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CATALYTIC EXTRACTION PROCESSING OF CONTAMINATED SCRAP METAL

Author:

Thomas P. Griffin
James E. Johnston

Contractor:

Molten Metal Technology, Inc.
51 Sawyer Road
Waltham, MA 02154

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4.2   Catalytic Extraction Processing of Contaminated Scrap Metal

CONTRACT INFORMATION

Contract Number   DE-AC21-MC30171

Contractor   Molten Metal Technology, Inc.
                                  51 Sawyer Road
                                  Waltham, MA 02154
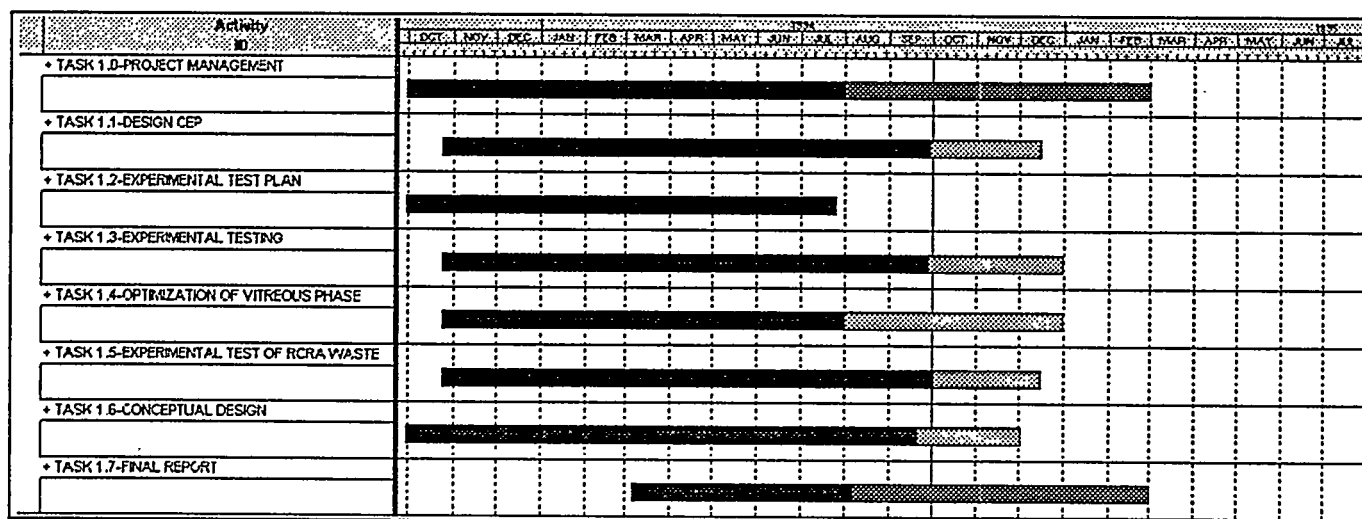   (617) 487-7681

Contractor Project Manager   Brian M. Payea

Principal Investigators   Thomas P. Griffin, Sc.D.
                                  James E. Johnston, Sc.D.

METC Project Manager   William J. Huber

Period of Performance   September 30, 1993, to February 28, 1995
Schedule and Milestones

Activity ID	OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL
◆ TASK 1.0-PROJECT MANAGEMENT																						
◆ TASK 1.1-DESIGN CEP																						
◆ TASK 1.2-EXPERIMENTAL TEST PLAN																						
◆ TASK 1.3-EXPERIMENTAL TESTING																						
◆ TASK 1.4-OPTIMIZATION OF VITREOUS PHASE																						
◆ TASK 1.5-EXPERIMENTAL TEST OF RCRA WASTE																						
◆ TASK 1.6-CONCEPTUAL DESIGN																						
◆ TASK 1.7-FINAL REPORT																						

OBJECTIVES

The contract was conceived to establish the commercial capability of Catalytic Extraction Processing (CEP) to treat contaminated scrap metal in the DOE inventory. In so doing, Molten Metal Technology, Inc. (MMT), pursued the following objectives:

- *Demonstration of the recycling of ferrous and non-ferrous metals* -- to establish that radioactively contaminated scrap metal can be converted to high-grade, ferrous and

non-ferrous alloys which can be reused by DOE or reintroduced into commerce.

