DECONTAMINATION OF METALS BY MELT REFINING/SLAGGING: FIRST YEAR PROGRESS REPORT

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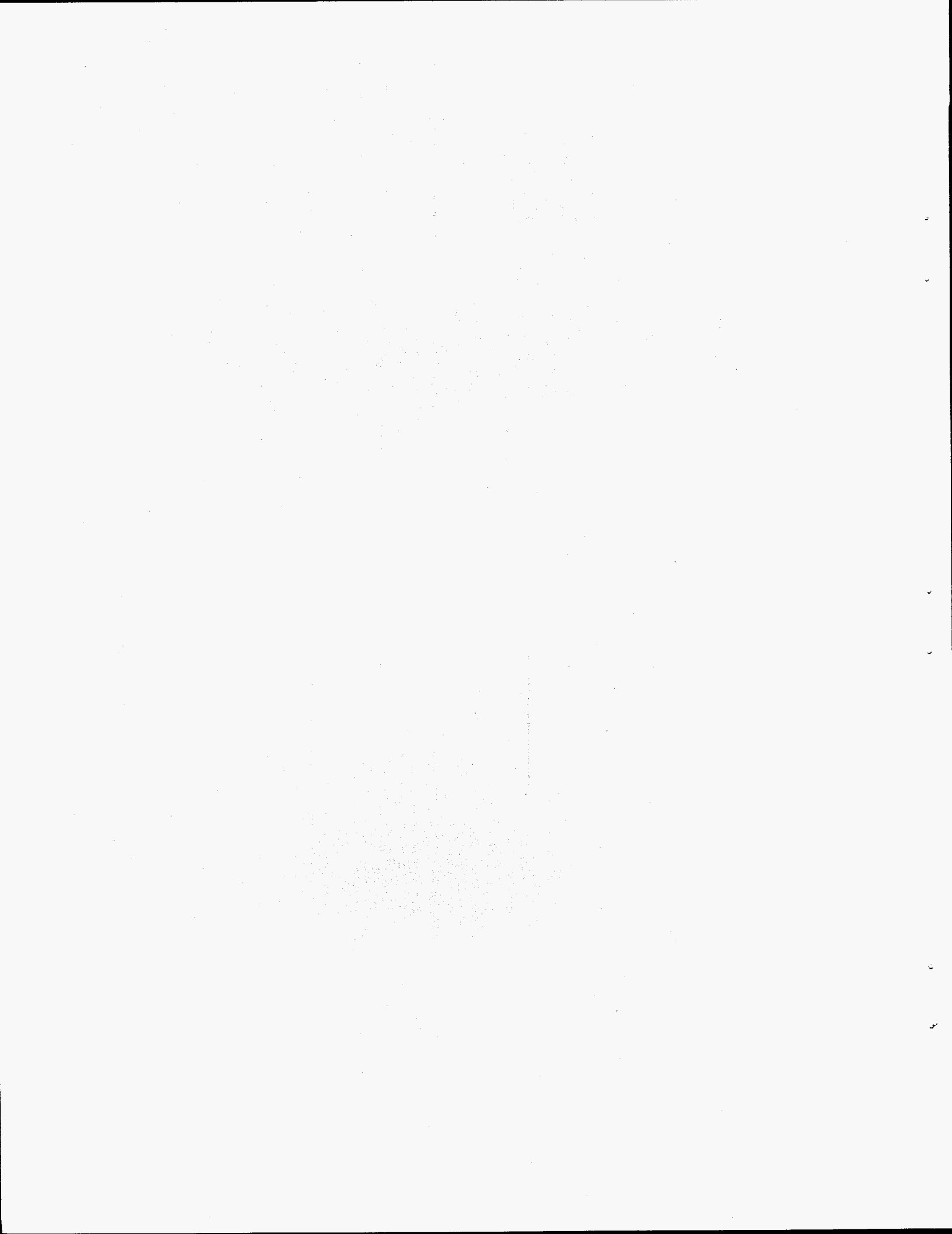**Westinghouse Idaho Nuclear Company, Inc.**

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EXECUTIVE SUMMARY

As the number of nuclear installations undergoing decontamination and decommissioning (D&D) increases, current radioactive waste storage space is consumed and establishment of new waste storage areas becomes increasingly difficult. The problem of handling and storing radioactive scrap metal (RSM) gains increasing importance in the DOE Environmental Restoration and Waste Management Program. To alleviate present and future waste storage problems, Westinghouse Idaho Nuclear Company (WINCO) is managing a program for the recycling of RSM for beneficial use within the DOE complex. As part of that effort, Montana Tech has been awarded a contract to help optimize melting and refining technologies for the recycling of stainless steel RSM. The scope of the Montana Tech program includes a literature survey, a decontaminating slag design study, small scale melting studies to determine optimum slag compositions for removal of radioactive contaminant surrogates, analysis of preferred melting techniques, and coordination of pilot scale melting demonstrations (100-500 lbs) to be conducted at selected commercial facilities. This program will identify methods that can be used to recycle stainless steel RSM which will be used to fabricate high and low level waste canisters for the Idaho Waste Immobilization Facility. This report summarizes the results of an extensive literature review and the first year's progress on slag design, small-scale melt refining of surrogate-containing stainless steel (presently only a three month effort), and pilot-scale preparation of surrogate master ingots.

There are a significant number of publications that include information on decontamination of radioactive scrap materials, e.g., a search of Chemical Abstracts alone shows over 350 publications. At this time approximately 280 publications have been identified that are related to the decontamination of metallic scrap. A large number of literature databases have been searched. Titles, abstracts, and publications have been recovered and reviewed. Information and experimental test results have been summarized in a previous publication (Worcester, et al, 1993) and will not be repeated in this report. Test work (both bench scale and larger scale) results described in the published literature to date demonstrate that slagging decontamination of uranium and plutonium from steel and stainless steel is a potentially effective treatment technology. Based on trends found in the literature, basic calcium-aluminum-silicate slags (with additives such as ferric oxide and calcium fluoride) appear to be effective steel decontaminators. Based solely on the presently available literature data optimum decontaminating slag compositions for stainless steel RSM cannot be specified.

The present research program involved selection of cerium, cesium, lanthanum, neodymium, strontium and cobalt as non-radioactive surrogates to represent radioactive constituents which might be found in RSM stored or still in use at DOE facilities. Selection was based on high temperature thermochemical similarities between the surrogates and anticipated radioactive contaminants found in RSM. Selected surrogates were added to a cold hearth plasma master melt to provide uniform starting material for subsequent small scale melt/slagging experiments. Cerium, lanthanum, and neodymium were successfully retained in the master melt at the 500 ppm level. Cesium and strontium were only retained in the master melt at the part per million concentration level. Cobalt was present in the initial stainless steel scrap (Type 304) and was not added as a surrogate, because of its interference with lanthanum detection by neutron activation. Melting fluxes were selected as a result of the literature search and thermochemical calculations performed using the CSIRO/MONASH Thermochemistry System. This program was then used to qualitatively predict the potential partitioning of surrogates into the metal, slag, and gas phases during experimental melting. A series of ten induction melt/slagging experiments were performed to explore the effectiveness of a "borate" steelmaking slag in removing surrogates from the master melt. Preliminary results show removal of surrogates to "low ppm" levels (in general, less than ten ppm) that match decontamination levels established in the literature for uranium. Additional analytical techniques are being pursued to establish surrogate levels in the "decontaminated metal." A 250-lb pilot scale cold hearth plasma melt was conducted to confirm the effectiveness of the "borate" slag. Analytical data from that melt are not yet available.

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SECTION ONE: INTRODUCTION

1.1. Background

As the number of nuclear installations undergoing decontamination and decommissioning (D&D) increases, current radioactive waste storage space is consumed and establishment of new waste storage areas becomes increasingly difficult. The problem of handling and storing radioactive scrap metal (RSM) gains increasing importance in the DOE Environmental Restoration and Waste Management Program. To alleviate present and future waste storage problems, Westinghouse Idaho Nuclear Company (WINCO) is managing a program for the recycling of RSM for beneficial use within the DOE complex. As part of that effort, Montana Tech has been awarded a contract to help optimize melting and refining technologies for the recycling of stainless steel RSM. The scope of the Montana Tech program includes a literature survey, a decontaminating slag design study, small scale melting studies to determine optimum slag compositions for removal of radioactive contaminant surrogates, analysis of preferred melting techniques, and coordination of pilot scale melting demonstrations (100-500 lbs) to be conducted at selected commercial facilities. This program will identify methods that can be used to recycle stainless steel RSM which will be used to fabricate high and low level waste canisters for the Idaho Waste Immobilization Facility. This report summarizes the results of an extensive literature review and the first year's progress on slag design, small-scale melt refining of surrogate-containing stainless steel (presently only a three month effort), and pilot-scale preparation of surrogate master ingots.

1.2. Literature Survey/Annotation

An extensive search of several computerized databases, collection and review of much of the published literature on melt/slag decontamination refining, annotation of the available literature and publication of the results have been completed as a part of the present study. The results of the literature review are summarized here and are reported in detail in a recently published report *Decontamination of Metals by Melt Refining/Slagging-An Annotated Bibliography* (Worcester, et al, 1993). The authors of the report summarized currently available radioactive scrap metal (RSM) decontamination melt refining technology, presented extensive flux composition versus final melt contaminant concentrations for a variety of ferrous and non-ferrous metals, analyzed melting methods conducive to slagging decontamination, proposed experimental directions for the WINCO/Montana Tech program and the Department of Energy's (DOE) Environmental Restoration and Waste Management

Program, and discussed aspects and needs (apparent to the Montana Tech team) to enable a successful research and development program. A summary of the annotation follows.

There are a significant number of publications that include information on decontamination of radioactive scrap materials, e.g., a search of Chemical Abstracts alone shows over 350 publications. Approximately 280 publications have been identified that are related to the decontamination of metallic scrap. Test work (both bench scale and larger scale) results described in the published literature demonstrate that slagging decontamination of uranium and plutonium from steel and stainless steel is a potentially effective treatment technology. Based on trends found in the literature, basic calcium-aluminum-silicate fluxes (with additives such as ferric oxide and calcium fluoride) appear to be effective steel decontaminators. Optimum decontaminating flux compositions cannot be specified based solely on the presently available literature data.

At present it appears that removal of most radionuclides by slagging and volatilization holds good possibilities for the treatment of steel scrap. The same slagging/volatilization possibilities appear to exist for stainless steel, except for the specific elements that constitute stainless steel. Radionuclides of iron, cobalt, nickel, manganese and chromium will be retained to a large degree in the metal product. These radionuclides could be incorporated in a melt from two potential sources: a) metal that was exposed to a neutron flux in a reactor, and/or b) metal that would have incompletely removed surface contamination containing these radionuclides.

The review revealed that the technological community has selected two technologies for large scale melt/consolidation of ferrous RSM, i.e., coreless induction and electric arc furnace (EAF) melting. The choice between these two technologies involves many factors. The main factors favoring coreless induction are better melt agitation, easier fume control, and rapid heatup. On the other hand, the EAF provides lower cost as heat sizes increase, accommodates larger scrap section sizes, allows for easier modification of melt composition, and provides a greater margin of reliability and safety because of the absence of the water cooled induction coil.

It appears quite obvious that melt decontamination alone will not provide steel which qualifies for free release, particularly if the trend reflected in Europe in 1989 (Janberg, 1990) toward lowering free release limits from 3.7 Bq/g to 0.1 Bq/g continues. Essentially none of the products (discussed in the large scale melting section of the literature review report) could be released under the criteria established in Europe in 1989. It might be argued that free or controlled release is not necessary. Consolidation of RSM and removal of volatile and easily oxidized radionuclides could be accomplished in DOE-controlled melting facilities. Melt

consolidated and characterized RSM from these facilities could then be released, on a controlled basis, to the steel industry for efficient incorporation into large heats for manufacture of nuclear waste or spent fuel canisters.

Although the present program deals specifically with stainless steel (Type 304) RSM, the authors included published information on the melting of stainless steel, mild steel, nickel, aluminum, uranium, copper, lead, zinc and plutonium in the literature review publication. Experience gained with melting and slagging these materials is directly applicable to radioactively contaminated stainless steel.

Several laboratory scale and large scale melt consolidation programs have been conducted during the past thirty years. Although the major tonnage has been produced by the treatment of mild steel, relatively large scale treatment efforts have also been conducted on stainless steel, nickel, and aluminum. Although the degree of cleanup varied from one program to the other, a large degree of success has been achieved by melt refining for reducing the concentrations of lanthanides, actinides, and most other fission products that are easily oxidized. On the other hand, melt refining to remove troublesome transition elements from stainless steels, such as cobalt and technetium, has met with little success. Efforts to decontaminate aluminum have also been much less successful, as might be expected from the consideration of the thermodynamic properties of the radionuclide-aluminum systems.

1.3. Status of Large-Scale Melt Consolidation/Refining

Considerable large scale melt consolidation experience exists for melt consolidation/refining of ferrous RSM. Both arc and coreless induction furnaces of up to 20 tonne capacity have been employed. Since many of these tests were for volume reduction, very limited slag composition data were reported. A summary of large scale world wide ferrous melt consolidation/refining programs is presented in Table 1.1, pages 4 and 5.

