The second method presents a normalized percent recovery. This method scales the percent recovery and effluent slag percent recovery is 100 percent. Using this method, the percent recoveries of lead, zinc, and cadmium are 95.8, 89.7, and 99.6, respectively.

6.6 HRD FLAME REACTOR PROCESS RELIABILITY

The HRD Flame Reactor process consists of five sections: (1) the feed system, (2) the Flame Reactor, (3) the slag separator, (4) the combustion chamber, and (5) the oxide product recovery system. The Flame Reactor, slag separator, and combustion chamber had no operational problems that affected their performance during the demonstration. The feed system had one feed system jam that did not affect the SITE Demonstration results. However, HRD reports that the oxide product recovery system was undersized for the feed rate used during the demonstration.

During Run 1, a feed screw conveyor was jammed for approximately 30 minutes. The other feed conveyor rate was increased to keep the feed rate to the reactor constant. Because

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MASS BALANCE CLOSURE AND RECOVERY OF METALS PRESENT IN THE WASTE FEED (percent)

Analyte	Mass Balance Closure	Oxide Product Recovery ¹	Normalized Oxide Product Recovery ²
Aluminum	88.9	2.27	2.56
Antimony ³	113	81.1	71.5
Arsenic ³	68.7	51.6	75.1
Barium ³	72.3	7.90	10.9
Beryllium ⁸	58.6	23.9	40.7
Cadmium ³	75.3	75.0	99.6
Calcium	74.5	7.48	10.0
Chromium ^{3,4}	90.6	34.6	38.2
Copper	83.5	20.9	25.1
Iron	74.6	7.53	10.1
Lead	81.2	77.7	95.8
Magnesium	83.5	3.46	4.14
Manganese ³	87.0	8.50	9.77
Mercury ³	9.44	4,49	47.6
Potassium	103	69.8	68.0
Selenium ³	33.2	17.3	52.0
Silicon ⁴	73.6	31.2	42.3
Silver ³	230	191	83.0
Sodium	73.5	30.9	42.0
Thallium ³	99.0	7.11	7.19
Tin	66.1	56.6	85.6
Zinc	89.2	80.0	89.7

Notes:

¹ In this calculation the weight percent of the metal in the effluent slag is the mass balance closure minus the oxide product recovery.

- ² In this calculation the weight percent of the metal in the effluent slag is 100 minus the normalized oxide product percent recovery.
- ³ Analyte is present in the waste feed at less than 0.1 weight percent.

4 Silicon and chromium analytical results from HRD's analytical procedure were used.

Run 1 was discarded (because of temperature and pressure fluctuations in the stack gas), the demonstration results were not affected.

The oxide product recovery system consists of a shell and tube heat exchanger, a baghouse, an induced draft fan, and a stack. This equipment was sized to handle the gases generated by the HRD Flame Reactor processing 20,000 tons per year of EAF dust. However, for reasons explained below, when processing waste feed during the SITE Demonstration at a rate of only 7,880 tons per year (0.9 tons/hour or 30 pounds per minute), the capacity of the oxide product recovery system was exceeded.

During each demonstration test run, the Flame Reactor was forced to shut down because of back pressure at the slag tap hole. Under normal conditions, the reactor operates under a slightly negative pressure to prevent escape of gases, including CO and metal vapors. The negative pressure is maintained by the induced draft baghouse blower. If this blower is unable to draw a sufficient draft, the process reactions quickly cause a pressure rise which results in the escape of gases.

During the demonstration test runs, the heat exchanger restricted the flow of off-gases causing back pressure at the slag tap hole and subsequent shutdown of the reactor. The water-cooled shell and tube heat exchanger was obtained as salvage from a nearby zinc smelter. Approximately 20 percent of its tubes have been intentionally sealed because they are broken due to corrosion and leak water. There were no problems at the beginning of each test run because the system was cool and the refractory material lining the system before the heat exchanger behaved as a heat sink, lowering the temperature and, therefore, the gas volume through the heat exchanger. As the refractory material heated, the temperature of the gases entering the heat exchanger increased until the gas volume was so high that a large pressure drop occurred across the heat exchanger and the induced draft baghouse blower was unable to compensate.

The tap hole back pressure usually occurred during the demonstration after about 4 hours of steady operation. At this time, the control room operator manually shut down the Flame Reactor. The system was cooled by drawing ambient air through the oxide product collection system. At the same time, oxide which accumulated in the heat exchanger tubing was removed to reduce restrictions. The total time of each shut down was 2 to 3 hours.

For a full-scale Superfund site remediation project, the gas handling capacity of the oxide

product recovery system could be increased to allow the process to run 24 hours/day with regular maintenance.

Another problem developed when, on the second day of the demonstration, the cooling tower began leaking noncontact cooling water. Although the addition of makeup water was required to maintain the necessary level in the tower, the problem did not affect the operation of the cooling system.

6.7 STACK MONITORING AND EMISSIONS SAMPLING RESULTS

During the HRD SITE Demonstration, stack gases were sampled for metals, HCl, and particulate emissions, and were continuously monitored for SO₂, nitrogen oxides (NO_x), O₂, CO₂, CO, and THC. The metals and particulate emissions were determined using an EPA Modified Method 5, isokinetic, multiple metals sampling train. HCl emissions were determined by a single point EPA Method 26 sampling train. The continuous emission monitors used the following: EPA Method 6C for SO₂, EPA Method 7E for NO_x, EPA Method 3A for O₂ and CO₂, EPA Method 10 for CO, and EPA Method 25A for THC. All the standard EPA methods can be found in 40 CFR 60, Appendix A, and the multiple metals train is discussed in the Methods Manual for Compliance with the Boilers and Industrial Furnaces (BIF) Regulations [40 CFR 266, Appendix IX].

6.7.1 Introduction to the BIF Rule

On February 21, 1991, the final BIF rule was published [40 CFR 266, Subpart H; 56 FR 7134-7240]. This rule is the applicable or relevant and appropriate requirement (ARAR) that the air emissions from the HRD Flame Reactor may be required to meet. Therefore, a brief introduction to the rule is presented before stack monitoring and emissions sampling are discussed. The BIF rule became effective on August 21, 1991.

The HRD Flame Reactor is classified as a smelting, melting, and refining furnace by the BIF rule [56 FR 7143]. However, smelting, melting, and refining furnaces that process hazardous waste solely for metal recovery are conditionally exempt from the majority of 40 CFR 266, Subpart H regulations, and therefore, need only comply with 40 CFR 266.101 (Management Prior to Burning) and 40 CFR 266.112 (Regulation of Residues). These furnaces are conditionally exempt because (1) EPA does not believe it prudent to regulate a whole potential class of devices and wastes that it has not fully evaluated and (2) EPA wishes to study further whether regulating these furnaces under the Clean Air Act may be more appropriate, particularly if technology-based controls on toxic air emissions are likely to apply.

Even though EPA might classify the HRD Flame Reactor as conditionally exempt because the BIF rule promulgated risk-based emission levels for metals and HCl, the state or federal permitting authority could possibly apply these standards by imposing the omnibus authority of RCRA [40 CFR 270.32(b)(2) and RCRA Section 3005(c)(3)] to protect human health and the environment. Therefore, the BIF regulatory limits for metals, particulate, and HCl emissions are presented below.

The BIF rule established a three-tiered permitting structure to control emissions of HCl, chlorine (Cl₂), and 10 toxic metals listed in Appendix VIII of 40 CFR 261. The list of 10 toxic metals is further broken down into four carcinogenic metals (arsenic, beryllium, cadmium, and chromium) and six noncarcinogenic metals (antimony, barium, lead, mercury, silver, and thallium). Tier I of the three-tiered permitting structure limits feed rates, Tier II sets emission rate screening limits, and Tier III requires a site-specific risk assessment. EPA expects the majority of facilities to elect to comply with Tier III standards to obtain more flexible permit limits.

Tier III standards require 1) emissions testing to determine the emission rate for each metal and 2) air dispersion modeling to predict the maximum, annual, off-site, ground-level concentration for each metal. These concentrations are then compared to the acceptable ambient levels specified in Appendix IV and V of the BIF rule [56 FR 7223]. Because dispersion modeling is beyond the scope of the SITE Demonstration, actual Tier III limits for the HRD Flame Reactor were not calculated; therefore, Tier II screening limits will be presented. These limits are not the regulatory limits for the Flame Reactor and are presented for comparison purposes only. In addition, because the HRD stack is shorter than the Flame Reactor building, and because the surrounding terrain within 5 kilometers (3.1 miles) of the stack equals or exceeds the elevation of the physical stack height, the Tier II screening limits are the conservative (restrictive) limits.

The HRD Flame Reactor may be subject to additional air emissions regulations when EPA promulgates regulations under the authority of the Clean Air Act Amendments of 1990. The Clean Air Act Amendments concerning hazardous air pollutants may potentially address many of the same sources regulated under 40 CFR 266. For example, the New Source Performance

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Standards (NSPS) of Section 111 of the Clean Air Act may be ARARs for a HRD Flame Reactor unit installed at a Superfund site, especially if the pollutants emitted and the technology employed are sufficiently similar to a pollutant and source category regulated by the NSPS. Also, EPA has established National Emissions Standards for Hazardous Air Pollutants (NESHAPS) for arsenic, beryllium, and mercury for certain categories of sources [40 CFR 61].

6.7.2 Metal Emissions

The metals emissions in the stack gas were calculated from the EPA Modified Method 5 sampling train data. The Modified Method 5 sampling train collects two types of samples. The first type, or "front-half," is solid matter collected on a filter. The second type, or "back-half," collects gaseous emissions by absorbing them in an acid solution. The analytical results, shown in Table 13, are the sum of both halves. Table 13 presents the metals emission rates for the blank run and the three valid test runs (Runs 2, 3, and 4), as well as the BIF Rule Tier II screening limits. The Tier II screening limits are presented for comparison only. EPA believes that most facilities will choose to comply with the less restrictive Tier III limits. Tier III limits are not presented because they involve site-specific dispersion modeling and risk analysis.

The HRD Flame Reactor emitted lead, chromium, and arsenic at rates above the Tier II screening limits during the SITE Demonstration; however, the detection limit for arsenic is too high for comparison to Tier II limits. The Tier II levels presented are restrictive because of the short stack and the complex terrain. (See Section 6.7.1 of this report.)

6.7.3 HCl Emissions

HCl emissions during the HRD Flame Reactor Demonstration were between 38.5 and 46.4 pounds per hour (lb/hr). This high emission rate could be expected because the Flame Reactor had no acid gas control system, and the waste feed contained, on average, 2.46 percent chloride by weight. The BIF rule has promulgated risk-based emission limits on HCl. The Tier II screening limit is 0.091 g/sec (0.72 lb/hr) [56 FR 7232]. The addition of a wet scrubber should control HCl emissions to below the applicable standards.