- *Immobilize radionuclides* -- that CEP will concentrate the radionuclides in a dense vitreous phase, minimize secondary waste generation and stabilize and reduce waste volume.

- *Destroy hazardous organics* -- that CEP will convert hazardous organics to valuable industrial gases, which can be used as feed gases for chemical synthesis or as an energy source.

- *Recover volatile heavy metals* -- that CEP's off-gas treatment system will capture volatile heavy metals, such as mercury and lead.

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

BACKGROUND INFORMATION

Technology Overview

CEP is an innovative and proprietary technology that allows organic, organometallic and inorganic waste streams to be recycled into useful resources of commercial value. At the core of CEP is a liquid metal bath which acts as a catalyst and solvent in the dissociation of the feed and the synthesis of products. Upon introduction to the bath, feeds dissociate into their constituent elements and go into metal solution. Once in this dissolved state, addition of co-reactants enables reformation and partitioning of desired products.
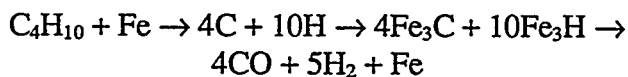
The CEP process can be conceptually divided into two stages.

- 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 are readily dissolved in the metal bath. These soluble elements form dissolved intermediates.

- Product synthesis: Through the addition of select co-reactants or by controlling operating conditions, the dissolved elemental intermediates can be reacted to form desired products of commercial value. These reactions are driven by thermodynamic forces.

In order to demonstrate the reaction pathway in the CEP system, consider the case of the introduction of an organic feed, such as the type commonly contaminating scrap metal, into a molten metal bath. The organic's reaction pathway is essentially dissociation into a dissolved carbon intermediate ($\underline{C}$) which can then be selectively reacted with oxygen to form CO. Schematically, the reaction pathway can be depicted as follows:

$$\text{Feed} \rightarrow \underline{C} \rightarrow M_XC \rightarrow \text{products}$$

or, taking an organic as the feed and iron as the metal:

$$C_4H_{10} + Fe \rightarrow 4C + 10H \rightarrow 4Fe_3C + 10Fe_3H \rightarrow$$
$$4CO + 5H_2 + Fe$$

Under typical CEP operating conditions both solution and reaction thermodynamics are important driving forces for product formation. For example, the production of synthesis gas is due to the selective addition of oxygen and the effectiveness of the dissolved carbon intermediate as a reductant. This phenomena is best illustrated

by the Gibbs free energy diagram shown in Figure 1. The left vertical axis is the free energy which is plotted versus temperature. Each line on the diagram represents the reaction of an element with oxygen to form an oxide. At any given temperature, the lower a line is on the diagram, the more favorable the reaction is. This diagram, therefore, represents the relative stability of various oxides when other elements are present. Hence, Group VIII and other transition elements are readily reduced to form metal alloys in typical CEP systems and the uniformly reducing environment of CEP can be maintained through the reaction of carbon with oxygen to form carbon monoxide.

As indicated, this diagram is for pure elements and their oxides. It shows, however, the general trends for reduction/oxidation reactions in CEP and demonstrates the flexibility which can be achieved through select reactant addition and operating parameter manipulation. MMT bases actual thermodynamic predictions upon the activities of species in metallic and oxide solutions and has developed proprietary in-house equilibrium and non-equilibrium models to predict reactant and product behavior.

