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Decontamination and Decarburization of Stainless and Carbon Steel by Melt Refining

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DISCLAIMER

DECONTAMINATION AND DECARBURIZATION OF STAINLESS AND CARBON STEEL BY MELT REFINING

EXECUTIVE SUMMARY

THE PROBLEM

With many nuclear reactors and facilities being decommissioned in the next ten to twenty years the concern for handling and storing Radioactive Scrap Metal (RSM) is growing. Upon direction of the DOE Office of Environmental Restoration and Waste Management, Lockheed Idaho Technology Company (LITCO) is developing technologies for the conditioning of spent fuels and high-level wastes for interim storage and repository acceptance, including the recycling of Radioactive Scrap Metals (RSM) for beneficial re-use within the DOE complex.

The current RSM inventory for the Idaho National Engineering Laboratory (INEL) is estimated at 1.0 million kilograms which include 175,900 kilograms as iron or carbon steel, 294,300 kilograms as stainless steel. RSM steel and stainless steel projections for Decontamination and Decommissioning (D&D) for the INEL are estimated to be 23,759,600 kilograms and 37,613,100 kilograms, respectively. Nichols has estimated that the annual generation of RSM for the entire DOE complex will be approximately 109,000,000 kg (120,000 tons) beginning in 1999-2000.

MONTANA TECH PROGRAM

In February 1993, WINCO (previous INEL Metal Recycle Program manager) contracted with Montana Tech of the University of Montana to develop and demonstrate technologies for the decontamination of stainless steel RSM. This program was designed to complement and support other INEL Recycle Program efforts with the Oregon Graduate Institute (OGI), Sandia National Laboratories, Newport News Shipbuilding, Savanah River Site, Colorado School of Mines, and the Northwest Consortium (OGI, Teledyne Wah Chang Albany, Northwest Pipe and Casing, Sacramento Municipal Utility District, and Portland General Electric).

The general objectives of the Montana Tech research program included conducting a literature survey, performing laboratory scale melt refining experiments to optimize decontaminating slag compositions, performing an analysis of preferred melting techniques, coordinating pilot scale and commercial scale demonstrations, and producing sufficient quantities of surrogate-containing material for all of the laboratory, pilot and commercial scale test programs. Later on, the program was expanded to include decontamination of carbon steel RSM. Specific objectives of the Montana Tech research program included the following components:

- Review the literature as it relates to decontamination of radioactive elements from stainless steel and carbon steel. Prepare an annotated summary of the published literature. (Two reports were issued during the contract period.)

- 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).

- Apply the results of the laboratory studies to pilot scale studies and commercial scale studies to demonstrate effective decontamination technology(s) for slag/melt refining. This phase included melting of pilot-scale quantities (several hundred pounds) and commercial scale quantities (several thousand pounds) of surrogate-containing stainless and carbon steel (surrogate preparation techniques insured introduction of measurable quantities of non-oxidized surrogates into all master alloys) for demonstration programs.

Each research program (steel and stainless steel) has been completed. Results of these programs are presented in this report, and other publications issued during this program are listed in **Section 1.3**

PROGRAM RESULTS

Radionuclides with oxide free energies of formation (based on one mole of oxygen gas) that are significantly lower than the free energies of formation for the steel constituent oxides potentially can be removed from the RSM by Melt Refining/Slagging. This melt refining process has been proven effective in agreement with the results found in the literature and based on the results of the Montana Tech research program. Radionuclides with high vapor pressure (strontium and cesium) were also removed.

Surrogates used in the present study included an isotopic mixture of cerium, strontium, neodymium, lanthanum, and cesium. Cesium and strontium represent radioactive isotopes of their own 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.

Melting fluxes were chosen from the literature and thermochemical calculations performed using the CSIRO/MONASH Thermochemistry Software. The results for both the stainless and carbon steel research programs indicate that induction melting in an open atmosphere will (with and without the presence of flux additions) sufficiently lower the surrogate concentration levels of the master surrogate ingot to below 1.0 ppm after five minutes at a melting temperature of 1600°C. This result has been demonstrated on the scale of a few pounds up to approximately one ton.

After demonstration of removal of surrogates, it became apparent that it was desirable to produce stainless steel that met low carbon requirements to increase product utility and value. For many applications, i.e. long term waste and fuel containers, SS304 with a carbon content greater than 0.03 % is unacceptable for welded components. Therefore, a series of pilot scale experiments (200-250 pounds) utilizing vacuum induction melting (VIM) have been performed to demonstrate the effective removal of surrogate elements and to investigate the lowering of carbon to specification levels. The results show that effective decontamination of the surrogate elements and the lowering of carbon content (from approximately 1000 ppm to 300 ppm) can be achieved in one melting step in a vacuum environment using either ferric oxide (magnetite) additions or carbon dioxide gas surface sparging. Additional advantages of VIM demonstrated during the program were: minimization of slag formation to minimize the quantities of radioactive materials which must subsequently be disposed of, and positive control of fume and offgas during the melting operation.

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SECTION ONE

INTRODUCTION

1.1. BACKGROUND

With many nuclear reactors and facilities being decommissioned in the next ten to twenty years the concern for handling and storing Radioactive Scrap Material (RSM) is growing. Upon direction of the DOE Office of Environmental Restoration and Waste Management, Lockheed Idaho Technologies Company (LITCO), formerly Westinghouse Idaho Nuclear Company (WINCO), is developing technologies for the conditioning of spent fuels and high-level wastes for interim storage and long term repository acceptance, including the recycling of RSM for beneficial re-use within the DOE complex (T.E. Bechtold, 1993). The current RSM inventory for the Idaho National Engineering Laboratory (INEL) is estimated at 1.0 million kilograms of which 175,900 kilograms consists of iron or carbon steel, and 294,300 kilograms of stainless steel. RSM steel and stainless steel projections for Decontamination and Decommissioning (D&D) for the INEL are estimated to be 23,759,600 kilograms and 37,613,100 kilograms, respectively. (T.E. Bechtold, 1993). In a recent report which addressed the entire DOE complex and the nuclear power industry, Nichols estimated approximately 109,000,000 kilograms (120,000 tons) of RSM would be available annually for recycle or burial beginning in 1999-2000. (F. Nichols, 1995)

In February, 1993, WINCO awarded a task order for the development and demonstration of technology for the decontamination of stainless steel RSM to Montana Tech of the University of Montana. (Since October, 1995, management of the INEL Metal Recycle program has changed from WINCO to Lockheed Idaho Technologies Company (LITCO)). The contract objectives for Montana Tech are further described in Sections 2.1.

1.2. RADIONUCLIDES IN NUCLEAR POWER REACTORS

The contamination present in RSM can be either volumetric or surface contamination. Certain elements present in both stainless and carbon steel can become activated from the neutron flux during normal reactor operations, thus causing volumetric contamination. Surface contamination is often due to radioactive elements from reactor and/or spent fuel storage environments that are present in "Crud" (Atteridge, 1994, Dyer, 1994) that is deposited or forms on the surface. This "Crud" is a corrosion product from within the reactor vessel or from a "leaking" nuclear fuel rod.

In a recent report, Dyer and others listed types of radioactive contaminants possible in nuclear reactor systems. Dyer assumes that 1000 days would be required before RSM could enter the recycling process; therefore, the removal of radionuclides with half-lives less than 50 days should not be considered because radionuclide reduction of over a million times (9.54E-7) will occur in a period of 1000 days. (N.C. Dyer, 1994) The radionuclides of concern in nuclear power reactors (half-lives longer than 50 days) for decontamination are presented in Table 1.1. These nuclides are separated into three groups: gamma emitters, non-gamma and low-energy gamma emitters, and transuranics.

TABLE 1.1. RADIONUCLIDES FOUND IN NUCLEAR POWER REACTORS (LIMITED TO HALF-LIVES LONGER THAN 50 DAYS), Dyer (1994)

NUCLIDES	HALF-LIFE (DAYS)	MODE OF PRODUCTION
FOR GAMMA EMITTERS:		
Mn-54	3.1E+2	Activation of iron
Co-57	2.7E+2	Activation of nickel
Co-58	7.1E+1	Activation of nickel
Co-60	1.9E+3	Activation of cobalt
Zn-65	2.4E+2	Activation of zinc
Kr-85	3.9E+3	Fission/Fuel
Zr-95	6.4E+1	Fission/Fuel and Activation of Zr-94
Nb-94	7.4E+6	Fission/Fuel then Activation of Nb-93
Ru-106 & D	3.7E+2	Fission/Fuel
Ag-108m	4.6E+4	Activation of silver
Ag-110m	2.5E+2	Activation of silver
Sb-124	6.0E+1	Activation of antimony
Sb-125	1.0E+3	Activation of tin
Cs-134	7.5E+2	Fission/Fuel then Activation of Cs-133
Cs-137	1.1E+4	Fission/Fuel
Ce-144 & D	2.8E+2	Fission/Fuel
Eu-152	5.0E+3	Fission/Fuel
Eu-154	3.2E+3	Fission/Fuel

NUCLIDES	HALF-LIFE (DAYS)	MODE OF PRODUCTION
Eu-155	1.8E+3	Fission/Fuel
FOR NON-GAMMA OR LOW-ENERGY GAMMA EMITTERS:		
H-3	4.5E+3	Activation of deuterium or lithium
C-14	2.1E+6	Activation of nitrogen
S-35	8.7E+1	Activation of sulfur or chlorine
Ca-45	1.6E+2	Activation of calcium
Fe-55	9.9E+2	Activation of iron
Ni-59	2.7E+7	Activation of nickel
Ni-63	3.7E+4	Activation of nickel
Sr-89	5.1E+1	Fission/Fuel
Sr-90 & D	1.0E+4	Fission/Fuel
Y-91	5.9E+1	Fission/Fuel
Nb-93m	5.3E+3	Fission/Fuel
Mo-93	1.3E+6	Activation of molybdenum
Tc-99	7.8E+7	Fission/Fuel
I-129	5.7E+9	Fission/Fuel
Pm-147	9.6E+2	Fission/Fuel
FOR TRANSURANICS:		
PU-238	3.2E+4	Fission/Fuel
Pu-239	8.8E+6	Fission/Fuel
Pu-240	2.4E+6	Fission/Fuel
Pu-241	5.3E+3	Fission/Fuel
Am-241	1.6E+5	Fission/Fuel
Cm-242	1.6E+2	Fission/Fuel
Cm-244	6.6E+3	Fission/Fuel

T.E. Bechtold (1994) noted that the allowable release of decontaminated materials has not been fully established at the present time, "The Nuclear Regulatory Commission (NRC) attempted to initiate a *de minimus* free release policy for decontaminated metals, but public opposition to the policy has prevented any free release of materials with detectable radioactivity. A court tort deciding in favor of a claim for damages resulting from radiation exposure could establish strict liability, and hold the original generator liable for damages. The risk of this type of ruling could make NRC licensees extremely cautious about releasing contaminated material for conversion to consumer products. ...In view of continued public resistance to participation in efforts to frame clear and explicit regulatory guidance, and in light of the potential for product liability, the best available option for RSM recycle would appear to be the fabrication of products which would remain under DOE or NRC operational controls." (T.E. Bechtold, 1994)

1.3. PUBLICATIONS RESULTING FROM THIS STUDY

The reader is referred to the following publications that resulted from the steel and stainless studies (listed in alphabetical order):

- Paolini, D.J., "Decontamination of Metals by Melt Refining/Slagging", MSc. Thesis in Metallurgical Engineering at Montana Tech of the University of Montana, 128 p., May 1995.

- Weldon, T.A., "Decontamination of Metals by Melt Refining/Slagging", MSc. Thesis in Metallurgical Engineering at Montana Tech of the University of Montana, 131 p., June 1994.

- Webber, D., "Decontamination and Decarburizationof Stainless Steel by Vacuum Induction Melting," MSc.Thesis in Metallurgical Engineering at Montana Tech of the University of Montana, In Progress, 1996.

- Worcester, S.A., Twidwell, L.G., Paolini, D.J., Weldon, T.A., Mizia, R.E. (Ed.), "Decontamination of Metals by Melt Refining/Slagging-An Annotated Bibliography", WINCO-1138, INEL-DOE, 89 p., 1993.

- Worcester, S.A., Twidwell, L.G., Paolini, D.J., Weldon, T.A., Mizia, R.E. (Ed.), "Decontamination of Metals by Melt Refining/Slagging: First Year Progress Report", WINCO-1198, INEL-DOE, 47 p., 1994.

- Worcester, S.A., Twidwell, L.G., Paolini, D.J., Weldon, T.A., Mizia, R.E., "Decontamination of Metals by Melt Refining/Slagging", Second International Conference on Materials Engineering for Resources, ICMR'94 AKITA, October 12-14,1994, Society of Mat'ls Engr for Resources of Japan and Res. Inst. of Nat. Resources, pp 62-75, 1994.

- Worcester, S.A., Twidwell, L.G., Paolini, D.J., Weldon, T.A., Mizia, R.E., "Decontamination of Metals by Melt Refining/Slagging", Proc. Vacuum Metallurgy Conf. on Liquid Metal Processing and Casting, Sante Fe, N.M., Sept. 11-14, 1994, 14 p., 1994.
- Worcester, S.A., Twidwell, L.G., Paolini, D.J., Weldon, T.A., Mizia, R.E. (Ed.), "Decontamination of Metals by Melt Refining/Slagging: An Annotated Bibliography Update on Stainless Steel and Steel," DOE De-AC07-94ID13223, INEL-95/0123, 1995.
- Worcester, S. A., Twidwell, L.G., Webber, D. Mizia, R. E. "Decontamination and Decarburization of Stainless Steel by Vacuum Induction Melting," accepted for presentation at "Spectrum'96 Nuclear and Hazardous Waste Management International Topical Meeting", Seattle, WA, August 1996.

1.4 PUBLICATIONS RESULTING FROM COMPANION STUDIES

The reader is also referred to the following publications that resulted from other INEL Metal Recycle Program-sponsored programs (listed in alphabetical order)

- Atteridge, D.G., Buckentin, J., J. Carter, Davis, H.L., Devletian, J.H., Scholl, M.R., Turpin, R.B., Webster, S.L., Mizia, R.E. (Ed.), "Refining Technology for the Recycling of Stainless Steel Radioactive Scrap Metals: FY 94 Bi-Annual Report," INEL-DOE, WINCO-1224, 97 p., 1994.
- Bechtold, T.E. (Editor), "WINCO Metal Recycle Annual Report, FY 1993," INEL-DOE, WINCO-1172, 77 p., 1993.
- Bechtold, T. E. (Editor), "INEL Metal Recycle, Annual Report" INEL-94/0067, September 1994.
- Buckentin, J. M. R., "Melt Decontamination of Radioactive Stainless Steel by Electroslag Remelting", PhD. Thesis in Materials Science at Oregon Graduate Institute of Science and Technology, 241 p., March 1996
- Dyer, N.C., Bechtold, T.E. (Editor), "Radionuclides in United States Commercial Nuclear Power Reactors", WINCO-1191, INEL-DOE, 26 p., 1994.
- Frost, R. H., "Refining Technologies for Radioactive Stainless Steel Scrap", Final Report Contract No. C86-110877-009, Colorado School of Mines, 61 p., 1996.

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SECTION TWO

RESEARCH PROGRAM

2.1. OBJECTIVES

General objectives of the Montana Tech research program included: a literature survey, laboratory scale melt refining experiments to optimize decontaminating slag compositions, analysis of preferred melting techniques, coordination of pilot scale and commercial scale melt demonstrations, and providing pilot and commercial scale quantities of surrogate-containing steels for subsequent demonstration programs. Specific objectives of the Montana Tech research program included the following components:

- Review the literature as it relates to decontamination of radioactive elements from carbon and stainless steel. Prepare annotated summaries of the published literature. (Worcester, 1993 and 1995)
- Evaluate melt technologies and chose those appropriate for the present study.
- 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).
- Apply the results of the laboratory research program to pilot scale studies at commercial facilities to demonstrate effective decontamination technology(s) for slag/melt refining. (Worcester, et al, 1994)

2.2. LITERATURE SURVEY/ANNOTATION FOR STAINLESS AND CARBON STEEL

Two separate literature annotations have been completed by the Montana Tech research team. The first was an extensive search of 12 databases, reviewing over 280 published literature reports pertaining to the decontamination refining of stainless steel, annotating the articles and publishing the results (Worcester, 1993). The second literature evaluation consisted of reviewing, annotating, and publishing results for steel decontamination refining, and updating the stainless steel annotation from 1993 to 1995 (Worcester, 1995). Relevant comments resulting from the literature reviews are presented below.

A conclusion resulting from the review of published literature by Worcester (1993, 95) was that test work (both bench scale and larger scale) demonstrated that slagging decontamination of uranium and plutonium from steel and stainless steel is an effective treatment technology. Laboratory test work performed at Montana Tech and large scale test work supervised by Montana Tech personnel (Worcester, et al, 1994) have further demonstrated (using surrogates for the radioactive nuclides) effective decontamination to concentrations less than one part per million using induction melting (in air and in a vacuum). Other test work in associated programs included; electroslag melting laboratory test work performed at the Oregon Graduate Institute (Atteridge, et al, 1994; Buckentin, 1996) and at the Colorado School of Mines (Frost, 1996).

Based on trends found in the literature, basic calcium-aluminum-silicate slags (with additives such as calcium fluoride or ferric oxide) appeared to be effective RSM decontaminators. However, the recent work of Worcester (1994), Weldon (1994) and Paolini (1995) demonstrated that flux composition is not very important when the decontamination is conducted in refractory-lined induction melting furnaces.

From the literature review 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 the major consitutents (iron, cobalt, nickel, chromium) will be retained to a large degree in the metal product.

Tritium removal was not considered in the keyword search nor was analytical data provided in any of the publications reviewed. This issue was the subject of a joint LITCO/Savannah River Technical Center (SRTC) research initiative and the reader is referenced to that initiative. (Imrich, 1994)

The technological community has selected two technologies for melt/consolidation of RSM, coreless induction and electric arc furnace (EAF) melting. The choice between these two technologies involves many factors. The main factors favoring coreless induction include better melt agitation, easier fume control, and rapid heat up. These factors are particularly important when considering an initial consolidation/homogenization melt of RSM, and are the primary reasons why induction melting was selected for most of the "large scale" RSM melting described in the literature. 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. According to Reimann (1991), an induction furnace produces only 20% as much effluent dust as an EAF of similar capacity. In the authors opinion, the reduction of effluent dust should be a major factor in furnace selection. This is of significance when designing a capture system which will control the dispersal of a significant portion of the long-lived radionuclides (e.g., Cs-137).

It appears quite obvious that melt decontamination alone will not provide RSM which qualifies for free release to the private sector, 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 publications describing large scale melting treatment) could be released under the criteria established in Europe in 1989. It is suggested that free or controlled release is not necessary; and that 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 nuclear fuel storagecontainers. (Worcester, et al, 1994) In addition, elimination of volatile and easily oxidized elements from recycle heats minimizes the problems involved in fabrication of useful components such as waste containers and canisters.

The availability of stainless steel RSM at INEL and other DOE sites and the need for stainless steel for waste or nuclear fuel storage canisters present a unique opportunity. Methods for consolidating stainless steel RSM can be developed on a commercial scale while developing protocol for disposal of carbon steel scrap at a later date. Carbon steel might also be combined with characterized nickel RSM to produce additional quantities of stainless steel for use within the DOE program (Mizia, 1993). This approach has been pursued by Manufacturing Sciences Corporation. (Nichols, 1994) Montana Tech is currently involved in a program with MSE, Inc to demonstrate the conversion of surrogate-containing carbon steel scrap into stainless steel meeting low carbon requirements.

Analysis of the literature suggests the following approach:

- Decontaminate and melt stainless steel RSM into heats of sufficient size to minimize radionuclide characterization and analytical costs while casting the material into suitable shapes for recycle into a limited release remelt program. These products could be used to fabricate components for the nuclear industry.

- Such an approach would provide volume reduction while establishing protocol for at least limited release into the commercial scrap market. One of the problems associated with trying to do on-site casting of stainless heats for fabrication into canisters is the small heat size inherent in such an application. Small heat sizes significantly drive up production costs while increasing certification costs and complexity without improving quality.

> Even if the largest U.S. RSM furnaces were used for ingot casting, heat size would only be 20 tons. Fabrication and quality control costs for such small heats would be prohibitive. On the other hand, if characterized first melt RSM ingots were released to a commercial stainless melter/fabricator for use as scrap addition to heats, quality could be improved, with minimal risk, by relying on the melting and fabrication expertise of the steel industry.

The program suggested in the original bibliography (Worcester, 1993) follows:

- "Decontaminate and melt RSM within the DOE complex into a configuration which is acceptable for use in the commercial scrap market, for use as shielding blocks, or for land disposal. Melting parameters would be optimized for transfer of radionuclides into slag and fume, homogenizing the melt, and minimizing slag inclusions.

- Release heats which meet release specifications to a commercial stainless melter/fabricator for combination with non-contaminated melt stock into large heats for fabrication into DOE program products. These products might include 55-gallon drums for low-level nuclear waste disposal, Hot Isostatic Pressed (HIP) canisters for Idaho Chemical Processing Plant (ICPP) waste immobilization, overpack canisters for ICPP-HIP canisters, and multi-purpose containers for storage of spent nuclear fuel.

- Use non-qualifying heats for internal use, land disposal, or remelting within the DOE complex. Remelting might involve further melt refining, possibly by induction ladle metallurgy as proposed by Reimann (Reimann, 1991) or electroslag melting." (Worcester, et al, 1993)

An alternatively realistic approach is the establishment of a regional or national RSM processing center within the DOE complex equipped to decontaminate, melt refine, cast, roll, and final fabricate the hardware required for nuclear waste disposal.

This approach is supported by the following observations:

- Free release requirements will become tighter with time.

- The steel industry is unlikely to accept RSM-derived material for input to conventional facilities.