6.7.4 Particulate Emissions

Because the HRD Flame Reactor process uses a baghouse to capture the metal oxide

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Metal	Blank Run	Test Run 2	Test Run 3	Test Run 4	Tier II Screening Limits ¹	Above / Below
Antimony	0.50 ²	0.39 ³	0.35 ^{2,3}	0.37 ^{2,3}	14	Below
Arsenic	0.39 ²	0.29 ²	0.27 ^{2,3}	0.29 ^{2,3}	0.11	Above
Barium	0.041	0.55	0.72	0.62	2400	Below
Beryllium	0.0057 ^{2,3}	0.019 ^{2,3}	0.018 ^{2,3}	0.019 ^{2,3}	0.20	Below
Cadmium	0.12 ²	0.24 ²	0.17 ²	0.17 ²	0.26	Below
Chromium	0.053 ²	1.0 ²	0.70 ²	1.0 ²	0.040	Above
Lead	12	12 ²	12 ²	12 ²	4.3	Above
Mercury	0.041 ³	1.1	1.3	0.96	14	Below
Silver	0.015	0.19	0.013 ^{2,3}	0.014 ^{2,3}	140	Below
Thallium	0.72 ^{2,3}	2.3 ^{2,3}	2.2 ^{2,3}	2.3 ^{2,3}	14	Below

METAL EMISSION RATES OF THE HRD FLAME REACTOR (grams per hour)

Notes:

- ¹ Emission limits are based on emission of a single metal. Tier III standards based on site-specific dispersion modeling are less restrictive. (See Section 6.7.1 of this report).
- ² The concentration of the metal was below the analytical detection limit in the combined EPA Modified Method 5 sampling train back-half samples for this run.
- ³ The concentration of the metal was below the analytical detection limit in the combined EPA Modified Method 5 sampling train front-half samples for this run.

product, particulate emissions from the Flame Reactor should be low when the baghouse is maintained and operated properly.

During analysis of the demonstration samples, problems occurred with the gravimetric analysis, preventing accurate determination of the particulate emissions for all but the blank run. Therefore, a worst case analysis (when the concentration of a metal was below the analytical detection limit, the detection limit was used in the emissions calculation) of the test run particulate emissions was performed.

Particulate emissions are calculated from the sum of two gravimetric analyses. The first analysis is conducted on the filter. The EPA Method 5 sample train uses a filter that exhibits 99.95 percent efficiency on 0.3-micron dioctyl phthalate smoke. The filter is weighed before and after sampling. The resulting difference is equal to the particulate weight on the filter. The blank run and Run 3 were the only runs with positive differences. Negative numbers were replaced with 1 mg for a worst case analysis. The second gravimetric analysis is the acetone probe wash. The probe (that part of the EPA Method 5 train that carries the gas sample from the source to the filter) is rinsed with acetone to remove any particulate matter deposited on the probe. In the laboratory, the acetone is completely evaporated, and the residual is weighed. A laboratory error occurred, and thus residuals were weighed only to ± 10 mg. The blank run and Run 2 were the only runs without negative numbers. For a worst case analysis, each run was assumed to show 10 mg of dried acetone residual.

Even under a worst case scenario, the test run particulate emissions were lower than the particulate emissions for the blank run. The blank run particulate emissions were slightly higher than runs containing waste, because no oxide product was formed to act as seed nuclei for particle formation and growth. Therefore, the particles formed were smaller and were not captured by the baghouse. The sources of the blank run particulate emissions may include residue material in the system and lime used to condition the baghouse bags.

The permit limit specified in the EPA RD&D permit for particulate emission is 0.02 grains per dscf. As shown in Table 14, all particulate emissions were below this standard. Table 14 also presents the particulate emissions in lb/hr and in grains/dscf corrected to 12 percent CO_2 and 7 percent O_2 for comparison purposes.

PARTICULATE RESULTS

	Actual		Grains/dscf	Pounds	
Test Run	mg/dscf	Grains/dscf	12 percent CO ₂	7 percent O ₂	per hour
Blank	0.517	0.00797	0.0282	0.0786	0.522
21	0.191	0.00295	0.00887	0.0164	0.364
31	0.294	0.00454	0.0114	0.0233	0.548
41	0.213	0.00328	0.00894	0.0168	0.356

Notes:

Particulate emissions were calculated using a worst case scenario. dscf = dry standard cubic feet mg = milligrams

6.7.5 Continuous Emission Monitoring

Emissions of SO_2 , NO_x , O_2 , CO_2 , and THC were continuously monitored for the blank run and for each 6-hour test run. Table 15 presents the average emission for each run.

The HRD Flame Reactor currently has an air quality permit issued by PaDER that limits SO_2 emissions to less than 500 ppm for commercial operations. For the demonstration, for which the limit is not effective, the SO_2 emissions were below 500 ppm except for a 2-minute period during Run 2. The maximum SO_2 emission was 514 ppm, which occurred immediately following startup, after a system shut down was required to cool the oxide product recovery system.

6.8 HRD FLAME REACTOR OPERATING PARAMETERS

Table 16 shows the operating parameters for the Flame Reactor during the blank run and the three valid test runs. The three test runs were intended to be replicate runs. The operating parameters show that, within operating limits, the operating conditions were the same for all three runs.

6.9 THE HRD THERMODYNAMIC MODEL

HRD has developed a thermodynamic model for the HRD Flame Reactor process. The model was used to set Flame Reactor operating parameters for the shakedown runs. Because the SLS slag waste feed is different in chemical composition from the EAF dust used to develop the model, the results of the model were not extremely accurate. Without improvements, it is believed that the model can be used only to set preliminary operating conditions and to determine order of magnitude estimates of the required amount of fuel and oxygen.

In the HRD Thermodynamic Model, oxygen and natural gas flow rates are calculated, and oxide product recovery and effluent slag formation are estimated by entering waste composition data and expected operating conditions into the model. The waste composition data used were based on chemical analyses and the estimated mineralogy of the waste feed. The operating parameters used were the waste feed rate, fuel composition (natural gas assumed to be 100 percent methane), oxidant composition (the combined total gas input, about 80 percent oxygen and 20 percent nitrogen), estimated heat loss, target temperature, and carbon monoxide/carbon dioxide ratio. Using these data, the model calculated the required waste feed, oxygen, air, and

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Gas	Units	Blank Run	Test Run 2	Test Run 3	Test Run 4
SO ₂	ppm dry	ND	268	272	290
NO _x	ppm dry	173	16.0	15.8	18.5
O ₂	percent	19.6	18.5	18.3	18.3
CO2	percent	3.39	3.99	4.77	4.40
СО	ppm dry	4.17	ND	14.2 ¹	1.28
тнс	ppm dry, as propane	1.64	1.61	1.7	0.91

RESULTS OF CONTINUOUS EMISSION MONITORING (average concentrations)

Notes:

¹ The CO analyzer performed erratically during Test Run 3. Therefore, the CO data for Test Run 3 are suspect.

ND = Not detected

ppm = parts per million

FLAME REACTOR OPERATING PARAMETERS FOR THE SITE DEMONSTRATION

	Range of Values			
Operating Parameter	01	2 ¹	3 ¹	
Natural gas feed rate (scfm)	242-251	334-356	331-353	333-357
Oxygen feed rate (scfm)	404-413	618-651	586-659	629-676
Air feed rate (scfm)	159-162	158-170	157-173	155-161
Waste feed rate (lb/min [lb/test])	0	29.7 ² [10,700]	29.8 ² [10,800]	30.0 ² [10,800]
Reactor slag flow rate (lb/min [lb/test])	0	14.4 [5,170]	4.55 [1,640]	11.6 [4,160]
Combustion chamber temperature (°C)	308-329	315-733	215-832	423-726
Cooling chamber exit gas temperature (°C)	92-99	100-306	78-401	154-372
Oxide product flowrate (lb/min [lb/test])	0	6.67 [2,400]	6.25 [3,250]	8.92 [3,210]
Stack temperature (°C)	73-70	50-150	50-147	70-155

Notes:

Test Run number. Test Run 0 was the background run. Test Run 1 was not a valid run.
 Average feed rate for entire test calculated from the change in weight of the feed bins over time.

scfm = standard cubic feet per minute

lb/min = pounds per minute

lb/test = pounds per test

 $^{\circ}C = degrees Celsius$

natural gas flow rates, and estimated the oxide product recovery and effluent slag formation, based on the system achieving an equilibrium.

The operating and recovery information estimated from the HRD Thermodynamic Model, and the actual data from the demonstration test are presented in Table 17. As shown in Table 17, the HRD Thermodynamic Model was unable to predict with the same accuracy as with previous waste feeds (1) the necessary oxygen and natural gas flows, (2) the amount of oxide product recovered, (3) the amount of effluent slag produced, and (4) the percent recoveries of zinc and lead.

The flow rates necessary for oxygen and natural gas were significantly higher than predicted by the HRD thermodynamic model. The formation of effluent slag in the actual demonstration was much less than predicted by the model, and the recovery of oxide product was much greater. Although total oxide product recovery was greater than predicted, the recoveries obtained during the demonstration for zinc (89.7 percent) and lead (95.8 percent) were less than predicted by the model (99 percent and 99.6 percent, respectively).

HRD offered several explanations of why the model was not able to accurately predict the conditions of the demonstration. First, because the model was set up for EAF dust and not for SLS slag, the waste composition data for the SLS slag did not fit directly into the model. Therefore, HRD had to make several assumptions concerning the mineralogy of the SLS slag and adjust the waste composition data to facilitate using this data in the model.

Also, certain constituents (such as sodium) that are assumed by the model to partition entirely into the effluent slag were found to be present in the oxide product. This would partially explain the lower-than-predicted effluent slag formation and the higher-than-predicted oxide product recovery.

OPERATING AND RECOVERY DATA FROM THE HRD THERMODYNAMIC MODEL AND THE SITE DEMONSTRATION

	Oxygen. Flow (scfm)	Natural Gas Flow (scfm)	Feed Rate (lb/min)	Effluent Slag Formation (percent of feed)	Oxide Product Recovery (percent of feed)	Zinc Recovery (percent of total sinc)	Lead Recovery (percent of total lead)
HRD Model	488	208	30	62.6	8.3	99.0	99.6
SITE Demonstration	614	310	30	3 0.1	22.0	89.7 ¹	95.8 ¹

Notes:

¹ Because the HRD model assumes a 100 percent closure on the mass balance, the normalized percent recovery is presented. The raw percent recovery for sinc and lead are 80.0 and 77.7 percent, respectively.

scfm = standard cubic feet per minute

lb/min = pounds per minute

7.0 QUALITY ASSURANCE/QUALITY CONTROL

The overall quality assurance objective was to provide well-documented sampling and analytical data of known quality in support of the demonstration objectives. A QAPP was prepared to incorporate all of the elements of a Category II QAPP (EPA, 1987; EPA, 1991b). Specific QA targets for precision, accuracy, completeness, and detection limit are listed in Table 18 and are summarized in the sections to follow. These sections present the analytical methods used and data for holding times, blanks, matrix spikes and spike duplicates, laboratory duplicates, reference standards, and detection limits.

