WINCO-1224 UC-510

REFINING TECHNOLOGY FOR THE RECYCLING OF STAINLESS STEEL RADIOACTIVE SCRAP METALS
FY 94 BI-ANNUAL REPORT

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August 1994

Westinghouse Idaho
Nuclear Company, Inc.

PREPARED FOR THE
DEPARTMENT OF ENERGY
IDAHO OPERATIONS OFFICE
UNDER CONTRACT DE-AC07-84ID12435

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1.0 INTRODUCTION

The research addressed under this project is the recycling of metallic nuclear-related by-product materials under the direction of Westinghouse Idaho Nuclear Company (WINCO). The program addresses the recycling of radioactive scrap metals (RSM) for beneficial re-use within the DOE complex; in particular, this program addresses the recycling of stainless steel RSM. It is anticipated that various stainless steel components under WINCO control at the Idaho Falls Engineering Laboratory (INEL), such as fuel pool criticality barriers and fuel storage racks will begin to be recycled in FY94-95. The end product of this recycling effort is expected to be waste and overpack canisters for densified high level waste for the Idaho Waste Immobilization Facility and/or the Universal Canister System for dry (interim) storage of spent fuel.

The programmatic work reported herein is being carried out by the Center for the Application of Advanced Materials Science and Engineering Concepts (CAAMSEC) at the Oregon Graduate Institute of Science and Technology (OGI). The Center is closely associated with the Materials Science and Engineering (MSE) Department at OGI, and has been specifically set up to facilitate timely completion of research and development for sponsor-specific programs that may entail technology transfer.

The specific components of this problem area that are presently being, or have been, addressed by CAAMSEC are:

- the melting/remelting of stainless steel RSM into billet form;
- the melting/remelting initial research focus will be on the use of radioactive surrogates to study:
    - reduction of radioactive contamination by slagging refinement techniques,
    - flux selection studies based on thermochemical considerations; and,
- the cost effectiveness of RSM processing oriented towards privatization of RSM reuse and/or resale.

Other components of this problem that may be addressed under program extension are:

- the melting/remelting of carbon steel,
- the processing of billet material into product form which shall meet all applicable ASTM requirements; and,
- the fabrication of an actual prototypical product; the present concept of an end product is a low carbon Type 304/316 stainless steel cylindrical container for densified and/or vitrified high level radioactive waste and/or the Universal Canister System for dry (interim) storage of spent fuel.

The specific work reported herein covers the melting/remelting of stainless steel "scrap" metal into billet form and the study of surrogate material removal effectiveness by various remelting techniques.

1.1 BACKGROUND

The generic types of material that this research area thrust is directed towards are those contaminated with radioactive species, either as surface or volumetric contamination. The majority of these materials are related to nuclear reactor operations, both governmental and commercial, and nuclear material processing equipment, both primary ore reduction and concentration operations and post-irradiation nuclear fuel processing equipment. These materials are expected to have a wide range of potential contaminates; Table 1 (1) presents potential commercial reactor contaminants with half lives over 50 days while Table 2 (2) presents radionuclides expected in government controlled facilities.

In considering the radionuclides that would be of concern in the recycling of structural materials from nuclear-related facilities, it is important to consider how much time will have passed between shutting down a plant and the actual recycling effort. Time is a consideration because some radionuclides are short lived, and can be brought to acceptable

TABLE 1. Radionuclides Found in Commercial Nuclear Power Reactors (Limited to half-lives greater than 50 days) (1)

Nuclide	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
Eu-155	1.8E+3	Fission/Fuel

TABLE 1. (Continued)

Nuclide	Half-life (days)	Mode of Production
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

TABLE 2. Radionuclides Potentially Present in Government Controlled Nuclear Related Facilities[2]

Primary Contributors	Secondary Contributors	Tertiary Contributors
Co-60	C-14	Ca-45
Cs-137	Co-57	Co-58
Cs-134	Ni-59	Sr-90
Fe-55	Nb-93m	Eu-154
Mn-54	Ru-106	Eu-155
Ni-63	Ag-110m	
Sb-125	Ce-144	
Zn-65	Pu-241	

levels by the passage of time. Dyer has assumed that it would take at least 1000 days before any reactor material would enter the recycling process and therefore has limited his consideration to radionuclides with half-lives longer than 50 days (Table 1).(1) A radionuclide with a half life of 50 days would be reduced over a million times in 1000 days. Radionuclides may be classified according to their nuclear emissions. Gamma emitters are assumed to be the major problem in any recycling effort because the radiation they emit will only be decreased by metallic shielding. Non-gamma emitters are less of a problem as they can be shielded against by such things as plastic gloves unless they are released as small particles into the working area where they may be ingested by workers.

Alpha rays (α-rays) consist of streams of nuclei of 4 atomic mass units and a +2 charge (i.e. He^{++} ions). These are projected at great velocities from certain radioactive elements. Beta rays (β-rays) are streams of electrons travelling at a velocity that is a little less than the velocity of light. Gamma rays (γ-rays), unlike the α- and β-rays are not thought of as particles but rather of electromagnetic vibrations similar to light or X-rays. Gamma rays thus have neither mass nor electric charge.

The power of these rays to penetrate matter increases from α to β to γ. When any of these radiations impinge on matter they are partially or completely absorbed. Most α-rays are stopped by a sheet of paper, whereas, β-rays may only be stopped by a thin sheet of metal. Gamma rays, with the greatest penetrating capability, can only be stopped by thick lead or concrete walls.(3)

A combination of two factors, the intensity of radioactivity and the exposure time is called the dosage.(1) Non-gamma or low-energy γ emitters will have a small contribution to the radiation dose level a person receives from external sources but may be a major contributor to the radiation dose from internal sources if the radionuclide enters a persons body. The transuranic nuclides are α emitters and are of importance to the internal radiation dose, since α emitters cause a much higher internal dose per radioactivity amount than do β or γ emitters.