- It is unlikely available quantities of RSM will justify more than one large-scale processing facility. Canister quality will be enhanced by utilization of larger equipment. Quality and certification costs for containers will be significantly reduced on large heats while real quality will be improved. Consolidation of stainless steel RSM will undoubtedly introduce some carbon pickup, necessitating carbon blowdown in the VIM, as developed in this program, or secondary refining techniques such as AOD or VOD for economical processing of low carbon stainless steel. Such refining will not be necessary for carbon steel.

- Some radionuclides will not be removed by any practical melting process known today (e.g., Fe, Co, Mn).

- Stainless steel scrap can be consolidated at a cost, at least, on a break-even basis ($400/ton) with commercial market stainless steel (disregarding burial costs for RSM). Mizia (1994) analyzed allowable costs for stainless RSM recycle. In the most likely scenario, burial costs were pegged at $668/cubic foot. A savings of $35,000 per 20 short ton (empty weight) canister was estimated. This estimate allowed a $2.10/lb tolling charge and a 15% premium for fabrication of the canister from RSM. Projected savings are highly dependent upon burial costs. A recent report by Nichols of Manufacturing Sciences Corporation (as a subcontractor to MSE, Inc. (Nichols, 1995)) estimates RSM production costs at $1130/ton for hot rolled sheet. Assuming a generator transfer charge of $1500/ ton, and an RSM product sales price of 70% of commercial value, Nichols estimated a 22 to 44% return on investment for a 30,000 tpy dedicated RSM "minimill."

2.3. SURROGATES

Surrogates used in the present study included an 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. (Worcester, et al, 1994)

Elemental surrogate concentrations were added at 0.10 weight percent additions (1000 ppm). The surrogate concentration level achieved in the master alloys were in general in the range of 300-500 ppm. (Worcester, et al, 1994)

There have only been a limited number of test programs that have used surrogates to simulate the distribution of radioactive nuclides during melt refining. However, a few studies have been identified that relate directly to the present project. The literature that has been identified is presented in Table 2.1.

TABLE 2.1. SURROGATES USED FOR RADIOACTIVE NUCLIDES IN HIGH TEMPERATURE STUDIES

Radionuclide or Oxide	Surrogate	Comment	Reference
PuO_2	HfO_2	Simulate plutonium oxide in electroslag melting	Ochiai (1982)
Fe-55, Ni-59, Ni-63	Co-60	Melt experiments with β,γ-contaminated material	Schuster (1990)
PuO_2	UO_2	Resistance heating & arc melting techniques	Levitz (1975)
PuO_2	Rare Earth Oxides of Dysprosium, Terbium, Ytterbium	Simulate plutonium in soils in vitrification study	Stoots (1990)
PuO_2 and Transuranic Oxides	Dysprosium Oxide	Incinerator tests and Glove box tests	Shaw (1988) as referenced by McAtee (1991); Hooker (1981); Shaw (1988)
PuO_2	Rare Earth Oxides of Dysprosium, Neodymium, Ytterbium, Cerium	Vitrification and slagging in silicate melts	Bergsman (1991) as referenced by McAtee (1991)
PuO_2	Dysprosium Oxide	Vitrification and slagging in silicate melts	Weidner (1991) as referenced by McAtee (1991)
PuO_2	All Rare Earth Oxides (Especially Cerium)	Based on high temperature chemistry considerations	McAtee (1991)
PuO_2	Cerium Oxide	Simulate plutonium oxide distribution during plasma melting of contaminated soils	Whitworth (1993)

Various substitutes for radioactive nuclides have been selected, e.g.,

- Ochiai, et al (1982) investigated the distribution of HfO_2 (as a surrogate for PuO_2) in an electroslag melting study. They determined that the best initial slag was composed of 47% CaO, 48% Al_2O_3, 5% B_2O_3 (the silica content of the slag rose to approximately 20% after repeated exposure). The hafnium distributed primarily, 96%, to the slag phase. The final ingot contained 2.53 ppb hafnium.

- McAtee (1991) has reviewed the high temperature chemistry of plutonium and the rare earths. He quotes the work of Shaw (1988a, 1988b), Hooker (1981), Weidner (1991), and Bergsman (1991) who have used rare earth oxides as surrogates for plutonium oxide. Shaw (1988a) and Hooker have reported the use of dysprosium oxide in incineration tests. Shaw also reported the use of dysprosium oxide in a glove box scale study on excavated buried transuranic wastes. Bergsman (1991) and Weidner (1991) used rare earth oxides to simulate plutonium in in-situ vitrification studies. Weidner used dysprosium oxide in test work on in-situ vitrification of basaltic melts and Weidner found that the simulates dysprosium, neodymium, ytterbium and cerium oxides were uniformly distributed in the silicate melt product at approximately uniform concentrations.

- Stoots (1990) recommended the use of rare earth oxides of dysprosium, terbium and ytterbium as simulates for plutonium oxide in soils. This was a work plan for in-situ vitrification studies. Experimental data were not yet published at the time of this report.

- Whitworth is presently conducting a study at MSE in Butte, MT to investigate the distribution of plutonium oxide during the plasma melting of contaminated wastes and soils. Cerium oxide is being used as the surrogate for plutonium oxide. Results of early work are published. (Whitworth, et al, 1992)

- Schuster (1990) investigated the distribution of Co-60 in melt experiments performed on beta and gamma contaminated steel scrap. The distribution of cobalt was taken to be an effective indicator for the distribution of iron (Fe-55) and nickel (Ni-59, Ni-63).

- In a current RSM decontamination program, Atteridge and others (Atteridge, et al, 1994) state the surrogate choices for cesium and strontium were merely the naturally-occurring isotopic mixtures of these elements. The naturally-occurring isotopic mixtures of the rare earth elements cerium and neodymium were used because rare earth elements are the most abundant fission products and because these two elements could be used as surrogates for uranium and plutonium, respectively. The choices of Ce and Nd as substitutes for all rare earths were reasonable because, in general the reactivities and thermochemical properties of the rare earths are quite similar to one another; lanthanum was chosen as a general surrogate for these same reasons. Atteridge lists the free energies of stable oxides of radionuclides of interest and possible surrogate elements and states the choice of Ce as a surrogate for actinide elements is a common one.

- The suitability for Ce as a Pu surrogate has recently been discussed by Raraz, Mishra, and Averil. (Raraz, 1993)

- Worcester, et al (Worcester, 1994) present arguments similar to Atteridge for selection of Ce, La, and Nd surrogates and also present arguments for tracking cobalt in experimentation.

- Herbst, et al (Herbst, 1994) selected Hf as a surrogate for U based on thermodynamic and density considerations in their work on "Quantum-Catalytic" extraction at Molten Metal Technology Corporation.

- In a DOE report, Stockdale, et al (Stockdale, 1994) states the chief radioactive nuclides of concern in the treatment of mixed wastes are ^{239}Pu, ^{238}U, ^{235}U, ^{137}Cs, ^{103}Ru, ^{99}Tc, and ^{90}Sr. These nuclides are largely by-products of uranium enrichment, reactor fuel processing, and weapons program activities. ... The seven radionuclides listed can be simulated by a surrogate package containing stable isotopes of ruthenium, strontium, cesium, and cerium.

- Elert, et al (Elert, 1992) have summarized the ten radiologically most important radionuclides present (as a function of time) in decommissioning waste materials; their results are presented in Table 2.2.

- Dyer and Bechtold (1994) surveyed the types of nuclide contamination present in eleven pressurized boiling reactors (PWRs) and eight boiling water reactors (BWRs). They found that for the PWR reactor coolant, about 90% of the radionuclide activities are the radiocesium fission products with the other 10% being iron and cobalt activation products, Fe-55 and Co-60. For the BWR reactor coolant, about 91% of the activities are from Sb-125 which is an activation product of tin from the condenser tubing. The other 9% of the BWR reactor coolant activities is mainly from the activation products, Fe-55 and Co-60. For the samples of reactor component parts, between 86% to as much as 99% of the radionuclide activities are the activation products, Fe-55, Co-60, and Ni-63. This distribution of radionuclides for the reactor components appears to be the same whether the activities are contamination on the part surfaces or are contamination distributed within the part materials. In summary, for all the samples reviewed, the radionuclides that provided 1% or more of the total activities were: Mn-54, Fe-55, Co-60, Ni-63, Zn-65, Sb-125, Cs-134, and Cs-137. It appears that these would be the main radionuclides of concern for the recycling of material and stainless steel components from commercial nuclear power reactors in the United States.

TABLE 2.2. **THE TEN RADIOLOGICALLY MOST IMPORTANT RADIONUCLIDES AT DIFFERENT TIMES FOR SURFACE CONTAMINATION FOR DECOMMISSIONING WASTE (Elert, et al, 1992)**

+0 Years	+10 Years	+100 Years
Co-60	Co-60	Cs-137
Mn-54	Cs-137	Sr-90
Co-58	Sr-90	Ni-63
Cs-137	Fe-55	Co-60
Sr-90	Ni-63	Ni-59
Fe-55	Mn-54	Am-241
Zn-65	Cs-134	Pu-238
Ni-63	Ni-59	Pu-240
Cs-134	Am-241	Pu-239
Ce-144	Pu-238	Cs-135

2.4. THERMOCHEMISTRY

During the melt refining of the RSM the metal constituents will react with oxygen to form metallic oxides (oxygen can be supplied from various sources such as flux, air, and other oxides). The metal contaminant species react and form less dense oxides compared to the metal phase constituents and float to the surface to be collected by the slag. Two example reactions between metals and oxygen are illustrated below:

Equation (2.1) $2\ M + O_2 = 2\ MO_2$

Equation (2.2) $4/3\ M + O_2 = 2/3\ M_2O_3$

The free energy of formation is often used to determine the relative stability of the oxide and metallic species. Free energy is the driving force for thermodynamic equilibrium; therefore, the direction of a chemical reaction can be determined from the free energy relationship:

Equation (2.3) $\Delta G = \Delta G^\circ + RT \ln(Q)$

Equation (2.4) $\Delta G^\circ = - RT \ln(K)$, where

ΔG° = Gibb's Free Energy under standard state conditions
$R = 8.314$ J/gm mole
$T = {}^\circ K$

Equation (2.5) $Q = a_{products}/a_{reactants}$,

where

$a_{products}$ = The Product of the Activities of the Product Species

$a_{reactants}$ = The Product of the Activities of the Reactant Species

If the free energy is negative the reaction may (depending on the rate of reaction) proceed to the right and form the oxide species, but when the free energy is positive the reaction will not occur.

The basis for melt decontamination of the RSM is the high affinity of oxygen for the surrogate metals compared to the RSM metal constituents. In the presence of an oxidizing species the surrogate elements react first to form oxides before the metal constituents react to form oxides. This process has been described as "...the slag/melt refining program can be visualized graphically by considering the relative thermodynamic stability of the oxide phases for the slag constituents, steel constituents and the surrogate constituents. Relative qualitative 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." (Worcester, et al, 1994)

A simplified visualization can be made using Ellingham diagrams; e.g., the lower the free energy for a specific oxide (i.e., the more negative the free energy of formation) the greater the affinity of the metal for oxygen; therefore, the lowest oxide curve (on a plot of free energy versus temperature) represents the oxide that has the greatest thermodynamic probability of forming. Ellingham diagrams show that the surrogate elements have a greater affinity for oxygen than the steel and stainless steel elements. Ellingham plots for all the major constituents for both steel and stainless steel constituents (including cobalt) are presented in Figure 2.1. Cobalt is included since it is a contaminant in nickel and is a major gamma emitter source. An Ellingham plot is presented in Figure 2.2 for the constituents present in some of the fluxes used in the present study. The surrogate oxide Ellingham plot is presented in Figure 2.3. Note that the free energy curve for cesium oxide lies higher on the plot than the free energy curves for steel and stainless steel constituents. This suggests that cesium would not "getter" (form an oxide more stable than the stainless steel constituent oxides). However, cesium has a high volatility and is expected to be eliminated by vaporization from the molten melt. In Figure 2.4 the free energy of formation for the stainless steel oxides is compared to that of lanthanum oxide (representing cerium, lanthanum, and neodymium oxides). Note that lanthanum oxide is more stable than the stainless steel constituent oxides; therefore, lanthanum has a greater affinity for oxygen than do the stainless steel constituents.

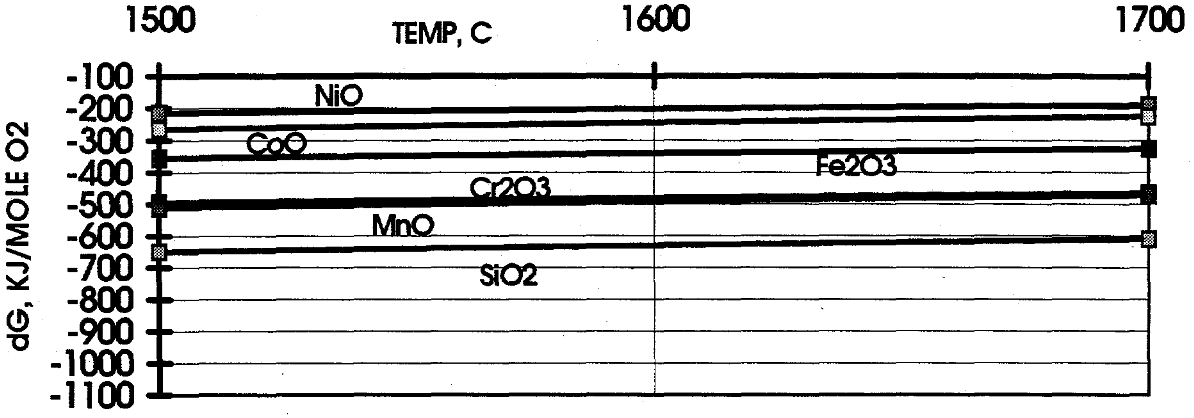

Figure 2.1. Ellingham Diagram for Stainless Steel Constituents (Worcester, et al, 1994)

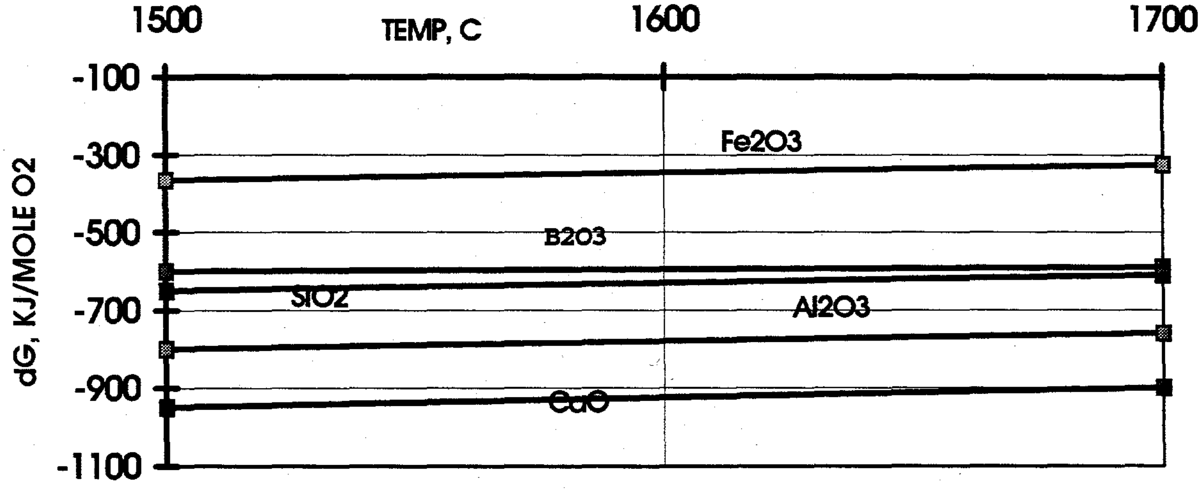

Figure 2.2. Ellingham Diagram for Slag Constituents (Worcester, et al, 1994)

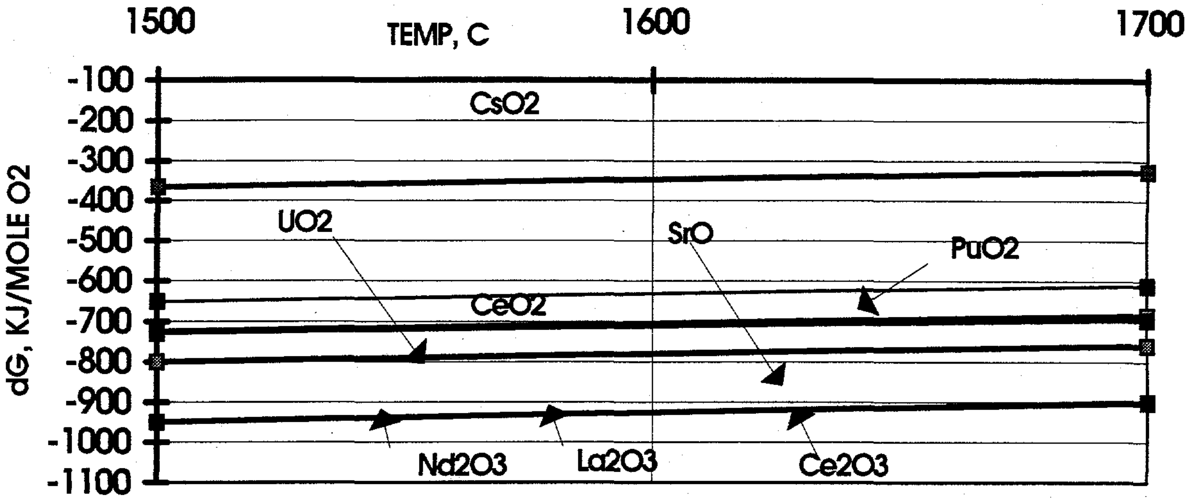

Figure 2.3. Ellingham Diagram for Surrogate Constituents (Worcester, et al, 1994)

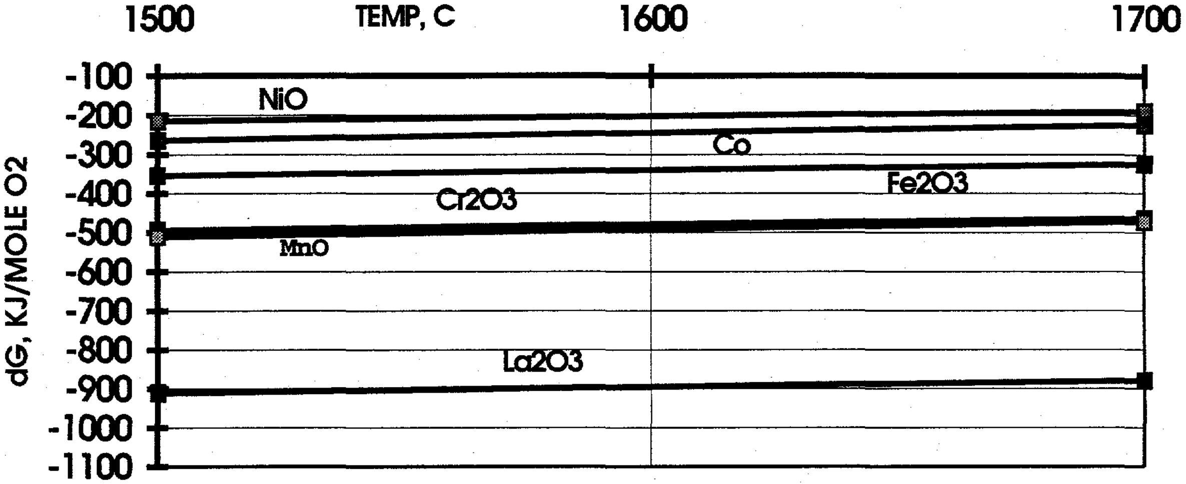

Figure 2.4. Free Energy of Formation for Lanthanum Oxide Compared to Steel Making Constituents (Worcester, et al, 1994)

2.5. CALCULATIONAL PROGRAMS

CSIRO/MONASH, a thermochemistry modeling program (Turnbull, 1992) for calculating high temperature equilibria, has been applied throughout the present study. The CSIRO/MONASH program provides the means for conducting various thermodynamic calculations for checking the thermodynamic feasibility of various proposed experiments. For example, questions similar to the following were considered: are the proposed conditions sufficiently oxidizing for removal of the surrogate elements without removing alloy constituents; will carbon be removed in preference to chromium, silicon, manganese; what is the effect of conducting the experiment in a vacuum; will a significant amount of fume be produced; what is the anticipated effect of raising or lowering the temperature; what is the anticipated effect of changing the flux composition?

There is presently insufficient thermodynamic data available for the surrogate constituents present in either the metal phase or in the slag solution to accurately model the distribution of surrogate elements between the metal, slag and gas phases on an exact quantitative basis. However, qualitative distributions can be determined that can be used as a guide for planning experimental test work. The metal/slag systems investigated in the present study included both stainless steel and carbon steel and a wide variety of slag/gas environments. The activities of the major slag constituents (CaO, SiO_2, Al_2O_3, Fe_2O_3) were assumed to be the same as in a steel refining slag (Elliott and McGleiser, 1963). The activities of the surrogate species in the slag solution (La_2O_3, Nd_2O_3,Ce_2O_3) were assumed to be ideal, i.e., their activities were taken to the same as their concentrations. The activities of the surrogate species in the steel solution were assumed to be ideal, i.e., their activity coefficients were assumed to be one. The activity coefficients for all the other species in the steel solution were modeled by using the Lupis-Elliott interaction coefficient formulation (Turnbull, 1992).