The importance of the metal bath as a solvent is demonstrated by considering the following competing reaction pathways upon injection of an organic feed into an iron bath:

$$2\underline{C} + O_2\ (g) \rightarrow 2CO\ (g)$$

$$2Fe(l) + O_2(g) \rightarrow 2FeO$$

$$FeO(l) + \underline{C} \rightarrow CO(g) + Fe$$
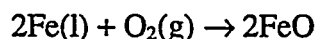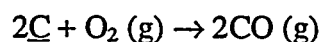
As outlined in Figure 1, thermodynamic forces favor the formation of carbon monoxide (CO) over iron oxide (FeO). The rate of these three reactions, however, is also dependent on the concentration of the dissolved carbon ([$\underline{C}$]). At very low carbon activity, iron oxide will be formed preferentially, while at high carbon concentrations, little, if any, FeO will be formed. The robust nature of the process is demonstrated by the wide range of operating conditions which favor the formation of carbon monoxide and preclude the formation of an oxidative environment.

A typical CEP integrated facility consists of a feed system, the Catalytic Processing Unit (CPU) or the reactor holding the liquid metal, followed by a hermetically sealed gas handling train and product recovery systems. All process components and equipment are adapted to chemical plant quality and process standards. Each subsystem can be adapted for the requirements of the feed processed and customer product specifications. For example, a chlorinated waste may not require an extensive metal product recovery system, but may require an HCl recovery and purification system in the gas handling train.
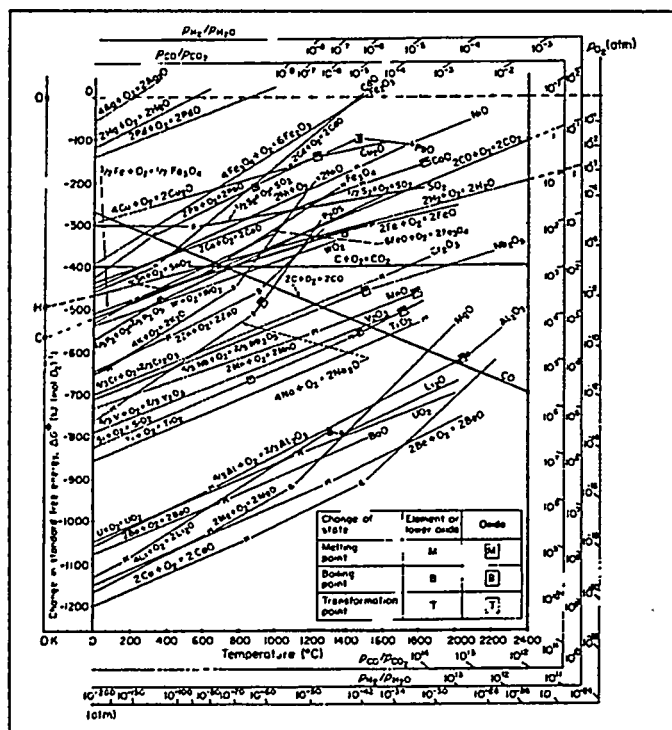

Figure 1. Gibbs Free Energy Diagram for Oxides

MMT is currently designing and constructing multiple CEP facilities, including an on-site closed-loop application for the chemical industry and a mixed waste (hazardous and radioactive) waste processing facility.

MMT operates a Recycling-Research & Development Facility in Fall River, Massachusetts. The facility houses four bench-scale units, four pilot-scale units, seven physical models and a commercial demonstration and prototype 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 and has sold the condensed phase products from this facility.

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 demonstrational campaigns, which may include several different

feed materials. Ongoing demonstrations in Fall River have shown the feed destruction and recycling capabilities of CEP. Specifically, CEP recycles waste into commercially valuable products while consistently achieving DREs $\geq 99.9999\%$. Trace components measure non-detect to the regulatory limits.

PROJECT DESCRIPTION

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

1.1 Design CEP system for recycling contaminated scrap metal

1.2 Formulate an experimental test plan

1.3 Experimental testing of surrogate radionuclide partitioning and bulk solids processing

1.4 Optimization of the vitreous phase

1.5 Experimental testing of RCRA wastes

1.6 Preparation of a conceptual design for a CEP facility for DOE's contaminated scrap metal

1.7 Preparation of a final report

Work on the individual tasks is nearly complete. Following contract signing, MMT first applied its proprietary thermodynamic, kinetic, and physical transport models to establish CEP design criteria for optimal processing of scrap metal contaminated with radionuclides and organics. Using equilibrium modeling, the homogeneous reactions occurring within individual phases and at the intra-phase interfaces, particularly with respect to the effect of uranium, plutonium and other radionuclides on the CEP system were researched. Using non-equilibrium modeling, MMT assessed

ways to enhance decontamination performance, component separation, and recovery potential using multi-phase processing.