Material contamination can be either external or internal. "Crud" accumulates on reactor piping surfaces and usually contains radioactive elements in the oxidized state, which are corrosion products from within the reactor vessel, or from "leaking"' nuclear fuel rods; processing piping contains residuals from the processing stream. Surface crud may be removable, or greatly reduced, by surface decontamination methods or a combination of surface contamination removal and remelt techniques, or by remelt techniques alone. Alloying elements in stainless steels, such as cobalt and manganese, can become activated due to the proximity of some steel components to neutron flux present during reactor operations. This is not surface contamination, but is incorporated within the steel itself and could never be removed by surface treatment operations. Activated material makes up only a small fraction of the total RSM to be decontaminated. The expectation is that internally activated products, such as Co, Fe, and Mn, can not be removed by either surface decontamination techniques or remelting techniques, and thus must be "decontaminated" by storage for sufficient half-lives to achieve desirable low residual levels of radioactivity.

The OGI research effort reported herein is directed toward low carbon 300 series austenitic stainless steels which have immediate potential for nuclear community reuse. The first step in reuse of RSM stainless steel is volume reduction by some type of primary melting technology. The program objective is to develop selected melt technologies for surface/volume decontamination as well as volume reduction.

Depending on the degree of contamination and the starting size and shape of RSM, it may be necessary to perform a first melting operation which consolidates and provides for significant volume reduction. This operation could be carried out in a number of ways including air atmosphere or inert atmosphere induction melting, electroslag remelting (ESR), vacuum arc remelting (VAR) and plasma arc remelting. Volume reduction melting may be combined with slag partitioning in the case of induction, electroslag and possibly plasma melting which would achieve some degree of partitioning of radioactive elements into the slag, or a second remelt operation specifically oriented towards radioactive element removal by slagging technology may be needed to reach the desired degree of decontamination.

There are several possible candidates for melting radioactive scrap metals including induction melting, ESR, VAR, electron beam (EB) melting, and cold hearth melting (plasma arc or EB). Each technique has advantages and disadvantages. Induction, plasma, and ESR melting have the ability to be run with a continuous slag covering. By adjusting the slag chemistry, it is possible to selectively extract unwanted species into the slag. The slag represents a relatively small volume which could then be disposed. Vacuum arc remelting has the advantage of low cost, relatively easy containment of radioactive species, low maintenance and the ability to extract volatile species (like tritium). Electron beam melting operates under a much higher vacuum than VAR and is often used to selectively extract high vapor pressure metallic species (elements with a low boiling point relative to the finished product). Electron beam melting is also capable of good containment, but maintenance and operating costs are higher because of the additional complexity of vacuum systems, electron gun maintenance, and feedstock preparation. Additionally, an EB hearth process can be used to segregate high density inclusions or elements (such as tramp UO_2 particles) from the melt.

This research program focuses on the assessment of the relative strengths and weaknesses of selected melting techniques, in particular ESR and VAR. A literature search is in progress to determine feasibility, from a thermodynamic as well as practical viewpoint, of the ability of various melt options to selectively remove radioactive species. Other considerations include likely degree of decontamination, positive containment and control of radioactive species, ease of operation and maintenance, and relative economics. Also of importance is the quality of the recycled steel, which should not only meet ASTM standards for microstructure and chemistry, but should also be as free of non-metallic inclusions if this is deemed necessary by the clean steel standards of possible customers. The need to meet ASTM or customer chemical and/or physical standards may require supplemental alloy additions, and/or possibly additional remelting cycles.

The OGI workscope is directed towards the following goals: 1) assessment of the feasibility of achieving 304L chemical specification requirements using a (combination of a) variety of remelting techniques; 2) assessment of the surrogate removal capabilities of various (combinations of) remelting techniques; 3) development of a mass balance for surrogate partitioning from results obtained in initial remelting activities; and, 4) development/assessment of thermochemical models to predict partitioning in various melt techniques.

The ESR and VAR remelting techniques are commercial processes proven to be capable of yielding billet chemistries within strict specification requirements. However, it is anticipated that it may take two remelts using these techniques to assure specification chemistries; a first remelt to volume reduce the supplied scrap material and a second remelt for adding specific alloying elements to assure chemistry specification compliance. Note that multiple remelts are routinely done in industry for chemistry control, grain size control, and inclusion/tramp element control. The ESR, as well as other slagging techniques, is expected to essentially remove all surrogates (to levels comparable or below starting stock and/or detection limits) while VAR, based on OGI research reported below, is expected to retain a reasonable level of surrogates; a VAR volume reduction remelt followed by a ESR radionuclide removal melt would be expected to yield a very acceptable product.

It is not presently obvious to OGI what remelting and/or combination of remelting techniques will be most efficient/effective in RSM volume reduction and/or reuse. Each of the various remelting techniques being studied under the WINCO multi-university research project appear to have advantages and disadvantages in the RSM volume reduction and reuse scenarios. Some techniques appear to maximize radioactive element removal, some appear to maximize remelting of various sized components and material chemistries with the minimum of RSM size reduction, and some appear to minimize equipment/facility/worker contamination potential. Thus the desire for OGI to study various techniques and various combination of techniques, as the OGI believes that it is quite possible that a double/triple melt of a given technique or a combination of techniques may be the most cost effective and/or minimize worker exposure.