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

- The CSIRO/MONASH calculational program was used to estimate the influence of oxygen on the presence of surrogate elements in stainless steel (under conditions of the plasma preparation of the Master Alloy). A more detailed discussion of this test work is presented in Section 3.4.1 (Master Ingot Preparation). Sufficient surrogate metals (lanthanum, cerium, neodymium) and fluorides (cesium and strontium) were initially added to dope the stainless steel to 1000 mg/kg (ppm). The results showed 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 was approximately the input amount of surrogate for lanthanum, cerium and neodymium, and zero for cesium and strontium. Also, the calculational results show that just a small amount of oxygen significantly reduces the concentration of the surrogate metals in the stainless steel. This was what was seen in the actual experimental results. The source of oxygen present in the plasma melt environment could be from stainless steel surface oxide deposits or from slight contamination of the inert shrouding gas. The results of the calculation show that only a relatively small amount of oxygen will force the distribution of the rare earth-surrogate elements to the slag phase which is in agreement with the experimental results. Experimentally 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 will oxidize, e.g., at an oxygen addition of 0.125 gram oxygen/100 gram stainless steel the chromium content of the slag is estimated (from calculations) to be about four percent, at an oxygen addition of 0.145 gram oxygen/100 gram stainless steel the chromium content of the slag is estimated to be about 14 percent, at 0.205 gram oxygen/100 gram steel the slag chromium content is estimated to be 36 percent. (Worcester, et al, 1994)

- A second example of the guidance gained by use of the thermodynamic model is in considering what fluxes should be used in the melt/slag experimental test work. Boron oxide addition to high melting flux oxides lowers the melting temperature of the oxide mixture and also increases the fluidity of the slag solution. Therefore, the presence of boron oxide is desirable. However, boron oxide is a relatively volatile oxide and may be lost from the slag phase. This possibility was checked by using the calculational program. The thermodynamic calculational results show that it should be anticipated that the borate content (present in one of the major slag compositions investigated) in the equilibrium slag will be considerably decreased (over the amount added with the input flux) by distribution to the gas phase (as much as 50-60% may be lost to the gas phase) and (a minor amount) to the stainless steel phase This occurrence will certainly influence the liquidus temperature of the slag. If a strongly oxidizing slag is used 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, it was anticipated that there may be a problem in keeping the slag fluid at 1600° C if the borate content was decreased (by loss to the gas phase) and/or the chromium oxide content was increased too high (by strongly oxidizing conditions). Both of these effects were noted in our experimental test results, i.e., most of the boron oxide was lost from the slag phase during the test and high chromium contents were noted when strongly oxidizing fluxes were utilized.

- Another example of the usefulness of the calculational program was its use in guiding the experimental test work in the pilot scale vacuum induction melt (VIM) study (calculated results and experimental results are presented in Section 4.1.3). This investigation was aimed specifically at lowering the carbon content to meet the low carbon stainless steel specifications, i.e., < 300 ppm, by using vacuum induction melting in the presence of carbon dioxide or magnetite (as the oxygen sources). The calculational and experimental results for anticipated and achieved carbon contents were in general agreement, especially for the magnetite study.

DECONTAMINATION AND DECARBURIZATION OF STAINLESS STEEL AND CARBON STEEL BY MELT REFINING

SECTION THREE

RESEARCH PROGRAM: LABORATORY SCALE TEST WORK (INDUCTION MELTING)

3.1. GOALS OF THE LABORATORY TEST WORK

The goals of the laboratory test work included:

- The development of a test protocol for induction melt decontamination that results in lowering each surrogate concentration to less than one part per million.
- The determination of the importance of several experimental variables prior to conducting larger demonstration verification tests. The variables investigated included: time, temperature, flux composition, and amount of flux.

3.2. LITERATURE SEARCH COMMENTS

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.

Variables that are expected to influence the decontamination efficiency of slagging include: temperature, time, initial contaminant concentration, slag composition, metal composition, and gas environment (oxygen potential). Equilibrium may or may not have been established in the individual slagging studies and the results were likely influenced by variables such as time of exposure, method of addition of radioactive constituents (metals, oxides, hydroxides, halides), initial concentration of radioactive constituents, slag/metal contact (static, dynamic), reaction with crucible materials, slag/metal disengagement technique (slag inclusions formed in the metal phase), and method of sampling final products (surface samples, core samples). None of the published studies reported the final slag composition, i.e., in general, only the composition of the initial flux has been reported. Therefore, because of the many differences in experimental techniques and the lack of complete characterization, the published test work results were reviewed from a phenomenological viewpoint.

Published laboratory and large scale test work results demonstrate that slagging is an effective decontamination technology for the removal of uranium and plutonium from stainless and mild steel. Based on trends found in the literature, basic calcium-aluminum-silicate slags with additives such as ferric oxide appeared to be effective steel decontaminators and, therefore, the major emphasis in the present laboratory study was placed on using these flux constituents.

3.3. EXPERIMENTAL TEST FACILITY

3.3.1. INDUCTION FURNACE

The investigators chose 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 installed and utilized a 15 KW/10 KHz induction furnace manufactured by the AJAX Magnethermic Corporation. 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 was operated in manual mode for the present test work, but Montana Tech has installed an automated system which now controls power output by melt temperature via the linear output signal of a two color pyrometer. The automated system digitally records power, current, frequency, time, and temperature during the melt cycle. The table mounted furnace houses a water cooled induction coil and is mechanically supported such that melts are manually poured from the furnace. (Worcester, et al, 1994)

3.3.2. CRUCIBLE SELECTION AND FABRICATION

A high alumina-chromium oxide refractory was chosen for fabrication of the furnace crucible used during the initial Montana Tech melt campaign. The refractory was 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 had 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 not melt which would lead 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 that deserve further consideration include: magnesia, chrome magnesite and alumina-magnesia. Because of budgetary and time constraints the only refractory studied in detail was the alumina-chromia material.

Furnace 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 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. (Worcester, et al, 1994)

3.3.3. TEMPERATURE MEASUREMENT

A Modline R Series Two Color Pyrometer manufactured by IRCON Inc. was 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 to the furnace power supply. Pyrometer measurement range is 900-2,000°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. (Worcester, et al, 1994)

3.4. MASTER SURROGATE INGOT AND FLUX PREPARATION

3.4.1. MASTER INGOT PREPARATION

3.4.1.1. STAINLESS STEEL MASTER INGOT PREPARATION

Master alloy ingots were prepared to supply the necessary feedstock for all subsequent test work. The master alloy was prepared by melting stainless steel in an inert gas shrouded plasma cold hearth furnace in the presence of surrogate elements (Ce, La, Nd) and surrogate fluorides (Sr, Cs). The preparation of the master alloy was preformed at the RETECH facility in Ukiah, California and the details of the preparation are presented below.

3.4.1.1.1. PREPARATION OF THE MASTER INGOT

The feedstock used to produce the master alloy ingots was prepared in the Montana Tech laboratories. The preparation required the fabrication of two 15.2-centimeter feedstock pipes. The feedstock pipes were constructed of 15.2-centimeter 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 15.2-centimeter pipes in order to provide the desired total mass. 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 132 and 135 centimeters, with a total weight of 84 and 86 kilograms, 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 argon in 3.2-centimeter 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 relatively homogeneous ingot, individual "packets" were welded along the length of the two pipes at 9.1-Kg equivalent intervals. The packet/pipe construction was then slid into the 15.2-centimeter feedstock pipe. Photographs of the assembling process are presented in Figures 3.1.-3.3

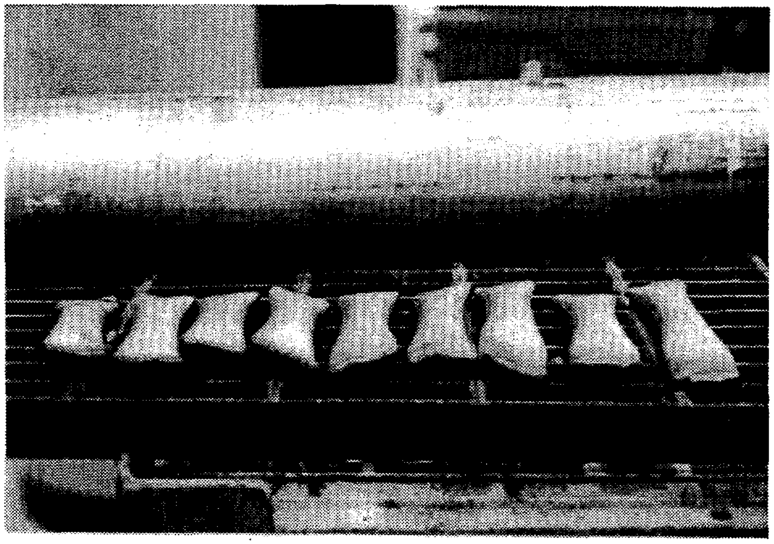

Figure 3.1. Photograph of the Pilot-Scale Feedstock Preparation Sequence: Welded Surrogate Package

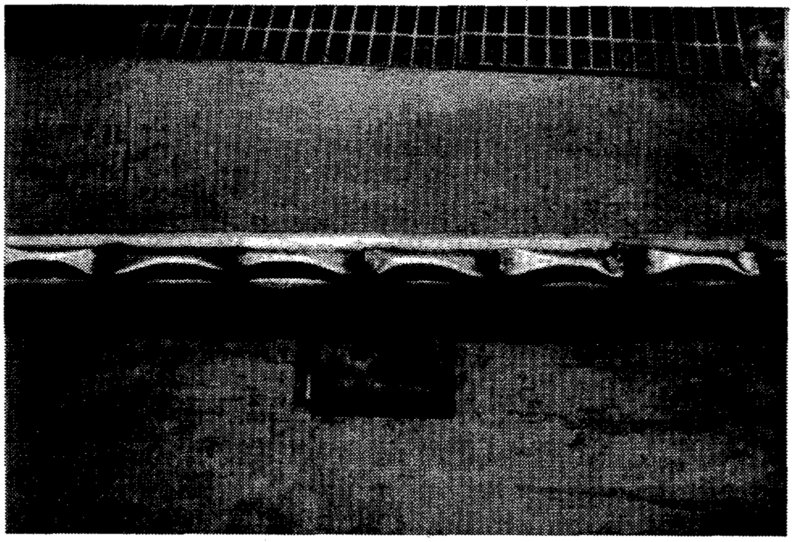

Figure 3.2. Photograph of the Pilot-Scale Feedstock Preparation Sequence: Surrogate Packages Welded to Insert Pipes

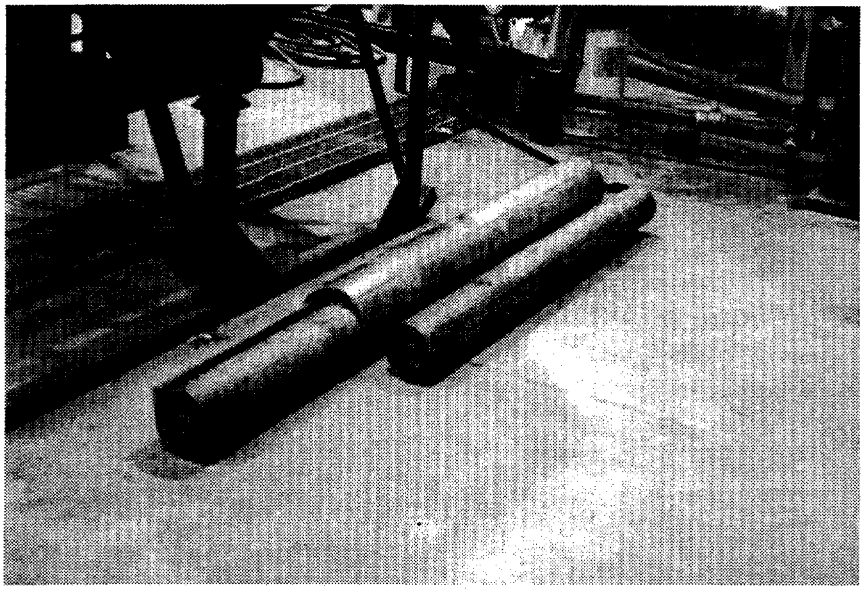

Figure 3.3. Photograph of the Pilot-Scale Feedstock Preparation Sequence: Final Feedstock Assemblage

The master ingot was prepared to provide sufficient surrogate containing stainless steel for all of the required laboratory scale experimental tests. The advantages of using plasma melting technology (in an inert atmosphere) 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 sectioning and sampling procedure is presented below.

3.4.1.1.2. SECTIONING, SAMPLING AND ANALYSIS OF THE MASTER INGOT

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. 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 3.4. 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 3.4. A photograph of the sectioned ingot is presented in Figure 3.5. Samples for elemental analysis (x-ray fluoescence and neutron activation) were taken from the edges and the centers of the three major sections as indicated in Figure 3.5. The analytical results (for the surrogate metal concentration and distribution) are presented in Section 3.4.1.1.3., Table 3.1.

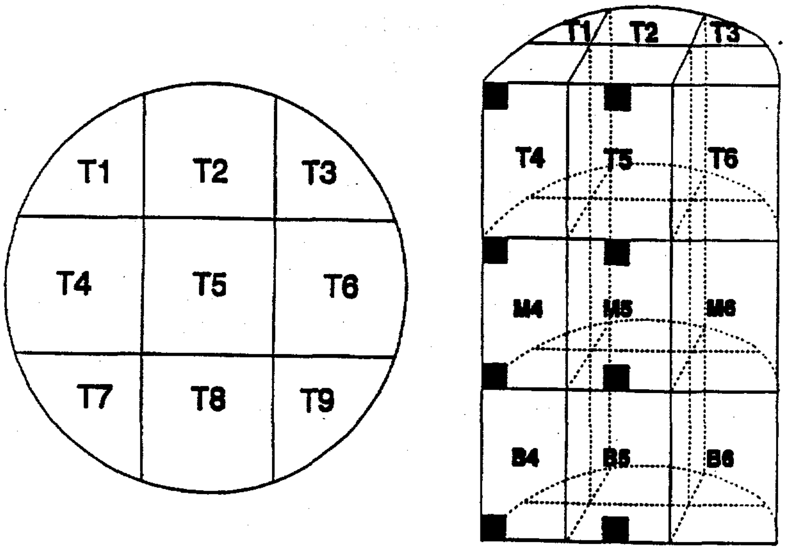

Figure 3.4. Schematic Diagram Depicting the Numbering Sequence Designation and Elemental Analysis Location of samples from the Master Ingot

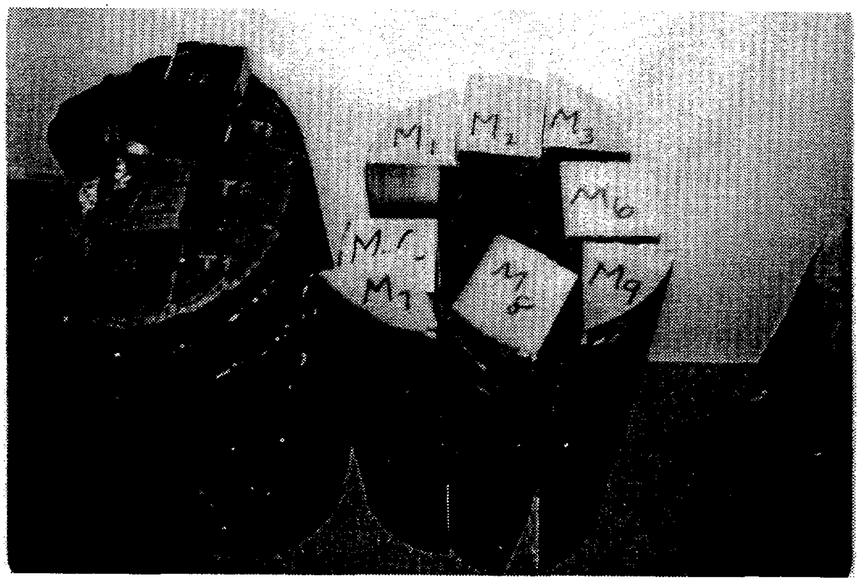

Figure 3.5. Photograph of the Sectioned Master Ingot

3.4.1.1.3. MASTER INGOT COMPOSITION AND DISCUSSION

TABLE 3.1. SURROGATE COMPOSITION OF THE STAINLESS STEEL MASTER INGOT (Worcester, et al, 1994)

SAMPLE (NUMBERING PER FIGURE 3.5)	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 D.L.=Detection Limit

The CSIRO/MONASH calculational program (Turnbull, 1992) was used to estimate the influence of oxygen on the presence of surrogate elements in stainless steel (under conditions of the RETECH furnace operation). 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 3.2. and for the slag phase in Table 3.3. Note (in Table 3.2) 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 (lost to the gas phase because of its relatively high volatility at elevated temperatures) and strontium (lost to the slag phase as strontium fluoride). Note also that a small additional 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 3.3).

TABLE 3.2. PREPARATION OF STAINLESS STEEL MASTER INGOT: METAL PHASE

ELEMENT	MEASURED, PPM IN METAL		CALCULATED(3), 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±11	1018	517	160	9	1	<1	<0.0
La	140±80	448±45	1018	534	199	12	2	<1	<0.0
Nd	357±100	630±32	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. 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 gram oxygen/100 gram stainless steel the chromium content of the slag is estimated to be about four percent, at an oxygen addition of 0.145 gram oxygen/100 gram stainless steel the chromium content of the slag is estimated to be about 14 percent, at 0.205 gram oxygen/100 gram steel the slag chromium content is estimated to be 36 percent. (Worcester, et al, 1994)

TABLE 3.3. PREPARATION OF STAINLESS STEEL 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. 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.

3.4.1.2. CARBON STEEL MASTER INGOT

A carbon steel master ingot was also assembled and plasma melted in a manner similar to the preparation of the stainless steel ingot. To facilitate obtaining feedstock for the small induction furnace, the 15.2-centimeter master ingot was forged (at Schlosser Forge) to a 4.4-cm round which was then sectioned for feed to the small induction furnace. Analytical results and surrogate predictions for the steel master ingot are presented in Table 3.4

TABLE 3.4. PREPARATION OF STEEL MASTER INGOT: METAL PHASE

ELEMENT	MEASURED, PPM IN METAL		CALCULATED[1], PPM IN METAL						
	MSM1	MSM2	GRAMS OXYGEN PRESENT/100 GRAMS OF STEEL						
			0.005	0.025	0.045	0.065	0.085	0.105	0.125
Cs	<DL	<DL	1.2	1.2	1.2	1.1	1.0	<1.0	<1.0
Sr	2	<DL	10.1	9.4	7.8	5.9	3.7	1.3	<1.0
Ce	170	230	676	436	188	60	14	1.0	<1.0
La	130	96	490	360	176	60	14	<1.0	<1.0
Nd	170	240	776	478	200	62	14	<1.0	<1.0

[1] CSIRO/MONASH program. Assumptions include: activity coefficients for all slag constituents assumed to be one. 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.

Calculated slag compositions for the carbon steel surrogate melt are included in Table 3.5. No analyses were performed on the slag phase obtained from the carbon steel master preparation surrogate melt.

TABLE 3.5. PREPARATION OF STEEL MASTER INGOT: SLAG PHASE

ELEMENT	MEASURED, % IN SLAG		CALCULATED, % OXIDES IN SLAG[1]						
	AS METALS	AS OXIDES	GRAMS OXYGEN PRESENT/100 GRAMS OF STEEL						
			0.005	0.025	0.045	0.065	0.085	0.105	0.125
Cs	N.A.	N.A.	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Sr	N.A.	N.A.	0.02 as SrO 2.7 as SrF_2	0.04 as SrO 2.5 as SrF_2	0.12 as SrO 4.2 as SrF_2	0.26 as SrO 6.3 as SrF_2	0.42 as SrO 8.2 as SrF_2	0.74 as SrO 10.4 as SrF_2	1.8 as SrO 13.1 as SrF_2
Ce	N.A.	N.A.	7.6 as Ce_2O_3 10.5 as CeF_3	24.0 as Ce_2O_3 4.3 as CeF_3	28.8 as Ce_2O_3 1.6 as CeF_3	29.0 as Ce_2O_3 0.99 as CeF_3	28.9 as Ce_2O_3 0.69 as CeF_3	28.5 as Ce_2O_3 0.43 as CeF_3	26.7 as Ce_2O_3 0.17 as CeF_3
La	N.A.	N.A.	0.24 as La_2O_3 68.7 as LaF_3	1.6 as La_2O_3 40.2 as LaF_3	6.5 as La_2O_3 28.7 as LaF_3	11.0 as La_2O_3 22.6 as LaF_3	14.3 as La_2O_3 18.2 as LaF_3	18.2 as La_2O_3 12.7 as LaF_3	22.2 as La_2O_3 5.6 as LaF_3

ELEMENT	MEASURED, % IN SLAG		CALCULATED, % OXIDES IN SLAG(1)						
	AS METALS	AS OXIDES	GRAMS OXYGEN PRESENT/100 GRAMS OF STEEL						
			0.005	0.025	0.045	0.065	0.085	0.105	0.125
Nd	N.A.	N.A.	10.2 as Nd_2O_3 0.06 as NdF_3	27.3 as Nd_2O_3 0.02 as NdF_3	30.1 as Nd_2O_3 <0.01 as NdF_3	29.8 as Nd_2O_3 <0.01 as NdF_3	29.4 as Nd_2O_3 <0.01 as NdF_3	28.8 as Nd_2O_3 <0.01 as NdF_3	26.7 as Nd_2O_3 <0.01 as NdF_3

1 CSIRO/MONASH program. Assumptions include: activity coefficients for all slag constituents assumed to be one. 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.

N.A.=Not Analyzed

3.4.2. FLUX PREPARATION

Flux constituents used in the laboratory scale test work included CaO, Al_2O_3, SiO_2, Fe_2O_3, $CaSiO_3$, $Ca(BO_3)_2$, and CaF_2. Each desired flux formulation (each formulation tested is presented in Section 3.5) was made by adding the appropriate amounts of each constituent. Powdered flux constituents were weighed and combined into a mixing bottle and then rolled for fifteen minutes to ensure that the constituents were homogeneously distributed. After mixing, the flux was poured around the metal charge prior to melting.

3.5. MELT/SLAG REFINING PROCEDURE

The master stainless steel ingots were sectioned as shown in the ingot map, Figure 3.5. After the master ingot was sectioned, pieces ranging from 680 to 1360 grams 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 carbon steel surrogate ingots were cut into approximately (900 gms) for subsequent melting experiments.