Following theoretical analysis and computer modeling, MMT's cadre of 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 (water and molten iron have essentially the same viscosity), and various oils and emulsions were used to simulate CEP's vitreous layer. The volatility of many expected components of DOE's contaminated scrap metal was modeled using dry ice particles in various sizes. Hundreds of physical model experiments were performed under the contract, and provided valuable information for use in designing the hot metal experiments and their associated reactor geometries.

Molten metal systems used in service to the contract ranged in size from small bench-scale units employing five pounds of metal, to large demonstration-scale experiments in a unit holding six thousand pounds of molten metal and ceramic. The normal course for the investigation was to verify initial chemistry on the bench-scale with a minimum number of process variables, and then proceed through pilot- to demonstration-scale systems to gradually introduce increasing levels of complexity into the equation.

As described in the contract statement of work, the actual experimental progression was well defined by the tasks set forth. Experimental verification of the ability of system engineers to set the process variables to effect partitioning of radionuclides to targeted phases was proven. Since uranium and the transuranic elements were specifically called out in the SOW, and earlier work predicted oxidation of those elements and their eventual inclusion in the ceramic phase, the work progressed toward the optimization of the

chemistry of the ceramic, to provide a stable, durable and predictable form for disposal or re-use. Shifting focus to the hazardous components of the subject contaminated scrap metal, the statement of work contained a series of efforts designed to verify CEP's ability to destroy the hazardous portion of the waste, and pave the way for future delisting efforts.

The combined results of the theoretical efforts and the experimental campaign served to inform a conceptual design for a facility to recycle contaminated scrap metal -- to produce decontaminated metal for re-use within the DOE complex, a syngas with significant fuel value and a ceramic product containing any uranium and transuranics in a durable final form.

RESULTS

Before designing the experiments to verify CEP's applicability to contaminated scrap metal, MMT undertook an extensive literature search to uncover previous work in related fields which could inform the experiments. Previous results reported in the literature using melt refining techniques with contaminated metals demonstrated that uranium and plutonium can be selectively removed from the metal phase and concentrated in a separable, vitreous oxide phase. Residual concentrations of 10nCi of such radioactive components had been achieved using the vitreous phase as the sole oxygen source to partition oxidized radioactive components from mild steel, stainless steel, nickel, copper and aluminum.

It was anticipated that CEP would offer superior capabilities to those of melt refining. Specifically, since CEP allows for co-feeds, such as oxygen, to be injected into the molten metal bath, the system provides for greatly enhanced oxidation of the radioactive components. In contrast, in melt refining, the vitreous phase is the only source of oxygen. Further, turbulence caused

by gas injection into the CEP bath facilitates mass transfer, leading to active partitioning of radionuclides.

MMT designed a series of bench scale experiments using radioactive surrogate materials to demonstrate the oxidation and partitioning of the 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-scale (250# metal bath) and demonstration-scale (2,000# and 6,000# metal baths). Hafnium was selected as the radioactive surrogate material due to its similarities in thermodynamic behavior (Figure 2) and physical properties (Table 1) 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, but was actually used as a feed material in several experiments and was also proven to effectively partition to the ceramic phase.

