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Catalytic Extraction Processing of Contaminated Scrap Metal

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Introduction

The U.S. Department of Energy issued a Planned Research and Development Announcement (PRDA) in 1993, with the objective of identifying unique technologies which could be applied to the most hazardous waste streams at DOE sites. The combination of radioactive contamination with additional contamination by hazardous constituents such as those identified by the Resource Conservation and Recovery Act (RCRA) pose an especially challenging problem. Traditional remediation technologies are increasingly becoming less acceptable to stakeholders and regulators because of the risks they pose to public health and safety. Desirable recycling technologies were described by the DOE as: (1) easily installed, operated, and maintained; (2) exhibiting superior environmental performance; (3) protective of worker and public health and safety; (4) readily acceptable to a wide spectrum of evaluators; and (5) economically feasible. Molten Metal Technology, Inc. (MMT) was awarded a contract as a result of the PRDA initiative to demonstrate the applicability of Catalytic Extraction Processing (CEP), MMT's proprietary elemental recycling technology, to DOE's inventory of low level mixed waste. This includes DOE's inventory of radioactively- and RCRA-contaminated scrap metal and other waste

forms expected to be generated by the decontamination and decommissioning (D&D) of DOE sites.

Objectives

In conjunction with the DOE, MMT designed a program to evaluate the commercial feasibility of Catalytic Extraction Processing to recycle and safely dispose of targeted portions of DOE's stockpiles of contaminated scrap metal. The contract included the following objectives:

- *Demonstrate recycling of ferrous and non-ferrous metals* -- establish that radioactive scrap metal waste can be decontaminated and converted to high-grade, ferrous and non-ferrous alloys for re-use.
- *Immobilize radionuclides* -- demonstrate that CEP will concentrate the radionuclides in a dense vitreous phase, minimize secondary waste generation, and stabilize and reduce waste volume.
- *Destroy hazardous organic constituents* -- demonstrate the conversion of hazardous organic compounds into valuable product gases, which could be used as chemical feedstocks or as an energy source.
- *Recover volatile heavy metals* -- demonstrate the capability of the gas

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handling train's design to capture and recover volatile heavy metals such as lead and mercury.

- *Establish that CEP is economical for processing contaminated scrap metal from the DOE inventory -- demonstrate that CEP is a complete processing and recycling technology, and is more cost-effective than competing technologies for processing contaminated scrap metal.*

Technology Description

Catalytic Extraction Processing (CEP) is a proprietary technology that allows waste materials of a wide range of chemical and physical forms to be processed leading to decontamination and resource recovery. For processing of radioactive and mixed waste streams, CEP permits both complete destruction of hazardous contaminants and controlled partitioning of radionuclides in a single step. This leads to the potential formation of one or more decontaminated product phases (fuel gas and/or metal alloys), as well as volume reduction and concentration of radionuclides in a stable condensed phase for final disposal. A typical CEP unit consists of a feed preparation system, the Catalytic Processing Unit (CPU) or the reactor holding the molten metal, followed by a gas handling and recovery train. Upon injection into the metal bath, feed materials dissociate into their elemental constituents aided by the catalytic and solvating properties of the liquid metal. Select addition of co-reactants or manipulation of operating conditions, together with the thermodynamically controlled reaction pathways, enables synthesis of products and/or partitioning of compounds into the desired phases.

The CEP process can be conceptually divided into two stages:

- Catalytic dissociation and dissolution: The catalytic effect of the molten metal bath causes complex compounds in the feed to be dissociated into their elements, which readily dissolve in the metal bath. These soluble elements form dissolved intermediates.
- Product synthesis/partitioning: Through the addition of select co-reactants or by controlling operating conditions, the dissolved elemental intermediates can be reacted to form desired products or made to partition to the desired phases. These reactions are driven by thermodynamic forces and solution equilibria.

The solubility of carbon in iron is key to CEP's processing of organic and organo-metallic feeds. Specifically, carbon from the dissociation of organic compounds in the feeds, readily dissolves maintaining a homogeneous reducing environment in the molten metal solvent for a large number of compounds including carbon dioxide, sulfur dioxide, water and a wide range of metal oxides. The reducing strength of dissolved carbon provides CEP the flexibility to recycle organics to synthesis gas, recover metals and inorganics such as halides, sulfur and phosphorus, and separate and concentrate transuranic compounds.

As outlined above, the molten metal bath in the CEP system ensures dissociation of the feed into 'singular' elemental intermediates. The partitioning of feed components and the synthesis of products of value is dependent on manipulating the reaction pathways of the dissolved elemental intermediates. Potential reaction pathways are controlled by reaction thermodynamics. The general thermodynamic characterizations of oxidation/reduction reactions are outlined below. Specific examples of feeds simulating contaminated scrap metal

relevant to typical CEP applications are discussed.

The starting point for this discussion is an overview of the Standard Gibbs Free Energy (ΔG°) changes accompanying typical reactions relevant to CEP. The reaction thermodynamics can be summarized graphically with the Gibbs Free Energy change plotted versus temperature, as shown in Figure 1. Such diagrams are used to predict the thermodynamic forces driving separation and recycling of key components in a typical CEP feed stream. Furthermore, these diagrams can be used to determine how operating conditions (temperature, pressure, bath composition) can be varied to synthesize desired products or effect partitioning of components.

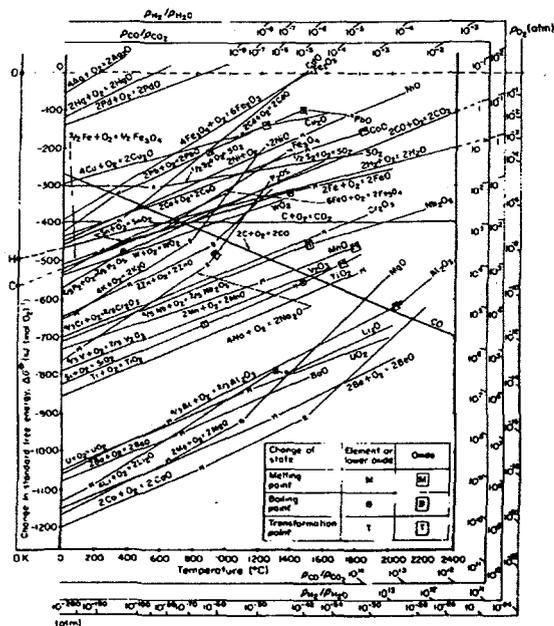


Figure 1
Gibbs Free Energies of Oxidation¹

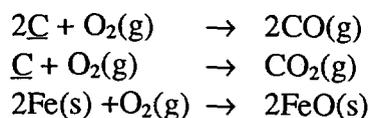
These correlations are for pure systems and provide only an approximation of the reaction thermodynamics guiding the process chemistry. Although beyond the scope of this

paper, MMT has in-depth understanding of the thermodynamic properties of higher order, non-ideal solution reaction chemistry. This knowledge is drawn upon by MMT for refining the CEP process chemistry and reactor design to meet specific applications.