Inspection of Table 1.1 reveals that varying degrees of final ingot contaminant concentration were achieved. It appears quite obvious from the large scale test work that melt decontamination alone will not provide steel which qualifies for free release, particularly if the trend reflected in Europe in 1989 (Janberg, 1990) toward lowering free release limits from 3.7 Bq/g to 0.1 Bq/g continues. In addition, very little data are presented in the scientific literature that provides insights into the actual removal efficiencies achieved. Starting ingot and final ingot contaminant concentrations are required for removal efficiency calculation. Slag removal efficiency is important when determining the slag/metal weight ratio needed for adequate melt cleansing. This lead the authors of this report to conclude that it would be desirable to establish contaminant input levels prior to individual melt/slag refining experiments. Therefore, a master ingot was prepared that contained

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known concentration of several selected surrogate elements (discussed in Section 3.2).

TABLE 1.1. SUMMARY OF LARGE-SCALE FERROUS MELT CONSOLIDATION/REFINING PROGRAMS

REFERENCE/COUNTRY/ (LOCATION)	TYPE/SIZE OF FURNACE	TOTAL WEIGHT MELTED	MATERIAL MELTED	INGOT CONTAMINANT LEVEL
Peulve (1992)/France/ (Marcoule)	Arc/15 tonne	2,580 tonne	Cast iron	"low-<several dozen Bq/g; contaminated< 3,000 Bq/g"
Sappok (1992)/Germany/ (Siempel-kamp)	Induction/ 20 tonne 3.2 tonne	2,000 tonne 2,500 tonne	Carbon and stainless steel	Not Reported
Mies (1991)/Germany	Same as above	500 tonne	Carbon steel	<0.3 Bq/g
Thoma (1990)/Germany/ (EIRAM)	Induction/2 tonne	150 tonne	Carbon steel	<1 Bq/g
Gomer (1985)/UK/ (Swinden, Grangetown, Sheffield)	Induction/0.5 tonne Arc/5 tonne and 150 tonne 3 tonne basic O_2	2 tonne diluted to approx. 22 then re-diluted	Carbon steel	2×10^{-6} uCi/g with dilution-then diluted to deminimus
Nakamara (1992)/Japan/ (JPDR)	Induction/0.5 tonne	Approx. 5 tonne (11 heats)	Carbon and stainless steel	Approx. 15 Bq/g in spiked ingots
Menon (1990)/Sweden/ (Studsvik)	Induction/1.5 tonne	190 tonne (93 heats)	90 % Carbon, 10 % stainless steel	<3.5 Bq/g for stainless
Mautz (1975a)/USA	Arc/10 ton	27,000 ton (2037 heats)	Carbon steel	0.4 ppm U Avg. 3.5 ppm max.
Mautz (1975a)/USA	Arc/10 ton	2,200 ton (218 heats)	Stainless steel	0.6 ppm U Avg. 3.2 ppm max.
Large, SEG (1993)/USA	Induction/20 ton	2,200 ton	Carbon steel (to be rolled into plate)	<10 mR/hr

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REFERENCE/COUNTRY/ (LOCATION)	TYPE/SIZE OF FURNACE	TOTAL WEIGHT MELTED	MATERIAL MELTED	INGOT CONTAMINANT LEVEL
Echols, SEG (1993)/USA	Induction/20 ton	2,735 ton	Carbon steel (cast to shield blocks)	<10 mR/hr
Larsen (1985a)/USA/ (INEL)	Induction/ 1,500 lb	78 ton (123 heats)	Carbon and stainless steel	21 pCi/g Avg.- 27 pCi/g max. Co-60

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SECTION TWO: RESEARCH PROGRAM

2.1. Objectives

The scope of the Montana Tech research program includes a literature survey, a decontaminating slag design study, laboratory scale melting studies to determine optimum slag compositions for cleansing radioactive contaminant surrogates from the stainless steel, analysis of preferred melting techniques, and coordination of pilot scale melting demonstrations (100-500 lbs) to be conducted at selected facilities. This program will identify methods that can be used to recycle stainless steel RSM which will be used to fabricate high and low level waste canisters for the Idaho Waste Immobilization Facility.

The specific objectives of the Montana Tech research program include the following components:

- Review the literature as it relates to decontamination of radioactive elements from stainless steel. Prepare an annotated summary of the published literature.

- Design appropriate slag formulations for use in a laboratory experimental study.

- Investigate the usefulness of calculational programs to predict the thermodynamic distribution of species between gaseous and condensed phases as a function of a number of system variables, e.g., temperature, impurity content, selected additive flux constituents, and gas composition.

- Conduct laboratory experimental studies and thermodynamic calculations to optimize the selection of appropriate slag formulations.

- Conduct laboratory experimental studies and thermodynamic calculations to optimize the selection of appropriate refractories for the selected slag formulation(s).

- Coordinate pilot scale studies at commercial facilities to demonstrate effective decontamination technology(s) for slag/melt refining.

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2.2. Approach to Program

2.2.1. Introduction

The literature provided little information on input RSM contaminant concentrations, which would allow prediction of RSM contaminant removal efficiencies. Slag removal efficiency is important when determining the slag/metal weight ratio needed for adequate melt cleansing. This lead the authors of this report to conclude that it would be desirable to establish contaminant input levels prior to individual melt/slag refining experiments. Therefore, a master ingot was prepared that contained known concentration of several selected surrogate elements. The approach selected for this effort involved melting a 300 pound Type 304 "master ingot" containing surrogates representing radioactive contaminants. This ingot was sectioned and analyzed chemically to characterize the surrogate concentration. These characterized sections provide the starting material for the laboratory scale (approximately two pounds) induction melt/slagging experiments. The following sections describe selection of surrogates and slags, and the thermochemical approach pursued.

2.2.2. Selection of Surrogates

Surrogates used in the present study include naturally occurring isotopic mixtures of cerium, strontium, neodymium, lanthanum, and cesium. Cerium and strontium represent radioactive isotopes of these elements, while neodymium, lanthanum, and cerium were chosen to simulate the metal/slag distribution characteristics of uranium, plutonium, radioactive isotopes of the lanthanide elements, and the other actinide elements.

Cobalt is an important radioactive isotope. Therefore, its distribution must be determined during the experimental study. A surrogate for cobalt is not necessary because it is present in austenitic stainless steels. The distribution of cobalt was followed in the experimental study but additional cobalt was not added to the stainless steel. Limiting the presence of cobalt was important in order to facilitate instrumental neutron activation analysis (INAA) analysis of other surrogates. (personal communications between Roman Schmidtt, Oregon State University and Sam Worcester, Montana Tech).

Analysis of surrogate constituents is important. Cobalt is effectively analyzed by INAA. Cerium is difficult to analyze at low concentration levels with INAA but can be analyzed by induction coupled plasma-mass spectroscopy (ICP-MS). Cerium was included as a surrogate to represent the +4 valence state of uranium and plutonium. Lanthanum, with a +3 valence state, can be detected at 10-100 ppb (personal communications between Dr. Scott Hughes, Idaho State University and Sam Worcester, Montana Tech). Neodymium, although not as easy to detect as

lanthanum, mimics americium and curium, two actinides of potential importance.

In order to insure that melt refining techniques could be applied to surface and volume contaminated RSM, it was decided that surrogates be incorporated into the master melt in the metallic form. This represents the worst case condition.

Two primary approaches were considered for making the master surrogate alloy: (1) plasma cold hearth melting, and (2) vacuum (or inert gas) induction melting using a graphite crucible. Plasma cold hearth melting was chosen because of the following advantages:

- Eliminates potential reaction of the surrogates with the crucible

- Requires a simple feed material configuration

- Requires a simple surrogate addition procedure.

It was advisable to add the lanthanide surrogates in the metallic form, since the oxides have elevated melting points (CeO_2, m.p. > 2600°C; La_2O_3, m.p. 2300°C; and Nd_2O_3, m.p. 2270°C), all well above the melting point of stainless steel. If these elements were added as oxides, they most certainly would report to the slag phase rather than to the melt phase.

Metallic strontium and cesium surrogate additions posed some different problems (as compared to cerium, neodymium, and lanthanum) as a result of their low melting and boiling points. Cesium melts at 26°C and boils at 670°C, therefore, addition in the metallic form will result in volatilization of cesium. Cesium compounds with lower volatilities (than cesium metal) were considered for surrogate addition, e.g., CsF, Cs_2O_4, Cs_2CO_3, and Cs_2CrO_4. Strontium melts at 800°C and boils at 1150°C, also making its metallic addition undesirable. Strontium compounds considered for surrogate addition included: SrF_2, $SrCl_2$, $SrCr_2O_4$ and $SrCO_3$. Cesium and strontium fluoride compounds were chosen to be used in ingot preparation.

Surrogate additions to the master melt feedstock were in accordance with Table 2.1.

TABLE 2.1. SURROGATE ADDITIONS

SURROGATE	ELEMENTAL ADDITION, Wt. %	FORM	ADDITION, Wt. %
Cerium	0.100	Metal	0.100
Lanthanum	0.100	Metal	0.100
Neodymium	0.100	Metal	0.100
Strontium	0.100	SrF_2	0.143
Cesium	0.100	CsF	0.114

2.2.3. Selection of Slags

Slags for decontaminating stainless steel containing surrogates were initially selected based on the work of previous investigators (as reported in the literature annotation publication, Worcester, et al, 1993, discussed in Section 1.3) and the selection was qualitatively validated by application of a thermodynamic equilibrium calculational program, e.g., the CSIRO/MONASH program.

Three flux compositions were initially recommended (Worcester and Twidwell, 1993a) for experimental study, e.g.,

- 30% SiO_2, 40% CaO, 10% Al_2O_3, 15% Fe_2O_3, 5% $Ca_2B_6O_{11}$, "borate"

- CaO-SiO_2-Al_2O_3-CaF_2 at a basicity index of 1.5, "fluoride"

- CaO-FeO-Fe_2O_3; nominally at 25% CaO, 40% Fe_2O_3, 35% FeO, "ferrite."

The first two listed fluxes are variations on normal steelmaking slag compositions, i.e., steelmaking slags are based on the constituents calcium oxide, silica, and aluminum oxide. Borate or calcium fluoride additions are included to provide increased slag fluidity. Ferric oxide is included in the flux formulation to increase the oxidative potential of the slag. The oxidative power of a given slag is dependent on its relative stability with respect to the oxide of the element to be recovered from a metal phase. In the present application (as is discussed in the following sections), the first flux (referred to here as the "borate" flux) will form a slag that is oxidizing to the surrogate elements. The more ferric oxide present-the more oxidizing the slag will be to the surrogates and to the stainless steel constituents. Therefore, the oxidizing power of the borate flux can be increased or

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decreased by controlling the ferric oxide content. The second listed flux (referred to here as the "fluoride" flux) will form a slag that will be oxidizing to the surrogate elements but not to the stainless steel major constituents (iron, chromium and nickel), i.e., this slag will have less oxidizing power than the "borate" slag. The third listed flux (referred to here as the "ferrite" flux) will form a slag that will have a very high oxidizing potential. Utilization of these three flux materials, therefore, provide the flexibility to the project for investigation of an extremely wide range of oxidizing potential slags.

From the thermodynamic calculational work and the laboratory and pilot-scale test work, it now appears that it is unnecessary to utilize a slag with a high oxidation potential.

2.2.4. Thermochemistry

The basis for the slag/melt refining program can be visualized graphically by considering the relative thermodynamic stability of the oxide phases for the slag constituents, the steel constituents and the surrogate constituents. Relative stability comparisons are normally made by constructing "Ellingham Diagrams", i.e., plots of free energy of formation of constituent oxides as a function of temperature.

The reactions of interest are depicted by the equations shown below:

$$2 M + O_2 = 2 MO_2$$

$$4/3 M + O_2 = 2/3 M_2O_3.$$
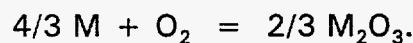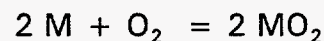
The free energy of formation for each individual oxide is based on one mole of oxygen gas (not per mole of oxide present).

The Ellingham plots for the major constituents of interest in the present study are presented in the following figures, e.g., Figure 2.1, stainless steel constituents; Figure 2.2, slag constituents; Figure 2.3, surrogate constituents. These figures can be used to illustrate that the surrogate elements have a greater affinity for oxygen than do the stainless steel constituent elements.

A simplified use of these diagrams is to consider that the lower an individual curve lies on the diagram, the more stable the oxide (in an oxidizing atmosphere), i.e., the more negative the free energy of formation the more stable the oxide. This is certainly an oversimplified generalization of the thermodynamics of the system because the actual thermodynamic description of the system depends on a number

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of factors, e.g., the constituents present, the constituent activities and interaction coefficients in the metal, slag, and gas phases. However, a qualitative estimate of the relative stability of metal oxides can be made by their relative positive in the Ellingham chart. The relative position of lanthanum (chosen to represent all the surrogate elements) oxide with respect to the steel constituent oxides is presented in Figure 2.4. Note that lanthanum oxide lies lower on the plot (lanthanum oxide has a lower free energy of formation than do the steel constituent oxides), i.e., lanthanum should react (with any oxygen in the system) to form lanthanum oxide in preference to the reaction of chromium, iron or nickel with oxygen. The relative position of lanthanum oxide with respect to the slag constituents (for a steel refining slag containing borate) is presented in Figure 2.5. Note that lanthanum oxide lies lower on the plot than the oxides for aluminum, boron and iron. Therefore, in a qualitative way, the surrogate element (dissolved in the stainless steel bath) should steal the oxygen away from the slag constituents, i.e., the less stable slag constituents should supply oxygen to the surrogate metals.