The metal sample was placed (usually approximately 400-900 gms) into the furnace crucible and its required flux poured around it (usually 2-5% flux was added). Flux compositions (and flux designations) used in the laboratory scale test work are presented below:

"Borate"-30%SiO_2, 40%CaO, 10%Al_2O_3, 15%Fe_2O_3, 5%$Ca_2B_6O_{11}$
"Borate" without Fe Oxide-13%CaO, 12%Al_2O_3, 68%$CaSiO_3$, 7%$Ca_2B_6O_{11}$
"Borate" without Borate-32%SiO_2, 10%Al_2O_3, 42%CaO, 16%Fe_2O_3
"Wollastonite"-100%$CaSiO_3$
"Fluoride"-30%SiO_2, 40%CaO, 10%Al_2O_3, 15%Fe_2O_3, 5%CaF_2
"Ferrite"-77.8%Fe_2O_3, 22.2%CaO
Calcium Fluoride-100%CaF_2.

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. 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. (Worcester, et al, 1994)

Slag and metal phase surrogate analysis for both steel and stainless steel were primarily performed using Induction Coupled Plasma/Mass Spectrometry (ICP/MS). The slag sampling was performed in two ways, i.e., one method was to recover the slag from the cast metal and slag after cooling. A second method consisted of sampling the slag in the molten state by plunging a cold metal rod into the molten slag and quickly withdrawing the rod. The adhering slag was then recovered. The second sampling method was preferred because metal contamination from the molten charge was minimized. The slag was then pulverized and submitted for analysis. Metal phase samples were obtained by drilling the cast ingot with a 3/8" drill bit to remove any surface oxidized metal; then metal shavings were obtained for analysis by drilling into the interior of the casting with a 1/4" drill bit. Most of the analyses were performed by Teledyne-Wah Chang Albany using Induction Coupled Plasma Mass Spectrometry (ICP-MS).

3.6. PRELIMINARY 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 Section 3.1.5. 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 wanted 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.

3.6.1. PRELIMINARY EXPERIMENTS: METAL PHASE

A series of 900 gram induction melts were performed by varying the time, temperature, and oxygen potential conditions. Thirty two laboratory scale experimental melts were performed on stainless and carbon steel in the induction furnace. The experimental results are presented in Tables 3.6 (for stainless steel) and 3.7 (for carbon steel). These melt tests provided quantitative information used to design the conditions for the larger pilot scale induction melt verification tests.

TABLE 3.6. EXPERIMENTAL CONDITIONS AND ANALYTICAL RESULTS FOR THE STAINLESS STEEL INDUCTION MELTS AT MONTANA TECH

EXPERIMENT CHARGE NUMBER (FIGURE 3.5)	TIME (MIN)	FLUX USED (CHARGE%)	SURROGATE IN METAL PHASE, PPM (Element subscript denotes concentration in Master Alloy)			Cr, Mn, & Si IN METAL PHASE, WT.% (Element subscript denotes concentration in Master Alloy)		
			La_{350}	Ce_{600}	Nd_{530}	$Cr_{18.7}$	$Mn_{1.42}$	$Si_{0.63}$
Temperature = 1500±50°C								
B5Tb	0.5	Borate w/o Fe Oxide (5%)	15	49	37	18.7	1.29	NA
T2Tb(1)	0.5	Borate w/o Boron (5%)	13	38	31	18.3	1.27	NA
B5Ta	5	Wollast.	0.47	1.5	1.1	18.4	0.76	NA
B1Ta	5	Fluoride (5%)	3.0	6.0	6.0	18.7	1.04	NA
B4Bb	5	Borate w/o Fe Oxide (5%)	3.3	9.2	7.6	18.8	1.28	NA
M5Ba	7	Borate w/o Fe Oxide (5%)	1.6	6.9	4.5	18.6	0.17	NA
B2Bb	15	Borate w/o Fe Oxide (5%)	<1.0	1.4	1.2	18.7	1.06	NA
Temperature = 1600±50°C								

EXPERIMENT CHARGE NUMBER (FIGURE 3.5)	TIME (MIN)	FLUX USED (CHARGE%)	SURROGATE IN METAL PHASE, PPM (Element subscript denotes concentration in Master Alloy)			Cr, Mn, & Si IN METAL PHASE, WT.% (Element subscript denotes concentration in Master Alloy)		
			La_{350}	Ce_{600}	Nd_{530}	$Cr_{18.7}$	$Mn_{1.42}$	$Si_{0.63}$
B3Bb	0.5	Fluoride (5%)	11.0	24.0	22.0	18.5	1.22	NA
B5Bb	5	Borate w/o Fe Oxide (25%)	2.0	4.0	<1.0	18.9	0.95	NA
M5Ta	4	None	0.55	2.40	2.20	NA	NA	NA
M5Bb	5	None (Argon)	1.80	14.0	6.20	NA	NA	NA
B5Mb	5	Borate (5%)	1.60	6.60	5.10	18.2	1.02	NA
M5Tb	5	Borate w/o Fe Oxide (5%)	1.60	6.30	<1.00	NA	NA	NA
B2Tb(1)	5	Borate w/o Boron (5%)	<1.0	<1.0	<1.0	18.4	1.23	NA
B4Ta(1)	15	Borate w/o Fe Oxide (5%)	<0.5	<1.0	<2.0	18.2 17.6*	1.08 1.05*	0.111 0.288*
T2Mb	30	Borate w/o Boron (5%)	<1.0	<1.0	<1.0	17.5	0.87	0.055
Temperature 1600 to 1690°C								
B5Ma	30	Borate w/o Fe Oxide (5%)	<1.00	<1.00	<1.00	16.6	0.52	NA
B5Ba	30	Borate (5%)	<1.00	<1.00	<1.00	17.1	0.55	NA
Temperature = 1700±50°C(2)								
B6Tb	5	Borate w/o Fe Oxide (5%)	<1.00	<1.00	<1.00	19.1	1.15	NA

EXPERIMENT CHARGE NUMBER (FIGURE 3.5)	**TIME (MIN)**	**FLUX USED (CHARGE%)**	**SURROGATE IN METAL PHASE, PPM (Element subscript denotes concentration in Master Alloy)**			**Cr, Mn, & Si IN METAL PHASE, WT.% (Element subscript denotes concentration in Master Alloy)**		
			La_{350}	Ce_{600}	Nd_{530}	$Cr_{18.7}$	$Mn_{1.42}$	$Si_{0.63}$
B6Ba	5(3)	Borate w/o Fe Oxide (5%)	<1.00	2.40	1.90	18.6	1.15	NA
B3Ta(1)	15	Borate w/o Fe Oxide (5%)	<1.0	<1.0	<1.0	17.5	0.87	0.055
T8Tb(1)	15	No Flux	<0.5	<1.0	<2.0	17.2	0.81	0.121
B1Tb(1)	15	Ferrite (5%)	<0.5	<1.0	<1.0	15.9 15.4*	0.59 0.60*	0.017 0.234*
T2Bb(1)	15	Calcium -Fluoride (100%)	<0.5	<1.0	<2.0	17.9 18.1*	1.02 1.25*	0.050 0.520*
B6Ta(1)	15	Borate w/o Fe Oxide (5%)	<0.5	<1.0	<2.0	18.2	1.06	0.066
B4Ba	15	Borate w/o Fe Oxide (5%)	<1.00	<1.00	<1.00	17.8	0.64	NA

(1) Experiments were performed in MgO crucibles.
(2) Melt temperature was held constant for these tests. The temperature in the previous tests were controlled to maintain a fluid slag.
(3) This 5 minute test was a duplicate test.

* Denotes that the data were obtained using the Spectro Analytical Instruments Spectro Lab F at AFFCO
NA: Not Analyzed
Fluxes: "Borate"-30%SiO_2, 40%CaO, 10%Al_2O_3, 15%Fe_2O_3, 5%$Ca_2B_6O_{11}$
"Borate" without (w/o) Fe Oxide-13%CaO, 12%Al_2O_3, 68%$CaSiO_3$, 7%$Ca_2B_6O_{11}$
"Borate" without Borate-32%SiO_2, 10%Al_2O_3, 42%CaO, 16%Fe_2O_3
"Wollastonite"-100%$CaSiO_3$
"Fluoride"-30%SiO_2, 40%CaO, 10%Al_2O_3, 15%Fe_2O_3, 5%CaF_2
"Ferrite"-77.8%Fe_2O_3, 22.2%CaO
"Fluoride"-100%CaF_2

Conclusions drawn from the above stainless steel data include the following:

- Temperature and time are important variables. At least 1600°C is necessary for effective surrogate removal; 1500°C is too low. When at 1600°C, five minute exposure is not sufficient for effective surrogate removal for any of the fluxes except the "Borate" (which contained ferric oxide), i.e., the stronger oxidizing condition provided by the ferric oxide does decontaminate the metal phase to <1 ppm for each surrogate. At fifteen and thirty minutes exposure the stronger oxidizing power of ferric oxide is not necessary to achieve effective surrogate removal, i.e., the "Borate" flux without ferric oxide was effective.

At 1700°C, short time exposure is all that is necessary, i.e., times between 5-15 appear to be effective without ferric oxide present.

The overall conclusion concerning effective surrogate removal is that higher temperature and strong oxidizing conditions (i.e., stronger than just air exposure) are necessary for effective decontamination in very short time periods. However, slightly longer times at more moderate temperature levels produce effective surrogate removal with and without the presence of flux, i.e., air is all that is needed for effective surrogate removal.

- Chromium is only slightly removed at 1600°C (for short exposure times), in the presence of "Borate" with ferric oxide (same conditions that effectively removed the surrogates). Chromium removal increased with temperature and time but was a function of type flux used, e.g., note that at 1700°C using the "ferrite" flux the chromium content in the metal phase was decreased to approximately 15.4%.

Manganese, in general, followed the same trend as chromium.

TABLE 3.7 EXPERIMENTAL CONDITIONS AND ANALYTICAL RESULTS FOR THE CARBON STEEL INDUCTION MELTS AT MONTANA TECH

TIME (MIN)	FLUX USED(1)	SURROGATE IN METAL PHASE, PPM(2) (Element subscript denotes concentration in Master Steel Ingot)					MN IN METAL PHASE, Wt. %(2)
		La_{213}	Ce_{200}	Nd_{205}	Sr_2	$Cs_{<1}$	$Mn_{0.75}$
Temperature = 1600±50°C							
5	(5%)	<1.0	<1.0	<1.0	<1.0	<1.0	0.23
15	(5%)	<1.0	<1.0	<1.0	<1.0	<1.0	0.077
30	(5%)	<1.0	<1.0	<1.0	<1.0	<1.0	0.021
Temperature = 1675±50°C							
5	(5%)	<1.0	<1.0	<1.0	<1.0	<1.0	0.094
15	(5%)	<1.0	<1.0	<1.0	<1.0	<1.0	0.044
15	NO FLUX	<0.5	<1.0	<2.0	<1.0	<1.0	0.26

1 Flux: 32%SiO_2, 42%CaO, 16%Fe_2O_3, 10%Al_2O_3

2 Element subscript denotes concentration in Master Alloy

Conclusions drawn from the above carbon steel data include the following:

- For carbon steel, as anticipated, all melting conditions produced removal of surrogates to below one ppm.

3.6.2. PRELIMINARY EXPERIMENTS: SLAGS

Analyses were performed on only a portion of the slags produced by the above described series of experiments. The results are reported in Table 3.8.

Comments concerning the stainless steel slag data presented in Table 3.8:

- There is apparent contamination of the slag by crucible MgO in samples T8Tb and BTTb.
- Chromium is relatively high in all the slags and highest in the slag formed from the strongest oxidizing flux, i.e., the "Ferrite" flux. The same comment applies to manganese.
- Surrogates (Ce, La, Nd) are present at much higher concentrations in the slag formed from the "Ferrite" flux.

TABLE 3.8. SLAG ANALYSES FOR THE EXPERIMENTAL INDUCTION STAINLESS STEEL TESTS

ELEMENT	SAMPLE ANALYZED							
	T8Tb (No Flux)	T2Bb (CaF_2 Flux)	T2Bb (Resample)	B6Ta (Borate, w/o Ferric Oxide)	BTTb (Ferrite Flux)	BTTb (Resample)	B3Ta (Borate, w/o Ferric Oxide)	B4Ba (Borate, w/o Ferric Oxide)
Al %	<0.1	<0.1	0.16/0.15	<0.1	<0.1	0.18/0.23	<0.1	<0.1
Ca %	<0.1	<0.1	0.45/0.58	<0.1	<0.1	0.41/0.42	1.3	<0.1
Co %	<0.1	<0.1	N.A.	<0.1	<0.1	N.A.	<0.1	<0.1
Cr %	24.5	21.2	N.A.	15.6	45.4	N.A.	19.7	18.6
Fe %	28.2	41.6	31.0/31.5	45.9	12.6	7.2/6.9	43.9	45.3
Mg %	5.10	1.20	N.A.	0.19	5.40	N.A.	0.93	0.56
Mn %	4.50	2.40	N.A.	0.82	10.1	N.A.	3.30	1.30
Si %	2.20	0.40	N.A.	<0.1	0.90	N.A.	1.30	0.27
Ce ppm	240	230	N.A.	83	1600	N.A.	390	150
La ppm	130	130	N.A.	64	1100	N.A.	30	120
Nd ppm	220	210	N.A.	79	1600	N.A.	380	140
Sr ppm	<5.0	6.7	N.A.	9.7	14	N.A.	68	<5.0

% = Weight Percent
ppm = Parts Per Million
N.A. = Not Analyzed

3.6.3. SLAG CHARACTERIZATION AND GENERAL OBSERVATIONS

Publications (from the computer data base search) did not report any final slag analyses or slag characterizations. The Montana Tech research team established the need to perform these procedures to determine element partitioning between slag constituents. Scanning Electron Microscopy/Energy Dispersive X-Ray Analysis (SEM/EDX) with standardless quantitative analysis software was used for the slag characterizations. Three slags, B5Ma, B5Tb and M5Tb were selected from the initial melt campaign for analysis. (Weldon, 1994)

Weldon (1994) reported in his M.Sc.Thesis the following: "Analysis of the slags show that dendrites high in chromium and manganese oxides exist in a variable composition matrix of Ca-Al-Si oxides along with varying amounts of chromium, manganese, and iron oxides. An SEM Digital Image of slag B5Ma is presented in Figure 3.6. In the image, the matrix is labeled "1", two metallic inclusions are labeled "3" and "6", and the dendritic oxide structures high in manganese and chromium are labeled "2", "4" and "5". Full standardless analyses for all numbered structures in the slag are located in Appendix B (Weldon, 1994), along with analyses obtained from slags B5Tb and M5Tb. All of the slags showed similar analyses and will be discussed collectively. It is assumed that all elements are present as oxides in the slag, except for metallic inclusions." (Weldon, 1994)

Surrogates cerium, lanthanum, and neodymium were detected in the slag matrix (composition varied over the range 0.28 to 1.76 weight percent). The surrogates cesium and strontium were not detected in any of the microstructural phases. SEM/EDX Standardless analysis provides only semiquantitative results and, therefore, the important result of this microstructural investigation is that the surrogates Ce, La, Nd are present in the matrix phase rather than in precipitated phases. However, this conclusion is only valid for the cooling conditions of the specific experiments. The microstructure present is, of course, very dependent on the rate at which the slag is cooled.

The matrix composition appears to vary with melt time (the chromium and manganese content in the three slag matrices increased with total melt time).

Dendrites high in chromium and manganese exist in the Ca-Al-Si oxide matrix. Chromium in the dendrites is present in the 49-59 weight percent range, manganese in the range 22-31 weight percent, and aluminum 3-7 weight percent (all based on oxide percentages). Surrogates were not detected in any of the dendrites. However, the present SEM/EDX system may not be able to detect the surrogates at very low concentrations, because of overlap problems between the Fe escape peak and the surrogate-La L_α peaks. A voltage sufficient to excite the surrogate K_α line (about 50-60 kV) was not available.

Oxidation potential and melt time may also effect the Cr-Mn dendrite formation by increasing the size of the dendrites. Precipitated phases present in the slag were noted to be larger for longer melt times and higher oxygen potential fluxes melts than for the short time low oxygen potential melts.

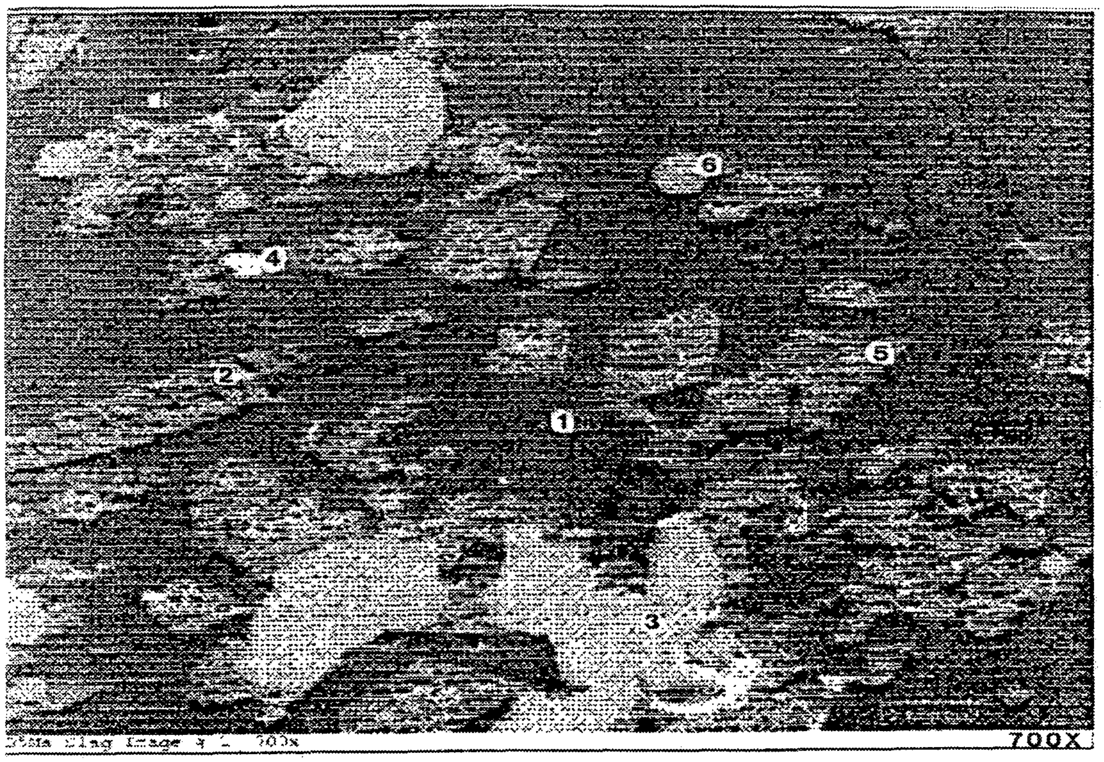

Figure 3.6. Digital SEM Image of Slag B5Ma. (Weldon, 1994)

Metallic inclusions were noted in the slags. The inclusions vary in composition from the starting metal to metallic particles that are essentially devoid of chromium and manganese. (Weldon, 1994)

3.6.4. ANALYSIS OF CRUCIBLE CORROSION DURING STAINLESS STEEL INDUCTION EXPERIMENTAL TEST MELTS

During the first melt campaign, ten stainless steel melts were made in a Scott-Ram 437A crucible for a total melt time of 100 minutes. Crucible wear for the entire program showed an average change in the crucible diameter of 0.077 mm per molten metal minute. These data were collected by measuring the diameter change at the molten metal/slag/crucible interface where there is the highest rate of crucible attack. Diametral corrosion was consistant over the entire diameter. 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. (Worcester, 1994). Later in the stainless steel melt campaign sacrificial fused MgO crucibles were utilized. The effects of crucible corrosion for the stainless steel melt campaign in MgO crucibles are presented in Table 3.9.

TABLE 3.9. RESULTS OF THE MgO CRUCIBLE CORROSION FOR THE STAINLESS STEEL MELT CAMPAIGN

EXPERIMENT IDENTIFICATION	CRUCIBLE CORROSION, CHANGE IN CRUCIBLE DIAMETER, cm	TIME, MIN	TEMP, °C	FLUX, (Wt.%)	VISUAL OBSERVATIONS
T2Tb	0.2	0.5	1500	Borate w/o Boron (5%)	Excellent ingot condition
B2Tb	0.2	5	1600	Borate w/o Boron (5%)	Slag adhered to metal, moderate surface oxide buildup
B4Ta	1.0	15	1600	Borate (5%)	Slag adhered to metal
T8Tb	0.3	15	1675	None	Excessive oxide products on metal surface
T2Bb	0.12	15	1675	Fluoride (5%)	Excessive oxide products on metal surface
B6Ta	0.3-1.3	15	1675	Borate (5%)	Slag adhered to ingot
B3Ta	0.3-1.0	15	1675	Borate (5%)	Slag adhered to ingot
B1Tb	0.3-1.0	15	1700	Ferrite (5%)	Slag adhered to ingot, good ingot condition

Flux: "Borate" without (w/o) Boron-32%SiO_2, 10%Al_2O_3, 42%CaO, 16%Fe_2O_3
"Borate"-30%SiO_2, 40%CaO, 10%Al_2O_3, 15%Fe_2O_3, 5%$Ca_2B_6O_{11}$
"Fluoride"-100%CaF_2
"Ferrite"-77.8%Fe_2O_3, 22.2%CaO

Crucible corrosion observations for the carbon steel campaign are summarized in Table 3.10.

TABLE 3.10. THE EFFECTS OF CRUCIBLE CORROSION FOR THE STEEL MELT CAMPAIGN

EXPERIMENT IDENTIFICATION	CRUCIBLE CORROSION (INCHES)	TIME (MIN)	TEMPERATURE (°C)	FLUX[(1)] (Wt.%)	CARBON CONTENT, Wt.%	COMMENTS
STM8994-2	0.031	5	1600	5%	0.02	Slag adhered to both crucible and metal, heavy ingot porosity

EXPERIMENT IDENTIFICATION	CRUCIBLE CORROSION (INCHES)	TIME (MIN)	TEMPERATURE (°C)	FLUX[1] (Wt.%)	CARBON CONTENT, Wt.%	COMMENTS
STM8994-3	0.062	15	1600	5%	0.08	Slag adhered to both crucible and metal, heavy ingot porosity
STM8994-5	0.38	30	1600	5%	<0.01	Slag adhered to crucible, good ingot condition
STM8994-4	0.12	15	1675	5%	0.01	Slag adhered to crucible, moderate ingot porosity
STM8994-6	0.12-0.38	5	1675	5%	0.10	Slag adhered to crucible, fair ingot condition
STM72694-1	0.062	15	1675	None	0.26	Slag adhered to both crucible and metal, ingot porosity

1 Flux: Borate w/o Boron-32%SiO_2, 10%Al_2O_3, 42%CaO, 16%Fe_2O_3

Crucible/slag corrosion comments are presented below:

- The expected trend of increased corrosion for longer melt times and higher melt temperatures was confirmed.
- Slag/crucible interaction increased for the MgO crucibles when the "borate" flux was used as compared to no flux in the melt, B3Ta/B6Ta versus T8Tb.
- Every MgO crucible thermally cracked during the melting process; therefore, MgO crucibles were not recommended for the subsequent pilot scale studies.