The fundamental physical chemistry principles of reaction thermodynamics and solution equilibria governing the processing of key feed components relevant to DOE waste streams will be presented. Specifically, processing of organic materials, metals, halides, and transuranics are discussed.

Organic Feed Conversion to Synthesis Gas

When an organic feed is injected into a CEP reactor, it dissociates and dissolves into elemental intermediates on contact with the molten iron solvent. Hydrogen will not dissolve in the metal solvent but will be released as a gas in the product off-gas stream. Addition of oxygen as a co-reactant will lead to the formation of synthesis gas. The production of synthesis gas is due to the effectiveness of the dissolved carbon intermediate as a reducing agent. This is best illustrated by the Gibbs Free Energy diagram (Figure 1). The oxides for which the free energy lines are above that of the formation of CO can be reduced by carbon. Therefore, when oxygen is added to a system containing carbon and iron at 2000°C, three competing reactions take place:



In this system, one can look at Figure 1 to identify that at 2000°C, the Gibbs Free Energy of reaction of carbon to carbon monoxide (-600 kJ/mol O₂) is lower than that involving carbon to carbon dioxide (-400 kJ/mol O₂) and iron to iron oxide (-250 kJ/mol O₂).

Therefore, due to thermodynamic forces CO will be formed preferentially to CO₂ and FeO when oxygen is injected into the carbon-iron melt.

A critical attribute of the CEP system is that a reducing environment is homogeneously maintained and neither carbon dioxide nor steam are formed. This is because in the presence of excess oxygen, wustite (iron oxide) formation is thermodynamically favored over carbon dioxide or steam formation. Therefore, in contrast to open flame organic feed processing systems such as coal gasification, the synthesis gas produced from CEP is of high quality with a CO/CO₂ ratio of 10,000:1 and an H₂/H₂O ratio of 2,000:1.

Metal Recovery

A significant advantage of CEP technology is its ability to recover and recycle metals from organo-metallic feeds. Consider an organo-metallic feed dissociating into its elemental constituents (e.g., C, H, M, where M is the metal) upon injection into the CEP reactor. As outlined above, both the carbon and the metal will readily dissolve in the molten metal solvent. If oxygen is added as a co-reactant, two reaction pathways are possible:

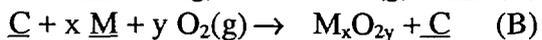
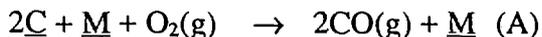


Figure 1 indicates which systems will proceed with formation of carbon monoxide (reaction pathway (A)) and which systems will proceed with formation of the metal oxide (reaction pathway (B)). Specifically, carbon monoxide formation is favored in systems containing metals such as nickel, cobalt and copper whose free energy of oxidation is higher than that of carbon. These metals can be recovered as alloys in the iron solvent. Metals with a free energy of oxidation lower than that of carbon (e.g., aluminum, calcium) will form oxides and partition into the ceramic phase.

Certain metals can either be recovered as metal alloys or as oxides in the ceramic phase depending on the operating conditions. For example, magnesium is reduced by carbon at elevated temperatures ($T \geq 1800^\circ\text{C}$, $P = 1 \text{ atm}$). However, at elevated pressures, magnesium oxide reduction by carbon, will not be favored.

Halogen Recovery

Under the Resource Conservation and Recovery Act (RCRA), chlorinated organic compounds of concern include the primary organic hazardous constituents (POHCs) in the waste. Carbon tetrachloride, chloroform, para-dichloro benzene, perchloroethylene, tetrachloroethane, 1,1,1-trichloroethane, trichloroethylene, methyl chloride, polyvinyl chloride (PVC), and polychlorinated biphenyls (PCBs) and all their intermediates and derivatives are among the common organic chlorinated compounds.

CEP technology can recover and recycle halogens from halogenated organic and inorganic feed streams without the formation of undesired by-products (e.g., chlorophenols, dioxins and furans). In order to demonstrate the recovery and recycling of halides in the CEP system, consider the case of a chlorinated organic feed stream. On injection into the molten metal bath, the feed will dissociate into dissolved elemental intermediates. Chlorine can be recovered and recycled as either a metal chloride or hydrogen chloride, or as chlorine gas in the absence of hydrogen. When a ceramic layer is introduced during CEP operation, thermodynamic control predicts predominant retention of chlorine in the ceramic phase under optimized conditions.

The two reaction pathways are:

- *Formation of Metal Chloride:* Calcium, in the form of calcium oxide, added to the

molten iron bath will form calcium chloride. The effectiveness of calcium as a chloride scrubbing agent is demonstrated by the Gibbs Free Energy of formation of common chlorides as a function of temperature diagram, shown in Figure 2. Calcium chloride is volatile under CEP operating conditions and will distribute itself in the gas product phase where it can be cooled and separated from the other gaseous components as a condensed solid. However, by manipulating the ceramic phase composition, the metal halide can be prevented from distributing into the gaseous phase.

- *Formation of Hydrogen Chloride:* In the absence of calcium, both hydrogen chloride and ferrous chloride will be formed as the free energy of formation for both compounds is of the same order of magnitude (Figure 2). If the CEP is operated at temperatures of 1500°C, the ferrous chloride will volatilize and be recovered as a condensed solid in the gaseous stream. If the CEP is operated at lower temperatures (1000°C) ferrous chloride can be recovered as a liquid in the vitreous phase.