1.2 MELT PARTITIONING

The heart of the success of RSM recycling is the ability to decontaminate the metal and render it suitable for re-use. Melt partitioning employs the use of a third agent to selectively remove an unwanted species from a molten pool of metal. During the production of iron and steels, a protective slag covering is maintained over the molten pool. The chemistry of the slag can be adjusted to selectively absorb unwanted species. Important variables include slag chemistry, the residence time the slag is in contact with the molten metal, and molten metal/slag temperatures.

Because one wishes to use slags as cleaning agents for radioactive melts, it is helpful to define a slag in terms of its basic functions and properties, which may then be modified in order to develop slags for ones specific purpose while still being capable of carrying out its other necessary functions. The four general functions of a slag are to protect the melt from the atmosphere, insulate the melt, accept unwanted components, and to act as a refining agent. The properties of a slag are basically threefold. It should have a lower melting point than the melt to maintain a slag of high fluidity; fluxes such as lime, CaF, or FeO may be added to lower the melting point of a slag. It must also have a lower specific gravity than that of the melt, so it floats on the molten metal. Of vital importance to this study is that the slag maintain a correct composition so that it can accept and react with impurities and be immiscible in the metal. ESR slags must also have conductivity within a specific range. Any changes made to the slag chemistry in computer models must be checked to make sure that basic slag properties and functionality are maintained.

It is possible that during the decontamination of RSM by melt refining techniques desirable species such as iron, chromium or nickel would be selectively removed in addition to the radioactive isotopes. This would necessitate replacing these elements in order to achieve compositional limits which meet specification requirements established by ASTM, ASME, etc. Dependable analysis would need to be carried out to determine depletion of alloy and trace elements which provide material such as 304L stainless steel with its basic mechanical and corrosion-resistant properties.

1.2.1 Melting methods

In considering the choice of a melting method for radioactive materials, several criteria become very important. The system must be as "closed" as possible, in order to control effluent dust and fumes. The system must have a controlled slag transfer method that can be performed remotely; the handling methods for this slag should be as simple as possible since the goal is to remove radioactive components to the slag. The initial melting process should be able to accommodate various scrap sizes and shapes, as cutting of scrap into small pieces requires much handwork and increases the potential for exposing workers to radioactivity. The ideal process should also allow easy modification of melt composition. The furnace itself should not become a source of contamination so that a highly radioactive melt could be made, followed by a less contaminated one, without further contamination of the latter melt. One source of this unintentional contamination would be refractory materials lining a melt surface, which, once contaminated, would contaminate every subsequent melt with which they came in contact. Finally, the process would have to have built in standards of safety and reliability so that worker radiation exposure should be as low as reasonably achievable (ALARA).

In any melting operation, certain parameters should be optimized, including homogenization of the melt, minimization of slag inclusions, and most importantly, the controlled transfer of radionuclides into slag and fume. Several variables are expected to influence the decontamination efficiency of slagging. These include temperature and time, the initial contaminant concentration, slag and metal composition, gas environment, predominance of static or dynamic slag/metal contact, as well as refractory interactions.

In order to clarify the relative merits and weaknesses of various melting processes, several popular processes are compared below.

1.2.1.1 Electroslag Remelting. The ESR technique may be used for a variety of metals and alloys provided appropriate fluxes and melting parameters are employed. In electroslag melting, the consumable electrode is melted into a water cooled copper crucible, Figure 1. Power for melting may be provided with either an AC or a DC power supply connected to the electrode. Before starting, turnings of the alloy to be melted are placed in the bottom of a water-cooled copper crucible. This crucible is fitted with a flange on top, to which the second power lead is connected. A portion of the flux is charged around the electrode prior to the start of the melt. Additional flux may be charged during melting through the top of the furnace. At the beginning of the melt, an arc is struck between the electrode and the

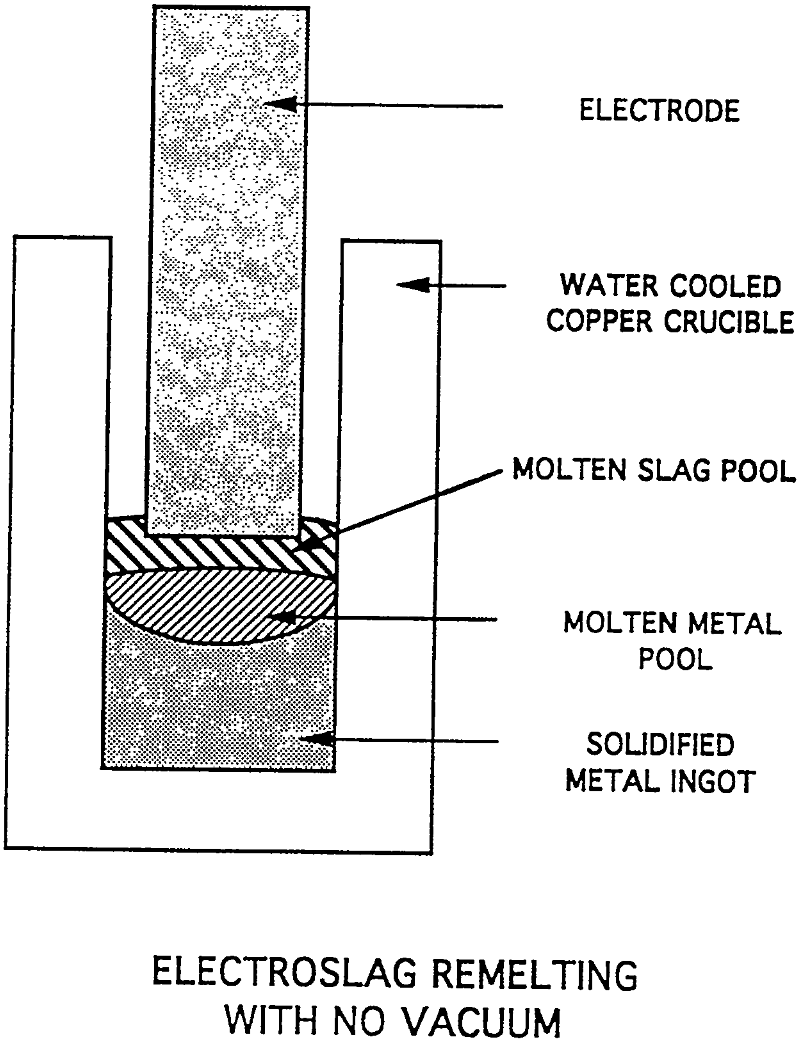


FIGURE 1. Schematic illustration of electroslag remelting process.