7.1 ANALYTICAL METHODS

In selecting appropriate methods to prepare and analyze the solid, liquid, and vapor phase samples from the HRD SITE Demonstration, the specific analytes of interest, the sample matrices, and the minimum detectable concentrations needed for the project were taken into account. Tables 19, 20, and 21 summarize the methods chosen. Most of the analytes were analyzed by using the EPA-approved methods or American Society for Testing and Materials (ASTM) methods as specified in the QAPP (EPA, 1990). Sulfur was analyzed by ASTM Method D3177 followed by EPA *Methods for the Chemical Analysis of Water and Wastes* (MCAWW) Method 300.0, instead of ASTM Method D4239 as originally specified, because it was determined during the laboratory audit that the method used would be more appropriate for samples with high metal content (ASTM, 1991; EPA, 1979).

Metals, TCLP metals, chloride, total organic carbon, Btu content, ash content, moisture content, and particle size distribution analyses were performed on the waste feed. Metals, TCLP metals, and moisture content analyses were performed on the effluent slag samples. Metals and moisture content analyses were performed on the oxide product samples. For the stack gas sample trains, particulate (metals sampling train), chloride (HCl sampling train), metals, and mercury (metals/mercury train) were quantified.

The standard EPA-approved digestion technique for metals preparation is SW-846 Method 3050 (EPA, 1986). However, because of potential analytical problems involving incomplete digestion, several alternative digestion methods were considered. Three methods,

QA OBJECTIVES FOR PRECISION, ACCURACY, COMPLETENESS, AND DETECTION LIMITS

Measurement	Matrix Type	Method Reference	Measurement Units	Detection Limits	Precision (RPD)	Accuracy (Percent Recovery)	Completeness (percent)
1. Metals	Solid ¹	SW-846 ³ Methods	mg/kg	Various ⁴	25	NA	90
	Gas ²	SW-846 ³ Methods	µg/dscf	Various ⁴	25	73-130	100
Metals (TCLP)	Solid (Waste feed and effluent slag samples)	SW-846 Methods	mg/L	Various ⁴	25	70-130	90
2. Chloride	Stack gas samples	SW-846 9252	ppm	1	25	70-130	100
3. Particulate	Stack gas samples	EPA Method 5	gram/dscf	0.0015 gram/ filter ⁵	NA	NA	90
4. Total Chloride	Solid	S₩-846 9252	percent	0.1	25	NA	90
5. Total Fluoride	Solid	ASTM D3761	percent	0.1	25	NA	90
6. Total Sulfur	Solid	ASTM D3177 and MCAWW 300.0	percent	0.1	25	NA	90
7. Total Carbon	Solid	Versar SOP	percent	0.1	25	NA	90
8. Total Organic Carbon	Solid	Versar SOP	percent	0.1	3 0	NA	90
9. Particle Distribution	Solid (Waste feed)	D422 ASTM	NA	NA	NA	NA	90
10. Moisture Content	Solid (Waste feed)	D2216 ASTM	percent	NA	30	NA	90

(sheet 1 of 2)

Notes:

- ¹ Metals analyzed in the solid samples (effluent slag, oxide product, and waste feed) include aluminum, antimony, arsenic, barium, beryllium, cadmium, calcium, chromium, copper, iron, lead, magnesium, manganese, mercury, potassium, silicon, silver, sodium, thallium, tin, and zinc.
- ² Metals analyzed in the stack samples include antimony, arsenic, barium, beryllium, cadmium, chromium, lead, mercury, silver, and thallium.
- ³ Test Methods for Evaluating Solid Waste, Volume One: Laboratory Manual, Physical/Chemical Methods; and Volume Two Field Manual, Physical/Chemical Methods, SW-846, Third Edition, Office of Solid Waste, U.S. Environmental Protection Agency, Document Control No. 955-011-00000-1, 1986.

QA OBJECTIVES FOR PRECISION, ACCURACY, COMPLETENESS, AND DETECTION LIMITS (sheet 2 of 2)

⁴ Typical instrument detection limits for metals analyzed by inductively coupled plasma atomic emission spectroscopy (ICP) using EPA Method 6010 were as follows:

Typical Detection Limits for Metals						
Metal	Liquid Matrix (µg/L)	Solid Matrix (mg/kg)	Impinger Contents (µg/dscf)	Filter (µg/dscf)		
Aluminum	25	6.5				
Antimony	30	8.5	0.26	0.030		
Arsenic	21 (4 for GFAA ⁶)	9.0	0.18	0.097		
Barium	1	0.5	0.0085	0.0037		
Beryllium	1	1	0.0086	0.011		
Cadmium	5	2.5	0.043	0.027		
Calcium	20	4.5				
Chromium	6	2	0.052	0.054		
Copper	5	2.5				
Iron	10	3				
Lead	33 (1 for GFAA⁶)	17.5	0.28	0.19		
Magnesium	500	5				
Manganese	4	1				
Mercury	$(0.2 \text{ for } \mathrm{CV}^7)$	$(0.1 \text{ for } CV^7)$	0.0086	0.0011		
Potassium	744	242				
Selenium	(3 for GFAA ⁶)	26				
Silicon		38				
Silver	5 (0.5 for GFAA ⁶)	1	0.0041	0.011		
Sodium	2 9	10				
Thallium	(1 for GFAA ⁶)	75	1.4	0.81		
Tin	13	6.5				
Zinc	2	1				

Note that the actual detection limits varied, depending on the concentration of the analytes present and the presence of any interference. The stack gas sampling trains generate liquid matrices for which the detection limits are listed. The detection limits for the impinger contents and filter were based on the average sample volume of Runs 2, 3, and 4 (55.5 dscf) and a final impinger volume of the system blank (475 ml).

⁵ Estimate of the detection limit was based on performing gravimetric analysis of the filter by using a scale accurate to 0.0001 grams.

⁶ Graphite furnace atomic absorption spectroscopy

⁷ Cold vapor atomic absorption spectroscopy

NA = Not applicable RPD = Relative percent difference $\mu g = microgram$ dscf = dry standard cubic foot mg = milligramL = liter

ANALYTICAL METHODS FOR SOLID SAMPLES (Waste Feed, Oxide Product, and Effluent Slag)

Analyte	Preparation Method ¹	Analysis Method ¹
Metals		
Mercury	7471	7471
Other metals: aluminum, antimony, arsenic, barium, beryllium, cadmium, calcium, chromium, copper, iron, lead, magnesium, manganese, potassium, selenium, silicon, silver, sodium, thallium, tin, and zinc	3050 ²	6010
Leachable Metals (use TCLP, Method 1311 to prepare extract)		
Mercury	7470	7470
Selenium	7740	7740
Other metals: arsenic, barium, cadmium, chromium, lead, and silver	3005	6010
Other Analytes ³		
Particle size distribution		ASTM D422
Moisture content		ASTM D22 16
Chloride		9252
Btu content		ASTM D2015
Ash content		ASTM D3174
Total organic carbon		Versar SOP ⁴
Total carbon		Versar SOP ⁴
Sulfur as sulfate		ASTM D3177, followed by MCAWW 300.0
Fluorine as fluoride		ASTM D3761
Chlorine as chloride		ASTM D3177, followed by MCAWW 300.0

Notes:

1 All methods are from SW-846 unless specified otherwise. 2 Method 3050 was modified to use 0.2 gram of sample instead of 1 gram.

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Analysis was completed only for samples from waste feed. 4 Versar SOP is included in Appendix F of this document.

ANALYTICAL METHODS FOR LIQUID SAMPLES (Decontamination Water and Equipment Rinsate Blanks)

Analyte	Preparation Method ¹	Analysis Method ¹
Metals		
Arsenic	7060/7740	7060
Lead	3020	7421
Mercury	7470	7470
Selenium	7060/7740	7740
Thallium	3020	7841
Other metals ²	3010	6010

Notes:

- ¹ All methods are from SW-846 unless specified otherwise.
- ² Other metals include aluminum, antimony, barium, beryllium, cadmium, calcium, chromium, copper, iron, magnesium, manganese, potassium, silicon, silver, sodium, tin, and zinc.

ANALYTICAL METHODS FOR GAS SAMPLES (Stack Gas)

		Front	Front Half		ack Half
Analyte	Sampling Method	Preparation Method ¹	Analysis Method ¹	Preparation Method ¹	Analysis Method ¹
Metals ²	Metals Method 5 ³				
Antimony Arsenic Barium Beryllium Cadmium Chromium Lead Mercury Silver Thallium		3050 3050 3050 3050 3050 3050 3050 3050	6010 6010 6010 6010 6010 6010 6010 7470 6010 7470	3010 3010 3010 3010 3010 3010 3010 3010	6010 6010 6010 6010 6010 6010 6010 6010
Particulate	Method 5 ³	Desiccation	Gravimetric		
Chloride	Method 26				9252
Moisture	Method 4				Gravimetric

Notes:

- ¹ All methods are from SW-846 unless specified otherwise.
- ² The 10 toxic metals listed in Section 3005(c)(3) of RCRA were the target analytes for the stack samples.
- ³ EPA, 1991a. The Method 5 sampling train has a front half (consisting of a probe and filter assembly) used to collect particulate, and a back half (consisting of impingers) to transfer metal vapors to a aqueous phase for analysis. Each half is analyzed independently and the results combined.

lithium tetraborate fusion, hydrofluoric acid dissolution, and a microwave bomb technique developed by HRD, were tested and evaluated before the final method was selected. Discussion of preliminary studies and rationale for comparing and selecting the various alternative digestion methods is presented in Section 6.1. A modified EPA Method 3050, with a reduced sample size (from 1.0 gram to 0.2 grams), was selected as the digestion method.

7.2 SAMPLE HOLDING TIMES

The dates of sample collection, preparation, and analysis are listed in Tables 22 and 23. These tables indicate whether sample holding times were met. The sample holding times specified in the analytical methods were met for all samples except for fluoride and sulfur in the waste feed samples and the mercury stack gas samples. Maximum holding times for fluoride and sulfur are 28 days. For this test the actual holding times for fluoride and sulfur were 62 and 63 days, respectively. Maximum holding time for mercury gas samples is 28 days. For this test the actual holding time was 34 days for all of the mercury samples.