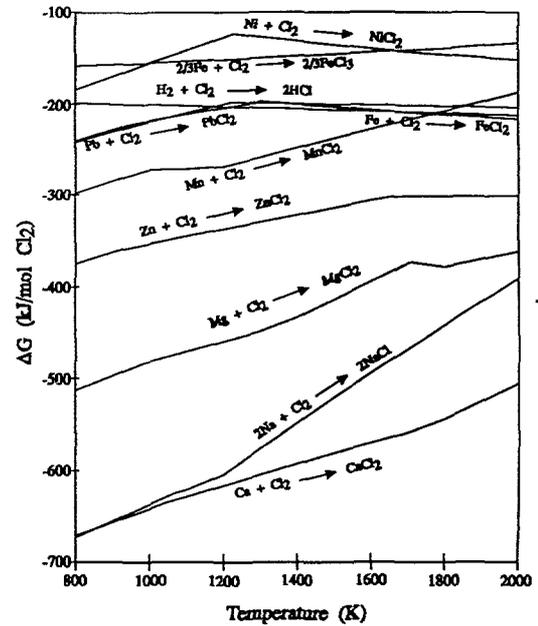


Figure 2
Chloride Free Energy Diagramⁱⁱ

Partitioning of chlorides in a metal/gas/ceramic phase system, however, must take into consideration the effects of mass transfer issues within the ceramic phase. Even though the free energy of reaction can be treated as a true measure of the driving force for the reaction, mass transfer issues can limit the extent of the reaction such that thermodynamic equilibrium is not achieved. In the case of chloride processing with a metal/CaO-Al₂O₃-SiO₂ ceramic phase, the formation of 'CaCl₂' in the ceramic phase is not only dependent on the activities of the constituents, but also influenced by ceramic phase viscosity, reaction-rate, and residence time of the gas in the ceramic phase. CaO-Al₂O₃-SiO₂ systems are of primary interest to MMT and have been extensively studied and optimized for potential capture of chlorides as CaCl₂.

The CEP flexibility in recovering halogens is a major advantage given the technical difficulties and expense associated with processing halogen-containing waste streams in

typical open flame combustion processes such as incineration. Halogen containing compounds tend to suppress combustion and are often characterized as non-combustible. Therefore, incineration of these chemicals can result in incomplete combustion leading to formation of highly toxic compounds. The free radical chemistry that occurs during combustion produces radical intermediates which can react to produce dioxins and furans.

Transuranic Recovery

An important advantage of the CEP technology is that it can separate and concentrate radioactive compounds from complex contaminated feeds while also recovering and recycling the non-radioactive components of the feed. This attribute of CEP has important implications in the decontamination of radioactive sites as well as the decommissioning of nuclear weapons and the byproducts of their manufacture. This implies that radioactively-contaminated components from DOE sites can be separated, highly concentrated and immobilized in a small volume that can be safely disposed of. Furthermore, feed components such as reducible metals (e.g., nickel, chromium, manganese) can be recovered as alloys while hazardous organic components can be effectively converted to a stable final form.

Table 1 shows that the Gibbs Free Energies of reduction by carbon of transuranic oxides are positive indicating that the reactions are not thermodynamically favored. It is this oxide stability that provides a mechanism for the partitioning of these radioactive species into the ceramic phase. Data collected from the literature demonstrates the partitioning of transuranic components from the metal to the vitreous phase. Specifically, residual concentrations ranging from 0.05 ppm to 2 ppm of such

radioactive components were achieved by others using diffusion of oxidizing, vitreous-forming agents to partition the radioactive components.

Table 1
Free Energies of Reduction of Transuranic Oxides

Reaction	ΔG (kJ/mol) at 2000K
$UO_2(s) + 2C(s) \rightarrow 2CO(g) + U(l)$	167.104
$PuO(s) + C(s) \rightarrow CO(g) + Pu(l)$	100.305
$PuO_2(s) + 2C(s) \rightarrow 2CO(g) + Pu(l)$	111.377
$Pu_2O_3(s) + 3C(s) \rightarrow 3CO(g) + 2Pu(l)$	463.122
$ThO_2(s) + 2C(s) \rightarrow 2CO(g) + Th(s)$	283.740
$ZrO_2(s) + 2C(s) \rightarrow 2CO(g) + Zr(s)$	156.339

Experimental Feed Conversion Demonstrations

The processing and conversion of organic, organo-metallic and inorganic compounds in mixed waste streams into stable materials has been demonstrated theoretically in the discussion above. In addition to the theoretical analysis, MMT has collected extensive experimental data in bench-scale and pilot plant units and in commercial-scale metallurgical systems. The experimental data validates the theoretical predictions and confirms CEP's capabilities to generate high quality products.

The physical chemistry of CEP, specifically, the solution equilibria and the formation of a 'singular' dissolved intermediate in the reaction pathway, ensures that complete dissociation of feed streams occurs and that product synthesis and recycling can be controlled and manipulated. Therefore, the molten metal, acting as a homogeneous catalyst and solvent with high chemical inertia, renders CEP a highly flexible and robust recycling technology.

Approach

To achieve the objectives set forth in the contract, the scope of work was divided into seven tasks:

1. Design CEP system for recycling contaminated scrap metal
2. Formulate an experimental test plan
3. Experimental testing of surrogate radionuclide partitioning and bulk solids processing
4. Optimization of the vitreous phase
5. Experimental testing of RCRA wastes
6. Preparation of a conceptual design for a CEP plant for processing DOE's contaminated scrap metal
7. Preparation of a final report

Contract-sponsored technical development activities have been carried out at MMT's Recycling Research and Development Facility in Fall River, MA. The facility houses CEP reactor systems including bench- and pilot-scale units, physical models, and a commercial-scale demonstration unit. This state-of-the-art facility is fully permitted by the Commonwealth of Massachusetts for recycling demonstrations using hazardous and non-hazardous materials as CEP feeds. MMT has received recycling certifications from the Massachusetts Department of Environmental Protection for the processing of RCRA and organometallic feeds.

Bench- and pilot-scale experimental units are used to confirm theoretical modeling predictions, establish product quality, determine appropriate materials of construction, assess design parameters and confirm fundamental

process chemistry. Many of these systems, including the Advanced Processing Units (APUs) which are appropriate for small commercial-scale operations, are operated round-the-clock for two to three-week experimental campaigns. Physical models are used to study fluid dynamics and transport phenomena, reactor flow patterns, unique reactor configurations, and final design parameters.