base plate but is immediately covered by the flux. When the flux has completely melted and the arc has been extinguished, the power is increased and the flux temperature exceeds the liquidous temperature of the electrode, which begins to melt. Metal droplets drop through the slag and collect in a pool on the baseplate of the mold and begin to solidify. As the process continues, an ingot is formed with a molten pool of metal on top of the solidified ingot and beneath the rising layer of molten flux. The molten slag in contact with the water cooled mold solidifies to form a skin between the crucible and the ingot. This skin protects the crucible by becoming a heat barrier between the melt and the copper.(4)

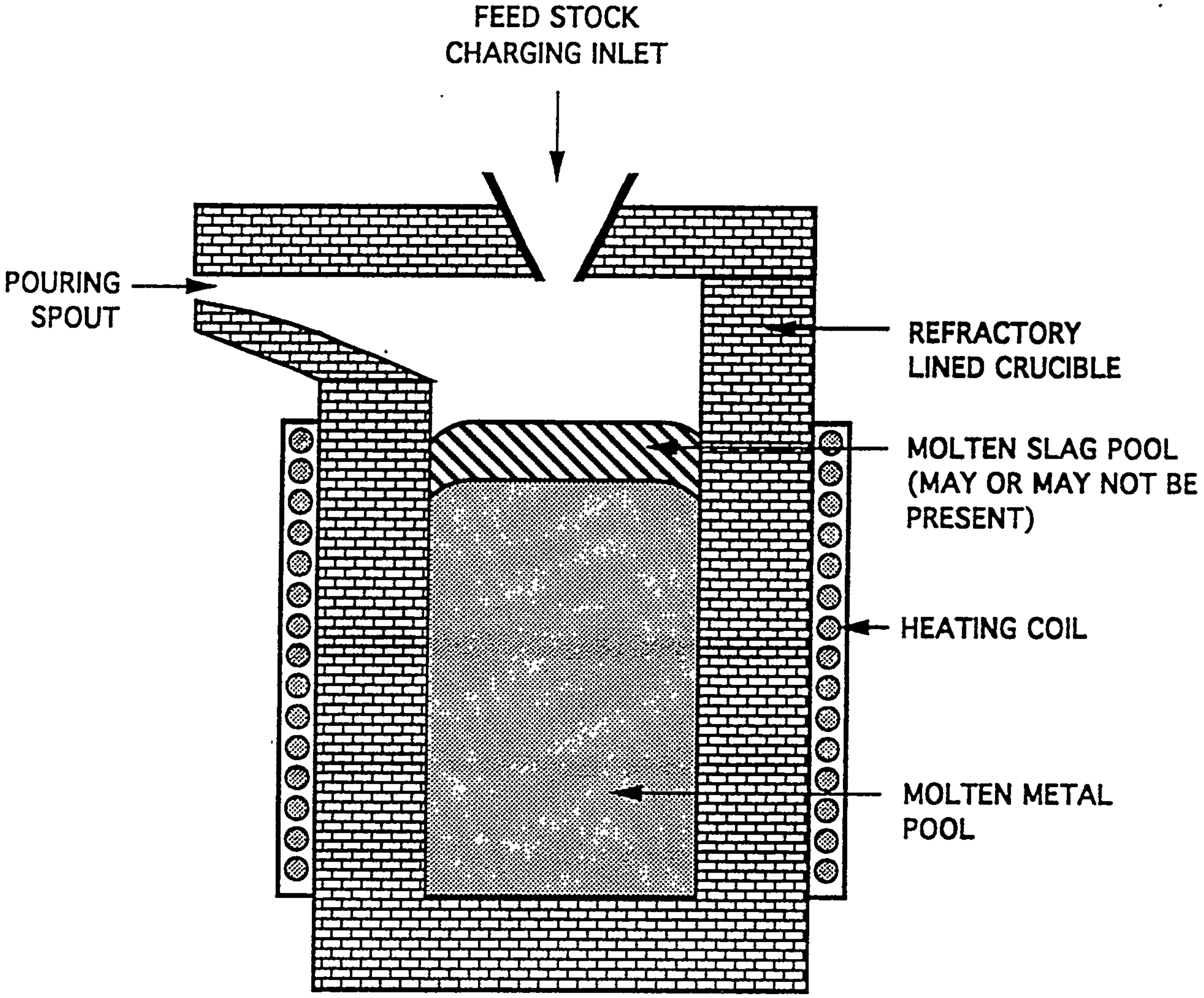
As a process for the safe, economical removal of radionuclides into a slag phase, ESR has many benefits. The slags in ESR tend to be hotter than in other melting processes, which is expected to have a beneficial effect on reaction kinetics. Metal/slag contact in ESR is very good in terms of promoting completion of reactions. As the electrode melts, drops of molten metal fall through a slag layer which completely surrounds the molten drop, oxidizing the most reactive species and capturing them into the slag. At the interface between the molten metal pool at the top of the ingot and the slag layer, reactions have another chance to take place.