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 concentration. 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.
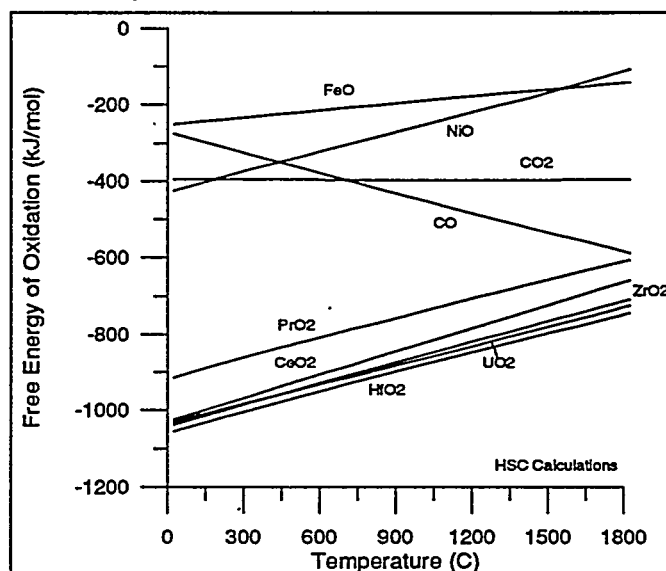

Figure 2. Identification of Radionuclide Surrogate

Table 1. Physical Properties of Uranium and Surrogates

Element	Oxide		Metal	
	m.p. (°C)	Density	m.p. (°C)	Density
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 exceeded the contract's 98% objective in all experimental trials with detection of any trace amounts limited by the LDL. Table 2 summarizes the results. V1 refers to aluminosilicate vitreous compositions while V2 refers to borosilicate vitreous compositions. Exact details of the optimum vitreous phase composition are proprietary.

Table 2. 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 demonstrate uniform distribution of any trace amounts of hafnium across the metal (Figures 3a and 3b). This indicates that transport to and incorporation in the oxide phase is very efficient under CEP operating conditions.

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 4a 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 4b, where hafnium is uniformly distributed. This is the desired vitreous radionuclide capture and stabilization.
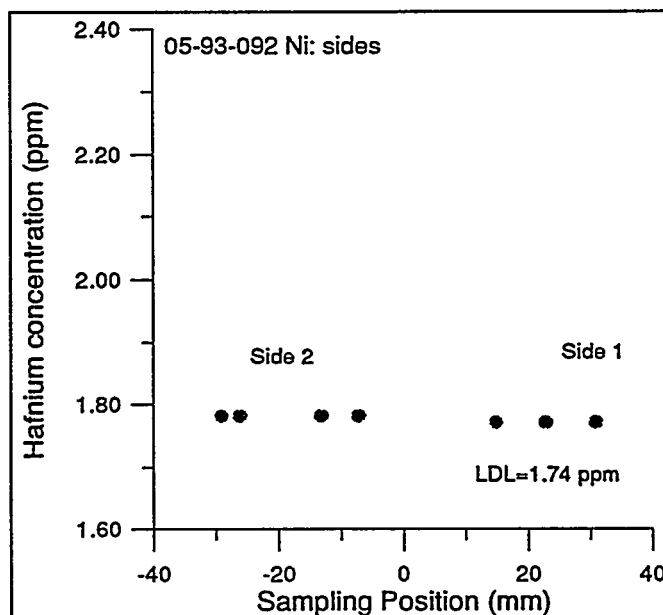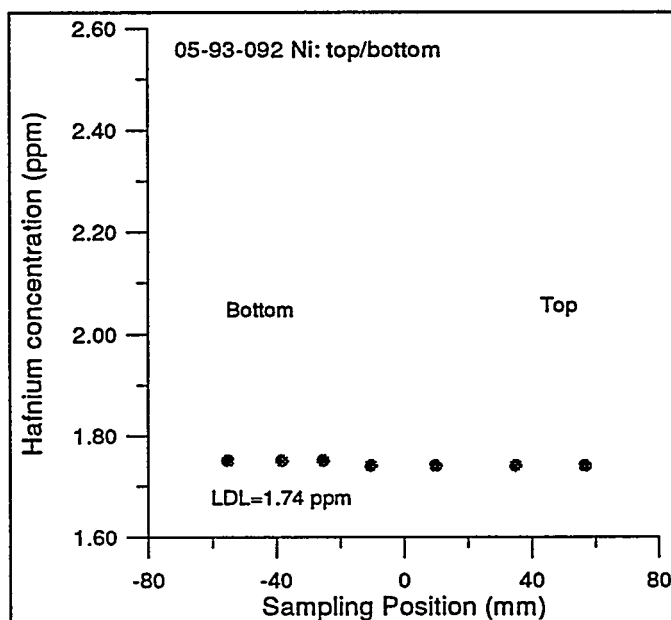