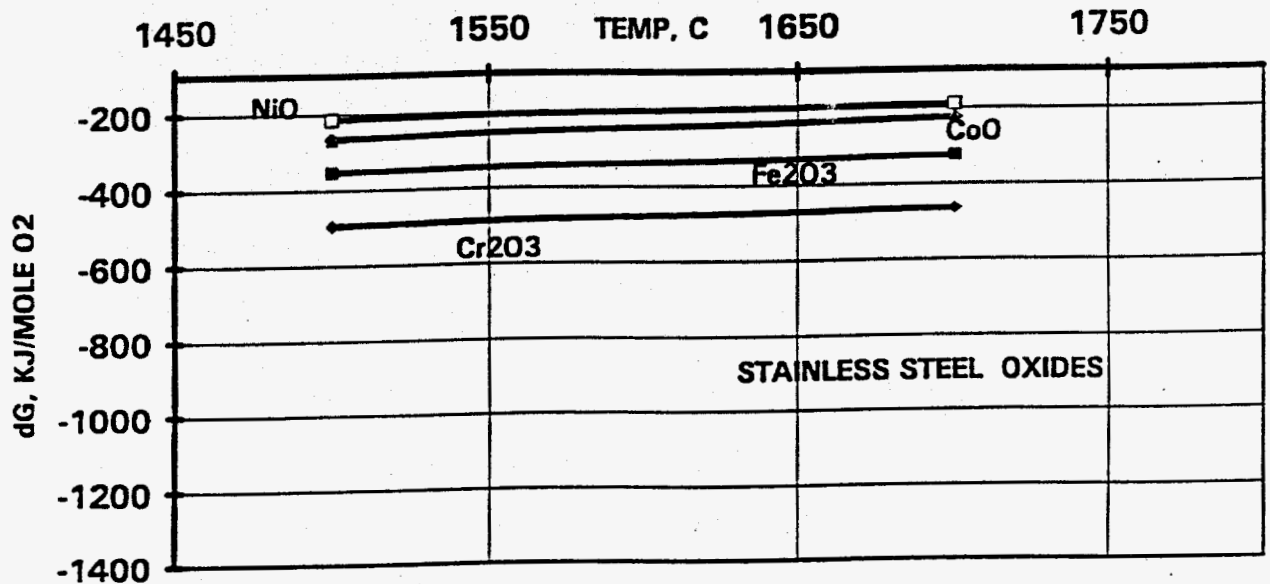Figure 2.1. Ellingham Diagram for Stainless Steel Constituents

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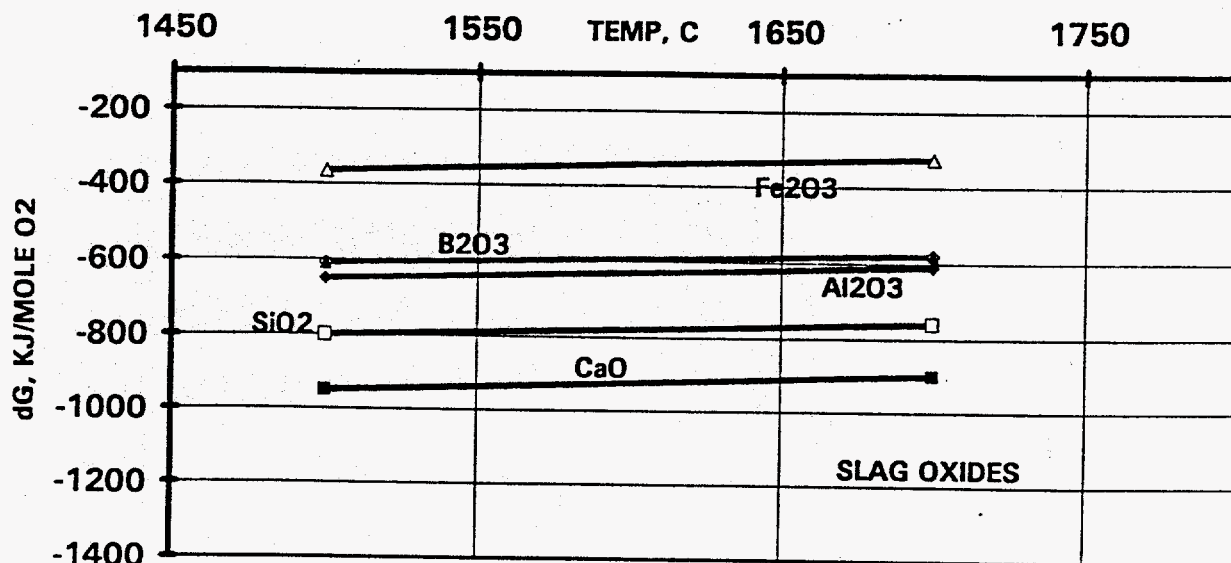
Figure 2.2. Ellingham Diagram for Slag Constituents
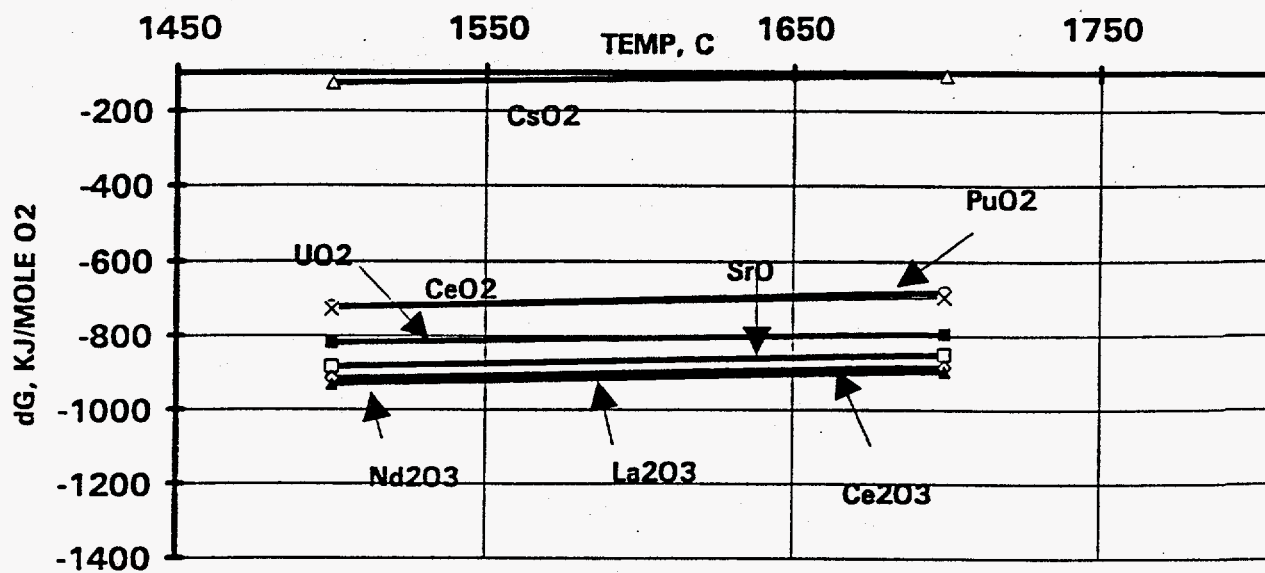
Figure 2.3. Ellingham Diagram for Surrogate Constituents

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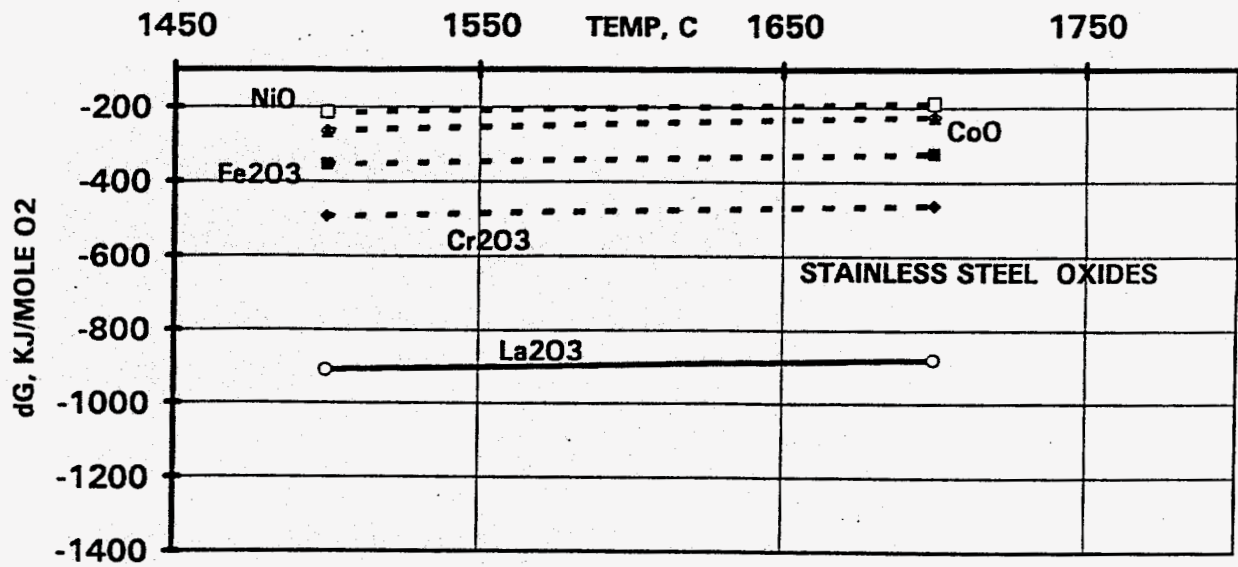
Figure 2.4. Relative Free Energy of Formation for Lanthanum Oxide Compared to Steel Making Constituents
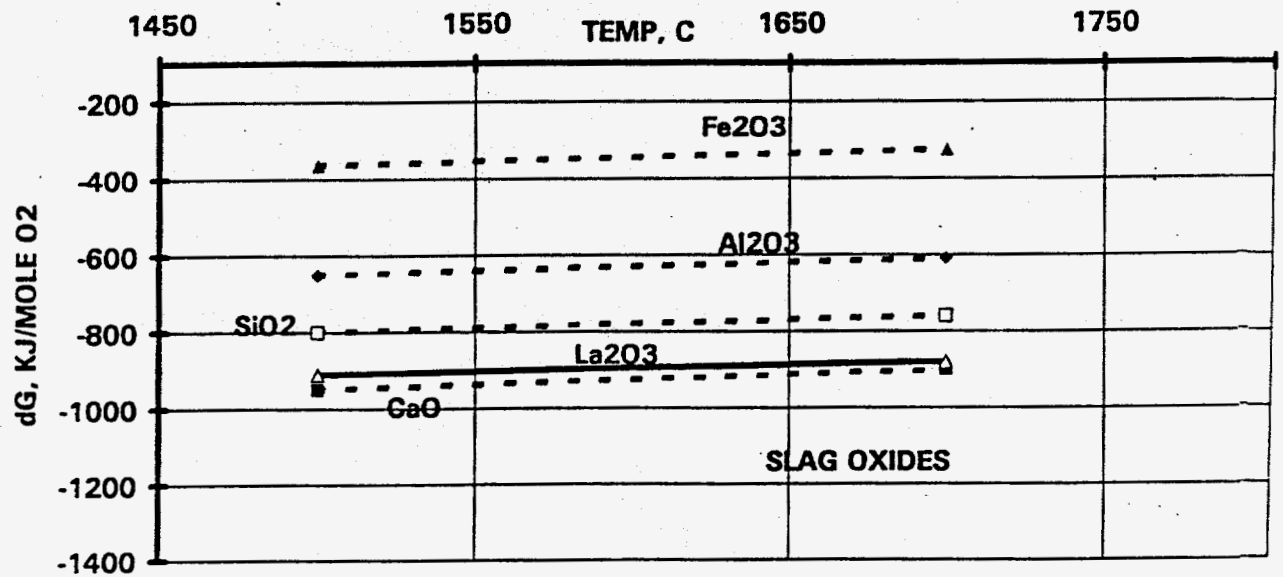
Figure 2.5. Relative Free Energy of Formation of Lanthanum Oxide Compared to Slag Forming Constituents

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2.2.5. Calculational Programs

A review of the usefulness of two thermochemistry calculation programs, CSIRO/MONASH (developed by the Australian Cooperative Science and Industry Research Organization over the past 15 years) and HSC (developed by Outokumpu Oy in Finland), has been made. This does not imply that the programs have been evaluated to determine if the calculational results will predict accurately experimental results for metal decontamination by slag cleansing. Insufficient thermodynamic data (especially for rare earth constituents in slags) presently exist for use of the programs as true modeling programs (although they have the capability for handling the calculations once the data are available). The value of the calculational programs is that they allow the user to rapidly calculate multicomponent complex reaction equilibria. It is up to the user to correctly set up scenarios that give results that can be useful in guiding and limiting required experimental test work.

The CSIRO/MONASH program is not very user friendly (one cannot point a mouse and click menus to accomplish the calculations). However, once the operational procedure is mastered the program has extensive calculational flexibility. The HSC program is Windows based, menu driven and very easy to use. However, it does not have the calculational flexibility of the CSIRO/MONASH program.

Both programs are very useful in asking "what if" questions and each provides the user guidance tools that should be useful in limiting the number of experimental studies and in interpreting and understanding the experimental results. Several example uses of the CSIRO/MONASH calculational program are presented below.