Although the fluoride and sulfur waste feed sample holding times were exceeded by more than a month, it is believed that the quality of data were not compromised. The waste feed samples were collected from a waste pile that had been in place for many months before sample collection occurred, therefore, exceeding the holding time is believed to make little difference.

Holding times for the mercury stack gas samples were exceeded by 6 days, because the samples were held until consensus was reached by HRD and EPA regarding which analytical method should be used.

7.3 MATRIX SPIKE/MATRIX SPIKE DUPLICATE RECOVERIES

Matrix spike and matrix spike duplicates were performed on the TCLP analyses for waste feed, effluent slag, and stack gas samples from Run 2 to ensure the accuracy and precision of these analyses. Matrix spikes were not analyzed for metals because of the high metal content (greater that 10 percent) of the samples. When matrix concentrations are very high, normal spiking concentrations cannot be used as they would be overwhelmed by the high concentration of the analyte in the sample. In addition, it would be very hard do dissolve such high concentrations of analytes to accurately prepare such solutions. In addition, special spiking solutions are very expensive. Therefore, duplicates were determined not to be appropriate by the analytical

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DATES OF SAMPLE COLLECTION, PREPARATION, AND ANALYSIS FOR PROCESS SAMPLES (sheet 1 of 4)

Sample/Analyte	Holding Time	Collection Date	Preparation/ Extraction Date	Analysis Date	Holding Tìme Met?
Waste Feed					
<u>Metals</u>	6 months ¹				
Run 1, Hr. 1-7		3/20. 3/21	•-		Archived
Run 2, Hr. 1-6		3/21		6/27	Yes
Run 3, Hr. 1-6		3/22		6/27	Yes
Run 4, Hr. 1-6		3/23		6/27	Yes
Run 2, Hr. 2 (Field Dup.)		3/21			Archived
TCLP Metals	6 months				
Run 1, Hr. 1-7		3/20, 3/21			Archived
Run 2, Hr. 1-6		3/21	$4/3, 7/11^2$	4/10-4/12, 7/11 ²	Yes
Run 3, Hr. 1-6		3/22	4/3,7/11 ²	$4/10-4/12, 7/11^2$	Yes
Run 4, Hr. 1-6		3/23	4/3, 7/112	4/10-4/12, 7/112	Yes
Run 2, Hr. 2 (Field Dup.)		3/21			Archived
<u>Total Chloride</u>	28 days				
Run 1, Hr. 1-7		3/20, 3/21			Archived
Run 2, Hr. 1-6		3/21	4/16	4/18	Yes
Run 3, Hr. 1-6		3/22	4/16	4/18	Yes
Run 4, Hr. 1-6		3/23	4/16	4/18	Yes
Run 2, Hr. 2 (Field Dup.)		3/21			Archived
<u>Fluoride</u>	28 days				
Run 1, Hr. 1-7		3/20, 3/21			Archived
Run 2, Hr. 1-6		3/21	5/17	5/24	No
Run 3, Hr. 1-6		3/22	5/17	5/24	No
Run 4, Hr. 1-6		3/23	5/22	5/25	No
Run 2, Hr. 2 (Field Dup.)		3/21			Archived
<u>Sulfur</u>	28 days				
Run 1, Hr. 1-7		3/20, 3/21			Archived
Run 2, Hr. 1-6		3/21	4/25, 5/21	5/23	No
Run 3, Hr. 1-6		3/22	5/21-22	5/24	No
Run 4, Hr. 1-6		3/23	5/22-23	5/25	No
Run 2, Hr. 2 (Field Dup.)		3/21			Archived
<u>Total Carbon</u>	6 months				
Run 1, Hr. 1-7		3/20, 3/21			Archived
Run 2, Hr. 1-6		3/21		$4/18, 5/24-25^2$	Yes
Run 3, Hr. 1-6		3/22		4/18, 5/24-25 ²	Yes
Run 4, Hr. 1-6		3/23		4/18, 5/24-252	Yes
Run 2, Hr. 2 (Field Dup.)		3/21			Archived

DATES OF SAMPLE COLLECTION, PREPARATION, AND ANALYSIS FOR PROCESS SAMPLES (sheet 2 of 4)

				<u>74</u>	
			Preparation		Holding
	Holding	Collection	Extraction	Analysis	Time
Sample/Analyte	Time	Date	Date	Date	Met?
Waste Feed (continued)					
TOC	6 months				
Run 1, Hr. 1-7		3/20, 3/21			Archived
Run 2, Hr. 1-6		3/21		$4/10, 5/24-25^{-1}$	Yes
Hun 3, Hr. 1-6		3/22		4/10, 0/24-20	T es V
Run 4, Hr. 1-6		3/23		4/10, 8/24-28	I es Anabiwod
Run 2, Hr. 2 (Fleid Dup.)		5/21			Alcinveu
Ash Content	6 months				
Abir Content	0 months				
Run 1, Hr. 1-7		3/20, 3/21			Archived
Run 2, Hr. 1-6		3/21		4/12	Yes
Run 3, Hr. 1-6		3/22		4/12	Үев
Run 4, Hr. 1-6		3/23		4/12	Yes
Run 2, Hr. 2 (Field Dup.)		3/21			Archived
Moisture Content	6 months				
Run 1, Hr. 1-7		3/20, 3/21			Archived
Run 2, Hr. 1-6		3/21		4/9	Yes
Run 3, Hr. 1-6		3/22		4/9	Yes
Run 4, Hr. 1-6		3/23		4/9	Yes
Run 2, Hr. 2 (Field Dup.)		3/21			Archived
Particle Size Distribution	6 months				
Dun 1 17- 1 7		9/20 9/21			Archived
Run 1, nr. 1-7 $Run 2 Ha 1 G$		3/20, 3/21		5/20-6/6	Var
Run 3 Hr. 1-6		3/22		5/20-6/6	Yes
$Run \mathbf{A} Hr 1_{6}$		3/23		5/29-6/6	Yes
Run 2 Hr 2 (Field Dup)		3/21			Archived
		-,			
Btu Content	6 months				
Run 1, Hr. 1-7		3/20, 3/21			Archived
Run 2, Hr. 1-6		3/21		6/27	Yes
Run 3, Hr. 1-6		3/22		6/27	Yes
Run 4, Hr. 1-6		3/23		6/27	Yes
Run 2, Hr. 2 (Field Dup.)		3/21			Archived
<u>Chlorine</u>	6 months				
		0/00 0/00			A
Kun I, Hr. 1-7		3/20, 3/21	 E/01 00	5/99 94	Archived
Run 2, Hr. 1-6		3/21	0/41-26 5/91_99	0/20-24 5/92	Ver
$\mathbf{R}_{\text{UD}} \mathbf{A} = \mathbf{H}_{\text{E}} 1_{-6}$		3/22	5/22-23	5/25	Yea
Run 2 Hr 2 (Field Dun)		3/23	V/ 44- 63		Archived
nun 2, nr. 2 (rield Dup.)		5/41	_	-	ALCHIVEL

DATES OF SAMPLE COLLECTION, PREPARATION, AND ANALYSIS FOR PROCESS SAMPLES (sheet 3 of 4)

Sample/Parameter	Holding Time	Collection Date	Preparation/ Extraction Date	Analysis Date	Holding Time Met?
Effluent Slag			<u></u>		
Metals	6 months ¹				
Run 1, Hr. 1-7 Run 2, Hr. 1-6 Run 3, Hr. 1-6 Run 4, Hr. 1-6 Run 2, Hr. 2 (Field Dup.)		3/20, 3/21 3/21 3/22 3/23 3/21		6/26 6/26 6/26 	Archived Yes Yes Yes Archived
TCLP Metals	6 months				
Run 1, Hr. 1-7 Run 2, Hr. 1-6 Run 3, Hr. 1-6 Run 4, Hr. 1-6 Run 2, Hr. 2 (Field Dup.)		3/20, 3/21 3/21 3/22 3/23 3/21	4/8 4/8 4/8 	4/15-4/17 4/15-4/17 4/15-4/17 	Archived Yes Yes Yes Archived
Moisture Content	6 months				
Run 1, Hr. 1-7 Run 2, Hr. 1-6 Run 3, Hr. 1-6 Run 4, Hr. 1-6 Run 2, Hr. 2 (Field Dup.)		3/20, 3/21 3/21 3/22 3/23 3/21	 	5/13 5/13 5/13 5/13	Archived Yes Yes Yes Archived
Oxide Product					
<u>Metalş</u>	6 months ¹				
Run 1, Composite of Hr. 1-6 Run 1, Hr. 7 Run 2, Composite of Hr. 1-3 Run 2, Composite of Hr. 4-6 Run 3 Run 4 Run 2, Composite of Hr. 1-3 (Field Duplicate)		3/20 3/21 3/21 3/21 3/22 3/23 3/21	 	6/27 6/27 6/27 6/27 6/27	Archived Archived Yes Yes Yes Yes Archived
Moisture Content	6 months				
Run 2 Composite Run 3 Run 4		3/21 3/22 3/23		4/11 4/11 4/11	Yes Yes Yes

DATES OF SAMPLE COLLECTION, PREPARATION, AND ANALYSIS FOR PROCESS SAMPLES (sheet 4 of 4)

Sample/Analyte	Holding Time	Collection Date	Preparation/ Extraction Date	Analysis Date	Holding Time Met?
Blanks					
<u>Metals</u>	6 months ¹				
Sand Blanks		3/19			Archived
Equipment Blank - Oxide Product (Run 1)		3/20		4/24	Yes
Equipment Blank - Effluent Slag (Run 2)		3/21		4/24	Yes
Air Blank (Run 2) Equipment Blank - Feed		3/21		4/24	Yes
(Run 3)		3/22		4/24	Yes
Waste		3/23		4/24	Yes
TCLP Metals	6 months				
Sand Blanks		3/19			Archived

Notes:

1 The holding time for mercury is 28 days. 2

This sample was reanalyzed.