There are no refractories in ESR to become contaminated, thereby forming another type of radioactive waste. A lack of refractories also means that there are no refractory interactions to compete with metal/slag interactions. Ease of slag removal is also a benefit of ESR. Most of the slag solidifies on the top of the ingot when the melt is finished. A thin layer of slag solidifies between the ingot and the mold. Because the slag is easily removed from the metal, it would be convenient to package and store the radioactive slag robotically to avoid human exposure. This would be much more difficult and expensive if a liquid slag were involved, as would be the case in other processes. Ease of fume capture in ESR would permit the effective capture of volatile isotopes such as Cs-137 and Sr-85.

The ESR lends itself quite nicely to process control. Nafziger(3) noted that the partitioning of elements between the metal and the slag is different under AC and DC conditions. By studying the effect of current type, current density, and voltage on various partition coefficients, one may be able to control the ESR process so that the radioactive species are pushed into the slag.

1.2.1.2 Induction Remelting. Solid conducting materials can be heated in three different ways by an electric current: (a) the indirect method in which the conducting material is heated by radiation and convection from resistors which carry the current; (b) the direct method where the current is passed directly from a power source through the conducting material; and (c) the induction method in which current is induced in the steel by an external induction coil and the conducting material acts as a secondary circuit for the current generated by the external induction coil(5), Figure 2. This current may also be used to stir the melt once the charge is molten. Water coils surround the furnace. Induction melting permits, but does not require the use of a slag. Induction furnaces are refractory lined, so reactions between the refractory and the metal and the refractory and the slag will occur. Such reactions will cause the presence of refractory particles in the melt, as well as the radioactive contamination of refractories. Slag is removed by skimming, often by manual operations. Because these furnaces need to be opened for molten slag removal, sealing them is difficult and fumes and dust will escape during the slag skimming process.

1.2.1.3 Direct Electric Arc Remelting. The direct electric arc furnace is three phase AC or DC. Heat is produced by arcing between the electrodes and the charge, Figure 3. These furnaces usually employ a water cooled, movable roof section through which three consumable graphite electrodes may be lowered for melting. The roof section swings away from the furnace for the charging of scrap and swings back for melting. This movable roof and the electrode ports make sealing the furnace difficult and dust and fume release is a



INDUCTION REMELTING

FIGURE 2. Schematic illustration of air induction remelting process.

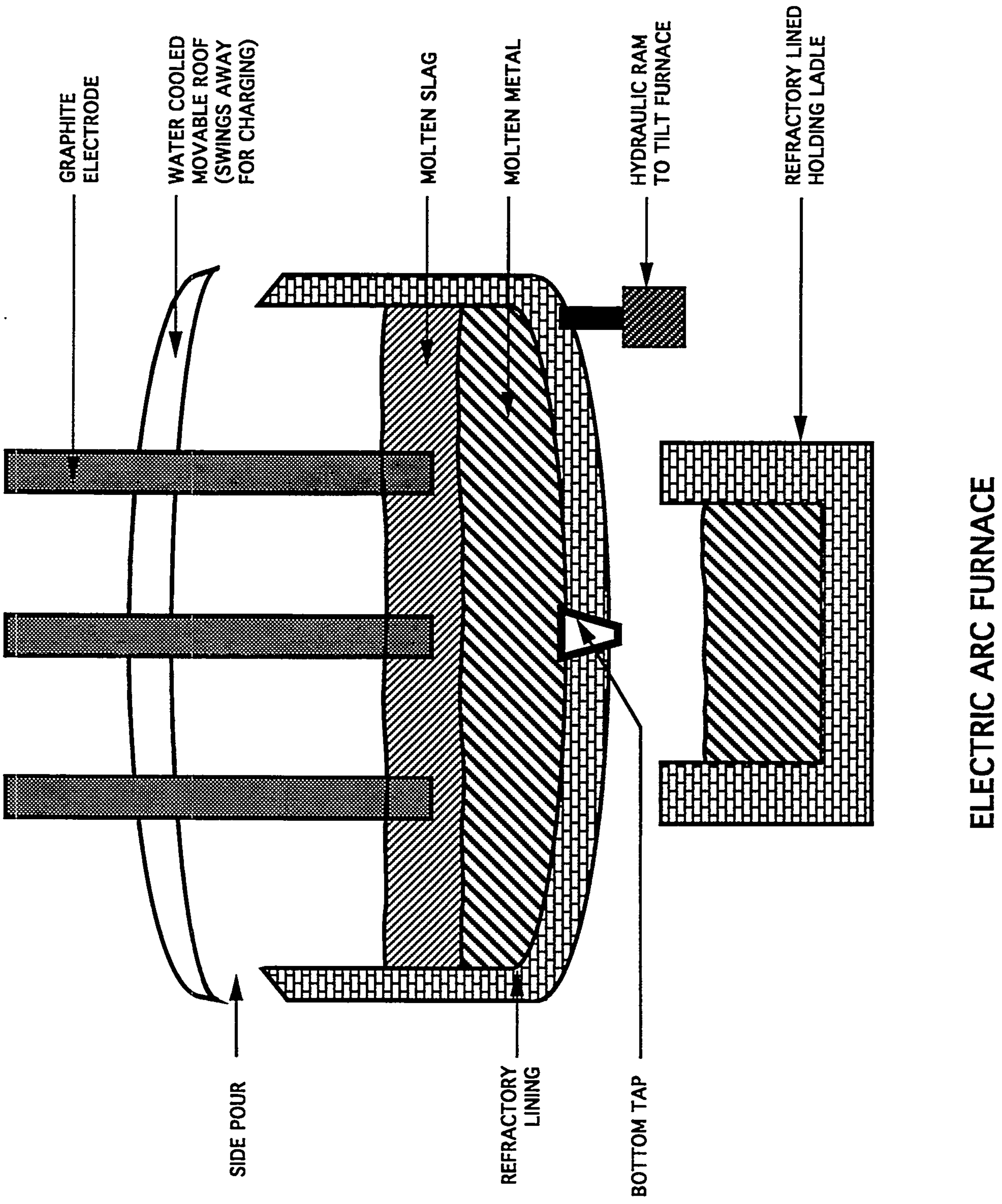


FIGURE 3. Schematic illustration of direct electric arc remelting process.