3.7. ATTAINMENT OF THE LABORATORY TEST WORK GOALS

As stated previously the goals set forth for the laboratory experimental program included:

- The development of a test protocol for induction melt decontamination that results in lowering each surrogate concentration to less than one part per million.
- The determination of the importance of several experimental variables prior to conducting larger demonstration verification tests. The variables investigated included: time, temperature, and flux composition.

The stated goals have been achieved. A test protocol has been developed for treating surrogate bearing carbon and stainless steel that results in attaining surrogate concentrations that are less than one milligram per kilogram of steel, i.e., 1 ppm . This protocol has been applied to larger scale demonstration verification melts with successful results (described in Sections 4.1 and 4.2).

DECONTAMINATION AND DECARBURIZATION OF STAINLESS STEEL
AND
CARBON STEEL BY MELT REFINING

SECTION FOUR
STAINLESS STEEL PILOT AND COMMERCIAL SCALE TEST WORK

4.1. PILOT SCALE PLASMA AND VACUUM INDUCTION MELTING TEST PROGRAM

Two pilot scale melt programs were conducted; one utilizing a two torch cold hearth plasma melt furnace and one utilizing a vacuum induction furnace. A description of the facilities, test procedures and test results are presented and discussed below. The intent of the pilot scale test work was to demonstrate that the basic information generated during the laboratory scale test work could be utilized in pilot scale tests and subsequently in commercial scale treatment systems.

4.1.1. GOALS OF THE PILOT SCALE TEST WORK

The goals of the pilot scale stainless steel test work included:

- The evaluation of whether effective surrogate removal could be accomplished using plasma torch melting under controlled oxidation potential conditions (applied to approximately two hundred pounds of surrogate-loaded stainless steel).

- The evaluation of whether effective surrogate removal and carbon reduction could be accomplished without appreciable chromium loss by vacuum induction melting (VIM) under controlled oxygen potential (applied to approximately two hundred pounds of surrogate-loaded stainless steel).

4.1.2. PLASMA PILOT SCALE MELT TEST PROGRAM

A number of experimental tests were performed in the RETECH (Ukiah, California) facility. Master alloy ingots were melted in various gaseous environments with and without the present of flux materials (i.e., the oxidizing potential in the tests was varied over a wide range) to investigate the degree of surrogate removal by controlling the oxidizing potential during the period. The melt procedure and the test results are presented in the following sections. The same plasma facility was utilized for this test program as that utilized for the preparation of the Master Ingots (See Section 3.4.1.)

4.1.2.1. DESCRIPTION OF THE MELT PROCEDURE

The melt procedure described previously for preparation of the Master Ingot (Section 3.4.1) is essentially the same procedure utilized for conducting the plasma controlled oxidation test work.

The major differences were that the gas atmosphere was modified and/or flux material was added to the melt chamber in order to control the oxidizing potential in the furnace environment. A detailed description of the melt procedure is presented by Paolini (1995) in his M.Sc. thesis. For the purposes of this report the initial conditions and melt procedure are described individually for each test in the following sections.

4.1.2.2. CONTROLLED OXIDATION MELT WITH AN OXIDIZING FLUX

A series of tests were conducted at RETECH in Ukiah, California utilizing their two torch plasma cold hearth melting facility. The experimental test program and results are summarized in the following sections.

4.1.2.2.1. INITIAL CONDITIONS FOR FIRST MELT/FLUX EXPERIMENT

The first pilot scale surrogate-removal melt was performed March 3, 1994 at RETECH, Inc. This test was designed to examine the effect of oxidation potential (by controlling flux addition) in removing surrogates La, Nd, Ce, Sr, and Cs from stainless steel without crucible interaction. The oxidation potential was controlled in the test by addition of the following fluxes:

- Stage One: No flux present (reference stage)
- Stage Two: "Borate" flux without ferric oxide
- Stage Three: "Borate" flux.

The melt test was conducted in RETECH's two-torch cold hearth plasma furnace in a helium atmosphere. Using this facility, the oxidizing potential of the slag could be assessed without interference from crucible material (because the hearth and mold crucible were both water cooled copper) and atmospheric gases. The procedure used consisted of melting approximately 30 kilograms of stainless steel without flux (Stage One), then melting a similar amount of stainless steel doped with an oxidizing flux (Stage Two); then melting a similar amount of stainless steel doped with a more oxidizing flux (Stage Three). Stage One and Two melting was conducted sequencially without stopping. The melting was then discontinued and the system opened up so that a slag sample could be collected after Stage Two melting. The system was then closed and Stage Three melting was performed.

In Stage One 32 kilograms of stainless steel feedstock was melted in the presence of packets of surrogate containing elements. No flux was present. Stage One melting had two purposes, i.e., to fill the hearth with surrogate containing metal and to demonstrate that melting stainless steel feedstock with surrogates would produce a high surrogate containing metal phase (similar to the master alloy in surrogate content). The major goal of Stage One was to demonstrate that the furnace helium (nonoxidizing) atmosphere was not oxidizing enough to oxidize the surrogates.

the metal phase for surrogate content provided the reference state for determining the effect of flux additions.

In Stage Two a 45.4 kilogram section of feedstock (containing surrogate packets) plus 2% flux without the presence of iron oxide (11.8% Al_2O_3, 35.3% SiO_2, 49.1% CaO, and 3.8% B_2O_3) was melted. The purpose of Stage Two melting was to demonstrate that a mildly oxidizing flux would result in at least partial surrogate removal.

In Stage Three a 45.4 kilogram section of feedstock (containing surrogate packets) plus 2% "Borate" flux containing 15% iron oxide (10% Al_2O_3, 30% SiO_2, 41.8% CaO, 3.2%B_2O_3, and 15% Fe_2O_3) was melted. The purpose of Stage Three melting was to demonstrate that a more aggressive oxidizing flux would result in greater surrogate removal.

Surrogates were added to the melt stock (during the melting process) in the same manner used for the master melt described in Section 3.4.1. Flux was present in 6.4 centimeter diameter Type 304 stainless steel tubes (attached to the ingot) that melted as the ingot was fed to the torches. Calcium borate was present as "Gerstley Borate," calcium silicate as "Wollastonite (100% $CaSiO_3$)," aluminum oxide as alumina and iron oxide as ferric oxide. (Worcester, 1994)

The ingot was continuously fed to a torch that melted the metal into a water cooled hearth. The rate of metal feed was controlled by this torch. The melt rate was held to approximately 20 centimeters/hour at steady state. The metal pool was kept molten by continuously exposing the hearth metal to the hearth torch. Periodically the hearth metal was fed into an extractable-bottom mold by melting a hearth dam of solidified metal that existed between the hearth and the extractable-bottom ingot crucible. The metal in the ingot mold was kept molten by a second torch that continuously rotated over the surface of the mold metal.

4.1.2.2.2. TEST RESULTS

Results from these tests showed less effective surrogate removal than that achieved during the laboratory air induction melt study. Analytical results for the metal and slag phases are presented in Tables 4.1 and 4.2 respectively. (Weldon, 1994)

4.1.2.2.2.1. METAL ANALYSES

Analysis of the metal phase revealed that decontamination levels achieved in the previous open atmosphere induction melts were not met by this test series; even though the oxygen potentials supplied by the fluxes in Stages Two and Three were calculated (by the CSIRO/MONASH program) to be sufficient to oxidize all of the surrogates from the melt. Metal phase analyses were performed using ICP-MS.

TABLE 4.1. FIRST FLUX CONTROLLED OXIDATION METAL PHASE ANALYSES

SAMPLE*	CE, PPM	LA, PPM	ND, PPM	CS, PPM	SR, PPM	CO, WT.%	CR, WT.%	MN, WT.%
Stage One: No Flux	570	270	650	<1	1.5	0.075	18.7	1.4
Stage Two: NFe1	360	150	290	<1	<1	0.078	18.6	1.40
Stage Two: NFe2	250	100	240	<1	<1	0.073	18.6	1.40
Stage Two: NFe3	120	64	110	<1	16	0.074	18.6	1.42
StageThree: Wfe1	360	160	340	<1	<1	0.076	18.7	1.41
Stage Three: WFe2	250	220	300	<1	<1	0.073	18.8	1.40
Stage Three: Wfe3	53	22	35	<1	<1	0.071	18.3	1.48

* Stage One, No Flux is the baseline for the other tests; no flux was used. The results compare favorably with the composition of the Master Alloy (Ce 522±136, La 432±77, Nd 658±144),.
Stage Two, NFe denotes borate flux without ferric iron present (less oxidizing slag formed).
Stage Three, WFe denotes borate flux with ferric iron present (more oxidizing slag formed).

Numbering sequence 1,2,3 denotes increasing slag/metal contact time. Higher numbered samples designate metal that was contacted with accumulated slag throughout the test melt period, i.e., sample 3 was taken from the top of the final product ingot).

Comments concerning the test results are presented below:

- The concentration of surrogates in the stainless steel in the absence of fluxing agents compared favorably with the results obtained for the preparation of the "Master" alloy utilized in the previous laboratory induction tests.

- Increasing oxygen potential in the system increased surrogate removal from the melt. Final surrogate concentrations for the "Borate" flux containing ferric oxide were lower (Ce 53 ppm, La 22 ppm, and Nd 35 ppm) compared to the final surrogate concentrations for the non-ferric oxide containing "Borate" flux (Ce 120 ppm, La 64 ppm, and Nd 110 ppm). This trend was anticipated based on thermodynamic calculations. However, it was anticipated that lower surrogate concentrations would be achieved for both slag exposures.

- Slag/Metal contact time had a significant effect on the surrogate removal efficiency of the slags. For both of the borate slags, surrogate removal was not as effective as open air atmosphere melting in induction furnace systems.

furnace. For the same contact time during induction melting less than 1 ppm surrogate concentrations were achieved.

- Sr and Cs were significantly removed from the metal phase simply by melting the stainless steel. Sr and Cs concentrations were <1.0 and 1.5 ppm, respectively, without the addition of flux. The flux addition to the melt brought the Sr concentration to below 1 ppm. Sample NFe3, one of the highest oxygen potential samples, showed Sr at 16 ppm, but this sample result is inconsistent with all the other results.

- Co concentration in the metal phase remained constant throughout all stages of the controlled oxidation testing.

- Cr and Mn concentrations in the metal phase did not appear to be affected by the oxidizing action of the slag. However, both are shown to be present at significant concentrations in analysis of the slag phase. (Weldon, 1994)

4.1.2.2.2.2. SLAG ANALYSES

All slag samples were collected from the indicated areas of Figure 4.1 for the RETECH plasma melts. The slag generally was loose on the metal surface except around the outer edges of the hearth. The slag analytical results are presented in Table 4.2.

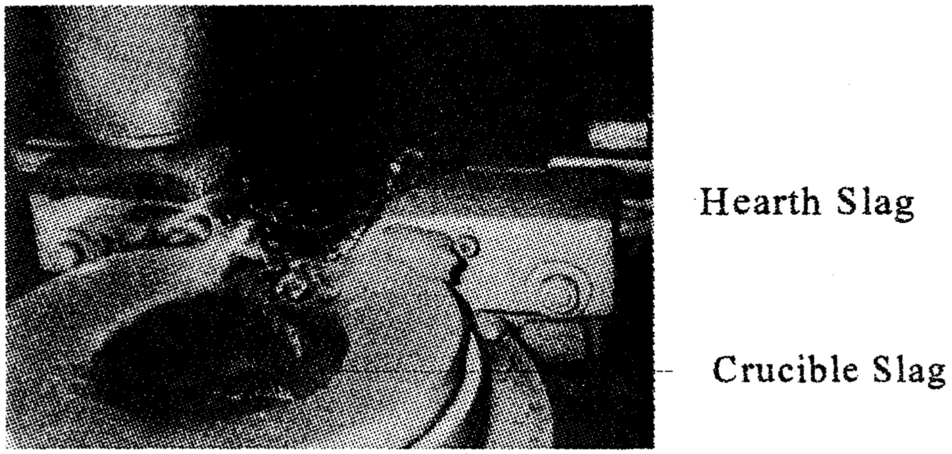

Figure 4.1. Slag Collection Points from the Retech Plasma Furnace

TABLE 4.2. FLUX CONTROLLED OXIDATION SLAG ANALYSES

TABLE 4.2. FLUX CONTROLLED OXIDATION SLAG ANALYSES (WELDON, 1994)

	SAMPLE			
	Hearth Slag (Borate Flux Without Iron Oxide)	**Crucible Slag (Borate Flux Without Iron Oxide)**	**Crucible Slag (Borate Flux With Iron Oxide)**	**Hearth Slag (Borate Flux Without Iron Oxide)**
Mass,(grams)	981	65	920	340
Starting Flux Composition[*]				
SiO_2 (Wt.%)	35	35	30	30
CaO (Wt.%)	49	49	42	42
Al_2O_3 (Wt.%)	12	12	10	10
Fe_2O_3 (Wt.%)	-	-	15	15
B_2O_3 (Wt.%)	4	4	3	3
Controlled Oxidation Melt Final Slag Composition: X-Ray Fluorescence				
Al (%)	4.6	4.6	4.5	3.5
Ca (%)	18.4	18.3	18.1	14.1
Si (%)	22.0	27.2	32.6	23.5
Cr (%)	0.6	0.6	1.1	0.8
Mn (%)	1.1	1.1	1.9	1.6
Fe (%)	0.6	0.6	0.7	0.5
Ni (ppm)	348	143	45	331
Sr (%)	2.5	2.3	3.0	6.8
Cs (ppm)	60	<15	18	300
Ce (%)	2.7	2.5	2.8	5.0
La (%)	2.7	2.5	2.8	6.2
Nd (%)	2.9	2.5	2.7	6.3
Co (ppm)	31	34	<15	<15
REFINED METAL INGOTS MAJOR SLAG CONSTITUENTS AS OXIDES: SEM/EDX STANDARDLESS QUANTITATIVE ANALYSIS				
Al_2O_3 (Wt.%)	9.8	9.4	8.4	7.6

	SAMPLE			
	Hearth Slag (Borate Flux Without Iron Oxide)	**Crucible Slag (Borate Flux Without Iron Oxide)**	**Crucible Slag (Borate Flux With Iron Oxide)**	**Hearth Slag (Borate Flux Without Iron Oxide)**
CaO (Wt.%)	45.0	40.4	41.1	35.5
SiO_2 (Wt.%)	29.9	26.7	30.1	29.8
Cr_2O_3 (Wt.%)	2.1	2.0	3.0	2.4
MnO (Wt.%)	1.8	1.6	2.6	2.4
FeO (Wt.%)	2.6	11.8	4.9	4.8
Ce_2O_3 (Wt.%)	2.9	2.5	3.2	5.0
La_2O_3 (Wt.%)	3.0	2.8	3.2	6.6
Nd_2O_3 (Wt.%)	2.8	2.7	3.4	6.0

* Flux was added at a rate equivalent to two weight percent of feed material.

The resultant slag was not continually removed from the plasma-arc furnace, but was allowed to cumulatively contact the hearth and crucible molten metal pools until all feed was consumed.

The cumulative slag collected for the ingot using 2% "Borate" with iron oxide and 2% "Borate" without iron oxide weighed 1259 and 1215 grams, respectively.

The following comments concerning the test results are presented below:

- Significantly more surrogate was recovered from the metal phase for the "Borate" flux containing ferric oxide (based on the hearth slag). This effect was noted for all of the surrogates.

- Cr and Mn were present in the slag phase and their concentrations increased with increasing oxidation potential of the flux. The metal analytical data showed no loss of chromium or manganese as a function of oxidizing potential (within the reproduciblity of the data). The differences are likely due to the fact that a small loss of chromium and manganese from a large mass of metal (approximately 40 kilograms of metal) resulted in measureable amounts in the small mass of slag (approximately 1200 grams).

- Ferric oxide added as flux was significantly reduced in concentration during the treatment process (indicating that it served its purpose as an oxidant).

- The final slag composition varied little for the major constituents from the starting flux, with only minor additions of chromium, manganese, and surrogate oxides. (Weldon, 1994)

4.1.2.2.2.3. DISTRIBUTION RATIO

Distribution ratios were calculated for the samples NFe3, and WFe3 and the values are presented in Table 4.3. The distribution ratio is defined as follows:

Distribution Ratio =

[Surrogate in the slag, ppm]/[Surrogate in the metal, ppm]

For example the D.R. for NFe3 is

D.R.(for Ce) = 25000/120 = 208

Note that the distribution ratio values are higher for the WFe3 exposure, i.e., the flux containing ferric oxide was more oxidizing to the surrogate elements than the flux without ferric oxide.

TABLE 4.3. DISTRIBUTION RATIOS FOR THE FIRST RETECH FLUX CONTROLLED OXIDATION MELT

Sample	Ce	La	Nd	Cs	Sr
NFe3	208	385	74	N.A.	1438
WFe3	528	1273	771	N.A.	N.A.
N.A. = Not Available					

4.1.2.3. SECOND CONTROLLED OXIDATION MELT WITH AN OXIDIZING FLUX

4.1.2.3.1. INITIAL CONDITIONS FOR MELT/FLUX EXPERIMENT

The second pilot scale controlled oxidation test was performed at RETECH, Inc. on May 26-27, 1994. This pilot scale test was similar to the first pilot scale test for controlling the oxygen potential with fluxes. The fluxes for this test series were chosen to provide more aggressive oxidizing conditions than were used in the first test series. The flux compositions for this test series consisted of the following:

- "Borate" Flux (5 wt.% added) with ferric oxide
  ($10\%Al_2O_3$, $15\%Fe_2O_3$, $5.9\%Ca_2B_6O_{11}$, $58\%CaSiO_3$, $11.1\%CaO$)

- "Ferrite" Flux (5 Wt.% added)
  (77.8% Fe_2O_3, 22.2%CaO)

The ferrite flux had the higher oxidizing potential.

The test melt was conducted in RETECH's two torch cold crucible plasma furnace. The two product ingots from the first controlled oxidation melt were remelted at the increased oxidation potentials to determine if additional surrogates could be removed. The melt stock consisted of the two 15.2 centimeter diameter, 45-kilogram ingots with fluxing agents tacked onto the sides in sealed stainless steel tubes. Additional compacted "Borate" flux (in a stainless steel container) was placed on the skull (the hearth metal that remained after the first test series) to provide the proper desired flux/metal ratio. During the melt, the molten metal and flux cover in the cold copper ingot crucible was magnetically stirred throughout the test period. The feedstock melt rate was held to approximately 20 centimeters/hour at steady state. The molten layer in the crubible ingot was maintained in the liquid state for an additional 30 minutes after all the feedstock had been transferred to the crucible. This "soaking" period was achieved by placing both torches over the top of the liquid in the mold crucible.

After the "Borate" exposure was complete the test was terminated and the product ingot and slag were recovered. The system was then closed and the second exposure utilizing "Ferrite" flux was conducted in a similar manner to the "Borate" exposure. The only noted difference between the two tests was that the soaking period for the "Ferrite" exposure was forty minutes.

4.1.2.3.2. TEST RESULTS

4.1.2.3.2.1. METAL ANALYSES

During the "soaking" period for the "Borate" test at least 3.8 centimeters of slag covered the crucible. It was anticipated that the extra 30 minutes of molten metal/slag contact should have allowed for adequate oxidation of the surrogates, but as the metal analysis (presented in Table 4.4) show the surrogate concentrations were still above 1.0 ppm.

TABLE 4.4. METAL ANALYSES FOR SECOND FLUX CONTROLLED OXIDATION MELT

ELEMENT	SAMPLE ANALYZED			
	BORATE FLUX		FERRITE FLUX	
	M52694T	M52694S	M52794T	M52794S
Co %	0.071	0.064	0.068	0.065
Cr %	18.8	19.1	17.7	18.5

ELEMENT	SAMPLE ANALYZED			
	BORATE FLUX		FERRITE FLUX	
	M52694T	M52694S	M52794T	M52794S
Mn %	1.31	1.27	0.91	1.07
Ce ppm	30	14	22	8.0
Cs ppm	<0.5	<0.5	<0.5	<0.5
La ppm	19	4.9	14	4.8
Nd ppm	24	13	20	7.8
Sr ppm	8.7	<0.5	4.5	0.8

% = Weight percent
ppm = Parts Per Million
Sample Identification: M52694T-Borate; metal from top of crucible ingot
M52694S-Borate; metal from side of ingot
M52794T-Ferrite metal from top of ingot
M52794S-Ferrite metal from side of ingot

Comments concerning the test results are presented below:

- Surrogate concentrations in the product ingots were significantly decreased from the starting concentrations. The surrogate concentrations at the slag/metal ingot surface were not very different in this test than in the First Flux Controlled Oxidation Melt test (for "Borate" with ferric oxide), i.e., the much greater oxidizing conditions supplied by the fluxes in the Second Flux Controlled Melts were not much more effective than the less aggressive oxidizing conditions supplied by the fluxes in the First Flux Controlled Melts.

- Ce, La, Nd, and Sr were all present at higher concentrations in the top of the ingot (compared to the samples taken from the side of the ingot) irregardless of the flux used.

- Some chromium and manganese was lost from the steel. A greater loss was produced by the more oxidizing conditions of the "Ferrite" flux.