DATES OF SAMPLE COLLECTION, PREPARATION, AND ANALYSIS FOR STACK SAMPLES (sheet 1 of 3)

Sample/Analyte	Holding Time	Collection Date	Preparation/ Extraction Date	Analysis Date	Holding Time Met?
Particulate	6 months				
Run 1 - Front Half Acetone					
Rinse		3/20		7/2, 7/8	Үев
Run 1 - Filter		3/20		6/13, 6/14, 8/7 ¹	Yes
Run 2 - Front Half Acetone					
Rinse		3/21		7/2, 7/8	Yes
Run 2 – Filter		3/21		6/13, 6/14, 8/7 ¹	Yes
Run 3 - Front Half Acetone					
Rinse		3/21		7/2, 7/8	Yes
Run 3 - Filter		3/21		6/13, 6/14, 8/7 ¹	Yes
Run 4 - Front Half Acetone		3/22		7/2,7/8	Yes
Rinse		3/22		6/13, 6/14 , 8 /7 ¹	Yes
Run 4 - Filter		3/23		7/2, 7/8	Yes
Run 5 - Front Half Acetone		3/23		6/13, 6/14	Yes
Rinse		3/23		7/2, 7/8, 8/71	Yes
Run 5 - Filter		3/23		6/13, 6/14	Үев
System Blank - Acetone Rinse		3/23		7/2, 7/8	Үев
System Blank - Filter					
Reagent Blank - Acetone	28 days				
HCI					
		3/20	3/20	4/11	Yes
Run 1 - Impinger 1-3 Contents and Rinse		3/20	3/20	4/11	Yes
Run 1 - Filter		3/21	3/21	4/11	Yes
Run 2 - Impinger 1-3 Contents and Rinse		3/21	3/21	4/11	Yes
Run 2 - Filter		3/21	3/21	4/11	Yes
Run 3 - Impinger 1-3 Contents		3/21	3/21	4/11	Yes
and Rinse			·	,	
Run 3 - Filter		3/22	3/22	4/11	Yes
Run 4 - Impinger 1-3 Contents		3/22	3/22	4/11	Yes
and Rinse		3/21	3/21	4/11	Yes
Run 4 - Filter		3/21	3/21	4/11	Yes
Reagent Blank - D.I. ² Water		3/23	3/23	4/11	Yes
Reagent Blank - 0.1N NaOH					
System Blank - Impingers 1-3	6 months				
Metals					
		3/20	7/9	7/11	Yes
Run 1 - Front Half HNO ₃		_			
Rinse		3/20	4/16	4/23	Yes
Run 1 - Impinger 1-3 Contents					
and Rinse					

DATES OF SAMPLE COLLECTION, PREPARATION, AND ANALYSIS FOR STACK SAMPLES (sheet 2 of 3)

Sample/Parameter	Holding Time	Collection Date	Preparation/ Extraction Date	Analysis Date	Holding Time Met?
Metals (continued)					
Run 2 - Front Half HNO ₃ Rinse		3/21	7/9	7/11	Yes
Run 2 - Impinger 1-3 Contents		9/21	4/16	4/78	Ves
and Kinse Run 3 - Front Half HNO.		5/21	4/10	4720	100
Rinse		3/21	7/9	7/11	Yes
Run 3 - Impinger 1-3 Contents		0/01	4/10	4/59	Var
and Rinse		3/21	4/16	4/23	Yes
Rinse		3/21	7/9	7/11	Yes
Run 4 - Front Half HNO3		ŗ	,		
Rinse		3/22	7/9	7/11	Yes
Run 4 - Impinger 1-3 Contents		8/77	4/16	4/23	Yes
and Rinse Run 4 - 0 1N HNO, Nozzle		5/22	4/10	4/20	100
Rinse		3/22	7/9	7/11	Yes
Run 5 - Front Half HNO ₃					
		3/23	7/9	7/11	Yes
Run 5 - Impinger 1-3 Contents		3/23	4/16	4/23	Yes
Run 5 - 0.1N HNO ₃ Nozzle		-,	-,	,	
Rinse		3/23	7/9	7/11	Yes
System Blank - 0.1N HNO ₃			7/0	7/11	Vec
Nozzle Rinse Research Blank 59 HNO /		3/23	1/9	1/11	165
10% H ₂ O ₂		3/23	7/9	7/11	Yes
Reagent Blank - D.I. ² Water		3/23	7/9	7/11	Yes
Reagent Blank - 0.1N HNO3		3/23	7/9	7/11	Yes
Reagent Blank - 8N HCl		3/23	7/9	7/11	Yes
Reagent Blank - Filter		3/23	7/9	7/11	IES
System Blank - Impinger 1-3 Contents and Pinge		3/23	4/16	4/23	Yes
System Blank - Front Half		-,	-/		
HNO ₃ Rinse		3/23	7/9	7/11	Yes
Mercury/Metals	28 days				
Run 1 - Impinger Rinse 1					
50 mL Aliquot					
Run 1 - KMnO ₄ /8N HCl Rinse		3/20	4/16	4/24	No ³
Run 2 - Impinger Rinse 1		3/20	4/16	4/24	No
50 mL Aliquot		3/21	4/16	4/24	No ³

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DATES OF SAMPLE COLLECTION, PREPARATION, AND ANALYSIS FOR STACK SAMPLES (sheet 3 of 3)

Sample/Parameter	Holding Time	Collection Date	Preparation/ Extraction Date	Analysis Date	Holding Time Met?
Mercury/Metals (continued)					
Run 2 - KMnO ₄ /8N HCl Rinse Run 3 - Impinger Rinse 1		3/21	4/16	4/24	No ³
50 mL Aliquot		3/21	4/16	4/24	No ³
Run 3 - KMnO ₄ HCl Rinse Run 4 - Impinger Ringe 1		3/21	4/16	4/25	No ³
50 mL Aliquot		3/22	4/16	4/24	No ³
Run 4 - KMnO./8N HCl Rinse		3/22	4/16	4/24	No ³
Run 5 - Impinger Rinse 1			-,		
50 mL Aliquot		3/23	4/16	4/24	No ³
Run 5 - KMnO ₄ /8N HCl Rinse		3/23	4/16	4/24	No ³
Reagent Blank - KMnO4		3/23	4/16	4/24	No ³
System Blank - KMnO ₄ /8N					
HCl rinse		3/23	4/16	4/24	No ³
System Blank - Impinger					
Rinse 1 50 mL Aliquot		3/23	4/16	4/24	No ³

Notes:

D.I. Water = distilled, deionized water

3 These samples were held for analysis until extraction method was selected.

I These filters were reweighed. 2

laboratory. For a spike to be recovered, it would have to be almost 25 percent of the sample concentration. Therefore, laboratory duplicates, as discussed in Section 7.5, were used. The chloride, metals, and mercury gas train samples, were analyzed for matrix spike (MS) and matrix spike duplicate (MSD) recoveries. MS analyses were also performed to determine chloride, fluoride, sulfur, and carbon recoveries from the Run 2 waste feed samples.

The target recovery window for all of the MS and MSD recoveries is 70 to 130 percent, and the specified range of relative percent differences (RPDs) for matrix spike duplicates is 0 to 25 percent. Tables 24, 25, and 26 show the sample results, spiked sample results, spikes added, percent recoveries, and relative percent differences for MS and MSD samples.

All recoveries were within the target recovery windows except the following TCLP metals: barium, cadmium, lead, and silver for waste feed; and silver for stack gases. Most of these samples were out of specification because they were spiked at inappropriate levels. Reanalyses were performed on the waste feed sample with the correct spike concentrations (that is equivalent to the regulatory levels for the RCRA Toxicity Characteristic [TC] rule, or 0.5 to 5 times the result if the result is less than half of the regulatory level). All of the reanalysis recoveries were within the target window of 70 to 130 percent.

For the stack gas sample, only the MS and MSD metal recovery results for silver analyzed by inductively coupled plasma atomic emission spectroscopy (ICP) were low (32.4 percent and 10.3 percent). This sample did not require reanalysis because silver was also analyzed by graphite furnace atomic absorption spectroscopy (GFAA) and the MS and MSD results were acceptable.

After reanalysis, all RPDs for spike duplicates were within the specified limits of 0 to 25 percent, except the stack gas sample that was not reanalyzed. The RPD for leachable silver in the stack gas sample analyzed by ICP was 104 percent, but the RPD for the GFAA silver analysis was 3.70 percent, which is well within the control limits.

7.4 LABORATORY DUPLICATES

Laboratory duplicate samples were divided in the laboratory and analyzed as an indicator of precision. One sample of each sample matrix (waste feed, oxide product, and effluent slag) from Run 2 was analyzed in duplicate for all analytes. Tables 27, 28, 29, and 30 contain laboratory duplicate results. The precision objective was an RPD of less than or equal to

TCLP MATRIX SPIKE RECOVERIES

		Matrix Spike		Matrix Spike Duplicate				
Analytes	Sample Result (mg/L)	Spiked Sample Result (mg/L)	Spike Added (mg/L)	Percent Recovery ¹	Spiked Sample Result (mg/L)	Spike Added (mg/L)	Percent Recovery ¹	Relative Percent Difference ²
			TCLP -	WASTE FEED				
Arsenic	< 210 ³	4.51	5.00	90.2	4.81	5.00	96.2	6.44
Barium ⁴	0.0165	197	200	98.6	195	200	97.5	1.12
Cadmium ⁴	16.1	18.1	2.00	97.7	18.0	2.00	95.0	2.80
Chromium	0.193	4.45	5.00	85.1	4.57	5.00	87.5	2.81
Lead ⁴	4.73	15.3	10.0	105	14.1	10.0	93.2	12.3
Mercury	< 0.010	0.186	0.200	93.2	0.186	0.200	93.2	0
Selenium	0.151	0.853	1.00	70.1	0.844	1.00	69.3	1.15
Silver ⁴	< 10.0	0.0176	0.0200	88.0	0.0163	0.0200	81.6	7.55
			TCLP - EI	FLUENT SLA	G			
Arsenic	0.616	4.70	5.00	81.7	4.51	5.00	77.8	4.89
Barium	0.200	88.9	100	88.7	86.0	100	85.8	3.32
Cadmium	< 0.0500	0.884	1.00	88.4	0.830	1.00	83.0	6.30
Chromium	< 0.0600	4.66	5.00	93.1	4.58	5.00	91.6	1.62
Lead	< 0.330	4.25	5.00	85.0	4.08	5.00	81.5	4.20
Mercury	< 0.0100	0.187	0.200	93.5	0.184	0.200	92.0	1.62
Selenium	0.0730	0.685	1.00	79.5	0.780	1.00	78.4	24.6
Silver	< 0.0530	0.795	1.00	79.5	0.780	1.00	78.0	1.90

Notes:

Percent recovery = (matrix spike concentration - sample concentration) x 100/matrix spike concentration

² RPD = (|matrix spike recovery - matrix spike duplicate recovery | x 100)/(matrix spike recovery + matrix spike duplicate recovery)/2

 3 < = Below detection limit ⁴ Reanalysis results are given

⁴ Reanalysis results are given for this metal.