2.2.5.1. Master Ingot

A master ingot was prepared to provide sufficient surrogate containing stainless steel for all of the required laboratory scale experimental tests. Description of the preparation and characterization of the master ingot are presented in Sections 3.2 and 4.1. This alloy was prepared by plasma melting (under helium) the desired surrogates and stainless steel. The advantages of this preparation procedure are that the oxygen content could be controlled and that the metal would not be contaminated by contact with crucible materials. The preparation procedure was successful and resulted in an ingot of stainless steel containing appreciable concentrations of lanthanum, cerium, and neodymium. The ingot analyses are presented in Table 4.1, Section 4.1.

The CSIRO/MONASH calculational program was used to estimate the influence of oxygen on the presence of surrogate elements in stainless steel. Sufficient surrogate metals (lanthanum, cerium, neodymium) and fluorides (cesium and strontium) were initially added to dope the stainless steel to 1000 mg/kg (ppm). It

was assumed in the calculation program that all slag constituent activity coefficients were one; the temperature was 1600°C; and that the oxygen input per 100 grams of stainless steel was varied. The analytical and calculational results are presented for the metal phase in Table 2.2 and for the slag phase in Table 2.3. Note that in the presence of only a minor concentration of oxygen (0.005 grams oxygen/100 grams stainless steel) that the calculated surrogate concentration in the metal phase is approximately the input amount of surrogate for lanthanum, cerium and neodymium, and zero for cesium and strontium (Table 2.2). Note also that a small amount of oxygen significantly reduces the concentration of the surrogate metals in the stainless steel. The source of oxygen present in the plasma melt environment could be from the stainless steel surface or from slight contamination of the inert shrouding gas. The results of the calculation do show that only a relatively small amount of oxygen will force the distribution of the rare earth-surrogate elements to the slag phase (Table 2.3).

TABLE 2.2. PREPARATION OF MASTER INGOT: METAL PHASE

ELEMENT	MEASURED, PPM IN METAL		CALCULATED, PPM IN METAL						
	Skull[1]	Ingot[2]	Grams Oxygen Present/100 grams of Stainless Steel						
			0.005	0.025	0.045	0.065	0.085	0.105	0.125
Cs	<DL	<DL	<0.0	<0.0	<0.0	<0.0	<0.0	<0.0	<0.0
Sr	<DL	<DL	<0.0	<0.0	<0.0	<0.0	<0.0	<0.0	<0.0
Ce	530± 60	352±1 1	1018	517	160	9	1	<1	<0.0
La	140± 80	448±4 5	1018	534	199	12	2	<1	<0.0
Nd	357± 100	630±3 2	1016	513	159	9	1	<1	<0.0

1 Skull sample analyzed by x-ray fluorescence, Ashe Analytics. The skull metal may not be representative of the master ingot.
2 Master ingot samples analyzed by neutron activation, Oregon State University.
3 CSIRO/MONASH program. Assumptions include: activity coefficients for all slag constituents assumed to be one except for CaO (0.056), SiO_2 (0.167). All surrogate constituent activity coefficients in the metal were assumed to be one. Other metal constituent activity coefficients in the metal were estimated by using the Lupis-Elliott interaction coefficient model.

TABLE 2.3. PREPARATION OF MASTER INGOT: SLAG PHASE

ELEMENT	MEASURED, % IN SLAG[1]		CALCULATED, % OXIDES IN SLAG[2]				
	As Metals	As Oxides	Grams Oxygen Present/100 grams of Stainless Steel				
			0.025	0.045	0.065	0.085	0.105
Cs	0.027	0.02 as CaF	<0.0	<0.0	<0.0	<0.0	<0.0
Sr	28.4	23.9 as SrF_2	18.6 as SrF_2	15.3 as SrF_2	14.2 as SrF_2	14.2 as SrF_2	14.2 as SrF_2
Ce	9.1	12.5	28.7	28.7	28.7	28.7	28.7
La	18.9	26.0	24.0	27.4	28.7	28.7	28.7
Nd	15.3	21.0	28.8	28.6	28.7	28.5	28.7

1 Slag chipped from skull metal. Analyzed by Ashe Analytics.
2 CSIRO/MONASH program. Assumptions include: activity coefficients for all slag constituents assumed to be one except for CaO (0.056), SiO_2 (0.167). All surrogate constituent activity coefficients in the metal were assumed to be one. Other metal constituent activity coefficients in the metal were estimated by using the Lupis-Elliott interaction coefficient model.

One of the questions of concern for subsequent melt/slag contact experiments was whether the surrogates would "getter" the oxygen from the available oxygen sources (the gas or slag atmosphere) in preference to the steel constituents. The master ingot preparation test results and the CSIRO/MONASH program calculational results have both demonstrated that the rare-earth surrogates were, indeed, distributed to the slag phase in preference to the steel component constituents (such as iron, chromium and nickel). Chromium oxide (the most stable oxide of the steel constituent elements) was not detected in the slag phase and the calculational results also show that chromium oxide would not form until a greater amount of oxygen was available than that required for oxidation of the surrogate elements. When the oxygen requirement for the surrogates is satisfied, then chromium oxidizes, e.g., at an oxygen addition of 0.125 gm oxygen/100 gm stainless steel the chromium content of the slag is estimated to be about four percent, at an oxygen addition of 0.145 gm oxygen/100 gm stainless steel the chromium content of the slag is estimated to be about 14 percent, at 0.205 gm oxygen/100 gm steel the slag chromium content is estimated to be 36 percent.

The successful preparation of a surrogate-bearing master ingot (in an inert gas atmosphere) has led to a pilot-scale test (recently conducted at RETECH, Ukiah,

CA). Results are now being collected and evaluated, i.e., a test to demonstrate the importance of controlling the melt oxygen potential. The test concept is described in Section 6.2 and calculational estimates for surrogate distribution are presented in Section 2.2.5.2.

2.2.5.2. Metal/Slag Calculations

The CSIRO/MONASH calculational program has been applied to the present metal/slag refining problem. There is insufficient thermodynamic data available for the metal phase and for the slag phase to accurately model the distribution of steel and surrogate elements between the metal, slag and gas phases. However, qualitative distributions can be determined that can be used as a guide for planning experimental test work. The metal/slag system presently being investigated is the stainless steel/calcium-aluminum-silicate-borate slag/gas combination. The slag composition considered was based on the flux recommended by Reimann (1991) (30% SiO_2, 40% CaO, 10% Al_2O_3, 15% Fe_2O_3, 5% $2CaO.3B_2O_3$) for decontamination of stainless steel (referred to subsequently as the "borate" flux or "borate" slag). The activities of the major slag constituents (CaO, SiO_2, Al_2O_3) were assumed to be the same as in a steel refining slag (Elliott and McGleiser, 1963). All other constituents were assumed to be ideal, i.e., their activities were taken to be the same as their concentrations. The activities of the surrogate species in the steel solution were assumed to be ideal, i.e., the activity coefficients were assumed to be one. All the other species in the steel solution were modeled by using the Lupis-Elliott interaction coefficent formulation (CSIRO, 1993). "Calculational" questions included: what is the composition of the "equilibrium" slag expected if the starting flux is the "borate" flux (the slag composition will definitely change and changes may be very important in determining the useful operating temperature of the slag/metal system); and will the input slag be oxidizing to the constituents in stainless steel (also will the surrogate elements be oxidized preferentially to the chromium)?

Examples of what can be learned (on a qualitative basis) from the equilibrium calculations are illustrated below:

- In a system where the only oxygen source is the slag constituents (no water vapor or atmospheric oxygen present), the surrogates will be effectively removed by reacting with the oxygen in the slag phase, i.e., the surrogates in the stainless steel will be oxidized by "gettering" the oxygen from the less stable slag constituent oxides. In fact, the presence of ferric oxide (proposed to be added to the slag composition to provide an oxygen source) does not appear to be thermodynamically necessary, i.e., the other slag constituents apparently can supply the required oxygen to the surrogate elements.

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- The borate content in the equilibrium slag may be considerably decreased (over the amount added with the input flux) by distribution to the gas phase and (a minor amount) to the stainless steel phase (as much as 50-60% may be lost to the gas phase). This occurrence will certainly influence the liquidus temperature of the slag. If a strongly oxidizing slag is used, like the calcium ferrite containing slag (as was proposed in the original test plan), then chromium in the stainless steel will oxidize (and will, therefore, be decreased in the metal phase) and the slag liquidus temperature will certainly be raised. Therefore, there may be a problem in keeping the slag fluid at 1600° C if the borate content is decreased and/or the chromium oxide content is increased too high (phase diagrams indicate so). As a result of these noted effects it may be desirable to change the flux/metal input weight ratio (to keep the chromium oxide content in the slag phase at concentrations that will be appropriate to maintain a useful liquidus temperature) or reduce the oxidizing potential of the input flux so that only sufficient oxidizer is present to remove the surrogate elements (La, Nd, Ce), and not chromium, from the metal phase, or increase the amount of borate in the feed flux (to keep the liquidus temperature below 1600° C).

- It is very interesting to note that in a system containing the "borate" slag/stainless steel that has an oxidant source other than ferric oxide (such as water vapor), the equilibrium slag composition could be greater than fifty percent chromium oxide (and, therefore, the slag would be a mixture of liquid phase and precipitated solid phase at 1600° C). This assumes, of course, that equilibrium would be attained.

- In a water vapor containing system, the borate would be essentially lost to the gas phase as a hydroxyl specie, i.e., BHO_2. Loss of borate would influence the liquidus temperature, i.e., a decreased borate content would tend to raise the liquidus temperature.

2.2.5.3. Controlled Oxygen Potential Melt/Slag Refining

A controlled oxygen potential pilot-scale test melt has recently been conducted at RETECH (March 3, 1994). The test procedure is presented in Section 6.2. The test included the use of the calcium-aluminum-silicate-borate flux formulation presented earlier. Calculations have been performed to qualitatively estimate the

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expected concentrations and distributions of each surrogate element. The calculational results are presented in Tables 2.4-2.6. Experimental results will be forthcoming.

STAGE ONE

Conditions:

- No slag added
- Inert gas furnace atmosphere
- Only oxygen source: surface oxides were assumed to be at 0.025 gm oxygen/100 gms stainless steel because that level of oxygen resulted in calculated surrogate concentrations consistent with what was actually measured.

TABLE 2.4. CONCENTRATION AND DISTRIBUTION OF SURROGATE ELEMENTS: NO FLUX ADDED (CALCULATED)

ELEMENT	CONCENTRATION		DISTRIBUTION, %		
	Metal, ppm	Slag, % Oxides	Metal	Slag, as Oxides	Gas
Cs	<0.00	<0.0	<0.0	<0.0	100.0 as CsF
Sr	<0.00	18.6 as SrF_2	<0.0	26.2 as SrF_2	73.8 as SrF_2
Ce	517	28.7	57.4	42.6	<0.0
La	534	24.0	65.5	34.5	<0.0
Nd	513	28.8	64.2	35.8	<0.0

STAGE TWO

Conditions:

- Two percent slag added ("borate" composition)
- Inert gas furnace atmosphere
- Oxygen source: Slag constituents; no ferric oxide present.

TABLE 2.5. CONCENTRATION AND DISTRIBUTION OF SURROGATE ELEMENTS: BORATE FLUX WITHOUT FERRIC OXIDE (CALCULATED)

ELEMENT	CONCENTRATION		DISTRIBUTION, %		
	Metal, ppm	Slag, % Oxides	Metal	Slag, as Oxides	Gas
Cs	8	<0.0	0.8	0.1	64.1 as Cs 35.0 as CsF
Sr	1	1.8 as SrF_2 4.7 as SrO	0.1	30.5 as SrO 63.6 as SrF2	5.2 as SrF2 0.5 as Sr
Ce	<0	6.0	<0.0	100.0	<0.0
La	<0	6.0	<0.0	100.0	<0.0
Nd	N.I.	N.I.	N.I.	N.I.	N.I.
N.I. = Not included in calculation because of restriction on number of elements that can be considered in the CSIRO/MONASH program.					

STAGE THREE

Conditions:

- Two percent slag added ("borate" composition)
- Inert gas furnace atmosphere
- Oxygen source: Fifteen percent ferric oxide and other slag constituents

TABLE 2.6. CONCENTRATION AND DISTRIBUTION OF SURROGATE ELEMENTS: BORATE FLUX WITH FERRIC OXIDE (CALCULATED)

ELEMENT	CONCENTRATION		DISTRIBUTION, %		
	Metal, ppm	Slag, % Oxides	Metal	Slag, as Oxides	Gas
Cs	7	<0.0	0.7	0.1	54.3 as Cs 44.9 as CsF
Sr	0.5	4.7 as SrF_2 1.7 as SrO	0.0	31.6 as SrO 63.3 as SrF2	4.8 as SrF2 0.2 as Sr
Ce	<0	5.5	<0.0	100.0	<0.0
La	<0	5.5	<0.0	100.0	<0.0
Nd	N.I.	N.I.	N.I.	N.I.	N.I.

N.I. = Not included in calculation because of restriction on number of elements that can be considered in the CSIRO/MONASH program.

The controlled oxygen potential pilot-scale test should yield information concerning the effect of oxygen potential on the distribution of the surrogate elements between the metal and slag phases. The "borate" (no ferric oxide) flux should effectively remove the surrogate elements. The "borate" (with fifteen percent ferric oxide) flux should demonstrate that not only are the surrogate elements removed from the stainless steel bath, but that the oxygen potential is high enough to also remove a significant portion of chromium from the stainless steel bath (undesirable in actual practice). The test will also provide information concerning the usefulness of the equilibrium calculational technique for qualitatively predicting the distribution of surrogate and steel constituents to the metal, slag and gas phases.