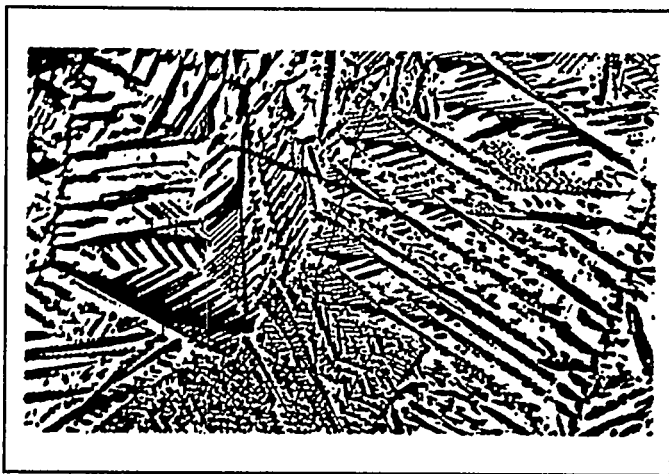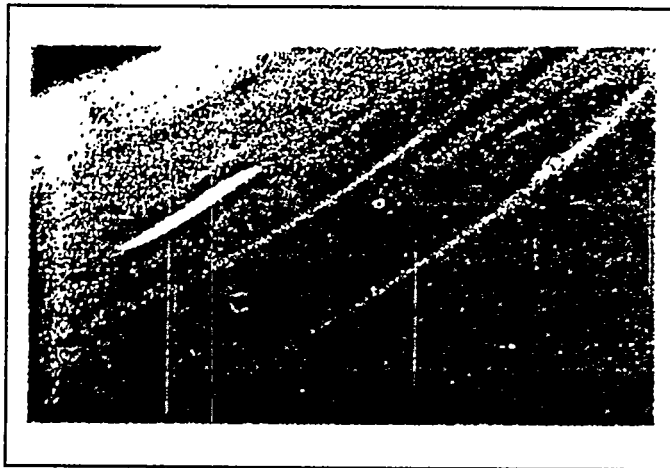**Figure 3a. Sampling across Radius of Metal**

Figure 3b. Sampling from Top to Bottom of Metal

Figure 4a. Backscatter Image: Phase Separation Exhibited

Figure 4b. Backscatter Image: No Phase Separation Exhibited

The investigation of the destruction capabilities of 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 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. Gaseous product generation utilizing an iron bath was demonstrated on a demonstration-scale prototype. Chlorinated waste feed surrogates and listed chlorinated waste streams were processed. Halogenated streams processed include contaminated metal components (including some chlorinated plastics) and RCRA-listed streams K019, K020 (heavy residuals from ethylene dichloride and vinyl chloride production) and F024 (chlorinated aliphatics). Chlorine partitioning as anhydrous hydrogen chloride and iron chloride were consistent with thermodynamic predictions and bench-scale data. Hydrocarbon components of the feed were converted to commercial-grade synthesis gas.

Throughout the demonstration-scale CPU and gas handling unit there are 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 analysis is performed to enable third-party analysis down to ppb levels via established EPA methods. Mass spectrometer samples are drawn on-line and gas composition measurements are taken every twenty seconds for feed-back process control.

Analysis of CPU off-gas product quality indicates that DREs $\geq$ 99.9999% are achieved for all feeds (Table 3). Chlorinated aromatics, plastics and straight-chain chloro-organics have been successfully converted to synthesis gas, ceramic products and hydrogen chloride. Data is also shown for CEP of aromatic species and organically-bound nitrogen to demonstrate the high DREs achievable for complex compounds and the preclusion of NO_x formation (LDL < 1 ppm), as confirmed by third-party evaluation.