The commercial-scale prototype is used primarily for customer and regulatory demonstrations and establishment of commercial design scenarios. MMT has processed a wide range of hazardous, characteristic, and surrogate waste feeds in the commercial prototype. The commercial prototype typically operates round-the-clock during one-week demonstration campaigns, which may include several different feed materials.

The demonstration-scale CPU and gas handling unit is equipped with approximately 2,000 monitored variables and 900 control loops linked into the computerized monitoring and control modules. Numerous sampling ports throughout the gas handling train enable full characterization of the product gas quality. Summa canister sampling is performed to enable third-party analysis down to ppb levels via established EPA methods (TO-14). Mass spectrometer samples are drawn on-line and gas composition measurements are taken every twenty seconds for feed-back process control.

To meet the PRDA objectives, MMT embarked on a parallel theoretical research program and engineering design development to supplement these experimental activities. MMT's proprietary thermodynamic, kinetic, and physical transport models were applied to establish CEP design criteria for optimal processing of scrap metal contaminated with

radionuclides and organic compounds. Equilibrium analysis was used to study the homogeneous reactions occurring within the individual phases. Non-equilibrium modeling was used to assess methods to enhance decontamination performance, component separation, and recovery potential using multi-phase processing.

Following theoretical analysis and computer modeling, the physical models were employed to verify predictions of hydrodynamic behavior of the system, including the specialized feeding of bulk solids into the bath. The physical models use water as a surrogate for molten iron, and various oils and emulsions were used to simulate CEP's ceramic layer. The volatility of some feed components in DOE's contaminated scrap metal was modeled using dry ice in various sizes. Hundreds of physical model experiments were performed under the contract, providing valuable data for use in designing bench-scale and pilot plant experiments.

The actual experimental progression was defined by the tasks outlined above. Experiments were designed to verify the CEP system's ability to effect partitioning of radionuclides to the targeted phases. Since inclusion of these radionuclides in the ceramic phase was predicted, concerted efforts were directed toward the optimization of the chemistry of the ceramic phase to provide a stable and durable form for disposal. In parallel, experimental processing of feeds containing RCRA contaminants was conducted to demonstrate CEP's capability to destroy hazardous organic constituents, paving the way for the delisting efforts.

The combined results of MMT's theoretical analysis, modeling studies, and experimental campaigns are currently being integrated to generate design specifications for a

commercial CEP plant for processing contaminated scrap metal. The plant design package will include a bulk solid feed subsystem, particulate handling subsystem, gas handling train, a process control plan for automated monitoring and control, and a risk/safety analysis for maximizing operational safety.

Results

Targeted Partitioning to Durable, Stable Form

Previously published studies have demonstrated the ability to partition radioactive components, such as uranium and plutonium, from the metal phase into a vitreous phase via melt refining. Residual concentrations ranging from 0.05 ppm to 2 ppm were achieved using diffusion of oxidizing, vitreous-forming agents to partition the radioactive components. Successful partitioning to less than 10 nCi/g levels (approximately < 0.1 ppm) has been demonstrated for uranium- and plutonium-contaminated metals. CEP offers the potential for superior performance, as the techniques involved in melt refining are completely incorporated and enhanced in CEP technology. Specifically, CEP incorporates active radionuclide partitioning through select co-reactant additions (e.g., oxygen) and enhanced mass transfer (e.g., convection), while melt refining is based upon 'passive' diffusion-based partitioning.

MMT designed a series of bench-scale experiments using radioactive surrogate materials to demonstrate the oxidation and partitioning of radionuclides between the metal and vitreous phases and to identify and optimize the effect of operating conditions on partitioning. The bench-scale experiments were followed by experiments on pilot- and demonstration-scale systems. Hafnium was

selected as a radioactive surrogate due to its similarities in thermodynamic behavior (Figure 3) and physical properties (Table 2) to uranium. Zirconium, although similar to uranium in the thermodynamic properties, was not chosen as the primary surrogate material because of its significantly lower density.

The experimental design parameters evaluated were metal system, gas environment and ceramic phase composition. Radioactive surrogate partitioning was measured using neutron activation analysis (NAA) for non-destructive trace analysis. The hafnium LDL was 0.2 ppm in iron and 2 ppm in nickel. X-ray fluorescence (XRF) was used for analysis of the vitreous phase composition. Metal samples were taken at different positions in the metal bath to ensure uniform decontamination. The contract objective was to demonstrate uniform metal decontamination above 98%. In addition, backscattered electron imaging and X-ray analysis were used to investigate the nature of the capture and stabilization of the radionuclide surrogate in the vitreous phase.

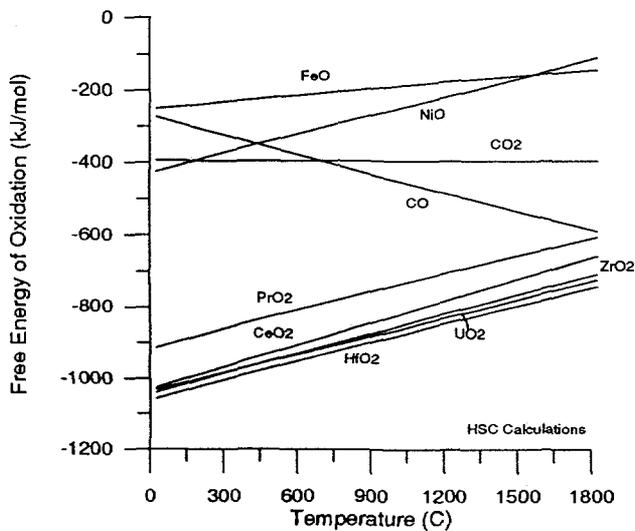


Figure 3
Identification of Radionuclide Surrogate

Table 2
Physical Properties of Uranium and Surrogates

Element	Oxide		Metal	
	m.p. (°C)	Density (g/cm ³)	m.p. (°C)	Density (g/cm ³)
U	2,878	10.96	1,132	19.05
Hf	2,758	9.68	2,227	13.31
Zr	2,715	5.6	1,852	6.49
Fe	1,369	5.7	1,535	7.86
Ni	1,984	6.67	1,455	8.90

Average decontamination of the metal samples were >99% and exceeded the contract's 98% objective in all experimental trials. The calculated decontamination factors were analytically limited with no radioactive surrogate detected in the metals. Table 3 summarizes the results. V1 refers to aluminosilicate vitreous compositions while V2 refers to borosilicate vitreous compositions.