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SECTION THREE: EXPERIMENTAL TEST PROGRAM

3.1. Experimental Test Facility

3.1.1. Description of Induction Melter

The investigators have chosen induction melting as the best melting method for laboratory scale testing in the scrap metal recycle program. Induction melting was chosen primarily because of the inherent melt stirring. Other advantages of induction melting are high heating rates, easier fume control, easy and fast start-up, and energy savings. Induction heating occurs by two energy loss mechanisms, Joule (I^2R losses) and magnetic hysteresis. When dealing with non-magnetic materials such as austenitic stainless steel, joule heating is the only energy loss mechanism. Joule heating is produced when electrical eddy currents are induced within a conducting material when it is placed in a dynamic magnetic field.

Montana Tech has installed a 15 KW/10 KHz induction furnace manufactured by the AJAX Magnethermic Corporation, see Figure 3.1. The furnace consists of two integrated units: first, a water cooled power supply operating on 480 V, 3-phase, 18 KVA power; and second, a table mounted 5-lb furnace connected to the power source through water cooled leads. An adjustable capacitor bank allows the operator to vary operating frequency and current ratios of the power source. Adjustability of the capacitor bank allows maximum furnace control when melting different size melts or when melting different kinds of metals. The power source is controlled by a rheostat dial on the control board when the furnace is operated in manual-control-mode. The operator's panel has direct reading frequency, power, and current meters. Because the furnace has automatic power control, operation learning is minimized and an inexperienced operator can become proficient in several melts. The furnace is currently operated in manual mode, but Montana Tech may develop a fully automated system which controls power output by melt temperature via the linear output signal of a two color pyrometer. The automated system would also digitally record power, current, frequency, time, and temperature during the melt cycle. The power supply unit is connected to a table mounted furnace through water cooled leads. The table mounted furnace houses a water cooled induction coil and is mechanically supported such that melts are manually poured from the furnace.
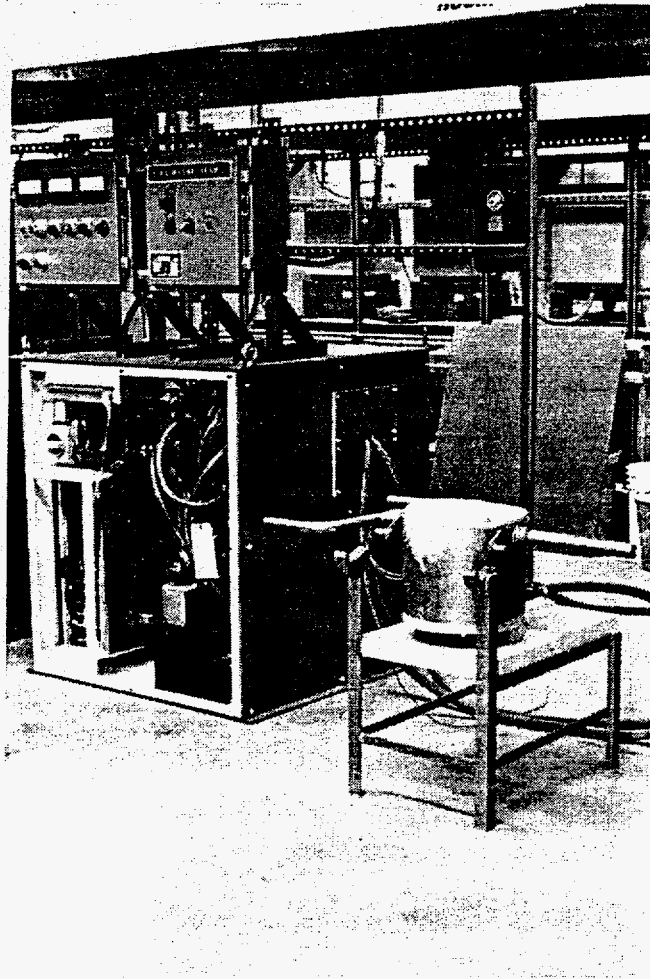
Figure 3.1. Photograph of the Induction Furnace Melt System

3.1.2. Temperature Measurement

A Modline R Series Two Color Pyrometer manufactured by IRCON Inc. has been installed above the furnace for temperature measurement. The two color pyrometer, also known as a ratio pyrometer, is insensitive to varying target material emissivity caused by dynamic target surface conditions or to a partially blocked optical path between the melt and the sensor by melt fumes. The pyrometer measures the intensities of two individual radiation wavelengths, and then computes actual temperature according to the ratio of these intensities. The pyrometer consists of two units: a sensing head, which is mounted directly above the induction table furnace; and an indicator unit, which is mounted onto the furnace power supply. Pyrometer measurement range is 900-1600°C and will tolerate a 95 percent reduction in radiation intensity. Temperature is digitally displayed on the indicator display, or can be fed into a controller via a 0-100 mVdc linear output signal for automated furnace control.

3.1.3. Induction Melter Crucible

3.1.3.1. Crucible Selection

A high alumina-chromium oxide refractory was chosen for fabrication of the furnace crucible used during the initial Montana Tech melt campaign. The refractory is Allied Mineral Products Scott-Ram Dri-Vibe 437A of composition Al_2O_3 86.9%, Cr_2O_3 7.5%, SiO_2 1.7%, TiO_2 3.2%, Fe_2O_3 0.2% and others 0.5%, and has a practical temperature limit of 1760°C. The primary application of the refractory as suggested by the manufacturer is coreless induction melting of stainless steel and other high temperature metals. During densification, the refractory's fused alumina base reacts with chromium oxide additive to form a chrome alumina solid solution resistant to slag and metal attack. The solidus of the refractory is approximately 2000°C.

Overall refractory selection was based on the resistance of the refractory to rapid chemical attack by both the slag and molten metal phases at furnace operating temperatures. The refractory must have adequate mechanical strength to withstand charging of the furnace, and likewise must have adequate thermal shock resistance to withstand the heating and cooling cycles, assuming sequential melting. Also, at the highest anticipated furnace operating temperature, the refractory must remain in the solid state, otherwise dissolution leads to failure. Reaction products of the refractory/melt interactions should not deleteriously contaminate the melt by decreasing the decontamination potential of the slag.

Regardless of refractory selection, some degree of chemical attack will occur at such high operating temperatures in an oxygen deficient melt. Thermodynamically it is predicted that the alumina-chromia refractory will show slight dissolution in the "borate" slag. The stability of the refractory, therefore, depends on the "kinetic" resistance of the crucible to the chosen slag environment. Other refractories are being considered, e.g., magnesia and chrome magnesite.

3.1.3.2. Crucible Fabrication

Crucibles used in the initial melt campaign were fabricated in a three-step process, where the first two steps involved the ramming of refractory into a green crucible, and the third was the densification process. The water cooled induction coil has a factory installed lining, which is the foundation of the crucible. In the first crucible fabrication stage, StarRam 140 (Al_2O_3 41.6%, CaO 1.08%, Fe_2O_3 1.35%, MgO 48.4%, SiO_2 7.6%) manufactured by American Refractories and Crucible Corporation, was rammed around a mold placed axially in the induction coil. This refractory was used to thermally protect the induction coil while providing mechanical support to the crucible refractory during melting. Following the molding of the StarRam 140, the liner mold was removed and a metallic crucible

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mold was placed within the liner. Next, Scott-Ram 437A was rammed between the metallic crucible mold and the insulating liner. After the layered ramming was completed, the green crucible was ready for densification.

During densification a stainless steel slug of metal was added to the inner metallic crucible mold. The temperature was slowly increased to 120°C and held for two hours and then slowly increased to 1300°C at a rate of 210°C per hour. After reaching the 1300°C temperature, furnace power was increased to melt the stainless steel slug and the metallic mold. The melt was then poured and subsequently discarded. After inspecting the refractory to ensure proper densification, the furnace crucible was deemed ready for melt testing. The entire densification process took a total of nine hours.

3.2. Preparation of Master Ingot

Montana Tech does not have facilities for handling radioactively contaminated material. Therefore, surrogate elements (to simulate radioactive contamination) were introduced into uncontaminated stainless steel (Type 304). The surrogate elements (cerium, cesium, lanthanum, neodymium, strontium) chosen for the present study were presented previously, Section 2.2.2.

The preparation of the surrogate/stainless steel master ingot was accomplished by melting stainless steel and surrogates in a cold hearth plasma melter located at RETECH, Inc. in Ukiah, California.

3.2.1. Preparation of Feedstock

The feedstock for the plasma melting was prepared at Montana Tech. The preparation required the fabrication of two six-inch feedstock pipes. The feedstock pipes were constructed of six-inch schedule-40 304 (in this study Type 304 is used to refer to both Type 304 and 304L) stainless steel pipe. Smaller diameter pipes and flat stock were placed inside the six-inch pipes in order to provide the necessary weight. All metal used in the feedstock construction, except for the surrogate elements and weld metal (ER308L), consisted of 304 stainless steel. The final lengths of the two pipe feedstock were 52 and 53 inches, with a total weight of 184.7 and 189.2 pounds, respectively.

Three of the surrogate elements (neodymium, cerium, lanthanum) were placed in the feedstock pipe in metal form. The other two surrogate elements (cesium and strontium) were added as cesium fluoride (CsF) and strontium fluoride (SrF$_2$). The surrogate metals were encapsulated in 1.25-inch stainless steel tubes, i.e., "packets." Sufficient surrogate elements were included to provide a final concentration in the steel product of 0.1 weight percent (1000 ppm). Packets were fabricated in a glove box containing an inert argon atmosphere. To achieve a

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relatively homogeneous ingot, individual "packets" were welded along the length of the two pipes at 20-lb equivalent intervals. The packet/pipe construction was then slide into the six-inch feedstock pipe. Photographs of the assembling process are presented in Figures 3.2-3.4.
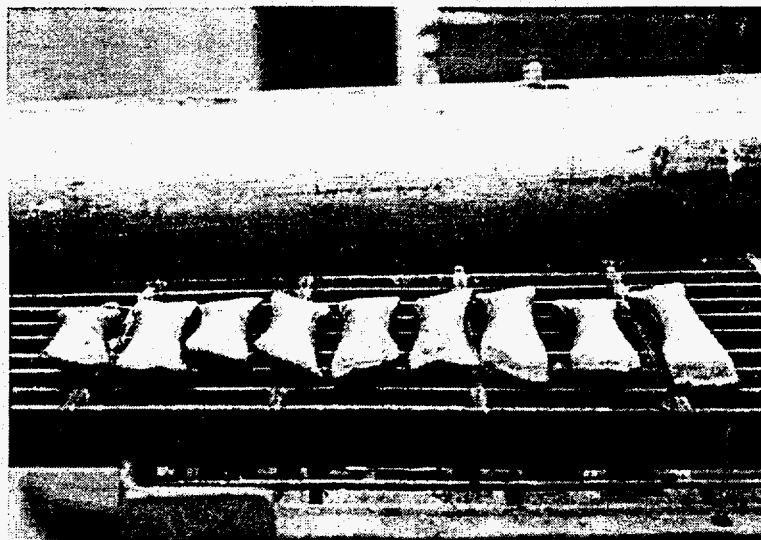
Figure 3.2. Photograph of the Pilot-Scale Feedstock Preparation Sequence: Welded Surrogate Package
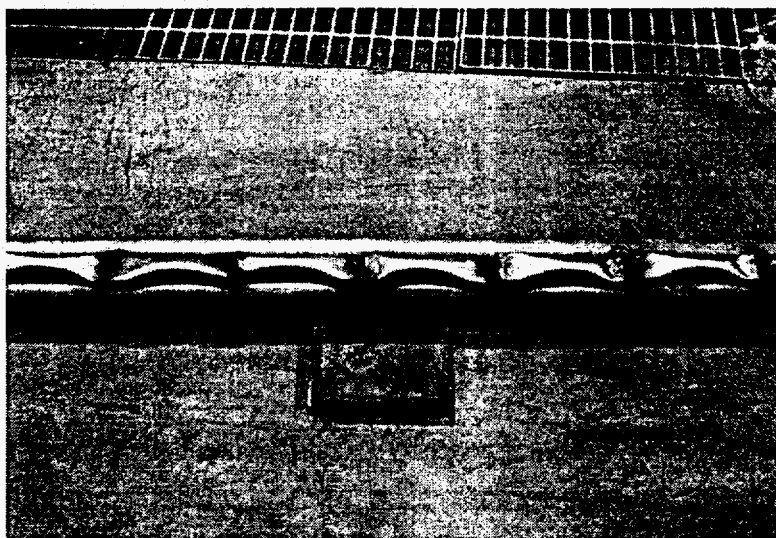
Figure 3.3. Photograph of the Pilot-Scale Feedstock Preparation Sequence: Surrogate Packages Welded to Insert Pipes
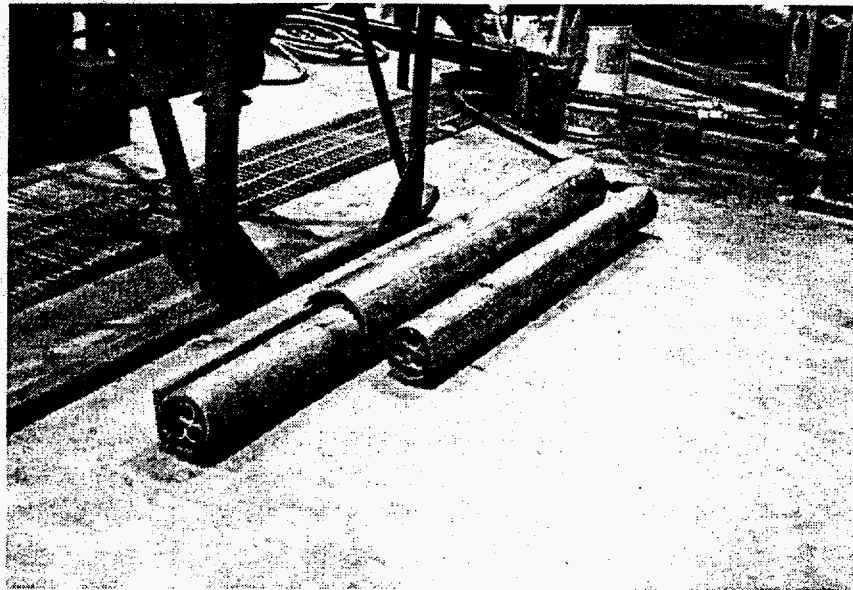
Figure 3.4. Photograph of the Pilot-Scale Feedstock Preparation Sequence: Final Feedstock Assemblage

3.2.2. Description of Plasma Furnace and Melt Procedure

The selection of a plasma cold hearth melter was based on the following characteristics: 1) controlled inert atmosphere melt chamber, 2) multiple plasma torches with computerized motion control, 3) melting and ingot solidification are performed in water cooled copper hearths and crucibles which prevents metal contamination.