problem. Direct electric arc furnaces are lined with refractories. Slag may be removed either by tilting the furnace and pouring it off, or by a bottom tap whereby the steel is tapped from beneath the slag.

During normal operations, fume and dust are generated by direct electric arc melting. Reimann (6) notes that an induction furnace produces 20% of the effluent dust produced by an electric arc furnace of similar capacity. Fume and dust resulting from melting contaminated steel will have concentrations of long lived radionuclides such as Cs-137, which pose a significant health risk.

1.2.1.4 Plasma Arc Remelting. Plasma heating uses an intense and controllable stabilized electric arc discharge as the source of energy and exploits its thermal advantages over fuel fired heating techniques. Furnace designs incorporating both single and multiple plasma torches have been developed. The Retech furnace features a dual hearth system with a torch operating in the transferred arc mode to each water cooled copper section. Material to be melted is fed into an upper water cooled copper hearth where primary melting is carried out, Figure 4. Heavy inclusions separate under gravity and molten material overflows into a water cooled withdrawal section. This section is equipped with a second torch for superheating which can be used to vaporize or dissolve the low density inclusions floating on the surface of the melt. This process has no refractories to interact with the melt. Plasma melting has the capacity to incorporate a slag, if desired.. However, volatilization during melting results in the potential for coating the complete melting chamber with condensed (radioactive) metal vapor.

1.2.1.5 Vacuum Arc Remelting. The VAR process is similar to the ESR process, except that the melting is done in vacuum and there is no slag, Figure 5. The vacuum enables this system to be "closed" in a very controlled way. As melting is done in a water cooled copper crucible, refractory interaction is not a problem. The inclusion content of ingots made by VAR may be higher than those made by ESR because of the lack of a slag layer.

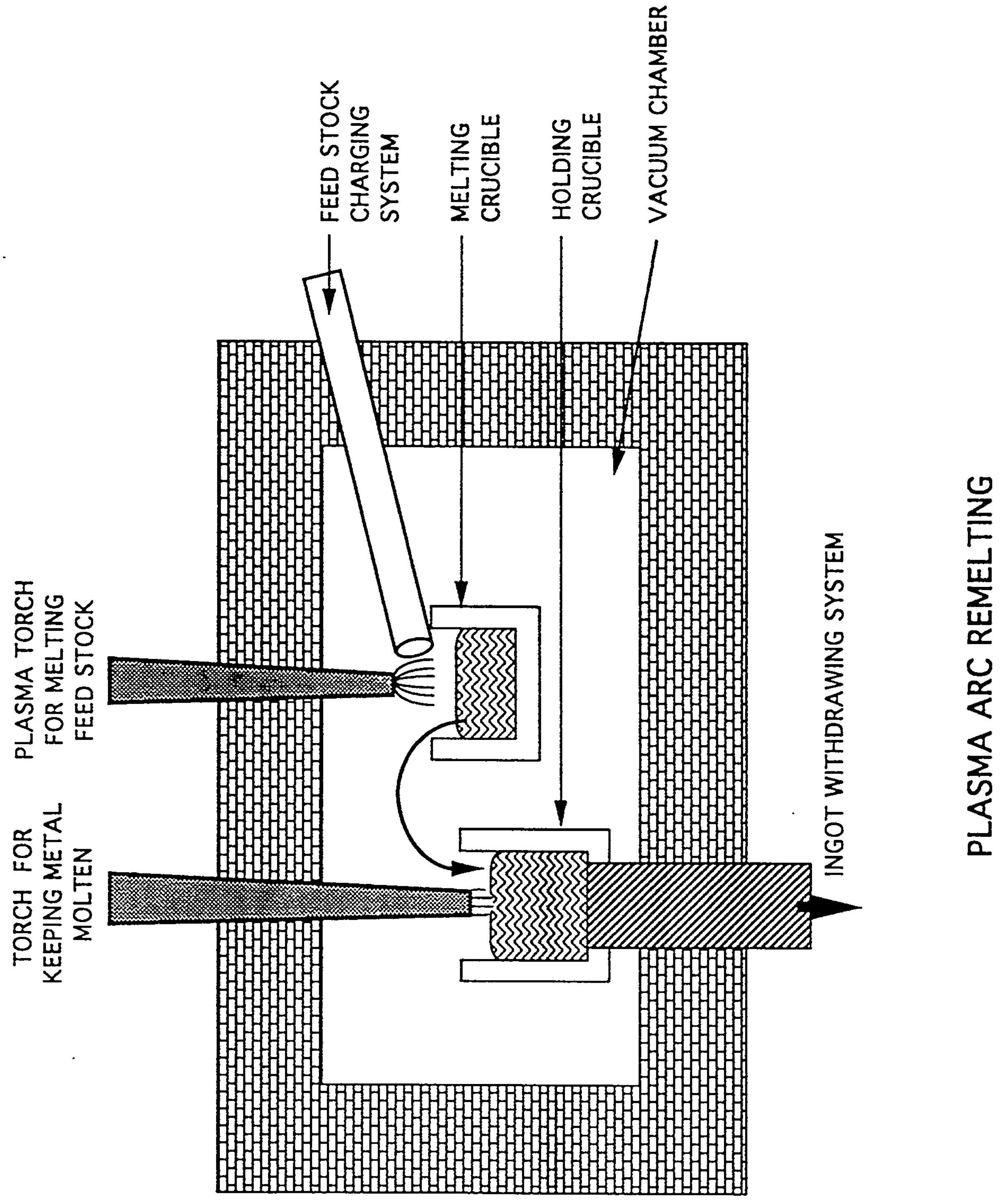


FIGURE 4. Schematic illustration of plasma arc remelting process.