			Matrix Spike	
Analytes	Sample Result (mg/L)	Spiked Sample Result (mg/L)	Spike Added (mg/L)	Percent Recovery ¹
Chloride	20.8	42.6	23.0	94.8
Fluoride	0.131	0.33 9	0.217	95.8
Sulfur	166	346	19 2	93.8
Total Carbon	120,000	365,000	236,000	104
Total Organic Carbon	150,000	325,000	156,000	112

WASTE FEED MATRIX SPIKE RECOVERIES

Notes:

¹ Percent recovery = (matrix spike concentration - sample concentration) x 100/matrix spike concentration mg/L = milligram per liter

MATRIX SPIKE RECOVERIES FOR STACK SAMPLES

		Matrix Spike		Matrix Spike Duplicate				
Sample/Analytes	Sample Result (µg/sample)	Spiked Sample Result (µg/sample)	Spike Added (µg/sample)	Percent Recovery ¹	Spiked Sample Result (µg/sample)	Spike Added (µg/sample)	Percent Recovery ¹	Relative Percent Difference ²
			METAI	S - STACK				
Antimony	20.6	2,350	2,460	91.6	2,360	2,460	91.9	0.327
Arsenic	< 13.4	2,350	2,460	92.1	2,310	2,460	90.8	1.42
Barium	29.5	1,280	1,270	98.5	1,280	1,270	98.0	0.509
Beryllium	< 0.64	1,220	1,270	95.5	1,210	1,270	94.9	1.05
Cadmium	< 3.18	1,190	1,270	93.8	1,170	1,270	92.2	1.72
Chromium	< 3.82	1,190	1,270	93.3	1,190	1,270	93.3	0
Lead	< 21.0	2,460	2,460	97.9	2,510	2,460	98.5	0.611
Silver	< 3.18	412	1,270	32.4 ²	132	1,270	10.3 ²	104 ²
Thallium	< 106	2,360	2,460	92.5	2,420	2,460	95.0	2.67
Silver by GFAA ³	0.68	2.08	1.27	110	2.03	1.27	106	3.70
METALS/Mercury - STACK ⁴	162	227	64.1	102	220	64.1	90.7	11.8
METALS/Mercury - STACK ⁵	9.62	13.9	3.42	124	13.7	3.42	119	4.12
Chloride - STACK	2,580	6,760	4,340	96	6,760	4,340	96	0

Notes:

¹ Percent recovery = (matrix spike concentration - sample concentration) x 100/matrix spike concentration

² This value is outside control limits (0 to 25 relative percent difference or 70 to 130 percent recovery).

³ GFAA = Graphite furnace atomic absorption spectroscopy

⁴ For impingers 1 through 3 -- see Section 5.3

⁵ For impinger 4 (special KMnO₄ impinger) -- see Section 5.3

< = less than

 $\mu g = microgram$

LABORATORY DUPLICATE RESULTS FOR GENERAL CHEMISTRY ANALYTES

Analyte	Sample Result	Duplicate Result	Mean Concentration	Relative Percent Difference ¹						
WASTE FEED (mg/kg)										
Chloride	29,100 mg/kg	29,300 mg/kg	29,200 mg/kg	0.685						
Chlorine	21,200 mg/kg	20,400 mg/kg	20,800 mg/kg	3.85						
Fluoride	138 mg/kg	124 mg/kg	131 mg/kg	10.7						
Sulfur	166,000 mg/kg	166,000 mg/kg	166,000 mg/kg	0						
Ash Content	82.2 percent	81.9 percent	82.0 percent	0.366						
Total Carbon	11.8 percent	13.2 percent	12.5 percent	11.2						
Total Organic Carbon	14.8 percent	15.3 percent	15.0 percent	3.33						
Moisture Content	3.23 percent	3.28 percent	3.26 percent	1.53						
Btu Content	2,020 Btu/lb	2,020 Btu/lb	2,020 Btu/lb	0						
Btu Content	1,760 Btu/lb	1, 710 Btu/ lb	1,740 Btu/lb	2.87						
Particle Size Distributio	n									
30 < X	9.45 percent	9.69 percent	9.57 percent	2.51						
60 < X < 30	8.28 percent	8.28 percent	8.28 percent	0						
100 < X < 60	7.58 percent	7.16 percent	7.37 percent	5.70						
200 < X < 100	8.69 percent	8.85 percent	8.77 percent	1.82						
325 < X < 200	1.94 percent	2.39 percent	2.16 percent	20.8						
325 < X	64.1 percent	63.6 percent	63.8 percent	0.784						

Notes:

1 Relative percent difference = (|sample result - duplicate result| + mean concentration) X 100 < = less than

mg/kg = milligram per kilogram Btu/lb = British thermal unit per pound

LABORATORY DUPLICATE RESULTS FOR WASTE FEED SAMPLES

Sample/Analyte	Sample Result (mg/kg)	Duplicate Result (mg/kg)	Mean Concentration (mg/kg)	Relative Percent Difference ¹						
WASTE FEED										
Aluminum	5,470	5,940	5,710	8.23						
Antimony	449	35 9	404	22.1						
Arsenic	1,040	414	729	86.5 ³						
Barium	846	865	856	2.22						
Beryllium	<1.00	<0.99	NC ²	NC ²						
Cadmium	512	370	441	32 .1 ³						
Calcium	6,820	6,860	6,840	0.585						
Chromium	98.3	66.7	82.5	38.3 ³						
Copper	2,590	2,080	2,340	22.0						
Iron	103,000	96,800	99,800	6.21						
Lead	51,600	44 ,000	47,800	16.0						
Magnesium	2,180	2,310	2,240	5.80						
Manganese	840	764	802	9.48						
Mercury	0.64	0.62	0.63	3.18						
Potassium	2,700	2,320	2,510	15.5						
Selenium	62.2	112	87.1	57.1 ³						
Silicon	2,000	3,610	2,800	52.1 ³						
Silver	5.38	1.58	3.48	109 ³						
Sodium	127,000	128,000	128,000	0.781						
Thallium	269	240	255	11.6						
Tin	2,950	2,800	2,880	5.21						
Zinc	6,810	4,630	5,720	38 .1 ³						

Notes:

1 Relative percent difference = (|sample result - duplicate result| \div mean concentration) x 100 2

NC = Not calculable

3 This value is outside of the control limits of 0 to 25 relative percent difference.

< = less than

mg/kg = milligram per kilogram
LABORATORY DUPLICATE RESULTS FOR OXIDE PRODUCT SAMPLES

Sample/Analyte	Sample Result (mg/kg)	Duplicate Result (mg/kg)	Mean Concentration (mg/kg)	Relative Percent Difference ¹					
OXIDE PRODUCT									
Aluminum	623	462	542	2 9.7 ²					
Antimony	1,230	1,260	1,240	2.42					
Arsenic	1,13 0	1,130	1,130	0					
Barium	275	267	271	2.00					
Beryllium	<0.95	<0.95	<0.95	NC					
Cadmium	1,370	1,370	1,370	0					
Calcium	2,340	1,860	2,100	22.8					
Chromium	308	308	3,08	0					
Copper	1,670	1,620	1,650	2.00					
Iron	31,800	31,300	31,600	1.58					
Lead	180,000	173,000	177,000	3.95					
Magnesium	348	334	341	4.10					
Manganese	282	279	281	1.07					
Mercury	0.136	0.165	0.150	19.0					
Potassium	7,410	7,450	7,430	0.538					
Selenium	65.9	65.0	65.5	1.53					
Silicon	1,130	1,230	1,180	8.47					
Silver	27.4	27.8	27.6	1.45					
Sodium	168,000	163,000	165,000	3.03					
Thallium	<71.4	<71.4	<71.4	NC					
Tin	6,870	6,800	6,840	1.02					
Zine	16,200	16,200	16,200	0					

Notes:

¹ Relative percent difference = (|sample result - duplicate result| ÷ mean concentration) X 100

² This value is outside of the control limits of 0 to 25 relative percent difference.

NC = Not calculable

< = less than

mg/kg = milligram per kilogram

LABORATORY DUPLICATE RESULTS FOR EFFLUENT SLAG SAMPLES

Sample/Analyte	Sample Result (mg/kg)	Duplicate Result (mg/kg)	Mean Concentration (mg/kg)	Relative Percent Difference ¹					
EFFLUENT SLAG									
Aluminum	14,300	14,800	14,500	3.45					
Antimony	103	93. 2	98.4	10.4					
Arsenic	104	89.6	97.0	15.2					
Barium	1,640	1,680	1,660	2.41					
Beryllium	<1.00	<1.00	<1.00	NC					
Cadmium	<2.50	<2.50	<2.5	NC					
Calcium	13,300	13,700	13,500	2.96					
Chromium	64.4	63.1	63.8	2.04					
Copper	3,570	3,660	3,610	2.49					
Iron	192,000	197,000	195,000	2.56					
Lead	1,560	1,640	1,600	5.00					
Magnesium	5,750	5,820	5,790	1.21					
Manganese	2,130	2,170	2,150	1.86					
Mercury	<0.10	<0.10	<0.10	NC					
Potassium	2,080	2,200	2,140	5.61					
Selenium	<26.0	40.8	NC	NC					
Silicon	2,170	2,600	2,390	18.0					
Silver	3 .06	4.53	3.80	38.6 ²					
Sodium	150,000	154,000	152,000	2.63					
Thallium	535	599	567	11.4					
Tin	766	786	776	2.58					
Zinc	1,270	1,310	1,290	3.10					

Notes:

Relative percent difference = (|sample result - duplicate result| ÷ mean concentration) X 100
This value is outside of the control limits of 0 to 25 relative percent difference.

NC = Not calculable

< = less than

mg/kg = milligram per kilogram

so percent for total organic carbon and moisture content, and less than or equal to 25 percent for all other analytes. When sample results were less than 5 times the detection limit, the control limit was less than or equal to 100 percent.

In the waste feed duplicate sample analyzed for metals and silicon, all RPDs were within the control limits of less than or equal to 25 percent (or 0 to 100 percent for low concentration samples) except arsenic, cadmium, chromium, silicon, silver, and zinc (86.5, 32.1, 38.3, 52.1, 109, and 38.1, respectively). Silver results were less than five times the detection limit, so the RPD of 109 percent is just outside the control limits of 0 to 100 percent. For metals analysis of the oxide product, only the RPD of 29.7 percent for aluminum was greater than 25 percent. The moisture content duplicate of 49.2 percent RPD for the oxide product was within the limit of 100 percent RPD for sample results near the limit of detection. For metal analysis of effluent slag, all RPDs were less than or equal to 25 percent except for silver (38.6 percent). Data that fall outside of the quality control (QC) limits have been flagged as such, and the EPA Project Managers have been notified.

7.5 FIELD DUPLICATES

Field duplicates were collected during Run 2, and archived, as specified in a November 2, 1990 memo concerning changes to the HRD SITE QAPP (EPA, 1990). Because a large number of waste feed (18 samples), oxide product (3 samples), and effluent slag (18 samples) samples were collected and analyzed, the collection of duplicate samples was redundant and the field duplicates were not analyzed.