The plasma melting procedure consisted of pre-melting 80-lb of feedstock on the hearth. Once the hearth melting was completed a second plasma torch was played on the molten metal surface to initiate stirring. When the hearth was full a second plasma torch, in conjunction with the first plasma torch, started a process of melting the feedstock and drawing the molten metal into the cold copper crucible. The second plasma torch continued stirring the molten metal in the crucible until the first plasma torch provided ample molten feedstock metal in the hearth. With a sweeping motion the second plasma torch again drew the excess molten feedstock from the hearth into the crucible. This process was repeated until the first of the six-inch pipe feedstock was consumed. The plasma furnace was then opened to recharge the feed chute with the second six-inch pipe feedstock and the same melting process was continued until the second six-inch pipe feedstock was consumed. The process is depicted in a series of photographs, Figures 3.5-3.7.

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The resulting final product was a cast ingot six-inches in diameter by forty-inches in length weighing approximately 300 pounds.
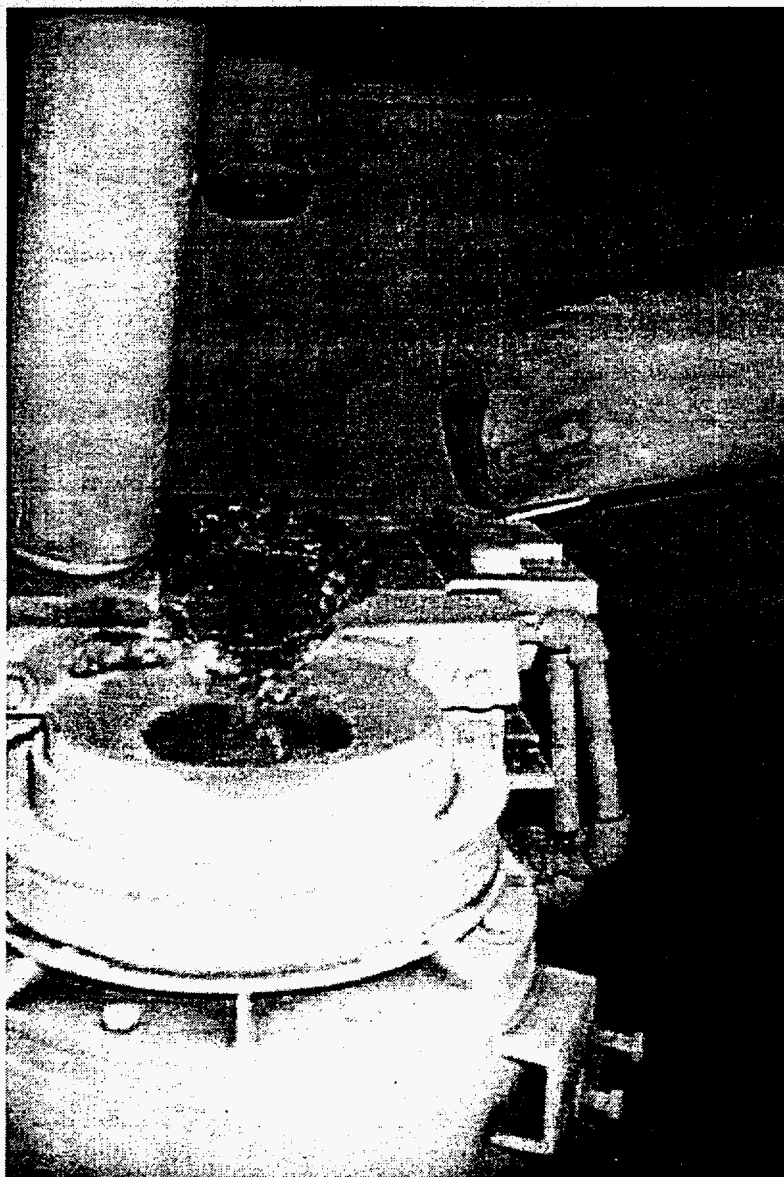
Figure 3.5. Photograph of the RETECH Plasma Melting Unit: Plasma Torch, Hearth, and Feedstock Pipe
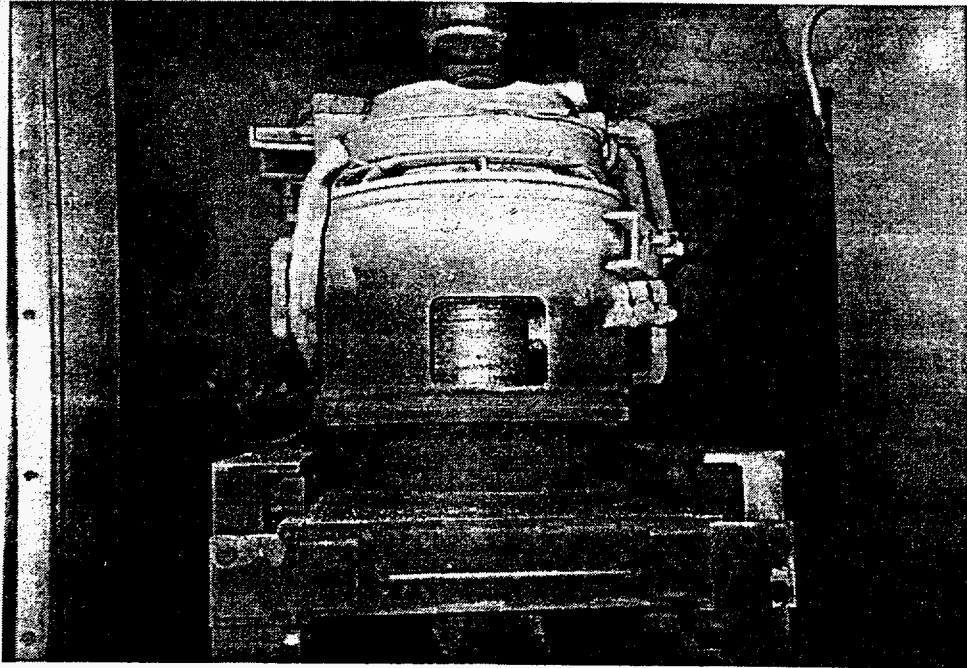
Figure 3.6. Photograph of the RETECH Plasma Melting Unit: Hearth Area and Ingot Mold
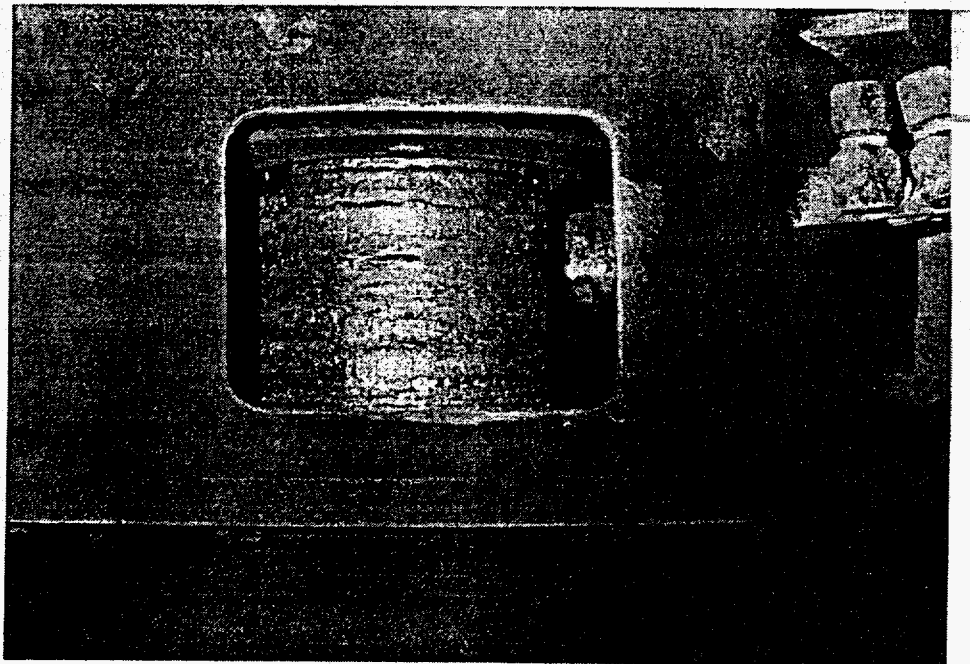
Figure 3.7. Photograph of the RETECH Plasma Melting Unit: Final Ingot in Mold

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3.2.3. Description of Sectioning and Sampling

The cast ingot from the RETECH Plasma Melter was shipped to Oregon Graduate Institute (OGI) for sectioning. The ingot was sectioned by OGI (along its length) into three approximately equal sections, i.e., three sections were produced that weighed approximately 100-lbs each, and then sampled. The sections were designated top, middle, and bottom, i.e. the top refers to the top of the ingot as the ingot came out of the mold. Sample designation for various positions in the ingot are presented in Figure 3.8. Each major section (each 100-lb section) was further sectioned along its length into nine minor sections each with a diagonal length of no more than 2.5-inches as shown in Figure 3.8. Samples for elemental analysis (as described in Section 3.2.4.) were taken from the edges and the centers of the three major transverse sections as indicated by the filled boxes of Figure 3.8. The analytical results (for the surrogate metal concentration and distribution) are presented in Section 4.1.
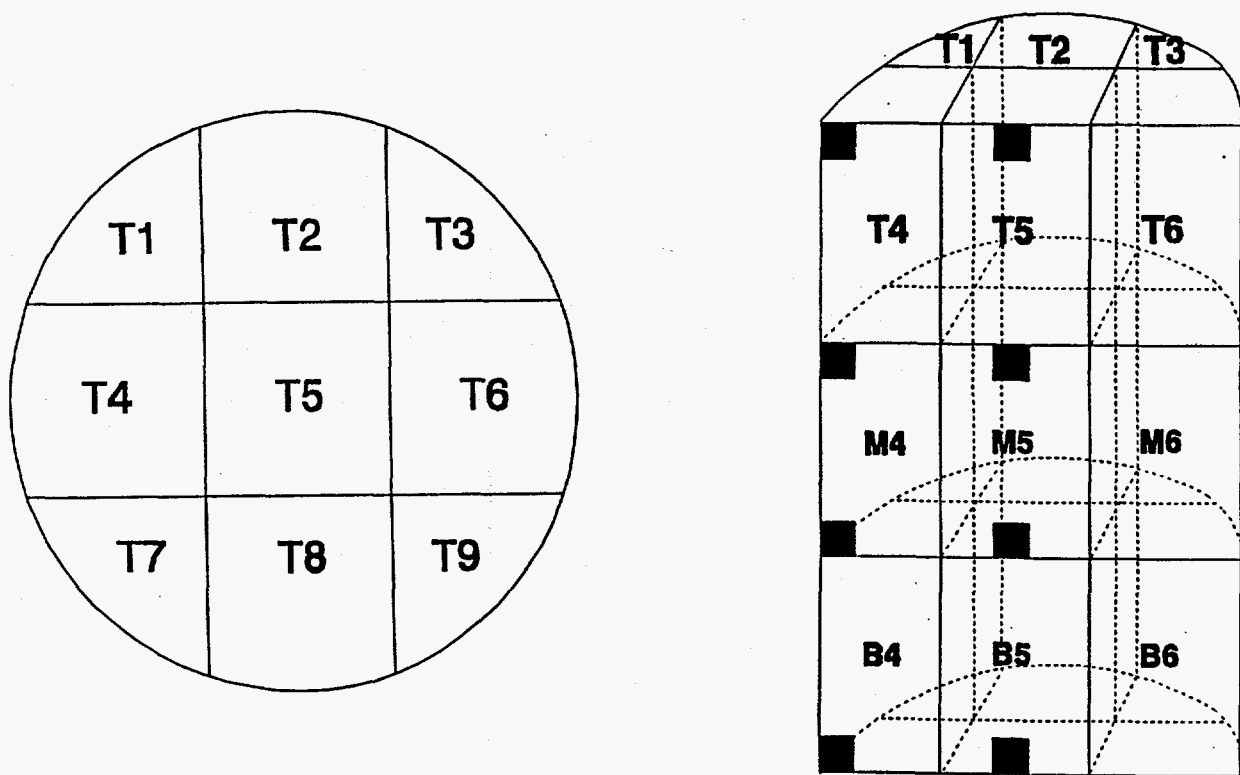
Figure 3.8. Schematic Diagram Depicting the Numbering Sequence Designation and Elemental Analysis Location of the Sample for the Master Ingot (Note: Shaded areas indicate the elemental analysis location.)