Table 3
Radionuclide Partitioning

Metal	Vitreous Phase	Decontamination
Iron	V1	≥ 99.62%
Nickel	V1	≥ 99.76%
Iron	V2	≥ 99.08%

Samples taken at different positions in the metal bath demonstrated uniform distribution of any trace amounts of hafnium across the metal (Figure 4 and Figure 5). This indicates that radioisotope transport to and incorporation in the oxide phase is very efficient under CEP operating conditions.

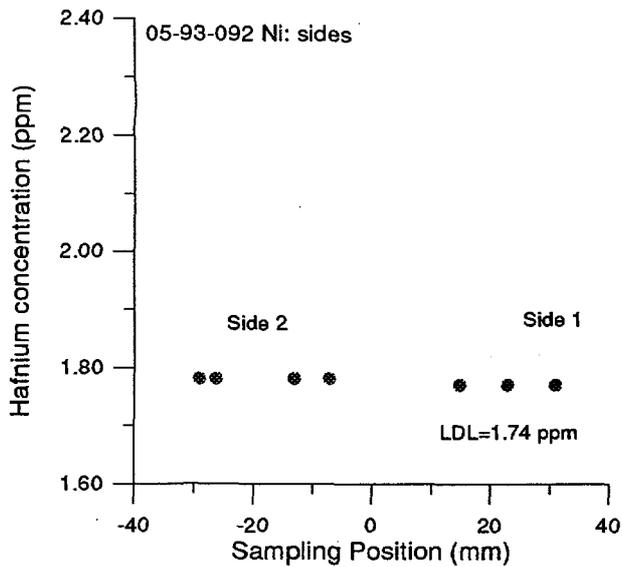


Figure 4
Sampling across Radius of Metal

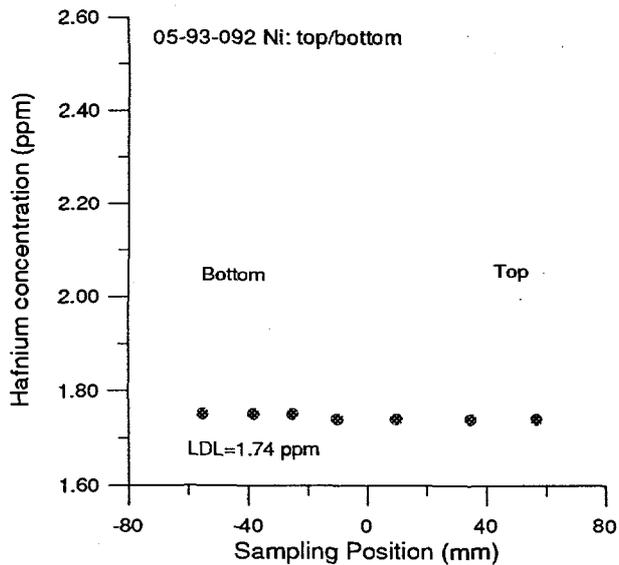


Figure 5
Sampling from Top to Bottom of Metal

Ceramic samples were analyzed using backscatter electron imaging to identify the nature of the radionuclide capture and stabilization in the ceramic phase. This work indicated that operating conditions and vitreous phase composition can affect radionuclide

capture and stabilization. Figure 6 shows the backscatter image of a vitreous sample which has separated into hafnium rich and hafnium poor regions. This is in contrast to the vitreous sample shown in Figure 7, where hafnium is uniformly distributed. CEP conditions have been identified to achieve this desired vitreous radionuclide capture and stabilization mechanism.

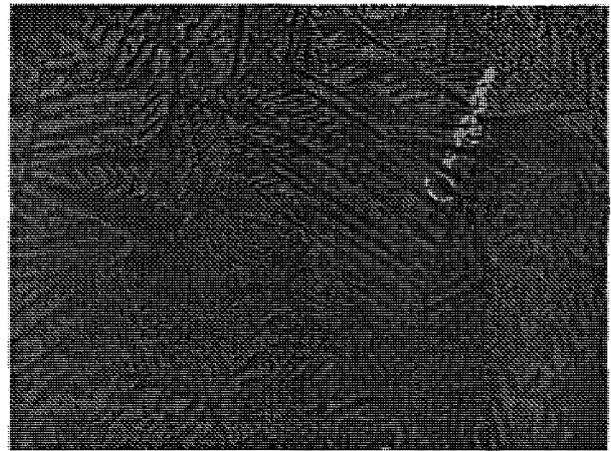


Figure 6
Backscatter Image: Phase Separation Exhibited



Figure 7
Backscatter Image:
No Phase Separation Exhibited

Processing of RCRA Contaminants

The investigation of CEP's conversion and immobilization capabilities for RCRA components of contaminated scrap metal feeds has been well proven during the experimental campaign of this contract. MMT brought to the contract a solid foundation of understanding of the behavior of toxic and halogenated feeds in CEP, and proceeded to optimize the chemistry of the system for the feeds anticipated. Efforts began on bench-scale apparatus, and subsequent prototype trials validated bench-scale results.

CEP has been demonstrated on a range of RCRA-listed wastes as well as characteristic and RCRA-like surrogate material (Table 4) including high-molecular weight aromatics, chlorinated organics, organically-bound nitrogen species (isocyanates), plastics, and organometallics. The technology's environmental performance has been demonstrated during actual waste processing to meet and surpass current and proposed regulatory standards. Specifically, DREs >99.9999% were achieved for principle organic

hazardous constituents (POHCs). NO_x and SO_x were not detected in the product gases to detection limits of 3 ppm. Condensed phase non-leachable products, both ceramic and metal phases, of marketable composition were generated. Dioxins were not detected to the targeted regulatory limit of 0.1 ng 2,3,7,8 TCDD TEQ/ Nm^3 .

Currently the effectiveness of hazardous waste treatment technologies is regulated by the EPA by measuring the concentration of hazardous materials in the after-process wastewater and non-wastewater. All processes have to ensure that organic constituent concentrations in individual wastewater and non-wastewater streams are lower than the regulated limits set by EPA. CEP demonstrations surpass the current limits even when compared with the Best Demonstrated Available Technology (BDAT). CEP was recently approved by EPA (on October 24, 1994) as a non-combustion technical equivalent (BDAT) for eight RCRA-listed isocyanate waste codes (K027) for which incineration had previously been mandated as the commercially available BDAT technology.