4.1.2.3.2.2. SLAG ANALYSES

The "Borate" slag had a much higher fluidity than the "Ferrite" slag. The quantity of slag recovered from product ingot using 5% "Borate" flux and 5% "Ferrite" flux was 1832 and 3124 grams, respectively. The slag phase analyses are presented in Table 4.5.

TABLE 4.5. SLAG ANALYSES OF SECOND FLUX CONTROLLED OXIDATION MELT

ELEMENT	SAMPLE ANALYZED			
	BORATE FLUX		FERRITE FLUX	
	S52694H	S52694I	S52794H	S52794I
Al (%)	5.41	1.41	5.57	1.09
B (%)	0.44	0.17	0.17	0.13
Ca (%)	30.4	19.0	33.4	16.8
Cr (%)	2.84	10.8	1.99	11.2
Fe (%)	0.39	6.91	0.31	5.64
Mn (%)	3.33	7.16	2.21	7.06
Mo (%)	<0.05	<0.05	<0.05	<0.05
Na (ppm)	<150	<150	<150	<150
Nb (%)	<0.05	0.11	0.06	0.12
Ni (%)	<0.05	<0.05	<0.05	0.07
Si (%)	15.9	10.8	15.7	9.73
Ce (%)	0.92	0.33	0.92	0.32
Cs (ppm)	6.2	2.1	<1.0	<1.0
La (%)	0.74	0.22	0.73	0.21
Nd (%)	0.81	0.31	0.82	0.30
Sr	0.35 %	800 ppm	0.34 %	600 ppm

% = Weight percent
ppm = Parts Per Million

Sample Identification: S52694H-Borate; slag from hearth
S52694I-Borate; slag from ingot

S52794H-Ferrite; slag from hearth
S52794I-Ferrite; slag from ingot

The cumulative slag collected from the product ingot using 5% Borate flux and 5% Ferrite flux weighed 1832 and 3124 grams, respectively.

Comments concerning the test results are presented below:

- The Al, Ca, Ce, La, Nd, Si, and Sr concentrations for both fluxes were significantly higher for the hearth slags than for the crucible slags.
- The Cr, Fe, Mn, and Nb concentrations for both fluxes were significantly higher for the crucible slags than for the hearth slags.
- The surrogate concentrations in the slag were independent of the oxidizing power of the fluxes. The surrogate concentrations in the slag from the First Controlled Oxidation Tests were almost double the concentrations in the slags from the Second Controlled Oxidation Tests. These lower concentrations are the result of lower surrogate concentrations in the starting metal and larger amounts of flux present in the second test.
- Chromium and Mn contents for the crucible slags were much higher than the contents for the hearth slags; probably because of the longer soaking times in the ingot crucible.

4.1.2.3.2.3. DISTRIBUTION RATIO

Distribution ratios are presented in Table 4.6 for the Second Controlled Oxidation Melts. The distribution values are significantly lower than those reported in Table 4.3, even though the oxidizing conditions for the borate and ferrite fluxes were greater than those in the previous test. This may be because the two product ingots from the first controlled oxidation melt were used as starting material for the second controlled oxidation test. Also, a greater mass of flux was added in this test (5%) compared to the first test (2%).

TABLE 4.6. DISTRIBUTION RATIOS FOR THE SECOND CONTROLLED OXIDATION MELT

SAMPLE	FLUX TYPE	Ce	La	Nd	Cs	Sr
M52694T	Borate	110	116	129	N.A.	92
M52794T	Ferrite	145	150	214	N.A.	133
N.A.: Not Available						

4.1.2.4. CONTROLLED OXIDATION MELT: 2% O_2

A third pilot scale surrogate removal test was performed at RETECH. This test was designed to investigate the use oxygen as the oxidant. Flux was not used. Two percent O_2 was injected on the surface of the hearth metal through the plasma torch, i.e., the injection gas contained 2% oxygen, 98% helium.

4.1.2.4.1. INITIAL CONDITIONS FOR MELT: 2% O_2 EXPERIMENT

Two ingots of approximately 114 kilograms each were melted under injected O_2. The metal feed rate was held approximately constant at 28 centimeters/hour for the first half of the melt and at 15-20 centimeters/hour for the second half of the melt. The feedstock utilized was master alloy ingots.

4.1.2.4.2. TEST RESULTS

The results from the 2% O_2 controlled oxidation melt test work verified that surrogate removal via O_2 is more effective than by use of an oxidizing flux. The metal and slag analyses are presented in Tables 4.7 and 4.8.

4.1.2.4.2.1. METAL ANALYSES

Metal phase surrogate concentrations show that the final surrogate concentrations were not lowered to the levels achieved by induction melting in air. The expected result that slower feed rate should result in lower surrogate concentrations was achieved. The metal phase analyses are presented in Table 4.7.

TABLE 4.7. METAL PHASE ANALYTICAL RESULTS FOR THE 2% O_2 CONTROLLED OXIDATION MELT

ELEMENT	SAMPLE ANALYZED			
	MELT RATE (28 CENTIMETERS/HOUR)		MELT RATE (15-20 CENTIMETERS/HOUR)	
	M72094-1 TOP OF INGOT	M72094-4 BOTTOM OF INGOT	M72094-3 BOTTOM OF INGOT	M72094-2 TOP OF INGOT
Al (%)	<0.01	<0.01	<0.01	<0.01
B (%)	<0.01	<0.01	<0.01	<0.01
Ca (%)	<0.01	<0.01	<0.01	<0.01
Cr (%)	18.4	18.3	18.3	18.2
Fe (%)	69.0	69.0	69.1	69.1
Mn (%)	1.40	1.51	1.33	1.44
Si (%)	0.18	0.23	0.22	0.23

ELEMENT	SAMPLE ANALYZED			
	MELT RATE (28 CENTIMETERS/HOUR)		MELT RATE (15-20 CENTIMETERS/HOUR)	
	M72094-1 TOP OF INGOT	M72094-4 BOTTOM OF INGOT	M72094-3 BOTTOM OF INGOT	M72094-2 TOP OF INGOT
Cs (ppm)	<1.0	<1.0	<1.0	<1.0
La (ppm)	290	51	18	6.3
Nd (ppm)	280	92	23	6.2

(%) = Weight percent
(ppm) = Parts per million by weight

Comments concerning the test results are presented below:

- For the melt rate at 28 cm/hr the surrogate (Ce, La, and Nd) concentrations varied from 51 to 290 ppm; while, the surrogate concentrations for the 15-20 cm/hr melt rate varied from 6.2 to 33 ppm.
- For the melt rate of 28 cm/hr the surrogate removal by gaseous oxygen was less than the flux controlled oxidation melts (which was conducted at approximately 20 cm/hr, Table 4.4). For the melt rate of 15-20 cm/hr the surrogate removal by gaseous oxygen was approximately the same when compared to the flux controlled oxidation melts at the same rate (Table 4.4.).
- Chromium and Mn were only slightly decreased for both feed rates.

4.1.2.4.2.2. SLAG ANALYSES

Only one slag sample was sent for analysis, i.e., the final slag present at the end of the test period. The slag analytical data are presented in Table 4.8

TABLE 4.8. SLAG ANALYSES FOR 2% O_2 CONTROLLED OXIDATION MELT

SLAG SAMPLE	ELEMENTS ANALYZED							
	Al (%)	Cr (%)	Fe (%)	Mn (%)	Si (%)	Ce (ppm)	La (ppm)	Nd (ppm)
S11994-2*	0.4	11.1	4.4	11.0	7.8	180	170	950

* The slag sample is from the slag collected at the end of the test period.

The weight of slag recovered was 454 grams.

4.1.2.4.2.3. DISTRIBUTION RATIO

Distribution ratios are presented in Table 4.9 for the 2% O_2 controlled oxidation melt.

TABLE 4.9. DISTRIBUTION RATIO FOR THE 2% O_2 CONTROLLED OXIDATION MELT

Sample	Ce	La	Nd	Cs	Sr
M72094-2	20	27	153	N.A.	N.A.
N.A.-Not available					

4.1.2.5. CONTROLLED OXIDATION MELT: 5% O_2

4.1.2.5.1. INITIAL CONDITIONS FOR MELT: 5% O2 EXPERIMENT

Another controlled oxidation test consisted of increasing the injected O_2 content from 2% to 5%. The feedstock was the ingot product from the 2% O_2 melt. The melt rate was held at 20 centimeters per hour for one half of the melt time but was then increased to 41 centimeters per hour for the remaining half of the experiment.

4.1.2.5.2. TEST RESULTS

The increase in the oxygen feed rate caused a notable difference in the final ingot surrogate concentrations, especially cerium. Only cerium, lanthanum and neodymium were analyzed in the metal phase (since the other elemental concentrations in the metal phase for previous melts did not appear to be effected by the oxidizing action of O_2). Analytical results for the metal and slag products are presented in Tables 4.10 and 4.11, respectively.

4.1.2.5.2.1. METAL ANALYSES

By increasing the O_2 to 5% the final concentrations of the surrogates dropped significantly from the 2% O_2 test as shown in Table 4.10. The results however still did not achieve the decontamination levels achieved by induction melting in an air atmosphere (except for cerium).

TABLE 4.10. METAL ANALYSES FROM 5% O_2 CONTROLLED OXIDATION MELT

ELEMENT	SAMPLE ANALYZED				
	MELT RATE (41 CM/HOUR)		MELT RATE (20 CM/HOUR)		
	M9294-1 TOP	M9294-2 BOTTOM	M9294-3 TOP	M9294-4 MIDDLE	M9294-5 BOTTOM
Ce (ppm)	<1.0	<1.0	<1.0	<1.0	<1.0
La (ppm)	7.4	22	<1.0	1.8	33
Nd (ppm)	11	28	1.2	2.8	78
(ppm) = Parts Per Million					

Comments concerning the test results are presented below:

- As anticipated the surrogate concentrations for the 20 cm/hr melt rate are lower than for the 41 cm/hr except for sample M9294-5 which may have contained a slag inclusion in the metal sample.
- The difference between the Ce concentration levels and La, Nd concentration levels is unusual since Ce is the least stable oxide of the three surrogates.

4.1.2.5.2.2. SLAG ANALYSES

Since the metal analyses for this pilot scale test melt were above 1.0 ppm for the surrogate concentrations only one slag sample was analyzed. The slag sample is a combination of the hearth slag from both the melt rate tests.

TABLE 4.11. SLAG ANALYSES FOR 5% O_2 CONTROLLED OXIDATION MELT

SLAG SAMPLE	ELEMENTS ANALYZED							
	Al (%)	Cr (%)	Fe (%)	Mn (%)	Si (%)	Ce (ppm)	La (ppm)	Nd (ppm)
S11994-3*	0.4	10.5	9.6	7.6	6.5	180	160	920

* The slag sample is a combination of the ingot slag from both melt rate tests.

The total combined slag collected for the ingot using 5% O_2 weighed 227 grams.

4.1.2.5.2.3. DISTRIBUTION RATIO

The distribution ratio for the 5% O_2 are presented in Table 4.12.

TABLE 4.12. DISTRIBUTION RATIO FOR THE 5% O_2 CONTROLLED OXIDATION MELT

Sample	Ce	La	Nd	Cs	Sr
M9294-1	>180	22	84	N.A.	N.A.

N.A.-Not available

M9294-1 is a metal sample selected at the 20 cm/hr melt rate.

The slag data used to generate the distribution ratio values are from a blend of slag from both melt rates.

4.1.2.6. CONTROLLED OXIDATION MELT: 5% AND 10% O_2 (WITH A REFRACTORY LINING)

4.1.2.6.1. INITIAL CONDITIONS FOR MELT: 5 AND 10% O_2 EXPERIMENT

The fifth pilot scale controlled oxidation melt consisted of injecting 5% (for half the test period) and 10% O_2 (for half the test period) across the hearth from an auxiliary port instead of injecting the O_2 through the plasma torches. The cold hearth was lined with the same chromia-alumina refractory that was used in the Montana Tech induction furnace. This refractory was rammed to fit the crucible but was not sintered. The refractory was installed so that superheating could be achieved in the molten pool; therefore, mimicking the superheating conditions achieved in the experimental induction tests. A new master surrogate ingot was used for this melt, weighing 114 kilograms. The master ingot contained approximately 400 to 500 ppm of La, Ce, and Nd. The metal feed rate was approximately 20 centimeters/hour.

4.1.2.6.2. TEST RESULTS

The results from this experiment were significantly different than what was anticipated. Surrogate concentrations in the resulting ingot varied over the range from 67 to 210 ppm. The analytical results for both of the metal and slag are presented in Tables 4.11 and 4.12, respectively.

4.1.2.6.2.1. METAL ANALYSES

The metal phase was analyzed only for the surrogate elements. The unanticipated results presented in Table 4.13 suggest that the attempt to provide superheating in the hearth metal was not successful.

The reason that surrogate concentrations are so high when the oxidation conditions appear to be appreciable is yet unknown.

TABLE 4.13. METAL PHASE ANALYSES FOR 5 AND 10% O_2 WITH REFRACTORY CONTROLLED OXIDATION MELT

ELEMENT	SAMPLE ANALYZED	
	10% O_2 AT 20 CM/HOUR	5% O_2 AT 20 CM/HOUR
	M102494-1	M102494-2
Ce (ppm)	75	130
La (ppm)	67	210
Nd (ppm)	79	210

(ppm) = Parts Per Million

Comments concerning the test results are presented below:

- A chromia-alumina refractory hearth liner was used to allow superheat in the molten metal in the hearth, but the refining effectiveness of this modification did not increase the effectiveness of surrogate removal.

- The 5 and 10% O_2 that was injected across the hearth from an auxiliary port instead of the O_2 through the plasma torches may have been a less effective way to supply oxygen for the decontamination reactions.

4.1.2.6.2.2. SLAG ANALYSES

The slag phase analyses are presented in Table 4.14 for both the hearth slag and the crucible slag.

TABLE 4.14. SLAG ANALYSES FOR 5 AND 10% O_2 OXIDATION MELT WITH REFRACTORY

Elements	Sample Analyzed	
	5-10% O_2 Hearth Slag S11994-6	**5-10% O_2 Crucible Slag S11994-5**
Al (%)	0.5	0.30
Cr (%)	12.5	14.2
Fe (%)	10.7	9.8
Mn (%)	7.8	13.2
Si (%)	4.8	5.3
Ce (ppm)	180	29000
La (ppm)	160	28000
Nd (ppm)	940	32000

% = Weight Percent
ppm = Parts Per Million

The slag collected from the product ingot weighed 2065 grams.

4.1.2.6.2.3. DISTRIBUTION RATIO

Distribution ratios are presented in Table 4.15 for the 5-10%% O_2 controlled oxidation melt.

TABLE 4.15. DISTRIBUTION RATIO TABLE FOR THE 5 AND 10% O_2 CONTROLLED OXIDATION MELT

Sample	Ce	La	Nd	Cs	Sr
M102494-1	2.4	2.4	12	N.A.	N.A.

N.A.-Not available

M9294-1 is a metal sample selected at the 20 centimeters/hour melt rate with 10% O_2

The slag data used to generate the distribution ratio values is a composite slag from both oxygen melts.

4.1.2.7. CONTROLLED OXIDATION MELT: 10% O_2

4.1.2.7.1. INITIAL CONDITIONS FOR MELT/10% O_2

A final controlled oxidation melt was performed at RETECH which consisted of injecting 10% O_2 through the plasma torch. Argon was used as the inert gas instead of helium. The ingot resulting from the previous test (Section 4.6) was remelted as the feedstock for this test. The feedrate was approximately 20 centimeters/hour.

4.1.2.7.2. TEST RESULTS

Results from the controlled oxidation melt have provided surrogate concentration results that are similar to the open atmosphere induction results. Several samples were taken from the test products for analysis, i.e., the ingot, the top of the skull, and the bottom of the skull. Analytical results for the metal and slag are presented in Tables 4.15 and 4.16, respectively.

4.1.2.7.2.1. METAL ANALYSES

Analysis of the metal phase revealed that effective surrogate oxidation had occurred. The metal analyses results are presented in Table 4.16.

Original analytical results for the product ingot showed a rather high surrogate concentration. The sample presumably had a slag inclusion present. This was believed to be the case because of the low surrogate concentrations in the skull top. Resampling of the ingot (samples M1695-D and M1695-E) confirmed that the sample was contaminated. The analysis of the hearth skull bottom are presented to demonstrate the difference in surrogate concentration across the skull thickness.

TABLE 4.16. METAL PHASE ANALYSES FOR 10% O_2 CONTROLLED OXIDATION MELT

ELEMENT	SAMPLE ANALYZED				
	MELT RATE OF 20 CENTIMETERS/HOUR				
	INGOT SAMPLE M1695-A	INGOT SAMPLE M1695-D[1]	INGOT SAMPLE M1695-E[1]	SKULL TOP M1695-B	SKULL BOTTOM M1695-C
Ce (ppm)	73	<1.0	<1.0	1.0	57
La (ppm)	64	<1.0	<1.0	<1.0	65
Nd (ppm)	80	<1.0	<1.0	<1.0	54

[1] Samples M1695-D and M1695-E were resamples taken from the center and the outside of the ingot after the ingot was cut axially in half to verify that there were slag inclusions in samples M1695-A and M1695-C.

Comments concerning the test results are presented below:

- The 10% O_2 at a 20 centimeters/hour melt rate has demonstrated decontamination of stainless steel to <1.0 ppm.
- The test has also demonstrated that supply of oxygen through the torch is much more effective than suppling it over the hearth surface.

4.1.2.7.2.2. SLAG ANALYSES

Slag analyses were not collected for this test.

4.1.3. VACUUM INDUCTION MELT PROGRAM

4.1.3.1. GOALS OF THE VIM PROGRAM

The goals for the vacuum induction melt (VIM) program included: effective removal of surrogates (to <1 ppm), and decarburization of the metallic solution to less than 300 ppm carbon by vacuum treatment in the presence of controlled quantities of air, carbon dioxide, or solid oxide. The desire was to selectively remove the surrogates and carbon without appreciable loss of chromium (which occurs when induction melting is conducted in air at ambient pressure). The authors sought to demonstrate that the goals could be met in a single step in reasonable time without the complications involved using bottom tapping or bottom blowing.

A series of eight VIM melts were performed in environments that contained different levels of oxidizing powers. The individual experimental conditions and test results are described in Section 4.1.3.3.

4.1.3.2. DESCRIPTION OF THE MELT FACILITY

The melting facility used for the vacuum induction experiments is located at the Retech, Inc. Manufacturing plant near Ukiah, California. The furnace consists of a water cooled coreless induction coil, power supply, vacuum chamber, and associated hardware.

An overall view of the VIM facility used for this work is presented in Figure 4.2. The induction coil is mounted to the door of the vacuum chamber, allowing easy access to the coil and the mold section of the chamber during loading, unloading, and cleaning, Figure 4.3. The power leads carry the cooling water to the coil through the coil tilt mechanism on the chamber door. A hydraulic motor is used to rotate the coil (crucible) clockwise and counter clockwise about the vertical position for casting. Samples were taken at intermediate times by rotating the crucible counter clockwise to pour molten metal into a prepositioned crucible (i.e., a crucible located on the side of the furnace chamber opposite the final melt mold).

The coil box, 18.5 by 18.5 by 22 inches high houses a ten-turn coil 14.5 inches inside diameter by 15 inches high. Allied Mineral Star Ram 313 was used to mud (cover) the coils for the first crucible fabricated while Minro Al A91 plastic was used to mud the coil for the second crucible used. Crucibles (inside the coil) were rammed (using Minro Al A52 dry ramming mix) into a steel tubing form. In-situ sintering of the refractory was accomplished in a conventional manner by melting and holding approximately 250 pounds of steel at 1600°C for one hour prior to casting. During the melting campaigns no measurable erosion of the 10.5-inch diameter by 14-inch high crucible was observed. Some crucible damage was inflicted during removal of adhered metal splatter from the upper sections of the crucible. Broken sections were successfully patched with A91 plastic.

An Ajax Phasor AC/DC Solid State Model #3-84 power supply converts 480 volt three phase to a single phase maximum output of 125 kilowatts, 400 volts, 4500 amps at 3,000 hertz. Load mismatch limited power to approximately 80%.

The induction furnace sits within a chamber that is 40-inches deep, 64-inches wide by 83-inches high. The vacuum chamber is water cooled and is evacuated by a Rootes blower backed by a 250 cfm Stokes mechanical pump. Mechanical and thermocouple gages provide vacuum measurements. The bottom of the coil is 48 inches above the floor and 13 inches from the door. Two view ports provide visual reference from the control deck located at the rear and top of the chamber. One view port allows the melt crucible to be observed while the second allows observation of the funnel during the pour. An alloy feeding system, consisting of six alloy hoppers and a retractable chute, provides for the addition of six different alloys during the melt without power or vacuum interruption. Process gases are introduced through a lance above the crucible or through several other ports in the furnace body.

Temperature measurements were taken with a two-color optical pyrometer and Type K thermocouples. Initial pyrometer calibration was confirmed with a Type R thermocouple. The thermal arrest observed during melting of the charge provided additional verification of the pyrometer.

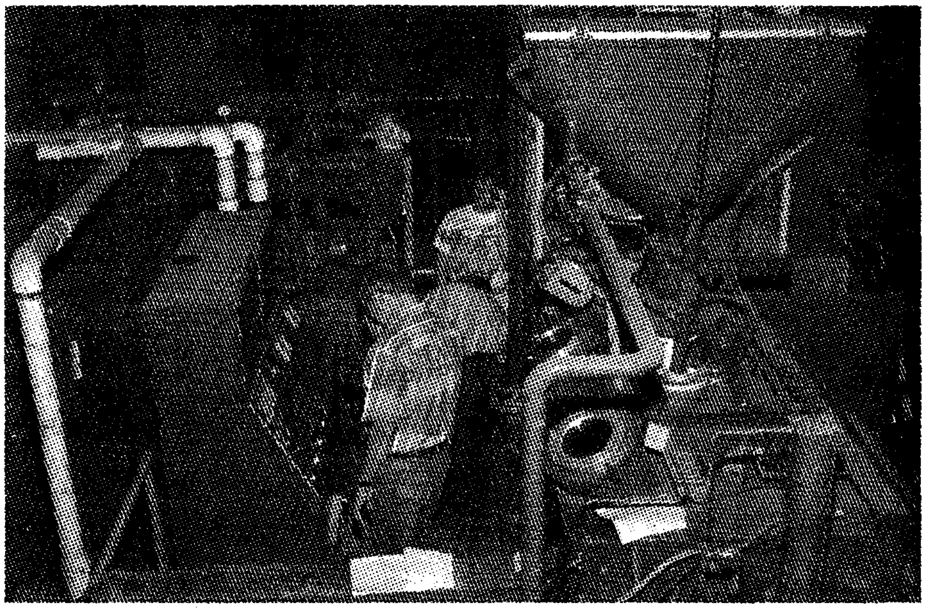

Figure 4.2 Overhead View of the Retech 125 KW VIM Showing Operator Console, View Ports. Gas Lance. and Alloy Feeder

Figure 4.3 The Retech VIM with the Door Open and a Mold Box in Place.