7.6 **REFERENCE STANDARDS**

The following reference materials were analyzed with each batch (Batch 1 was the waste feed samples, Batch 2 was the oxide product samples, and Batch 3 was the effluent slag samples) of metal samples: (1) lead blast furnace slag reference material, (2) Flame Reactor oxide reference material, (3) EURO-Standard 877-1 Furnace Dust reference material, (4) EURO-Enchantillon 876-1 certified reference material, and (5) National Institute of Science and Technology (NIST) 1633a Trace Elements in Coal Fly Ash certified standard reference material. Analytical results for the first four standards were compared to the certified values for an indication of accuracy. Because of the high level of metals in the demonstration samples, the NIST 1633a trace element standard was considered inappropriate. Relative standard deviations (RSD) and percent recoveries were calculated for each of three replicate samples - one analyzed with the waste feed samples

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(Batch 1), one analyzed with the effluent slag samples (Batch 2), and one analyzed with the oxide product samples (Batch 3). These results are shown in Tables 31, 32, 33, and 34. Reference material recoveries for each batch give an indication of accuracy for that particular batch or matrix; and although no acceptance criteria were specified, mean recoveries and RSDs give an indication of precision and accuracy for the entire metal analytical results.

For the lead blast furnace slag standard, mean recoveries for cadmium (62.0 percent), lead (83.8 percent), and zinc (126 percent) were all greater than 60 percent. Chromium had a mean recovery of only 17.7 percent. Although this recovery is very low, it is not an unexpected result for chromium digestion by Method 3050. The rationale for selection of this method is given in Section 6.1.

For the Flame Reactor oxide product, precision and accuracy were acceptable, with all recoveries greater than 75 percent and all RSDs less than 3 percent.

For EURO-Standard 877-1 furnace dust standard, all mean recoveries were greater than 75 percent except silicon (27.1 percent). Arsenic recovery was 214 percent. All RSDs were below 5 percent, except for these same constituents. The RSD for arsenic was 15.0 percent and the RSD for silicon was 9.76 percent. The analytical results for potassium were very close to the limits of detection.

For EURO-Enchantillon 876-1, all mean recoveries were greater than 75 percent, except for silicon (22.7 percent). All RSDs were less than 5 percent except for silicon, with an RSD of 6.34 percent.

One of the five reference materials, the NIST 1633a coal fly ash standard reference material, had low recoveries for every analyte except arsenic. This indicates that the Method 3050 digestion method is not appropriate for the coal fly ash matrix, probably because the matrix is resistant to the acid leaching procedure. However, the low recoveries of metals from the coal fly ash standard reference material do not necessarily transfer to the oxide product matrix samples. The coal fly ash standard contains only trace elements of metals, which is not comparable to the high concentration wastes associated with the Flame Reactor process. Thus, the NIST 1633a coal fly ash standard reference material does not appear to be an appropriate indicator of accuracy for the metal oxide product. Two other reference materials tested, the EURO 877-1 furnace dust standard and the HRD Flame Reactor oxide product standard, are much more similar

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COMPARISON OF CERTIFIED ASSAY VALUES AND LABORATORY RESULTS FOR LEAD BLAST FURNACE SLAG STANDARD REFERENCE MATERIAL

(weight percent)

Analyte	Certified Value	Batch 1	Percent Recovery ¹	Batch 2	Percent Recovery ¹	Batch 3	Percent Recovery ¹	Mean Result	Relative Standard Deviation	Mean Percent Recovery
Cadmium	0.002	0.00150	75.0	0.00140	70.0	0.00082	41.0	0.00124	29.6	62.0
Chromium ²	0.035	0.00659	18.8	0.00615	17.6	0.00580	16.6	0.00618	6.4	17.7
Lead	1.360	1.21	89.0	1.13	83.1	1.08	79.4	1.14	5.75	83.8
Zinc	10.110	10.0	98.9	18.9	187	9.25	91.5	12.7	42.2	126

Notes:

¹ Percent recovery = (certified concentration value - sample concentration) x 100/certified concentration value

² It was recognized during method selection that chromium results would be biased low by using EPA Method 3050 for sample digestion;

however, this method was selected for its overall applicability to digestion and analysis of a variety of metals, including lead and zinc, which were critical to the project.

COMPARISON OF CERTIFIED ASSAY VALUES AND LABORATORY RESULTS FOR FLAME REACTOR OXIDE STANDARD REFERENCE MATERIAL (weight percent)

Analyte	Certified Value	Batch 1	Percent Recovery ¹	Batch 2	Percent Recovery ¹	Batch 3	Percent Recovery ¹	Mean Result	Relative Standard Deviation	Mcan Percent Recovery
Cadmium	0.562	0.494	87.9	0.487	86.6	0.490	87.2	0.490	0.716	87.2
Chromium	0.033	0.0258	78.2	0.0270	81.8	0.0268	81.2	0.0265	2.42	80.3
Lead	7.23	6.54	90.4	6.86	94.9	6.73	93.1	6.71	2.40	92.8
Zinc	35.8	35.2	98.3	36.5	102	36.1	101	35.9	1.86	100

Notes:

¹ Percent recovery = (certified concentration value - sample concentration) x 100/certified concentration value

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COMPARISON OF CERTIFIED ASSAY VALUES AND LABORATORY RESULTS FOR EURO-STANDARD 877-1 FURNACE DUST STANDARD REFERENCE MATERIAL (weight percent)

Analyte	Certified Value	Batch 1	Percent Recovery ¹	Batch 2	Percent Recovery ¹	Batch 3	Percent Recovery ¹	Mean Result	Relative Standard Deviation	Mean Percent Recovery
Aluminum	0.044	0.0378	85.9	0.0395	89.9	0.0370	84.1	0.0381	3.36	86.4
Arsenic	0.014	0.0345	246	0.0312	223	0.0256	183	0.0304	15.0	214
Calcium	3.23	2.85	88.2	2.86	88.5	2.66	82.4	2.79	4.04	86.4
Chromium	0.017	0.0147	86.5	0.0143	84.1	0.0136	80.0	0.0142	3.94	83.5
Copper	0.025	0.0221	88.4	0.0219	87.6	0.0211	84.4	0.0217	2.44	86.8
Iron	62.07	60.5	97.5	60.8	98.0	58.3	93.9	59.9	2.28	96.5
Lead	1.00	0.785	78.5	0.835	83.5	0.767	76.7	0.796	4.42	79.6
Magnesium	0.28	0.235	83.9	0.244	87.1	0.232	82.9	0.237	2.63	84.6
Manganese	1.37	1.19	86.9	1.19	86.9	1.12	81.8	1.17	3.46	85.2
Potassium	0.058	< 0.023	<39.7	0.0688	119	< 0.023	< 39.7	NC	NC	NC
Silicon	1.08	0.263	24.4	0.320	29.6	0.295	27.3	0.293	9.76	27.1
Sodium	0.23	0.219	95.2	0.227	98.7	0.228	99.1	0.225	2.18	97.8
Zinc	1.16	0.929	80.1	0.934	80.5	0.861	74.2	0.908	4.49	78.3

Notes:

¹ Percent recovery = (certified concentration value - sample concentration) x 100/certified concentration value

< = less than

NC = not calculated

TABLE 34 COMPARISON OF CERTIFIED ASSAY VALUES AND LABORATORY RESULTS FOR EURO-ENCHANTILLON 876-1 STANDARD REFERENCE MATERIAL

(weight percent)

Analyte	Certified Value	Batch 1	Percent Recovery ¹	Batch 2	Percent Recovery ¹	Batch 3	Percent Recovery ¹	Mcan Result	Relative Standard Deviation	Mean Percent Recovery
Aluminum	0.34	0.283	83.2	0.279	82.1	0.268	78.8	0.277	2.81	81.5
Arsenic	0.023	0.0252	110	0.0242	105	0.0229	99.6	0.0241	4.77	105
Cadmium	0.13	0.108	83.1	0.106	81.5	0.101	77.7	0.105	3.45	80.8
Calcium	3.43	3.11	90.7	3.03	88.3	2.85	83.1	3.00	4.43	87.5
Chromium	0.17	0.138	81.2	0.135	79.4	0.127	74.7	0.133	4.28	78.2
Copper	0.42	0.377	89.8	0.365	86.9	0.360	85.7	0.367	2.38	87.4
Iron	24.85	21.9	88.1	21.5	86.5	20.3	81.7	21.2	3.92	85.4
Lead	7.82	6.37	81.4	6.66	85.2	6.18	79.0	6.40	3.78	81.8
Magnesium	1.31	1.10	84.0	0.0504	3.85	1.11	84.7	0.753	80.9	57.5
Manganese	2.84	2.48	87.3	2.40	84.5	2.29	80.6	2.39	4.00	84.2
Potassium	1.63	1.40	85.9	0.0514	3.15	1.39	85.3	0.947	81.9	58.1
Silicon	1.72	0.363	21.1	0.398	23.1	0.411	23.9	0.391	6.34	22.7
Sodium	1.98	1.85	93.4	1.83	92.4	1.83	92.4	1.84	0.625	93.4
Tin	0.094	0.0832	88.5	0.0824	87.7	0.0816	86.8	0.0824	0.971	87.7
Zinc	23.29	21.8	93.6	21.0	90.2	21.0	90.2	21.3	2.17	91.3

Notes:

¹ Percent recovery = (certified concentration value - sample concentration) x 100/certified concentration value

to the oxide product matrix and should be more true indicators of accuracy than the coal dust reference material.

7.7 FIELD BLANKS, EQUIPMENT BLANKS, AND SYSTEM BLANKS

The field blanks consisted of sand. These blanks were collected before the test but, at the direction of the EPA Project Managers, were not analyzed. Equipment blanks were collected and analyzed for the oxide product sample scoop rinsate, effluent slag sample scoop rinsate, and feed equipment rinsate. An air blank was also collected and analyzed, as was a sample of the decontamination solution.

For each type of stack gas sample (metals, particulate, HCl), system blanks and reagent blanks were collected and analyzed. System blanks were below detection limit for all metals except barium, chromium, and silver. All reagent blanks were below detection limit except for barium and mercury in the hydrochloric acid and chromium in the nitric acid/peroxide mixture.

The barium and chromium in the system blanks was probably carried over from the reagent blanks. For both metals, the system blank contamination was lower than the reagent blank contamination. Contaminants were detected at up to five times the detection limit, with sample concentrations approximately five times the blank concentration. Even when blank contamination was included with the sample results, barium was well below the Tier II Screening Limits, and chromium was well above the screening limits. Adjusting the data for blank contamination would not make a difference in the outcome of the emissions analysis.

Silver was high in the system blank and mercury was high in the HCl reagent blank. There is no known explanation for this contamination. However, emissions for both metals are below the Tier II Screening Limits (based on the highest sample concentration) and there would be no change in the outcome of the emissions analysis even if the data was blank-corrected.