The environmental performance of CEP has also been demonstrated on chlorinated waste streams containing some of the most difficult to destroy hazardous constituents. The results of demonstration-scale processing of RCRA-listed waste F024 (chlorinated aliphatics) indicated that hazardous organic constituents in the feed were not detected in ceramic, metal and scrubber water, thereby surpassing the BDAT standards for all effluent streams (Table 5). Destruction Removal Efficiency (DRE) on multiple organic hazardous constituents exceeded 99.9999%, which surpassed the current regulations mandating DREs >99.99% (Table 6). Trace constituents were not detected to the targeted regulatory limit of 0.1 ng/ Nm^3 TEQ.

Table 4
Major Feeds Processed at the Demonstration Prototype

Feed	Waste Minimization Performance			Environmental Performance		
	Product Recovery	% of feed Recycled	Residual	DRE	TCLP	Off-Gas
Representative Nonhazardous Feeds						
Polystyrene/ Graphite	Syngas	99% to syngas	Dust Negligible	≥99.9999%	N/A	PICs < LDL ¹ of 1 ppm; CO ₂ <1% NO, SO ₂ < LDL of 100 ppm
Chlorotoluene/ Heavy Organics	Syngas Ceramic	87% to syngas 12% to ceramic	Dust Negligible	≥99.9999%	Passes TCLP	PICs < LDL of 1 ppm; CO ₂ < 1% NO, SO ₂ < LDL of 100 ppm
Dimethyl Acetamide/ Heavy Organics	Syngas Nitrogen	96% to syngas 3% to nitrogen	Dust Negligible	≥99.9999% (based on THC)	N/A	PICs < LDL of 1 ppm; CO ₂ < 1% NO, SO ₂ < LDL of 100 ppm ² NO _x , SO _x < LDL of 1 ppm ³
Representative Hazardous Waste Feeds						
Industrial Biosolid Waste	Syngas Nitrogen Ceramic Ferroalloy	70% to syngas 8% to nitrogen 20% to ceramic 1% to ferroalloy	Dust Negligible	≥99.9999% (based on THC)	Passes TCLP	PICs < LDL of 1 ppm CO ₂ < 1% NO _x , SO _x < LDL of 3 ppm Trace <0.1 ng/Nm ³ TEQ ⁷
Surplus Metal/Weapon Componentry	Syngas Ceramic Ferroalloy	25% to syngas 8% to ceramic 63% to ferroalloy	Dust Negligible	N/A	Passes TCLP	PICs < LDL of 1 ppm CO ₂ < 1% NO, SO ₂ < LDL of 100 ppm ² Trace <0.1 ng/Nm ³ TEQ ⁷
K019/K020 ⁴ / Chlorobenzene/ Fuel oil	Syngas	76% to syngas 23% to ceramic	Dust Negligible	≥99.9999%	Passes TCLP	PICs < LDL of 1 ppm CO ₂ < 1% NO, SO ₂ < LDL of 100 ppm ²
K027 ⁵	Syngas Ferroalloy (Fe - Ni)	93% to syngas 5% to nitrogen <1% to ceramic <1% to ferroalloy	Dust Negligible	≥99.9999%	Passes TCLP	PICs < LDL of 1 ppm CO ₂ < 1% NO, SO ₂ < LDL of 100 ppm ²
F024 ⁶ / Fuel oil/ Chlorotoluene	Syngas HCl gas	82% to syngas 13% to HCl gas <1% to ceramic	Dust Negligible	≥99.9999%	Passes TCLP	PICs < LDL of 1 ppm CO ₂ < 1% NO, SO _x < LDL of 100 ppm ² Trace <0.1 ng/Nm ³ TEQ ⁷
¹ LDL = Lower Detection Limit.			⁴ EPA listed hazardous waste stream: ethylene dichloride/vinyl chloride heavy ends.			
² As measured by on-line mass spec. Lower detection limit to 1 ppm was confirmed as in footnote 3.			⁵ EPA listed hazardous waste stream: toluene diisocyanate distillation residues.			
³ As measured by third party analytical equipment placed on-line.			⁶ EPA listed hazardous waste stream: chlorinated aliphatic hydrocarbons.			
			⁷ Dioxins and furans non-detectable to the targeted regulatory limit of 0.1 ng/Nm ³ TEQ.			

Table 5
CEP Performance in BDAT Constituents Conversion (F024 Processing)

Constituents	Feed (mg/l)	Non-Wastewater Regulations			Wastewater Regulations	
		Ceramic ³ (mg/kg)	Metal ² (mg/kg)	Non-Waste-water (mg/kg)	Scrubber Water (mg/l)	Wastewater (mg/l)
1,1,2-Trichloroethane	18,000	ND ¹ (0.0075) ²	ND (0.0075)	6.0	ND (0.0015)	0.054
Tetrachloroethene	9,700	ND (0.0075)	ND (0.0075)	6.0	ND (0.0015)	0.056
Chlorobenzene	12,000	ND (0.018)	ND (0.018)	6.0	ND (0.0035)	0.057
1,2-Dichloroethane	6,800	ND (0.0075)	ND (0.0075)	6.0	ND (0.0015)	0.21
1,1,2,2-Tetrachloroethane	11,000	ND (0.005)	ND (0.005)	6.0	ND (0.001)	0.057
Trichloroethene	24,000	ND (0.005)	ND (0.005)	6.0	ND (0.001)	0.054
Xylenes	610	ND (0.005)	ND (0.005)	3.0	ND (0.001)	0.32
1,1,1,2-Tetrachloroethane	1,000	ND (0.025)	ND (0.025)	6.0	ND (0.001)	0.057
Hexachlorobutadiene	3,600	ND (0.025)	ND (0.025)	5.6	ND (0.001)	0.055
Naphthalene	900	ND (0.025)	ND (0.025)	5.6	ND (0.001)	0.059

¹ND = Not Detected.
²(n) where n is the lowest detection limit.
³In a commercial facility processing F024, the metal and ceramic would be products, not wastes subject to LDR standards.
 These data are provided to demonstrate CEP conversion of BDAT constituents.