4.1.3.3. TEST MELTS

All tests were conducted at a nominal temperature of 1600° C. The temperature was maintained manually by controlling the power input into the molten metal. Temperature was monitored using an IRCON two-color pyrometer. Time zero was taken to be when the melt temperature first reached 1600° C. The experimental tests conducted are listed below: (The experimental procedure is presented in Section 4.1.3.4.; the experimental conditions and experimental results are presented and discussed in Sections 4.1.3.5.1-4.1.3.5.2.)

- VIM 1: Vacuum Melting at One Torr for 0.5 Hour at Temperature.
- VIM 2: Vacuum Melting at a Carbon Dioxide Pressure of 75 Torr: Carbon Dioxide Blown into Chamber During Heat up and for 0.5 Hour at Temperature.
- VIM 3: Vacuum Melting at a Carbon Dioxide Pressure of 75 Torr: Carbon Dioxide Blown into Chamber During Heat up and Then Onto the Molten Surface for 0.5 Hour at Temperature.
- VIM 4: Vacuum Melting at 75 Torr Pressure of Air During Heat up. Carbon Dioxide Blown onto Molten Surface at Test Temperature for 1.0 Hour While Maintaining 75 Torr Pressure.
- VIM 5: Vacuum Melting at 50 Torr (Air) with Air Blown onto the Molten Surface for 1.0 Hour While Maintaining 50 Torr.
- VIM 6: Vacuum Melting (<2 Torr) for 1.0 Hours at Temperature with the Addition of 0.25-Pounds of Magnetite at Time Zero.
- VIM 7: Vacuum Melting (<2 Torr) for 1.0 Hours with the Addition of 1.0 Pound of Magnetite at Time Zero and 1.0 Pound at Thirty Minutes.
- VIM 8: Vacuum Melting (<2 Torr) for 1.5 Hours with the Addition of 1.0 Pound of Magnetite at Time Zero and 1.0 Pound at Each of Three 25 Minute Intervals.

4.1.3.4. TEST PROCEDURE

The experimental procedure consisted of placing approximately 250 pounds of stainless steel surrogate master melt ingot into a rammed alumina crucible. Sand molds were positioned in the furnace housing so that casting could be accomplished under a vacuum. The system was closed and a vacuum pulled on the chamber before power was applied. The desired conditions (type of gas, mass flow of gas, addition of magnetite) were established in the system either prior to ingot melting or subsequent to ingot melting. After the desired test exposures were completed the metal was poured under vacuum in the pre-positioned sheet-bar mold. The metal was allowed to cool (usually overnight) before breakout. The metal was removed from the mold and sampled at various positions for determination of surrogate and carbon concentrations. A detailed description of each test is presented in Section 4.1.3.5.

4.1.3.5. TEST RESULTS

The results of this series of tests are presented in the following sections;

4.1.3.5.1. Baseline Data: Vacuum Exposure
4.1.3.5.2. Gas Oxidizers: Carbon Dioxide or Air
4.1.3.5.3. Solid Oxidizer: Magnetite

4.1.3.5.1. BASELINE DATA: VACUUM EXPOSURE

VIM 1

Approximately 270 pounds of stainless steel master melt ingot was melted in the vacuum induction furnace, without the addition of any oxidizing species, to provide background data for the VIM series of tests. The conditions and experimental results are presented in Table 4.17. Note that surrogates were removed to below one part per million but that carbon was unaffected.

Most of the VIM tests were modeled using the CSIRO Thermochemistry calculational software. The input elements and their concentrations are listed in column four, Table 4.17. The calculational program assumptions included the following: temperature = 1600° C; pressure as measured during the test; the reference state for all slag constituents was the dissolved oxide constituents in the liquid state; reference state for the molten metal constituents was the dissolved elemental species; activity coefficients for slag constituents were assumed to be one; the Lupis solution model was used to describe the interaction coefficients in the molten metal; interaction coefficients for all species were taken from Lupis (Lupis, 1983) except for the rare earth surrogate elements; the temperature dependence of the infinitely dilute solution activity coefficients for the surrogate elements were assumed to be equivalent to that of aluminum; and the interaction coefficients for the surrogate elements were assumed to be equivalent to aluminum.

Note (Table 4.17) that the calculated surrogate concentrations show essentially no surrogate removal for the metallic phase, whereas, the measured surrogate concentrations in the metallic phase were all less than 1 ppm. This results indicates that there was an oxygen source in the system, i.e., probably surface oxidation products were present on the input ingot. The calculated carbon content is the same as the input carbon content and is essentially the same as the measured value showing that the oxygen source was not sufficient to decarburize the steel bath.

TABLE 4.17. VIM 1: VACUUM INDUCTION MELTING OF STAINLESS STEEL

VIM 1

CONDITIONS:

Date: 5/23/95
Temp: 1600-1650 C
Atm: Vacuum
Pressure: < 2 Torr
Ingot: 269.5 Pounds
Time at Temperature: 0.5 Hour

RESULTS:

ELEMENT	INGOT, %	IN	IN	IN	OUT	CALC
	WT%	LBS	GMS	PPM	PPM*	ppm
C	0.04	0.10	43.31	353	337	353
Fe	70.09	188.90	85760.49	700927	-	699500
Cr	17.80	47.97	21778.83	178000	182000	177700
Ni	10.50	28.30	12847.07	105000	-	104800
Si	0.29	0.78	354.82	2900	3000	2894
Mn	1.28	3.45	1566.12	128000	11200	12800
Ce, ppm	677.00	0.18	82.83	677	<1	675
La, ppm	740.00	0.20	90.54	740	<1	738
Nd, ppm	507.00	0.14	62.03	507	<1	506

* Average of Two Separate Samples

4.1.3.5.2. GAS OXIDIZERS: CARBON DIOXIDE OR AIR

VIM 2, VIM 3, VIM 4, VIM 5

Several tests were conducted to investigate surrogate removal and decarburization of stainless steel using gaseous oxidants, e.g., carbon dioxide (VIM 2, VIM 3, VIM 4) and air (VIM 5).

The VIM 2 test was performed by adding carbon dioxide to the vacuum chamber at a sufficient rate to maintain a pressure of approximately 50 torr. The test conditions and the experimental results are presented in Table 4.18.

Note that surrogate removal was successful but that carbon removal was not effective. In fact, the carbon content increased in the product ingot. The reason for this was that carbon dioxide was blown into the chamber as the ingot steel was heating, i.e., carbide formation on the steel surface likely occurred during the heat-up stage and insufficient time (only one half hour) was allowed for the oxidation (by carbon dioxide) of the increased carbon content. Thermodynamic calculations confirm this possibility. It was later experimentally demonstrated that this was the case (See VIM 4 results).

TABLE 4.18. VIM 2: VACUUM INDUCTION MELTING OF STAINLESS STEEL IN THE PRESENCE OF CARBON DIOXIDE

VIM 2

CONDITIONS:

Date: 8/8/95
Temp: 1600-1650
Atm: Vacuum, CO2 (1.1 SCFM) Blown into Chamber During Melting and for 0.5 Hrs While at Temperature
Pressure: 50 Torr
Ingot: 257 pounds
CO_2 Input: 2000 grams
Time at Temperature: 0.5 Hours

RESULTS:

ELEMENT	INGOT	TOTAL	TOTAL	IN	OUT
	WT%	LBS	GMS	PPM	PPM*
C	0.0354	0.08	35.12	354	416
Fe		152.74	69342.28	699022	-
Cr	17.8	38.89	17657.42	178000	180000
Ni	10.5	22.94	10415.90	105000	-
Si	0.29	0.63	287.68	2900	2800
Mn	1.28	2.80	1269.75	12800	11800
Ce, ppm	677	0.15	67.16	677	<1
La, ppm	740	0.16	73.41	740	<1
Nd, ppm	507	0.11	50.29	507	<1

* Average of Two Separate Samples

VIM 3 was conducted under essentially the same conditons as VIM 2 except the carbon dioxide was sparged onto the surface of the molten metal for approximately one-half hour. The results are presented in Table 4.19. Note that the results are similar to VIM 2, i.e. the surrogates were effectively removed but the carbon content increased.

TABLE 4.19. VIM 3: VACUUM INDUCTION MELTING OF STAINLESS STEEL IN THE PRESENCE OF CARBON DIOXIDE

VIM 3

CONDITIONS:

Date: 8/9/95
Temp: 1350-1600° C (Test Aborted, Low Temperature)
Atm: Vacuum, CO2 (0.9 SCFM) Blown into Chamber During Heat up (1 Hr) and on Surface (1.0 SCFM) for 0.5 Hrs While at Temperature
Pressure: 55 Torr
Ingot: 257.5 pounds
CO_2 Input: 5000 grams
Time at Temperature: 0.5 Hour

RESULTS:

ELEMENT	INGOT WT%	TOTAL LBS	TOTAL GMS	IN PPM	OUT PPM*
C	0.0354	0.08	35.12	354	426
Fe		152.74	69342.28	699022	-
Cr	17.8	38.89	17657.42	178000	178000
Ni	10.5	22.94	10415.90	105000	-
Si	0.29	0.63	287.68	2900	3400
Mn	1.28	2.80	1269.75	12800	12800
Ce, ppm	677	0.15	67.16	677	<1
La, ppm	740	0.16	73.41	740	<1
Nd, ppm	507	0.11	50.29	507	<1

* Average of Two Separate Samples

VIM 4 test work was conducted to demonstrate that carbon dioxide must not be sparged into the system until the metal is molten. The test conditions were similar to VIM 3 except carbon dioxide was not supplied until a molten bath formed. Sparging carbon dioxide onto the surface was continued for one hour. The results are presented in Table 4.20.

Note that surrogates (the goal was to lower the surrogate concentration to less than one ppm) and carbon (the goal was to lower the carbon concentration to less than 300 ppm) were successfully removed from the stainless steel without the oxidation and removal of chromium or nickel. The model calculations are also in qualitative agreement with the experimental results (except for silicon).

Air sparging was also investigated, VIM 5. The test conditions and experimental results are presented in Table 4.21. Air was sparged onto the surface of the molten metal for one hour at approximately one CFM. The results show that better molten metal/gas contact is required to lower the surrogates and carbon to the desired concentrations. It is also evident that air sparging results in a greater loss of chromium from the metal phase than when carbon dioxide is used as the oxidant.

4.1.3.5.3. SOLID OXIDIZER: MAGNETITE

Several tests were conducted to investigate surrogate removal and decarburization of stainless steel using magnetite as a solid oxidant, e.g., VIM 6, VIM 7, VIM 8.

VIM 6, VIM 7, VIM 8

Magnetite was tested as a solid oxidant for selectively removing the surrogates and carbon in preference to chromium. Various amounts of magnetite were added to the molten stainless baths under the conditions presented in Tables 4.22 through 4.24.

The stoichiometric requirement of magnetite for removal of the surrogates (to less than one ppm) and carbon (to less than 300 ppm) is approximately one pound (for 250 pounds of feed metal). Note that for acceptable surrogate and carbon removal two pounds were experimentally required. However, the quantity of magnetite required has not been optimized. Much of the magnetite added to each experimental test was deposited in a splatter ring located just above the molten metal surface. The proper mode of introduction of the solid oxidant into the molten bath has yet to be determined.

TABLE 4.20. VIM 4: VACUUM INDUCTION MELTING OF STAINLESS STEEL IN THE PRESENCE OF CARBON DIOXIDE

VIM 4

CONDITIONS:

Date: 9/30/95
Temp: 1600-1650
Atm: Vacuum, CO2 on Surface for 1 Hr at 1 SCFM
Pressure: 0.1 Atm
Ingot: 220 pounds; Flange 16 pounds; Pipe 14 pounds
CO2 Input: 3338.6 grams
Time at Temperature: 1.0 Hour

RESULTS:

ELEMENT	INGOT	FLANGE	PIPE	INGOT	FLANGE	PIPE	TOTAL	TOTAL	IN	OUT	CALC
	WT%	WT%	WT%	LBS	LBS	LBS	LBS	GMS	PPM	PPM*	PPM
C	0.11	0.23	0.09	0.24	0.04	0.01	0.29	133	1175	226	171
Fe				161.06	15.74	13.93	190.74	86594	762942	-	746500
Cr	18.00			39.60	0.00	0.00	39.60	17980	158400	160000	150100
Ni	10.40			20.13	0.00	0.00	20.13	9139	80520	89800	93370
Si	0.32	0.27		0.70	0.04	0.00	0.75	339	2989	4500	680
Mn	1.34	1.10	0.41	2.95	0.18	0.06	3.18	1444	12726	9700	8953
Ce, ppm	210.00	1.70		0.05	0.00	0.00	0.05	21	186	<1	<1
La, ppm	200.00	1.50		0.04	0.00	0.00	0.04	20	176	<1	<1
Nd, ppm	280.00			0.06	0.00	0.00	0.06	28	246	<1	<1

* Average of Three Separate Samples

Flange and pipe added as susceptors

TABLE 4.21. VIM 5: VACUUM INDUCTION MELTING OF STAINLESS STEEL IN THE PRESENCE OF AIR

VIM 5

CONDITIONS:

Date: 9/27/95
Temp: 1600-1650
Atm: Vacuum, Air on Surface for 1 Hr at 2 SCFM
Pressure: 50 Torr
Ingot: 218.5 pounds; Flange 16 pounds; Pipe 14 pounds
Air Input: 970 grams O2; 3396 grams N2
Time at Temperature: 1.0 Hour

RESULTS:

ELEMENT	INGOT	FLANGE	PIPE	INGOT	FLANGE	PIPE	TOTAL	TOTAL	IN	OUT	CALC
	WT%	WT%	WT%	LBS	LBS	LBS	LBS	GMS	PPM	PPM*	PPM
C	0.10	0.23	0.09	0.23	0.04	0.01	0.28	126.20	1116	566	9
Fe				151.99	15.74	14.53	182.26	82746.64	731679	-	704000
Cr	18.00			39.60	0.00	0.00	39.60	17978.40	158972	165300	152800
Ni	10.40			22.88	0.00	0.00	22.88	10387.52	91851	94800	92620
Si	0.32	0.27		0.70	0.04	0.00	0.75	339.23	3000	4200	890
Mn	1.34	1.10	0.41	2.95	0.18	0.06	3.18	1444.36	12772	11800	9686
Ce, ppm	210.00	1.70		0.05	0.00	0.00	0.05	21.10	187	1	<1
La, ppm	200.00	1.50		0.04	0.00	0.00	0.04	19.99	177	<1	<1
Nd, ppm	280.00			0.06	0.00	0.00	0.06	27.97	247	2	<1

* Average of Three Separate Samples

Flange and pipe added as susceptors

TABLE 4.22. VIM 6: VACUUM INDUCTION MELTING OF STAINLESS STEEL USING MAGNETITE AS AN OXIDANT

VIM 6

CONDITIONS:

Date: 6/27/95
Temp: 1550-1600° C
Atm: Vacuum
Pressure: 1.2 Torr
Magnetite Addition: 0.25 pounds at T=0. Planned T=15 min. Addition Misfed
Ingot: 241 pounds
Total Magnetite Addition: 0.25 Pounds
Time at Temperature: 0.5 Hour

RESULTS:

ELEMENT	INGOT	TOTAL	TOTAL	IN	OUT	CALC
	WT%	LBS	GMS	PPM	PPM*	PPM
C	0.03	0.08	36.43	333	394	307
Fe		168.28	76398.00	698247	-	726400
Cr	17.80	42.90	19475.69	178000	182000	162700
Ni	10.50	25.31	11488.47	105000	107000	95950
Si	0.31	0.75	339.13	3100	-	2833
Mn	1.29	3.11	1411.44	12900	11100	11780
Ce, ppm	830.00	0.20	90.81	830	16	18
La, ppm	640.00	0.15	70.02	640	14	17
Nd, ppm	950.00	0.23	103.94	950	31	18

* Average of Two Separate Samples

TABLE 4.23. VIM 7: VACUUM INDUCTION MELTING OF STAINLESS STEEL USING MAGNETITE AS AN OXIDANT\

VIM 7

CONDITIONS:

Date: 9/14/95
Temp: 1600-1650
Atm: Vacuum
Pressure: 2 Torr
Magnetite Addition: 1 pound at T=0, 1 pound at T = 0.5 Hr
Ingot: 215.5 pounds
Total Magnetite Addition: 2 Pounds
Time at Temperature: One hour

RESULTS:

ELEMENT	INGOT	TOTAL	TOTAL	IN	OUT	CALC FOR 1 LB FE3O4	CALC FOR 2 LBS FE3O4
	WT%	LBS	GMS	PPM	PPM*	PPM	PPM
C	0.11	0.23	103.71	1062	946	211	7
Fe		150.51	68331.32	698420		691800	69630
Cr	17.90	38.57	17512.82	179000	178000	182300	181300
Ni	10.40	22.41	10175.05	104000	103700	106000	105800
Si	0.32	0.69	313.08	3200	3700	3261	2767
Mn	1.36	2.93	1330.58	13600	10800	13860	13370
Ce, ppm	220.00	0.05	21.52	220	<1	7	<1
La, ppm	210.00	0.05	20.55	210	<1	9	<1
Nd, ppm	290.00	0.06	28.37	290	<1	8	<1

* Average of Two Separate Samples

TABLE 4.24. VIM 8: VACUUM INDUCTION MELTING OF STAINLESS STEEL USING MAGNETITE AS AN OXIDANT

VIM 8

CONDITIONS:

Date: 9/25/95
Temp: 1600-1650
Atm: Vacuum
Pressure: 1 Torr
Magnetite Addition: 1 pound at T=0, 25 min, 45 min, 65 min
Ingot: 219 pounds
Total Magnetite Addition: 4.0 Pounds
Time at Temperature: 1.5 Hours

RESULTS:

ELEMENT	INGOT	TOTAL	TOTAL	IN	OUT	CALC FOR 1 LB FE304	CALC FOR 2 LBS FE304	CALC FOR 4 LBS FE304
	WT%	LBS	GMS	PPM	PPM*	PPM	PPM	PPM
C	0.11	0.23	105.39	1060	264	202	4	3
Fe		152.95	69441.11	698420		699100	701200	716200
Cr	17.90	39.20	17797.25	179000	175300	179500	178700	176200
Ni	10.40	22.78	10340.30	104000	103700	104300	104100	99960
Si	0.32	0.70	318.16	3200	3500	3209	2724	1769
Mn	1.36	2.98	1352.19	13600	9000	13630	13150	119400
Ce, ppm	220.00	0.05	21.87	220	<1	18	<1	<1
La, ppm	210.00	0.05	20.88	210	<1	22	<1	<1
Nd, ppm	290.00	0.06	28.83	290	<1	21	<1	<1

* Average of Three Samples

4.1.3.6. SUMMARY OF VIM TEST WORK

The vacuum induction melt test work has demonstrated that surrogate elements can be effectively lowered to below one part per million by melting in a vacuum, by sparging carbon dioxide into the vacuum chamber or onto the molten metal surface, by sparging air onto the molten metal surface, and by the addition of magnetite to the molten metal bath. The test work has also demonstrated that decarburization of the melt can be accomplished by sparging carbon dioxide onto the molten metal bath or by the addition of magnetite to the molten metal bath. Both removal of surrogate elements and decarburization can be accomplished without loss of chromium in reasonable process times without use of immersed sparging or bottom blowing.

4.1.4. ATTAINMENT OF GOALS FOR THE PILOT SCALE TEST WORK

The goals of the pilot scale test work included:

- The evaluation of whether effective surrogate removal could be accomplished using plasma torch melting under controlled oxidation potential conditions (applied to approximately two hundred pounds of surrogate loaded stainless steel).

  Attainment of goal: The pilot scale plasma melt tests demonstrated that effective surrogate removal (< 1 ppm) was achieved under the following specific conditions: feed rate, 20 cm/hr; 10% O_2 supplied through the torch during melting.

- The evaluation of whether effective surrogate removal and carbon reduction could be accomplished by vacuum induction melting (VIM) under controlled oxygen potential (applied to approximately two hundred pounds of surrogate loaded stainless steel).

  Attainment of goal: The VIM series of tests demonstrated that surrogate elements can be effectively lowered to below one part per million by melting in a vacuum, by sparging carbon dioxide into the vacuum chamber or onto the molten metal surface, by sparging air onto the molten metal surface, and by the addition of magnetite to the molten metal bath. The test work has also demonstrated that decarburization of the melt can be accomplished by sparging carbon dioxide onto the molten metal bath or by the addition of magnetite to the molten metal bath. Both removal of surrogate elements and decarburization can be accomplished in a single melting step without appreciable loss of chromium from the metal phase.

4.2. COMMERCIAL SCALE AIR INDUCTION MELT TEST PROGRAM

Two commercial scale air induction melt programs were conducted; one at the Anaconda Foundry and Fabrication Company (AFFCO) in Anaconda, Montana and one at Newport News in Newport, Virginia. A description of the facilities, test procedures and test results are discussed below.

4.2.1. GOALS OF THE COMMERCIAL SCALE AIR INDUCTION TEST WORK

The goals of the commerical scale test work were the demonstration and verification that the basic information generated during the laboratory scale test work could be successfully transferred to a full scale operational facility.