Table 3. Halogenated Feeds Processed at Demonstration Scale

| Feed | Waste Minimization Performance | | | Environmental Performance | | |
	Product Recovery	% of feed Recycled	Residual	DRE	TCLP	Trace
F024/ Fuel oil/ chlorotoluene	Syngas HCl gas	82% to syngas 13% to HCl gas < 1% to ceramic	Dust Negligible	≥ 99.9999%	Passes TCLP	PICs < LDL[1] of 1 ppm CO_2 < 1% NO, SO_x < LDL of 1 ppm
K019/K020[2]/ 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
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
Contaminated Metals	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
K027[3]	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

[1] LDL = Lower Detection Limit.
[2] EPA listed hazardous waste stream: ethylene dichloride/vinyl chloride heavy ends.
[3] EPA listed hazardous waste stream: toluene diisocyanate distillation residues.
[4] As measured by on-line mass spec.
[5] As measured by third party analytical equipment placed on-line.

A description of the demonstration-scale processing of RCRA waste F024 exemplifies prototype operations at MMT's Recycling-R&D Facility. The chlorinated waste mixture (17.6% Cl) shown in Table 4 was fed to the CPU. Oxygen was co-fed as a reactant to form CO and natural gas was fed as a tuyere coolant. An iron bath (2.5 wt% < [C] < 3.0 wt%; 2,600°F < T < 2,750°F) with a ceramic phase was employed.

Table 4. F024 Chlorinated Waste Feed Composition

Feed Component	Approximate Wt% of CPU Feed
F024 (RCRA chlorinated aliphatic waste)	21.6
Fuel Oil	63.6
Chlorotoluene	5.0
Chlorobenzene	9.8

Table 5. Gas Product Composition from Chlorinated Waste Processing

Gas Product Component	Approx. Mol%	Approx. Wt%
Hydrogen, H_2	47	6
Carbon Monoxide, CO	50	86
Hydrogen Chloride, HCl	3	7

Carbon Dioxide, CO_2, concentrations were < 1 mol%; Gas compositions based upon Ar tracer gas

The product gas composition, given in Table 5, shows the generation of products, synthesis gas and anhydrous HCl, from the chlorinated wastes. Material balance closure on the major feed constituents, C, H and O, was 94.5%, 100.1% and 103.6%, respectively.

The product gases were extremely pure. Total hydrocarbon concentrations (C_2+) in the off-gas were ≤ 5 ppm. Methane concentrations were

consistent with thermodynamic predictions ($\approx$ 50 ppm). NO_x and SO_x were not detected to the on-line lower detection limit of 3 ppm and 1 ppm, respectively. Summa canister samples from the off-gases, subjected to EPA TO-14 analysis, demonstrated destruction and removal efficiencies (DREs) of the principal organic hazardous constituent (POHC) $\geq$ 99.9999% (Table 6).

Table 6
DREs Based on Multiple Chlorinated
Organic Feed Constituents for CEP of F024

Feed Constituent	DRE
1,1,2-Trichloroethane	$\geq$ 99.9999%
Chlorobenzene	$\geq$ 99.9999%
1,1,2,2-tetrachloroethane	$\geq$ 99.9999%
Trichloroethene	$\geq$ 99.9999%
Note: Data based upon the consistent results of 10 different samples	

The demonstration-scale data verifies the thermodynamically-predicted partitioning of chlorine in an iron bath and establishes CEP's ability to generate high-quality products from chlorinated RCRA wastes. Chlorine was successfully recovered as anhydrous HCl. The feed conversion exceeded 99.9999% and the product gases contained no undesired species. The ceramic phase formed a non-leachable (TCLP), durable glass product.

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 dioxin: excess free O_2 ($\geq 10^{-3}$ 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).[i,ii,iii,iv] 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 O_2 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 a wide variety of aromatic feeds, isocyanates, chlorinated plastics (PVC and polystyrene) and chlorinated solvents. The DRE data is based upon third-party summa-canister analysis using TO-14 analysis.

FUTURE WORK

The optimization of Catalytic Extraction Processing for the recycling of contaminated scrap metal by the DOE will require further efforts in four areas: bulk solids addition, delisting of the product phases, separation of chemically similar metals and progression of the conceptual design.

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