Table 6
Destruction Removal Efficiency (DRE) for Listed Hazardous Constituents (F024 Processing)

Feed Constituent	Feed Concentration (mg/l)	Off-gas Concentration (ppm)	DRE
1,1,2-Trichloroethane	18,000	ND ¹ (0.00037) ²	≥99.9999%
Chlorobenzene	12,000	ND (0.00037)	≥99.9999%
1,2-Dichloroethane	6,800	ND (0.00044)	≥99.9999%
1,1,2,2-Tetrachloroethane	11,000	ND (0.00029)	≥99.9999%
Trichloroethene	24,000	ND (0.00038)	≥99.9999%
¹ ND=Not Detected		² (n) where n is the lowest detection limit.	

CEP reaction pathways, combined with the uniform and highly reducing environment maintained over a wide range of operating conditions, preclude the formation of dioxins, furans and other undesirable by-products. Research suggests that all of the following conditions must be present to promote the formation of dioxins: excess free O₂ (≥ 10⁻³ atm partial pressure), the presence of aromatic precursors, sufficient residence time in the temperature range around 300°C (572°F), and the presence of heterogeneous catalytic surfaces (e.g., particulates).^{iii,iv,v,vi} These essential conditions for formation of dioxins are either inherently absent or can be minimized through appropriate design and operation of the CEP system.

Extremely low oxygen concentrations in the CEP off-gas will inhibit the formation of dioxins. Oxygen partial pressure is continuously monitored in the prototype demonstration unit and is not detected. Thermodynamic evaluation of CEP reaction scenarios shows that partial pressures of O₂ can approach 10⁻¹⁵ atm.

CEP solution chemistry can ensure that all species pass through a dissolved intermediate

and preclude the formation of aromatic precursors. Table 4 shows that Destruction and Removal Efficiencies (DREs) are greater than 99.9999% for chlorinated plastics (PVC and polystyrene) and chlorinated solvents.

Monitoring Devices and Control Methods

The development of advanced models and techniques to monitor and control key process parameters is crucial to robust, automated CEP operation. System automation reduces the likelihood of operators' exposure to radioactivity, and allows better control of process variables and a more immediate response to system and feed variabilities. Areas of keen development interest include bath temperature control, bath composition control, containment system monitoring, and bath level, among others. Monitoring these properties through conventional means utilizes intrusive measurements. Carbon concentration and bath temperature can be directly measured using invasive sampling techniques, but these may interrupt the flow of operations and delay opportunities for feedback control. In addition, manual sampling and other conventional methods will increase risks to worker and public

health and safety. Therefore, MMT embarked on a technology development and implementation program under this contract to improve the reliability, operability, and degree of automation in CEP systems. The program encompasses improving existing and developing new on-line sensing and instrumentation devices, developing sophisticated control algorithms, and the selection and integration of inherently safe equipment and robust operating procedures.

Through the use of its dynamic and steady-state simulation models, detailed theoretical models describing local phenomena, and operational experience garnered from its demonstration-scale unit, MMT identified the key process and design parameters impacting CEP performance. A program was then set up to develop, test, and implement non-intrusive, continuous monitoring of these key parameters, which include bath temperature, carbon concentration, gas composition, ceramic composition, refractory thickness, bath level, bath pressure, dust loading, and headspace temperature. A market search was conducted to identify the most accurate, reliable, and cost-effective sensing devices. Sensing devices currently used in industry have been adapted to CEP systems, and new and novel sensing techniques have been implemented and are undergoing testing on pilot plant and demonstration-scale units to verify their accuracy and reliability. To complement these activities, MMT has developed commercial-quality on-line control modules, providing an easy-to-use operator interface.

Temperature Control. The primary objective of the bath temperature control strategy is to keep the bath molten and above a minimum acceptable temperature set primarily by the liquidus temperature of the bath. Secondary objectives are to minimize changes in the bath temperature and to operate at the

optimum temperature to minimize containment wear. The bath temperature is controlled by adjusting the power setting of the bath induction coil power supply. Closed-loop temperature control was successfully demonstrated with the controlled variable being the bath temperature and the controller output the power supply setting. The bath temperature is estimated using embedded thermocouples readings and the CET (Compensated Embedded Thermocouple) temperature model. The CET model is a proprietary software module developed in-house that can predict the bath temperature by solving the governing transient heat diffusion equations. The commercial-quality module has capabilities for digital filtering, sensor diagnosis, automatic rejection of erroneous thermocouple inputs, self-tuning, and automatic refractory thickness correction.

Other techniques for measuring the bath temperature are currently undergoing testing. Specifically, the feasibility of using a two-section (sapphire/quartz) infrared (IR) lightpipe sensor has been recently proven on the demonstration-scale unit. A lightpipe is a solid rod of high IR transmission characteristics, and good chemical stability at high temperatures. One end of the lightpipe rod is in direct contact with the melt, thus providing a path for IR radiation from the molten metal through the lightpipe. The IR emissions are collected by a re-imaging lens or a terminated fiber optic cable at the other end of the rod and carried via a fiber-optic cable to a dual-wavelength pyrometer. During testing, the lightpipe sensor showed immediate response to temperature perturbations and demonstrated stability against thermal cycling.

Delisting

CEP has been demonstrated on a range of RCRA-listed wastes as well as characteristic and RCRA-like surrogate material (Table 4)

including high-molecular weight aromatics, chlorinated organics, organically-bound nitrogen species, plastics, and organometallics. CEP's ability to provide complete destruction of the hazardous constituents while maintaining high regulatory integrity has been proven. Due to the unique set of regulations governing the processing of RCRA-listed materials, the disposal of a stable final form containing radionuclides but not exhibiting any RCRA characteristics would benefit from delisting. Delisting would provide increased flexibility in terms of disposal destination and cost.

A delisting petition has been prepared based on experimental data generated from pilot plant and demonstration-scale testing. The delisting petition is an upfront application for a generic delisting of the ceramic phase generated from CEP systems. Five representative mixed waste streams have been selected for delisting:

- Organic sludges: e.g., ORR MWIR 3090 (F001-F002 solvents, F006 electroplating waste); INEL ID-EGG-158:3
- Inorganic sludges: e.g., ORR MWIR 3004 (F006 electroplating waste); INEL ID-EGG-102:7 (toxic organic and metals with mercury)
- Soils and sediments: e.g., ORR MWIR 3151 (Pb, Hg); INEL ID-EGG-141:990
- Combustible debris: e.g., ORR MWIR 2028 (F003); INEL ID-EGG-114:337
- Scrap metals: e.g., INEL ID-EGG-132:20

The experimental results presented in support of the delisting petition included feed materials characterization, ceramic elemental composition, ceramic hazardous characteristics evaluation, toxicity characteristics leachability

procedures (TCLP) testing, and hazardous organic constituents concentration in the ceramic phase.