4.2.2. AFFCO DEMONSTRATION TEST

This commercial scale test (using a typical production foundry induction furnace) was conducted to demonstrate that induction melting would successfully verify the previous laboratory scale test results, i.e., that the surrogate concentrations would be lowered to less than one part per million. The test program was funded, designed, managed and supervised by Montana Tech personnel.

4.2.2.1. INITIAL CONDITIONS FOR THE AFFCO TEST

The test work was performed at AFFCO (located in Anaconda, Montana). The test involved melting 227 kilograms of master surrogate with 726 kilograms of 304 stainless steel in an open atmosphere induction furnace. AFFCO typically uses Allied Dri-Vibe 437A refractory as their crucible liner. This is the same liner used in the Montana Tech laboratory scale induction furnace. Before the melt, the induction furnace crucible was flushed with a charge of 301 stainless steel to clean up any previous contamination.

The test procedure consisted of placing ingots of master alloy and stainless steel in the crucible chamber (approximately 410 kilograms of master surrogate ingot and scrap metal were loaded into the induction furnace. Once this charge was molten additional stainless steel scrap was added until 953 kilograms of charge was present), heating in air to melt the charge, and holding in the molten state for a specific time. After the desired air exposure the molten charge was poured into previously prepared sand molds.

4.2.2.2. TEST RESULTS

The results for the large scale induction melt were very similar to the small scale tests performed earlier at Montana Tech. All surrogate concentrations were <1.0 ppm. Analytical results for the metal and slag are presented in Tables 4.25 and 4.26, respectively.

4.2.2.2.1. METAL ANALYSES

The results presented in Table 4.25 are for samples taken at timed intervals. Time zero was taken to be when the entire stainless steel charge was completely molten. Twenty one minutes before $t = 0$ the charge was almost completely molten and a sample was taken, $t = -21$ minutes. The analytical results for this time show that all the surrogate had been removed to below ICP detection limits. Notice also that the concentrations of both Cr and Mn are not significantly reduced. The longer the charge was held in the molten condition, the lower the Mn concentration. This is shown in Table 4.25, i.e., from $t = 0$ to $t = 78$ minutes the Mn concentration decreased from 1.52 to 1.41%. The Cr concentration remained at approximately 18.2% from $t = -21$ to $t = 78$ minutes.

TABLE 4.25. METAL PHASE ANALYSES FOR THE AFFCO COMMERCIAL SCALE MELT

ELEMENT	SAMPLE ANALYZED			
	t=-21 MIN M72094-5	t=0 MIN M72094-6	t=42 MIN M72094-7	t=78 MIN M72094-8
Al (%)	<0.01	<0.01	<0.01	<0.01
B (%)	<0.01	<0.01	<0.01	<0.01
Ca (%)	<0.01	<0.01	<0.01	<0.01
Cr (%)	18.2	18.3	18.2	18.2
Fe (%)	69.1	69.2	69.2	69.3
Mn (%)	1.52	1.53	1.45	1.41
Si (%)	0.30	0.30	0.30	0.29
Ce (ppm)	<1.0	<1.0	<1.0	<1.0
Cs (ppm)	<1.0	<1.0	<1.0	<1.0
La (ppm)	<0.5	<0.5	<0.5	<0.5
Nd (ppm)	<2.0	<2.0	<2.0	<2.0

(%) = Weight Percent
(ppm) = Parts Per Million

Comments concerning the test results are presented below:

- The AFFCO test melt verified the small scale experiments at Montana Tech. Surrogates were lowered to less than 1.0 ppm. Chromium, Mn and Si decreased only slightly with time.
- At t = 0 the surrogates were already <1.0 ppm.
- The creation of effluent fume and dust was minimal. However, no attempt was made to quantify the amount created.

4.2.2.2.2. SLAG ANALYSES

The slag analyses were performed by X-Ray fluorescence spectroscopy and the data are presented in Table 4.26. Slag samples were obtained by skimming the slag/(oxide products) from the molten metal surface, with a stainless steel bar, at various time intervals.

TABLE 4.26. SLAG ANALYSES OF THE AFFCO COMMERCIAL SCALE MELT

ELEMENT	SAMPLE ANALYZED t=-13 MIN. S72294-3	 t=4 MIN. S72294-1	 t=16 MIN. S72294-2
Mg (ppm)	8200	12500	11500
Al (ppm)	97000	144000	154000
Si (ppm)	221000	258000	249000
Ca (ppm)	3600	3600	4000
Cr (ppm)	25800	24400	22800
Mn (ppm)	47800	43800	41600
Fe (ppm)	1280	2800	1150
Co (ppm)	N.D.	N.D.	N.D.
Ni (ppm)	155	240	120
Sr (ppm)	20	34	30
Cs (ppm)	N.D.	N.D.	N.D.
La (ppm)	2600	756	575
Ce (ppm)	3420	1110	837
Nd (ppm)	2100	720	394

(ppm) = Parts Per Million
N.D. = Not Detected

Comments concerning the test results are presented below:

- The first skimming contained the highest surrogate loading. The loading decreased with time. Since the metal was essentially decontaminated at t = -21 minutes the decrease in surrogate content in the slag likely reflects dilution by "popcorn" additions.
- Strontium remained remarkably consistent with melt time.
- Chromium and Mn were relatively high in the slag even though little of either was lost from the metal phase. This effect is simply because such a small amount of slag is formed during treatment period.

4.2.2.2.3. DISTRIBUTION RATIO

Distribution ratios are presented in Table 4.27. The distribution ratio for metal sample M72094-5 (t = -21 minutes) was calculated using the slag sample S72294-3 (t = -13 minutes). The distribution ratio for metal sample M72094-6 (t = 0) was calculated using slag sample S72294-1 (t = 4 minutes). From the distribution ratios it is evident that most of the surrogates were oxidized early in the melting process, i.e., at least before t = -21 minutes.

TABLE 4.27. DISTRIBUTION RATIO TABLE FOR THE AFFCO COMMERCIAL SCALE OXIDATION INDUCTION MELT

Sample	Ce	La	Nd	Cs	Sr
M72094-5/ S72294-3	>3420	>5200	>1050	N.A.	N.A.
M72094-6/ S72294-1	>1110	>1512	>360	N.A.	N.A.
N.A.-Not available					

4.2.3. NEWPORT NEWS DEMONSTRATION TEST

This commercial scale test was conducted to demonstrate that induction melting would successfully verify the previous laboratory scale test results, i.e., that the surrogate concentrations would be lowered to less than one part per million. The test program was funded by WINCO (except for the analytical test work) under a Cooperative Research and Development Agreement (CRADA) with Newport News. The test plan was cooperatively designed by WINCO and Montana Tech personnel, managed and supervised by WINCO and Montana Tech personnel, and all analytical test work was coordinated and funded by the Montana Tech program.

4.2.3.1. INITIAL CONDITIONS FOR NEWPORT NEWS TEST

The second pilot scale stainless steel decontamination induction melt was performed at Newport News Shipbuilding and Dry Dock Company (NNS) in Newport, Virginia. The charge was composed of a 552 kilogram master surrogate ingot and 456 kilograms of AFFCO decontaminated stainless steel. Approximately 2% (20 kilograms) of "Borate" flux (32%SiO_2, 42%CaO, 10%Al_2O_3, and 16%Fe_2O_3) was added to the charge before heating the furnace. The same crucible refractory (Allied Dri-Vibe 437A) that AFFCO used was sintered into the NNS furnace for this pilot scale experiment. Background off-gas was monitored by WINCO personnel throughout the test period. Ferro-manganese and ferro-silicon additions were made to deoxidize the melt just prior to when the gate sample was taken.

4.2.3.2. TEST RESULTS

Near the end of the melt, molten metal leaked out the crucible side and on to the floor. This occurrance was most likely caused by incomplete high temperature sintering of the crucible mix prior to the test. The pour temperature from the tilt induction furnace to the ladle was only 2740°F. The metal phase analytical results are presented in Table 4.28.

4.2.3.2.1. METAL ANALYSES

The results of the NNS pilot scale melt were similar to the results achieved in the AFFCO melt. All of the surrogate concentrations were reduced to less than 1 ppm (except for Ce in sample M9994-1).

TABLE 4.28. METAL PHASE ANALYSES FOR THE NNS COMMERCIAL SCALE INDUCTION MELT

Element	Sample Analyzed		
	Prepour S1 T=-32 (Min) M9994-3	**Prepour S2 T=69 (Min) M9994-2**	**Gate Sample T=93 (Min) M9994-1**
Al (%)	<0.01	<0.01	<0.01
B (%)	<0.0005	<0.0005	<0.0005
C (ppm)	424	460	424
Ca (%)	<0.010	<0.010	<0.010
Co (%)	0.129	0.128	0.122
Cr (%)	18.21	18.10	18.05
Mn (%)	1.08	0.99	1.14
Si (%)	0.217	0.179	0.217
Ce (ppm)	<1.0	<1.0	1.4
Cs (ppm)	<1.0	<1.0	<1.0
La (ppm)	<1.0	<1.0	<1.0
Nd (ppm)	<1.0	<1.0	<1.0
Sr (ppm)	<1.0	<1.0	<1.0

(%) = Weight Percent
(ppm) = Parts Per Million

Comments concerning the test results are presented below:

- The final surrogate concentrations resulting from the large scale NNS melt were < 1 ppm. These results are similar to the large scale AFFCO melt test results and verify the Montana Tech laboratory study results.

4.2.3.2.2. SLAG ANALYSES

The analyses for the slag resulting from the NNS melt are significantly different from the AFFCO slag analyses. The slag analyses for the NNS pilot scale induction melt are presented in Table 4.29.

TABLE 4.29. SLAG ANALYSES FOR THE NNS COMMERCIAL SCALE INDUCTION MELT

ELEMENTS	SAMPLE ANALYZED
	SLAG S11994-4
Al %	0.7
Cr %	3.5
Fe %	1.1
Mn (%)	1.7
Si (%)	9.5
Ce (ppm)	190
La (ppm)	160
Nd (ppm)	930

% = Weight Percent
ppm = Parts Per Million

Comments concerning the test results are presented below:

- It has been noted in other test work that surrogate element concentrations in the slag phase (when essentially complete removal has occurred from the metal phase) are very low. It is our conclusion at this time that the surrogates are "gettered" out by the refractory crucible. Analysis of the induction crucible material has not been performed in this study.

4.2.3.2.3. DISTRIBUTION RATIO

Distribution ratios are presented in Table 4.30 for the NNS pilot scale melt. The distribution ratios for this test are considerable less than those reported for the other large scale test, i.e., the AFFCO test. The reason for the difference is because of the volume of slag present in each treatment was considerably different. The AFFCO test generated a relatively small amount of slag (no flux was added to the system, except "popcorn" was added to collect the slag immediately before skimming), whereas two percent flux was added prior to the melting test at Newport News.

TABLE 4.30. DISTRIBUTION RATIO TABLE FOR THE NNS COMMERCIAL SCALE INDUCTION OXIDATION MELT

SAMPLE	Ce	La	Nd	Cs	Sr
S11994-4/ M9994-2	>190	>160	>930	N.A.	N.A.
N.A.-Not available					

4.2.4. ATTAINMENT OF GOALS FOR THE COMMERCIAL SCALE AIR INDUCTION MELT TESTS

The goals of the commerical scale test work were the demonstration and verification that the basic information generated during the laboratory scale test work could be successfully transferred to a full scale operational facility. These goals were achieved by both of the commercial scale test programs, e.g., the surrogate concentrations were lowered to less than one ppm in both tests.

4.3. STAINLESS STEEL MELT PROGRAM: COMPARISON OF RESULTS

For the convenience to the reader compilations of the pilot scale cold hearth plasma, air induction test and commercial results are presented in Tables 4.31 and 4.32.

TABLE 4.31. COMPILATION OF PILOT SCALE AND COMMERCIAL SCALE MELT TESTS: METAL PHASE ANALYSES

SAMPLE ANALYZED	ELEMENT CONCENTRATION						
	Ce (ppm)	La (ppm)	Nd (ppm)	Cs (ppm)	Sr (ppm)	Cr (%)	Mn (%)
First Controlled Oxidation Plasma Melt With an Oxidizing Flux: ICP-MS (Fluxes: Borate and Borate Without Ferric Oxide-Two Weight Percent) Reference Section 4.1.2.2 for Details							
WFe1	360	160	340	<1.0	<1.0	18.7	1.41
WFe2	250	220	300	<1.0	<1.0	18.8	1.40
WFe3	53	22	35	<1.0	<1.0	18.3	1.48

SAMPLE ANALYZED	ELEMENT CONCENTRATION						
	Ce (ppm)	La (ppm)	Nd (ppm)	Cs (ppm)	Sr (ppm)	Cr (%)	Mn (%)
NFe1	360	150	290	<1.0	<1.0	18.6	1.40
NFe2	250	100	240	<1.0	<1.0	18.6	1.40
NFe3	120	64	110	<1.0	16	18.6	1.42
Second Controlled Oxidation Plasma Melt With an Oxidizing Flux: ICP-MS (Fluxes: Borate and Ferrite-Five Weight Percent) Reference Section 4.1.2.3 for Details							
M52694T	30	19	24	<0.5	8.7	18.8	1.31
M52694s	14	4.9	13	<0.5	<0.5	19.1	1.27
M52794S	8.0	4.8	7.8	<0.5	0.8	18.5	1.07
M52794T	22	14	20	<0.5	4.5	17.7	18.5
Controlled Oxidation Melt With 2% O_2 in Helium: ICP-MS Reference Section 4.1.2.4. for Details							
M72094-1	280	290	280	N.A.	N.A.	18.4	1.40
M72094-4	120	51	92	N.A.	N.A.	18.3	1.51
M72094-3	33	18	23	N.A.	N.A.	18.3	1.33
M72094-2	9.2	6.3	6.2	N.A.	N.A.	18.2	1.44
Controlled Oxidation Plasma Melt With 5% O_2 in Helium: ICP-MS Reference Section 4.1.2.5 for Details							
M9294-1	<1.0	7.4	11	N.A.	N.A.	N.A.	N.A.
M9294-2	<1.0	22	28	N.A.	N.A.	N.A.	N.A.
M9294-3	<1.0	<1.0	1.2	N.A.	N.A.	N.A.	N.A.
M9294-4	<1.0	1.8	2.8	N.A.	N.A.	N.A.	N.A.
M9294-5	<1.0	33	78	N.A.	N.A.	N.A.	N.A.
Controlled Oxidation Plasma Melt With 5% and 10% O_2 in Helium (With a Refractory Lining: ICP-MS) Reference Section 4.1.2.6 for Details							
M102494-1	75	67	79	N.A.	N.A.	N.A.	N.A.
M102494-2	130	210	210	N.A.	N.A.	N.A.	N.A.
Controlled Oxidation Plasma Melt With 10% O_2 in Argon: ICP-MS Reference Section 4.1.2.7 for Details							
M1695-A	73	64	80	N.A.	N.A.	N.A.	N.A.
M1695-B	<1.0	<1.0	<1.0	N.A.	N.A.	N.A.	N.A.

SAMPLE ANALYZED	ELEMENT CONCENTRATION						
	Ce (ppm)	La (ppm)	Nd (ppm)	Cs (ppm)	Sr (ppm)	Cr (%)	Mn (%)
M1695-C	57	65	54	N.A.	N.A.	N.A.	N.A.
M1695-D[1]	<1.0	<1.0	<1.0	N.A.	N.A.	N.A.	N.A.
M1695-E[1]	<1.0	<1.0	<1.0	N.A.	N.A.	N.A.	N.A.
Commercial Scale Air Induction Melt Performed at AFFCO: ICP-MS Reference Section 4.2.2 for Details							
M72094-5	<1.0	<0.5	<2.0	<1.0	N.A.	18.2	1.52
M72094-6	<1.0	<0.5	<2.0	<1.0	N.A.	18.3	1.53
M72094-7	<1.0	<0.5	<2.0	<1.0	N.A.	18.2	1.45
M72094-8	<1.0	<0.5	<2.0	<1.0	N.A.	18.2	1.41
Large Scale Air Induction Melt Performed at Newport News: ICP-MS Reference Section 4.2.3 for Details							
M9994-1	1.4	<1.0	<1.0	<1.0	<1.0	18.0	1.14
M9994-2	<1.0	<1.0	<1.0	<1.0	<1.0	18.1	0.99
M9994-3	<1.0	<1.0	<1.0	<1.0	<1.0	18.2	1.1
SAMPLE ANALYZED	**ELEMENT CONCENTRATION**						
	Ce (ppm)	**La (ppm)**	**Nd (ppm)**	**C (ppm)**	**Cr (%)**	**Si (%)**	**Mn (%)**
VIM: Vacuum Induction Melting Reference Section 4.1.3 for Details							
VIM 1	<1	<1	<1	353	18.2	0.29	1.28
VIM 2	<1	<1	<1	416	18.0	0.28	1.18
VIM 3	<1	<1	<1	426	17.8	0.34	1.28
VIM 4	<1	<1	<1	226	16.0	0.45	0.97
VIM 5	1	<1	2	566	16.5	0.42	1.18
VIM 6	16	17	18	394	16.3	0.28	1.18
VIM 7	<1	<1	<1	946	17.8	0.37	1.08
VIM 8	<1	<1	<1	264	17.5	0.32	0.90

(%) = Weight Percent
(ppm) = Parts Per Million
(1) Samples M1695-D and M1695-E were resamples taken from the center and the outside of the ingot after the ingot was cut axially in half to verify that there were slag inclusions in samples M1695-A and M1695-C.

TABLE 4.32. COMPILATION OF PILOT SCALE AND COMMERCIAL SCALE MELT TESTS: SLAG ANALYSES

SAMPLE ANALYZED	ELEMENT										
	Ce (%)	La (%)	Nd (%)	Cs (ppm)	Sr (%)	Al (%)	Ca (%)	Cr (%)	Fe (%)	Mn (%)	Si (%)
(Fluxes: "Borate" and "Borate Without Ferric Oxide"-Two Weight Percent) Reference Section 4.1.2.2 for DetailsFirst Controlled Oxidation Plasma Melt With an Oxidizing Flux: X-Ray Fluorescence											
Without Fe Hearth Slag	2.7	2.7	2.9	60	2.5	4.6	18.4	0.6	0.6	1.1	22
Without Fe Crucible Slag	2.5	2.5	2.5	<15	2.3	4.6	18.3	0.6	0.6	1.1	27.2
With Fe Crucible Slag	2.8	2.8	2.7	18	3.0	4.5	18.1	1.1	0.7	1.9	32.6
With Fe Hearth Slag	5.0	6.2	6.3	300	6.8	3.5	14.1	0.8	0.5	1.6	23.5
Second Controlled Oxidation Plasma Melt With an Oxidizing Flux:ICP-MS (Fluxes: "Borate" and "Ferrite"-Five Weight Percent) Reference Section 4.1.2.3 for Details											
S52694H	0.92	0.74	0.81	6.2	0.35	5.41	30.4	2.84	N.A.	3.33	15.9
S52694I	0.33	0.22	0.31	2.1	0.08	1.41	19.0	10.8	N.A.	7.16	10.8
S52794H	0.92	0.73	0.82	<1.0	0.34	5.57	33.4	1.99	N.A.	2.21	15.7
S52794I	0.32	0.21	0.30	<1.0	0.06	1.09	16.8	11.2	N.A.	7.06	9.73
Controlled Oxidation Plasma Melt With 2% O_2 in Helium: ICP-MS Reference Section 4.1.2.4 for Details											
S11994-2	0.018	0.017	0.095	N.A.	N.A.	0.4	N.A.	11.1	4.4	11.0	7.8
Controlled Oxidation Plasma Melt With 5% O_2 in Helium: ICP_MS Reference Section 4.1.2.5 for Details											
S11994-3	0.018	0.016	0.092	N.A.	N.A.	0.4	N.A.	10.5	9.6	7.6	6.5
Controlled OxidationPlasma Melt With 5% and 10% O_2 in Helium (With a Refractory Lining): ICP-MS Reference Section 4.1.2.6 for Details											
S11994-6	0.018	0.016	0.094	N.A.	N.A.	0.5	N.A.	12.5	10.7	7.8	4.8
S11994-5	2.9	2.8	3.2	N.A.	N.A.	0.3	N.A.	14.2	9.8	13.2	5.3
Commercial Scale Air Induction Melt Performed at AFFCO: X-Ray Fluorescence Spectroscopy Reference Section 4.2.2 for Details											
S72294-3	0.34	0.26	0.21	N.D.	N.A.	9.7	0.36	2.58	0.13	4.78	22.1
S72294-1	0.11	0.076	0.072	N.D.	N.A.	14.4	0.36	2.44	0.28	4.38	25.8

SAMPLE ANALYZED	ELEMENT										
	Ce (%)	**La** (%)	**Nd** (%)	**Cs** (ppm)	**Sr** (%)	**Al** (%)	**Ca** (%)	**Cr** (%)	**Fe** (%)	**Mn** (%)	**Si** (%)
S72294-2	0.084	0.058	0.039	N.D.	N.A.	15.4	0.40	2.28	0.12	4.16	24.9
Commercial Scale Air Induction Melt Performed at Newport News: ICP-MS **Reference Section 4.2.3 for Details**											
S11994-4	0.019	0.016	0.093	N.A.	N.A.	0.7	N.A.	3.5	1.1	1.7	9.5

(%) = Weight Percent
(ppm) = Parts Per Million
N.A. = Not analyzed
N.D. = Not detected

RECOMMENDATIONS FOR FUTURE WORK

1. Demonstrate the technology established on surrogates on full-scale VIM melts using selected radioactive scrap material.

2. Continue pilot scale induction melts to establish the kinetics of decarburization in VIM using gaseous and solid oxidizers.

3. Develop the use of cold hearth plasma melting for cutting, consolidation, and refining of surrogate-containing scrap material. This work will require optimization of torch design to allow polarity changes and use of oxidizing gases.

4. Conduct a basic study to investigate the influence of torch polarity on oxidation potential in cold hearth plasma melting.

DECONTAMINATION AND DECARBURIZATION OF STAINLESS STEEL AND CARBON STEEL BY MELT REFINING

SECTION SIX

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