3.2.4. Analytical Methods

The characterization of the master ingot has involved the use of four analytical methods: X-ray Fluorescence (XRF), Instrumental Neutron Activation Analysis (INAA), Inductively Coupled Plasma/Acoustic Nebulizer (ICP/AN), and Inductively Coupled Plasma/Mass Spec (ICP/MS). The surrogate metal detection limits for each of the analytical methods are presented in Table 3.1.

TABLE 3.1 ANALYTICAL DETECTION LIMITS FOR SURROGATE ELEMENTS

ANALYTICAL METHOD	SURROGATE METALS, PPM				
	Nd	Ce	La	Cs	Sr
XRF[1]	100	60	80	80	30
INAA[2]	<100	<100	<1.0	<10.0	<2500
ICP/AN[3]	<5	N.A.[5]	<5	N.A.	N.A.
ICP/MS[4]	<0.1	<0.1	<0.1	<0.1	<0.1

1	Ashe Analytics-Butte, MT
2	Oregon State University-Corvallis, OR
3	MSE-Butte, MT (Weiss G., 1994)
4	Teledyne Wah Chang-Albany, OR
5	N.A. - Not Analyzed

3.3. Flux Selection and Preparation

Basic calcium-aluminum-silicate slags with small additions of oxides or fluorides, such as B_2O_3, NiO and CaF_2 were identified in the literature search to be effective stainless steel decontaminators. The investigators selected these types of slags for their initial melt campaign based on data from the literature search.

Flux constituents (for the basic calcium-aluminum-silicate slags) used in the initial campaign are CaO, Al_2O_3, SiO_2 and B_2O_3; these oxides have melting temperatures of 2614, 2072, 1723, and 1860°C respectively. Stainless steel melts at approximately 1490°C, and this presents a problem, because the slag must be in liquid state during the decontamination exposures. Because the pure oxides melt at too high a temperature, lower melting compounds containing CaO, SiO_2 and B_2O_3 were identified and used for initial flux charging. Two compounds identified were calcium meta-silicate $CaSiO_3$ (m.p. 1540°C), and calcium meta-borate $Ca(BO_2)_2$ (m.p. 1154°C). It was anticipated that these compounds would lower the melting point of the pure oxide flux to below the melting temperature of stainless steel. The relevant phase diagrams show that this is the case.

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In powder form the flux constituents were weighed and combined into a mixing vessel, which was then agitated to ensure homogenous mixing. After the flux was mixed, it was poured around the metal charge in the furnace prior to melting, and then melted during the heating cycle of the melt.

3.4. Metal/Slag Refining Procedure

Master ingot steel obtained from Montana Tech's first RETECH cold-hearth plasma master melt was sectioned with reference to the ingot map described in section 3.2.3. After the master ingot was sectioned, pieces ranging from 1.5 to 3 pounds were removed and used for individual induction furnace slag/metal melt tests. By tracking master ingot specimens used in the melt testing, the starting sample surrogate concentrations were known for each individual melt test. The flux requirement for each melt test was then prepared by weighing and mixing the ingredients required for each specific test.

The metal sample was placed (usually consisting of 1-2 lbs) into the furnace and its corresponding flux poured around it (usually 2-5% flux was added). Once the furnace was loaded, furnace power was turned on and slowly increased to heat the metal charge without thermally stressing the crucible. Furnace power, current and frequency, temperature, and time were recorded throughout the heating and molten metal cycle. Three personnel were involved during each experimental melt to control the experimental conditions and record operating data.

During melting of the metal charge, the bottom of the samples heated at a faster rate than the top; therefore, temperature readings of the optical pyrometer were generally lower than the average sample temperature. The pyrometer detects the temperature at the top of the sample. The bottom of the samples heated faster due to a higher heat loss near the top of the crucible and because the sample was not located at the midline of the induction coil axis. Timing of the melt for the specified melt/slag interaction period was not begun until all of the metal was molten and displayed a rolling motion in the furnace. Once the charge was molten, furnace power was decreased to a level that would just maintain the rolling action. Operating the power output of the furnace in this manner minimized superheat. There was no obvious temperature gradient after the charge was molten.

Tests were conducted in an open atmosphere and in an argon atmosphere by flooding the crucible with argon. In the open atmosphere and argon melts, fumes that emanated from the furnace were removed from the optical pyrometer path by an exhaust system. Pyrometer accuracy was improved by using this procedure. Once molten metal/slag interaction times were satisfied, the molten slag/melt charge was poured into sacrificial crucibles that were pre-heated to 400°C. The charge was then allowed to solidify and cool. Metal and slag samples were then taken and prepared for chemical characterization.

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SECTION FOUR: EXPERIMENTAL RESULTS AND DISCUSSION

4.1. Surrogate Composition of Master Ingot

Master ingot surrogate concentrations were analyzed by XRF and INAA. Sample designations for the master ingot are defined in Section 3.2.3. The surrogate composition of the master ingot for each of the analysis techniques are presented in Table 4.1. From the analysis results provided in Table 4.1 it is clear that the surrogates, Ce, La and Nd, were successful dissolved in the master ingot. Cesium and Sr were not effectively retained in the master ingot. The volatilization loss of Cs and Sr is in agreement with literature results and with the calculated results (as presented in Table 2.2).

4.2. Metal/Slag Refining Experiments

4.2.1. Initial Conditions for Metal/Slag Experiments

Using an experimental plan designed to investigate decontamination effectiveness of the basic calcium-alumina-silicate slags, Montana Tech's initial melt campaign was performed following the melt/slag refining procedure as described in Sections 3.3 and 3.4. The experiment control variables were flux composition, metal/slag mass ratio, time, gas atmosphere, and oxygen potential in the melt. Non-controllable variables were alumina and chromium oxide content, which were present as contaminant from furnace crucible dissolution, and oxygen, available from molten metal contact with the open atmosphere. Large scale melting described in the literature has been subject to these non-controllable variables, and most likely, also will production scale RSM recycling. The investigators want to match large scale decontamination efforts in the newly installed laboratory induction furnace, therefore, melting in a crucible in the open atmosphere was considered an acceptable experimental procedure.

Under the experimental plan, ten preliminary melts were performed in the induction furnace system for initial data collection. These preliminary melt tests were designed to provide guidance to the program rather than to provide quantitative evaluations of the experimental system variables.

TABLE 4.1. SURROGATE COMPOSITION OF THE MASTER INGOT

SAMPLE (Figure 3.8)	SURROGATE ELEMENTS AND CONCENTRATIONS				
	Cs, ppm	Sr, ppm	Ce, ppm	La, ppm	Nd, ppm
T4E[1]	96	<D.L.[5]	479	352	851
M4EA[1]	<D.L.	<D.L.	680	499	577
M4EB[1]	<D.L.	<D.L.	330	500	420
M5CA[1]	<D.L.	<D.L.	749	435	826
M5CA[2]	<3.9	<2300	719	376	498
M5CB[1]	<D.L.	<D.L.	428	504	740
M5CB[2]	<3.9	<1900	507	343	416
T5CA[1]	<D.L.	<D.L.	490	330	620
T5CA[2]	<6.0	<2300	525	272	332
T5CA[3]	0.88	2.3	510	300	450
B5MB[1]	<D.L.	<D.L.	560	470	660
B5MB[2]	<4.8	<2400	770	417	546
B4EB[1]	<D.L.	<D.L.	460	370	570
Average[4]			522±136	432±72	658±144

1	Analysis results are from X-ray fluorescence Analysis, Ashe Analytics.
2	Analysis results are from Instrumental Neutron Activation Analysis, Oregon State University Radiation Center.
3	Analysis results are from ICP-Mass Spec, Teledyne Wah Chang Albany.
4	Averaged values are only for X-ray fluorescence analysis results.
5	Detection Limits are shown in Table 3.1

Acquisition conditions for the ten tests are presented in Table 4.2.

TABLE 4.2. EXPERIMENTAL CONDITIONS FOR THE PRELIMINARY MELT/SLAG TEST SEQUENCE

EXPERIMENT IDENTIFICATION	STARTING FLUX COMPOSITION (Wt. %)					FLUX AMOUNT (Wt. %)	TIME[1] (min)	ATM.
	SiO2	CaO	Al2O3	Fe2O3	B2O3			
B5Ba	30.00	41.75	10.00	15.00	3.25	5.0	10,25,30	AIR
B5Bb	35.29	49.12	11.76	-	3.82	25.0	2,10	AIR
B5Ma	35.29	49.12	11.76	-	3.82	5.0	30	AIR
B5Mb	35.29	49.12	11.76	-	3.82	5.0	5	AIR
B5Ta	51.73	48.27	-	-	-	4.9	5	AIR
B5Tb	35.29	49.12	11.76	-	3.82	5.0	0.5	AIR
M5Ba	35.29	49.12	11.76	-	3.82	9.5	7	AIR
M5Bb	-	-	-	-	-	NO FLUX	5	ARGON
M5Ta	-	-	-	-	-	NO FLUX	4	AIR
M5Tb	30.00	41.75	10.00	15.00	3.25	10.0	5	AIR
1 Total melt time or slag sampling interval								

4.2.2. Sampling Procedure

Following melt refining of the master ingot samples in each of the ten melts, samples of both the metal and slag phases were collected and sent to independent laboratories for analysis. Slag sampling was accomplished in two manners: first, samples were removed from the surface of each solidified ingot; and second, induction coil power was temporarily terminated during the melt cycle so a metal rod could be dipped into the melt, extracting slag from the melt surface. The latter procedure is the preferred slag sampling method because metal contamination of the sample is minimized.

Metal sampling was accomplished by generating metal shavings from the solidified ingots after first removing the oxidized outer layer. The outer oxidized layer was removed by drilling a hole through it and metal shavings from continued drilling were collected and analyzed.

4.2.3. Preliminary Test Results

Preliminary test results from the Montana Tech initial melt campaign have been encouraging from a phenomenological point of view that confirms thermodynamic calculational predictions. All experiments performed thus far show that the remaining surrogates will oxidize in the melt and report to the slag phase. Final ingot surrogate concentrations have been less than one ppm for lanthanum in two tests, and usually are less than 10 ppm for the remainder of the test melts. Scatter in the analytical data, especially for metals analysis, has been experienced. Sampling method and sample analysis technique are currently being investigated to determine the cause of the data scatter. The program has shown effective surrogate removal, however, due to the data scatter conclusions have not been drawn on trends that are dependent on slag chemistry, time, temperature, gas atmosphere, and other variables.

4.2.3.1. Metal

The metal phase for five of the test melts was analyzed by x-ray fluorescence to determine major element content in the metal and slag phases. The x-ray fluorescence analysis results are presented in Table 4.3, page 37. In the refined ingots, surrogate elements are not present in sufficient quantity to be accurately detected by x-ray fluorescence.

Surrogate contamination levels present in the metal phase after melt refining are presented in Table 4.4, page 38. Associations between final ingot surrogate concentration and experimental acquisition conditions cannot be made at this time because of the scatter in the data.

Some of the present surrogate data is consistent with final radionuclide contamination levels found in the literature. In experiment M5Ta, a no-flux containing melt, the final concentration of the surrogate lanthanum (0.55 ppm by ICP-MS) matches values obtained by Heshmatpour for uranium (0.65 ppm by Heshmatpour 1981a). In experiment B5Ta, high silica-calcium oxide containing flux, final melt concentration of lanthanum (0.47 ppm by ICP-MS and 0.4 ppm by neutron activation) matches published values in the literature for uranium by Heshmatpour (<0.01 ppm, Heshmatpour 1981a) and (0.28 ppm, Heshmatpour 1981a) and for plutonium by Copeland (0.5 ppm, Copeland 1981).

In work published by Heshmatpour, uranium was introduced into the melt by adding uranium oxide containing flux to metal charges. Decontamination levels obtained from surface contaminant introduction may be inherently higher, because the contaminant is already in the oxide state. Heshmatpour analyzed metal samples using Fast Neutron Activation Analysis (FNAA).