For a waste to be successfully delisted, the petition must demonstrate that the waste:

- does not meet the criteria for which it was listed
- does not exhibit any hazardous waste characteristics
- does not exhibit any additional factors including additional constituents which may cause the waste to be a hazardous waste

In preparing the delisting petition, MMT has followed the requirements for delisting petitions set forth in 40 CFR § 260.20 and § 260.22, as well as in relevant EPA guidance (such as the guidance manual for petitions to delist hazardous waste (EPA/530-R-93-007, March 1993)). These regulations and guidance specify the administrative information, waste characterization and waste management history, process information, waste sampling and analysis information, and ground water monitoring information that must be included in the delisting petition.

Containment Design

Containment system development has been the focus of an integrated and rigorous effort under this contract. An integrated program aimed at maximizing refractory life and optimizing containment handling for ease of operation has been developed. The program's focus has been on improving the containment system design, optimizing refractory materials selection, and developing a theoretical and empirical understanding of the mechanisms controlling lining degradation.

Refractory wear is the most important physical phenomenon faced in the CEP containment development program, as gradual wear processes will ultimately determine the longevity of CEP units. Therefore, the factors involved in refractory lining wear have been systematically addressed experimentally and theoretically. Containment system design has been found to be the most important component for combating refractory lining deterioration. Much of the initial development work in CEP containment has been focused on improving design methodology. Refractory reliability has shown a steady increase over the course of the contract. This has been due to a combination of improvements to refractory design, layout, heat-up practice, shell design and temperature control. Critical design improvements are being made on an ongoing basis. The results of these important developments are summarized below:

- Developed and implemented crucible-based modular containment system capable of simplified change-out to provide extended life and enable rapid and economical turnaround/replacement of worn components
- Developed application-specific crucible materials compatible with different feed types
- Developed alternative bath chemistry process control strategies based on the type of crucible used
- Thorough investigation of the interaction of refractory systems with halogenated species led to dramatic improvements in containment system longevity
- Developed methods, such as composite coatings and other chemical techniques, to

enhance the lifetime of the containment system

- Under development is a model to predict refractory life based on key operating parameters
- Demonstrated compatibility of refractory materials with MMT-developed ceramic phase systems (developed for stabilizing radionuclides)

Future Activities

Bulk Solid Feed Addition

One important area of development under the PRDA contract is the design of a robust system to process a wide variety of bulk solid materials. The capability to process bulk solids such as whole drums or similar-sized materials will increase the range of DOE feeds that can be processed by CEP and eliminate the need for size-reduction feed pre-processing systems. CEP reactor configuration systems are currently under development at MMT for top addition of bulk solid feed, including multi-zone reactors, lances, and other advanced reactor designs. Common to these concepts is the fact that they include multiple zones; a dissolution/volatilization zone and a gas polishing zone. Bulk solids are charged to the dissolution zone (receiving chamber) with a sufficient residence time to ensure complete volatilization of organic constituents and those species which will be volatile under CEP operating regimes. Subsequently, the volatilized gas is directed to the polishing zone (zone 2) to ensure that all portions of the feed proceed through the dissolved elemental intermediate state.

Earlier work on the physical models has established the feasibility of lance feed injection

and multi-zone processing. The effect of reactor geometry on feed dispersion, gas bubble dynamics, and residence time were investigated. During hot metal experimentation, materials and methods of construction to prolong lance and baffle life have been identified. Bench-, pilot-, and commercial-scale experiments have shown that top addition of bulk solids using non-optimized CEP reactor configurations is very promising. Optimization of reactor geometry is planned to verify initial modeling and experimental results.

Prior to additional hot metal testing, the physical water models will be utilized where better visualization, flexibility, and controllability of the experiments can be obtained. The first set of experiments will investigate the dependence of the maximum solids loading on conditions in the dissolution/volatilization zone and on the properties of the bulk feed (feed type and size). This characterization of zone 1 will allow the requirements for the second polishing zone to be determined for evaluation. The physical models use water as a surrogate for the molten iron. Feed surrogate materials will also be used to model the behavior of different types of feed materials.

Characterization of the polishing zone will proceed by initially conducting experiments on the water models. The objective will be to determine the parameters affecting the efficiency of the polishing zone. Advanced reactor concepts will be applied to evaluate different methods to enhance the rate of mass and heat transfer which will lead to increasing the efficiency of processing the volatilized gas generated in the first zone. This knowledge will then be applied in the design of the detailed configuration of the polishing chamber.

The experimental data generated by the aforementioned work will provide a valuable

basis for designing and conducting hot metal experiments on the pilot plant units. The primary objective will be to characterize the dissolution/volatilization zone for different feed types and sizes, and evaluate the performance of the different configurations developed for the polishing zone. This will include determination of the off-gas composition and generation rate as well as dust loading and composition as a function of key process variables. The data collected will characterize the volatilized gas generated in zone 1 and will determine the requirements for zone 2. In addition, the operability range of the system for materials for which dissolution and volatilization is mass or heat transfer-controlled will be determined experimentally. Specifically, the maximum solids loading will be determined as a function of feed rate, mass of metal in contact with the feed, the dissolution time, and reactor geometry. The maximum power supply capacity which will provide the energy required to dissolve and volatilize the feed materials will be determined. Although limitations exist on the maximum feedable materials (by reactor physical dimensions) and on the rate of volatilization (by the maximum capacity of the GHT), methods will be developed to scale-up the results to commercial-scale systems.

The experimental test program will proceed to assess the performance of the different reactor configurations developed for the polishing zone. Baffle reactors, series reactors, and other advanced multi-zone reactor concepts will be evaluated for their ability to effect a complete conversion of the bulk feed materials while maximizing the lifetime of the equipment. The most appropriate method for bulk solids processing will be determined based on environmental performance criteria and cost-effectiveness.

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