Most blank results were below or near the detection limit. None was greater than 10 times the detection limit. The levels of contamination found in the blanks are insignificant when compared to the actual samples.

7.8 BLANK AIR RUN

The HRD SITE Demonstration Plan specified that three background stack samples would be collected (EPA, 1990). However, before the demonstration began, the EPA Project Managers, with the concurrence of the EPA QA manager and EPA QA auditors, decided that only one blank run would be conducted. Although the QA auditors commented that one run would not be statistically significant (a minimum of three is required for statistical significance), the EPA Project Managers and the technology vendor both agreed that, because the background run was not truly representative of background contamination, only one background run would be conducted and that the three treatment runs would not be corrected for background contamination.

The blank run exhibited elevated metal and particulate emissions. For arsenic, antimony, and particulate, the blank run emissions were higher than the treatment run emissions. The three treatment runs were not corrected to account for the contaminant levels in the blanks, but the highest concentration sample results were used to determine whether or not permissible limits were exceeded.

7.9 METHOD BLANKS AND REAGENT BLANKS

One method blank, laboratory grade pure water that underwent all the sample preparation (EPA Method 3050 digestion) steps, was prepared for each set of metal samples of similar matrix (such as waste feed, oxide product, and effluent slag). Laboratory reagent blanks were analyzed for each batch of reagents.

A contamination level of greater than 10 times the detection limit was considered outside control limits. Most blanks had concentrations below the detection limit. All laboratory blanks with metals concentrations of greater than 10 times the detection limit are indicated below.

- The method blank for metals in the effluent slag had concentrations for calcium and magnesium of greater than 10 times the detection limit. The calcium concentration was 48.2 mg/kg, and the detection limit was 4.5 mg/kg. The magnesium concentration was 22.6 mg/kg, and the detection limit was 0.5 mg/kg.
- The sulfur reagent blank for waste feed had a concentration of 3,990 mg/kg and a detection limit of 10 mg/kg.

Because the average sample concentration of calcium and magnesium in the effluent slag was 13,000 mg/kg and 5,430 mg/kg, respectively; the relatively low levels of these metals detected in the method blank are not of concern. The level of contamination found in the sulfur reagent blank is also insignificant when compared with the actual samples, as the average concentration of sulfur in the samples was 52,500 mg/kg.

7.10 INSTRUMENT CALIBRATION

Calibration standards were prepared and analyzed, as stated in the QAPP, in accordance with specifications provided in the methods. All initial and continuing calibration verification recoveries were within control limits. All initial and continuing calibration blanks were below or near the detection limit. For metals, the levels of elements detected above the instrument detection limits in the various blanks may be considered typical of the method. All blank concentrations were less than 10 times the detection limit.

7.11 **DETECTION LIMITS**

Method detection limits were lower than analyte concentrations, allowing evaluation of all sample matrices. The typical instrument detection limits for metal sample analysis using ICP and GFAA are shown in Table 18. Detection limits varied, depending on sample matrix and sample size.

The particulate results had a higher detection limit than specified in the QAPP due to analytical problems with the particulate filter weights and the acetone blowdown weights. Seven filters were weighed after the SITE Demonstration (the blank run, 4 test runs, the system blank, and the reagent blank). Only three of these filters were found to have positive weight: the blank run (44.8 mg), Run 3 (7.0 mg), and the reagent blank (1.0 mg). The other filters had negative weights. The reason for this problem is unknown but is probably related to a weighing error. In addition, a weighing error occurred with the acetone blowdown residuals, which were only weighed to an accuracy of 10 mg, rather than to the 0.1 mg accuracy specified in the QAPP. A worst case value of 10 mg was used in all calculations for the acetone blowdown weight.

7.12 **REPLICATE ANALYSIS**

The HRD SITE Demonstration collected samples from three replicate runs (three runs operated under the same conditions). The analytical results from all three runs are combined for each matrix and presented in Tables 4 (waste feed), 8 (oxide product), and 10 (effluent slag). To determine variability associated with the HRD Flame Reactor process and the relationship to the sample matrices, standard deviations were calculated for metals based on 18 samples each for the waste feed and effluent slag and three samples for the oxide product.

For waste feed, all standard deviations were below 40 percent. Arsenic, selenium, silicon, and silver had RSDs between 25 percent and 40 percent.

Standard deviations for effluent slag showed much greater variability than standard deviations for waste feed. All RSDs were below 40 percent, except cadmium (68.0 percent), chromium (88.3 percent), and lead (45.6 percent). Antimony, arsenic, and selenium all had RSDs greater than 100 percent (115 percent, 111 percent, and 100 percent, respectively).

For the oxide product, all standard deviations were below 25 percent.

Possible explanations for the high variation in sample replicates, most of which occur in the effluent slag matrix, include the following:

- Nonhomogeneity of the sample matrix
- Analytical problems

Because effluent slag samples show more variability than the waste feed and oxide product samples, the problem is probably related to lack of sample homogeneity, especially because of the difficulty in preparing a composite sample from this matrix.

Most of the metals showing variability among samples collected over the entire testing period are classified as volatile metals (antimony, arsenic, cadmium, lead, selenium, and zinc). It is possible that variation in the results was affected by (1) temperature changes during processing, and (2) analysis that affected the amount of volatilization and, thus, the metals concentrations.

7.13 QUALITY ASSURANCE CONCLUSIONS

In general, most of the analytical results are credible based on the supporting QA/QC data and were of acceptable quality for evaluation of the demonstration objectives. The primary objectives that utilized the analytical results were as follows:

- Evaluate the technology's ability to treat waste materials to form a potentially recyclable metal oxide product and a nonhazardous fused slag
- Evaluate the system's reliability

These objectives involved the three primary constituents of concern; lead, zinc, and cadmium, which are of interest because of their hazardous nature and high toxicity, and also because the recovery of these metals in the oxide product is a major objective of the Flame Reactor technology. Lead is of greatest concern because it is present at high levels in the lead slag waste feed. Zinc is also of concern because much of HRD's previous data was generated from treatment of EAF dust containing high levels of zinc.

All accuracy and precision data for lead were within the specified control limits.

For cadmium and zinc in the waste feed, the relative percent difference between the sample and sample duplicate of the laboratory duplicate analysis was slightly high. Considering the good overall precision of the 18 replicate samples and the consistency of the concentrations of waste feed samples collected throughout the test, the precision of the waste feed measurements is believed to be better than the RPDs from the sample/sample duplicate analysis indicate. Thus, the duplicate RPDs were used as a conservative measure of the actual precision of the data.

The recovery of cadmium from the lead blast furnace slag reference material was only 62.0 percent. Although this one measure of accuracy indicates a possible low bias for cadmium in the effluent slag, the test objectives were not impacted for several reasons. First, the ability of the process to form a nonhazardous slag was determined in accordance with regulatory protocols on the basis of metals analysis using the TCLP test procedure. QC data for the TCLP analysis indicated a high level of accuracy. Second, the concentrations of recyclable metals in the metal oxide product were determined to be high enough for successful recovery based on the total metals data obtained. Even if cadmium is actually present at slightly higher levels than reported, the oxide product would still be suitable for metals recovery, so the test objective would not be affected.

The system's reliability in meeting the first objective was demonstrated by the replicate sample results.

The chromium and silicon results are known to be biased low (but supplemental results for split samples digested by mineral acid digestion are available for comparison). A high recovery value for arsenic from the EURO-877-1 furnace dust standard indicates that arsenic results may be biased high. However, these analytes are not as critical as lead, cadmium, and zinc, and no major test conclusions were based on the affected data.

There was also a problem with the quality of air emissions data for particulate (due to a measurement error), and the concentrations determined in the air blanks for metals and particulate showed high background levels (higher than the test run concentrations for particulate, arsenic, and antimony). These problems could have affected the secondary objective of air emissions assessment. However, low quality results for particulate provided numbers sufficient for worst-case evaluation of particulate emissions, and the highest concentration results were used to determine whether or not permissible particulate emissions limits were exceeded. Thus, the data available were sufficient for a worst-case assessment of particulate emissions, but data of higher quality would have allowed for a more comprehensive assessment.

Barium, chromium, and mercury were found in reagent blanks; and barium, chromium, and silver were found in system blanks, with all except silver at levels lower than the sample concentrations. The blank contamination had no effect on the outcome of the emissions analysis (i.e., whether Tier II Screening Limits were met).

8.0 COST OF DEMONSTRATION

The cost (rounded to the nearest \$100) of conducting the HRD SITE Demonstration was approximately \$532,900. This cost includes site characterization and preparation, collection and loading of the SLS slag at the NSR site in Atlanta, transportation of the SLS slag to the HRD Flame Reactor facility in Monaca, demonstration planning, demonstration field work, chemical analyses, and report preparation. The developer's portion of this cost was \$122,500, and the balance of \$491,100 was allocated to the SITE Program. EPA costs for labor and travel are not included in this cost breakdown.

8.1 EPA SITE CONTRACTOR COSTS

Each SITE Project is divided into two phases. Phase I is for planning and Phase II is for demonstration of the technology. Costs for each phase are presented below, along with a list of the activities performed during each phase. Phase I costs are actual costs incurred before the HRD SITE Demonstration; Phase II costs include actual costs plus estimates for labor to complete the Technology Evaluation Report, Applications Analysis Report, and the technology demonstration videotape.

8.1.1 Phase I: Planning

Phase I activities included the following:

- Site sampling and treatability testing
- Sampling and Analysis Plan development
- Demonstration Plan development
- Site subcontractor procurement
- Waste handling and transportation

Costs for Phase I are summarized below by cost category:

Labor	\$120,200
Equipment and supplies	9,900
Travel	5,600
Waste handling	<u>16,000</u>
TOTAL	\$151,700

8.1.2 Phase II: Demonstration

Phase II activities included the following:

- Site preparation, mobilization, and demobilization
- Sample collection and field oversight
- Chemical analysis (field and off-site)
- Report and videotape preparation
- Demonstration waste disposal

Costs for Phase II are summarized below by cost category:

Labor	\$294,200
Equipment and supplies	28,000
Travel	16,000
Waste disposal	<u>2,200</u>
TOTAL	\$340,400

8.2 **DEVELOPER COSTS**

This section presents costs incurred by HRD in preparing and conducting the demonstration. These costs including:

- Field work
- Consumables (primarily oxygen and natural gas)
- Utilities (mainly electricity)
- Equipment and supplies
- Analytical costs.

HRD costs for processing 72 tons of SLS slag during the demonstration are presented below:

Labor	\$46,500
Consumable	11,000
Utilities	9,000
Travel	1,100
Analytical	50,700
Equipment and supplies	4,200
TOTAL	\$122,500

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