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TABLE 4.3. FINAL INGOT COMPOSITION

SAMPLE	METAL COMPOSITION AFTER MELT TESTING BY X-RAY FLUORESCENCE													
	V (%)	Cr (%)	Mn (%)	Fe (%)	Ni (%)	Cu (%)	Mo (%)	Sn (ppm)	Sr (ppm)	Cs (ppm)	Ba (ppm)	Ce (ppm)	La (ppm)	Nd (ppm)
B5Ta-M1	0.042	18.40	0.76	69.40	10.90	0.13	0.21	66.10	<D.L.	<D.L.	<D.L.	<D.L.	<D.L.	<D.L.
M5Ba-M1	0.089	18.60	0.17	69.10	10.60	0.22	0.23	63.40	<D.L.	<D.L.	<D.L.	<D.L.	<D.L.	<D.L.
M5Bb-M1	0.069	18.50	1.31	68.80	10.80	0.20	0.23	81.40	<D.L.	<D.L.	<D.L.	<D.L.	<D.L.	<D.L.
M5Ta-M1	0.049	18.20	1.26	69.20	10.70	0.16	0.21	63.00	<D.L.	<D.L.	<D.L.	<D.L.	<D.L.	<D.L.
M5Tb-M1	0.065	18.10	1.02	69.60	10.70	0.15	0.20	63.10	<D.L.	<D.L.	35.90	<D.L.	<D.L.	<D.L.
D.L. = Detection Limit											20	40	35	100

TABLE 4.4. SURROGATE METAL CONCENTRATION IN REFINED METAL INGOTS

| SAMPLE | ANALYTICAL TECHNIQUE | | | | | | | STARTING FLUX COMPOSITION (Wt. %) | | | | | FLUX AMOUNT (Wt. %) | TIME (min) |
| | ICP-AN[1] | | I.N.A.A.[2] | | ICP-MS[3] | | | | | | | | | |
	La (ppm)	Nd (ppm)	La (ppm)	Co (ppm)	La (ppm)	Nd (ppm)	Ce (ppm)	SiO2	CaO	Al2O3	Fe2O3	B2O3		
B5Ba-M1	3.1	8.4	N.A.[4]	N.A.	N.A.	N.A.	N.A.	30.00	41.75	10.00	15.00	3.25	5.0	30
B5Ma-M1	16.7	36.2	N.A.	N.A.	N.A.	N.A.	N.A.	35.29	49.12	11.76	-	3.82	5.0	30
B5Mb-M1	0.5	3.5	N.A.	N.A.	N.A.	N.A.	N.A.	35.29	49.12	11.76	-	3.82	5.0	5
B5Ta-M1	N.A.	N.A.	0.4	800	0.47	1.1	1.5	51.7	48.3	-	-	-	4.9	5
B5Tb-M1	26/18	71/54	N.A.	N.A.	N.A.	N.A.	N.A.	35.29	49.12	11.76	-	3.82	5.0	0.5
M5Ba-M1	0.09	4.8	4.71	606	1.6	4.5	6.9	35.29	49.12	11.76	-	3.82	9.5	7
M5Bb-M1	N.A.	N.A.	1.64	625	1.8	6.2	14.0	-	-	-	-	-	NO FLUX	5
M5Ta-M1	N.A.	N.A.	1.57	574	0.55	2.2	2.4	-	-	-	-	-	NO FLUX	4
M5Tb-M1	0.5/6	4/16	1.36	585	1.6	<0.02	6.3	30.00	41.75	10.00	15.00	3.25	10.0	5

1   ICP-AN = ICP by Acoustic Nebulization
2   I.N.A.A. = Instrumental Neutron Activation Analysis
3   ICP-MS = ICP Mass Spectroscopy
4   N.A. = Not Analyzed

4.2.3.2. Slag

Slag analyses from the preliminary melt campaign are presented in Tables 4.5 and 4.6. Table 4.5 contains elemental slag analysis data for all slag samples using x-ray fluorescence, and ICP-MS and Direct Current Plasma (DCP) data for two select samples. In comparing the x-ray fluorescence data to the ICP-MS and DCP data, there is considerable differences even in the major constituents.

In Table 4.6 all slag constituents were considered oxides, and elemental analysis data obtained from x-ray fluorescence was converted to oxide percentages using stoichiometric oxygen to metal ratios. Converting the elemental data in this manner does not produce 100 percent oxide accountability.

4.3. Crucible Wear

During the first melt campaign, ten stainless steel melts were made in Scott-Ram 437A crucible for a total melt time of 100 minutes. Crucible wear for the entire program averaged 0.077 mm of crucible diameter per molten metal minute, measured at the molten metal/crucible interface where there is the highest rate of crucible attack. Diametral corrosion was homogenous as the maximum measured diameter difference was 0.60 mm. As measured after ten melts, the crucible diameter was 7.57 cm in one direction and 7.51 cm in another. Temperature varied from 1490°C during initial melting to 1690°C, during two 30 minute open atmosphere melts.

It was initially estimated that the crucible could be enlarged by wear to a maximum diameter of 7.63 cm before system integrity was compromised. The melt program was discontinued after ten melts due to cracking at the top of the crucible. The crucible wear did not reach the maximum diameter of 7.63 cm. Cracking occurred where the refractory failed to bond during densification. Crucible wear was measured using calipers at room temperature.

TABLE 4.5. SLAG ANALYSIS RESULTS FOR DIFFERENT ANALYTICAL TECHNIQUES

SAMPLE	ANALYSIS BY X-RAY FLUORESCENCE EXCEPT FOR SAMPLES LABELED ICP-MS														
	Al (%)	Si (%)	Ca (%)	Cr (%)	Mn (%)	Fe (%)	Ni (ppm)	Sr (ppm)	Nb (ppm)	Mo (ppm)	La (%)	Ce (%)	Nd (%)	Cs (ppm)	B (%)
B5Ba-S1	9.6	15.6	21.7	8.9	8.6	2.2	525	60	454	67	0.44	0.54	0.61	N.A.[2]	N.A.
B5Ba-S2	12.6	15.8	20.7	10.8	7.5	1.3	137	58	571	76	0.36	0.45	0.52	N.A.	N.A.
B5Tb-S1	10.9	15.5	29.5	3.2	4.5	4.3	843	76	126	135	0.35	0.43	0.49	N.A.	N.A.
B5Tb-S1[1]	8.1	11.2	25.5	3.7	4.2	4.4	N.A.	N.A.	N.A.	N.A.	0.61	0.98	0.89	2.5	0.6
B5Mb-S1	6.7	14.6	22.5	5.1	6.4	3.5	1100	67	216	136	0.33	0.41	0.45	N.A.	N.A.
B5Ma-S1	11.8	14.5	19.3	12.4	6.7	3.1	495	59	400	86	0.30	0.38	0.43	N.A.	N.A.
B5Ma-S1[1]	8.1	9.9	14.2	10.6	6.2	4.6	N.A.	N.A.	N.A.	N.A.	0.45	0.74	0.67	5.0	0.4
B5Ba-S1	16.0	13.6	14.9	10.9	5.7	2.7	236	41	431	61	0.27	0.33	0.38	N.A.	N.A.
B5Bb-S1	10.8	14.6	32.6	4.6	3.9	0.9	61	75	185	<D.L.[3]	0.18	0.23	0.26	N.A.	N.A.
B5Bb-S2	10.6	15.3	37.6	2.3	2.9	0.6	23	83	108	<D.L.	0.18	0.24	0.25	N.A.	N.A.

1   Ce, La, Nd and Cs Analyzed by ICP-MS; B, Cr, Al, Mn, Si, Ca and Fe Analyzed by DCP.
2   N.A. = Not Analyzed
3   D.L. = Detection Limit

TABLE 4.6. SLAG COMPOSITIONS: AS OXIDES

SAMPLE	SLAG COMPOSITION BY OXIDE STOICHIOMETRY CALCULATION[1], Wt. %									
	Al_2O_3	SiO_2	CaO	Cr_2O_3	FeO	SrO	La_2O_3	Ce_2O_3	Nd_2O_3	Total[1]
B5BA-S1	18.14	29.48	29.14	12.96	2.88	0.01	0.51	0.63	0.71	94.46
B5BA-S2	23.81	29.86	27.80	15.78	1.65	0.01	0.43	0.52	0.60	100.45
B5BA-S3	20.41	27.59	43.75	6.65	1.10	0.01	0.22	0.27	0.30	100.29
B5BB-S1	30.23	25.70	20.01	15.93	3.43	0.00	0.31	0.39	0.44	96.46
B5BB-S2	20.03	28.91	50.49	3.39	0.83	0.01	0.21	0.28	0.29	104.44
B5MA-S1	12.66	27.59	30.21	7.40	4.49	0.01	0.39	0.48	0.53	83.75
B5MB-S1	20.60	29.29	39.61	4.71	5.53	0.01	0.40	0.51	0.57	101.23
B5TB-S1	22.30	27.40	25.92	18.12	3.96	0.01	0.36	0.44	0.50	99.00
M5BA-S1	N.A.[2]	N.A.	N.A.	2.94	0.52	N.A.	0.96	0.58	0.71	5.71
M5TB-S1	N.A.	N.A.	N.A.	4.37	0.96	N.A.	0.68	0.46	0.66	7.13

1 Oxide stoichiometric calculations were based on x-ray fluorescence quantitative analysis data presented on an elemental basis. The oxide percentages were calculated for the thermodynamically stable oxide specie of the elements based on their x-ray fluorescence quantitative data. Oxide distributions were unknown, thus oxide percentage totals were not normalized to 100 percent.

2 N.A. = Not Analyzed

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SECTION FIVE: FIRST YEAR ACCOMPLISHMENTS

The first year of study has resulted in the following accomplishments:

- A literature survey on decontamination of radioactive scrap metal was published.

- Three slag compositions from the literature survey were chosen for further study.

- A review of thermochemical calculational computer programs was completed resulting in the purchase of the CSIRO Program.

- Personnel were trained in the use of the CSIRO Program .

- Thermochemical calculations were performed to predict potential partitioning of the surrogates between the metal, slag, and gas phases.

- A "Master Ingot" was produced by plasma cold hearth melting.

- The melt refining test facility was installed and tested.

- Operating procedures were developed for the test facility.

- Personnel were trained in test facility operation.

- Ten experimental melts of the "Master Ingot" were completed.

- Sampling and analytical procedures were developed to measure metal and slag compositions.

- A pilot scale, controlled oxygen potential melt/refining experiment was performed using the plasma cold hearth furnace.

- A preliminary experimental schedule was completed for the second years work.

SECTION SIX: FUTURE WORK

Future test work is outlined in the following sections.

6.1. Laboratory Test Work

The planned laboratory test work includes:

- Slag Chemistry Optimization;

  The laboratory test work planned for the final year of the project will be somewhat dependent on the results of the recently completed controlled oxidation potential pilot-scale experiment (See Section 6.2). It is anticipated that much less aggressive (lower oxidizing potential) slags (than have been tested to date) will be effective for surrogate removal from the stainless steel solutions. Therefore, the laboratory test work will emphasize the development of fluxes that have the appropriate oxidizing power and that have good handling characteristics.

- Experimental Procedure Optimization;

  - Overall Problem - Data Scatter

    The data scatter is possibly due to the present practice of pouring from the melt crucible to the mold. This procedure may result in minor amounts of metal entrapment in the slag and cross contamination from the melt crucible to subsequent melts.

  - Solution

    Future test work will be conducted in such a way that the products will be allowed to solidify in the furnace crucible, i.e., pouring will be unnecessary. Not only will the problem of entrapment be eliminated but more effective recovery of each phase will

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allow material balance calculations to be
performed and distribution ratios to be
determined more accurately.

The new product recovery procedure will be tested by repeating some of the earlier "borate" test work that showed the most promising results. "Fluoride" slag/melt experiments will be initiated. It is anticipated that the third "ferrite" flux will not be investigated due to its excessive oxidative potential.

6.2. Pilot Scale Test Work

The first pilot scale surrogate-removal melt was performed March 3, 1994 at RETECH, Inc. This test was designed to examine the effect of controlling oxidation potential in removing surrogates La, Nd, Ce, Sr, and Cs from stainless steel. The oxidation potential was controlled in three independent stages by controlling flux composition:

- Stage One: No flux present

- Stage Two: "Borate" flux without ferric oxide

- Stage Three: "Borate" flux with ferric oxide.

The thermochemical basis for this test was described in section 2.2.5.3. The melt test was conducted in RETECH's two-torch cold hearth plasma furnace in a recirculating helium atmosphere (described in Section 3.2.2). Using this technique, the oxidizing potential of the slag can be assessed without interference from crucible material and atmospheric gases. In the first stage a 70 lb section of feedstock containing only surrogates (no flux) to reconfirm the results of the first master melt (Section 4.1) was melted. In the second stage a 100 lb section of feedstock containing surrogates plus 2% by weight of flux containing 11.8% Al_2O_3, 35.3% SiO_2, 49.1% CaO, and 3.8% B_2O_3 was melted. In the third stage a 100 lb section of feedstock containing 2% by weight of flux containing 10% Al_2O_3, 30% SiO_2, 41.8% CaO, 3.2% B_2O_3, and 15% Fe_2O_3 was melted. The melt was interrupted after completion of each stage to provide a separate ingot from each feedstock. The ingot will be sectioned and sampled to evaluate surrogate removal. Experimental data will be forthcoming.

Surrogates were added to the melt stock in the same manner used for the master melt described in Section 3.2.1. Flux was added as dried powder in 2.5 inch diameter Type 304 stainless steel tubing with crimped ends. Calcium borate was added as "Gerstley Borate," calcium silicate as "Wollastonite," aluminum oxide as alumina and iron oxide as ferric oxide.

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Future pilot scale melts will be scheduled after sufficient experience is gained from laboratory induction melt experiments using "fluoride" fluxes.

SECTION SEVEN: TECHNOLOGY TRANSFER AND PRIVATIZATION

The results from the work to be conducted (as described in Sections 6.1 and 6.2) will be used as resource information for designing melt refining demonstrations using radioactive scrap metal from DOE facilities. Montana Tech will assist WINCO in developing test plans for these larger scale melts and provide technical assistance in areas such as furnace heat up rate, flux addition, slag chemistry, and sampling techniques. Montana Tech will assist WINCO in data evaluation and applicability of this melt refining technology for recycling of DOE RSM.

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