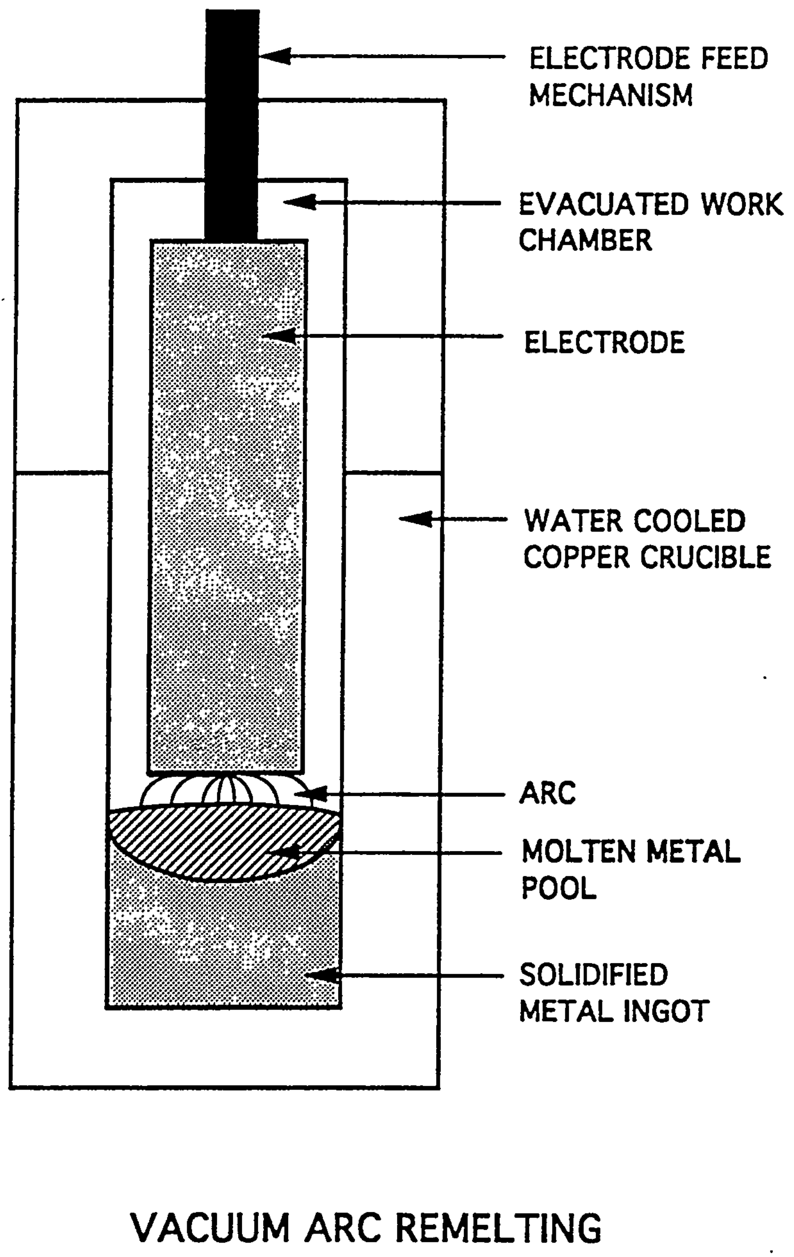


FIGURE 5. Schematic illustration of vacuum arc remelting process.

1.3 USE OF SURROGATES FOR RADIONUCLIDES

The radionuclides of interest in this work are fission products, which include rare earth elements, cesium, and strontium, and actinide elements, primarily uranium, plutonium, and americium. Due to the complication associated with experimental work involving radioactive materials that include, but are not limited to, disposal of wastes, ALARA considerations (keeping exposures As Low As Reasonably Achievable), and availability of laboratory facilities, surrogate elements will be used in the OGI study to mimic the chemical behavior of the radionuclides of interest. Some elements may be easily replaced without change in chemical reactivities. These elements are those that have naturally-occurring, essentially non-radioactive isotopic mixtures. Included among these are: cesium, strontium, and the rare earth elements (except promethium). The elements with atomic numbers greater than 83 have no non-radioactive isotopes; therefore, surrogate elements must be used if these are to be studied in a non-radioactive environment.

The choice of surrogate element is a function of a variety of considerations that include, but are not limited to, the chemical properties of the surrogate elements and phases formed by the reaction of those elements with other elements, the thermochemical properties of the surrogate elements and the phases formed by the reaction of those elements with other elements, availability of the surrogate elements, ease of handling of the surrogate elements, and ease of chemical detection of the surrogate elements. Of these considerations, those related to the chemical and thermochemical properties are probably the most important.

The abovementioned considerations were used to choose surrogates for the present work. 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. Table 3 lists the various stable oxides of the radionuclides of interest and oxides of possible surrogate elements. 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.(7) Neodymium was chosen as an actinide surrogate based on the chemical reactivity and thermochemical properties of the element and its compounds.

In order to quantify the suitability of any element to be used as a surrogate for another element, an index may be defined which is the ratio of the free energy of formation of the most stable oxide of the surrogate to that of the isotope of interest. The more closely this ratio approaches 1, the more suitable (at least in terms of free energy) is the surrogate to simulate the radionuclide. For example, the Suitability Index, S for the surrogate Nd to stand in for Pu is:

$$\mathbf{S = \Delta G^\circ Nd_2O_3 / \Delta G^\circ Pu_2O_3}$$

$$\mathbf{S_{1500C} = -310.675/-318.357 = 0.98}$$

This index should not be used alone in determining the suitability of a surrogate. Free energy data should either be normalized per mole of O, or compounds with equal ratios of reactive element atoms to O atoms should be used in determining S. A similar treatment of other properties of interest, such as melting and boiling points and lattice parameters, could also be performed in this fashion, with the resulting values being combined in a weighted fashion to arrive at the "best" surrogate for a given element. It is likely that the conclusions drawn from this type of treatment would be that different elements would be appropriate for mimicking different aspects of the behavior of an element; Raraz et. al. arrived at this conclusion in their previously mentioned work, identifying different surrogates to mimic various properties of Pu.(7)

TABLE 3. Free Energy Available for the Formation of Various Oxides at Three Temperatures. (8)

Stable Oxide	ΔG° at 1000 °C kcal/g atom of O	ΔG° at 1500 °C kcal/g atom of O	ΔG° at 2000 °C kcal/g atom of O
CsO_2	-18.705	-12.145	-7.217
Cs_2O	-29.979	-13.648	1.131
Cs_2O_2	-18.216	-8.746	0.307
Cs_2O_3	-21.743	-14.383	-8.009
Cs_2UO_4	-82.922	-70.261	-57.618
La_2O_3	-114.098	-102.783	-91.678
Nd_2O_3	-115.110	-103.558	-92.019
PuO	-107.790	-96.647	-86.074
PuO_2	-97.886	-87.257	-76.877
Pu_2O_3	-116.235	-106.119	-96.942
UO_3	-72.353	-62.245	-52.248
UO_3 (g)	-71.828	-61.461	-50.504
UO	-103.054	-90.559	-77.546
U_3O_8*	-81.781	-72.249	-167.673
U_3O_5*	-150.506	-143.858	-133.710
U_4O_9*	-94.509	-84.871	-75.373
UO_2	-103.554	-93.274	-83.018
ThO_2	-117.990	-107.125	-96.008
ThO	-119.146	-109.290	-99.685
SrO_2	-47.612	-37.566	-28.170
SrO	-111.424	-99.371	-87.667
AmO_2	no data	no data	no data

TABLE 3. (Cont.)

Stable Oxide	ΔG° at 1000 °C kcal/g atom of O	ΔG° at 1500 °C kcal/g atom of O	ΔG° at 2000 °C kcal/g atom of O
Am_2O_3	no data	no data	no data
$CeO_{1.72}$	-107.809	-96.076	-84.805
$CeO_{1.83}$	-104.241	-88.050	-81.010
CeO_2	-98.664	-86.477	-74.643
Ce_2O_3	-116.058	-105.001	-94.500
HfO_2	-105.453	-95.367	-85.652

*Extrapolated from 900K

Melting studies will be aimed at determining the partitioning of surrogate elements between metal and slag phases. Also of interest are the kinetics of radionuclide transfer to slag which may be controlled by a combination of diffusion to metal/slag interface and actual transfer across this interface. Because thermodynamic equilibrium is a function of temperature, the rate of formation of the species which are captured into the slag is temperature dependent also. The processes to be studied, specifically ESR, will provide data which may be used directly to predict partitioning of elements between the melt and the slag on a larger scale.

1.4. ANALYTICAL TECHNIQUES

After the surrogate remelting has taken place, analytical technique(s) for checking for residual surrogate concentration in the resultant billet and surrogate concentration in the slag must be employed. This could be as simple as standard alloy and trace species elemental determination, or as complex as neutron activation techniques. Issues to be addressed include degree of decontamination, residual byproducts generated, compositional control, and analytical techniques to assess the degree of decontamination achieved. OGI has made a considerable effort since program initiation on assessment of the attributes of various analytical techniques for both stainless steel and slag.

2.0 EXPERIMENTAL PROGRESS TO DATE

Experimental progress has included multiple scrap metal remelts, laboratory equipment construction, and plasma spray coating feasibility studies; all of these areas of research are discussed in detail below. A summary and brief description of all OGI remelt material to-date is given in Table 4. A summary of the material samples sent out for analysis and the various methods used for analysis is presented in Table 5. Selected analysis results are discussed in the various Experimental Progress To Date sections below, with an in depth discussion of analytical techniques presented in Appendix I "Assessment of Chemical Analysis Techniques."

2.1 SCRAP METAL MELTS

All material to date used in the OGI melting/remelting work came from the INEL site as "scrap" metal existing on the site and shipped to OGI by WINCO early in the last quarter of FY93. The scrap metal came from material purchased to go into an INEL processing facility that was never completed. The material was stored on site after purchase but never exposed to radioactive contamination. The approximately 10,000 pounds of metal sent to OGI was thought to be 304L stainless steel. Various metal alloys were purchased for facility construction, but specific alloy types were supposed to be kept separate.

The original OGI melts were made from random material selected from the INEL-furnished metal scrap, mostly tubing or narrow sheet stock. Subsequent chemical analysis of the resultant melted material indicated that material cross contamination had occurred, with some Nitronic 50 tubing being mixed with the 304L alloy tubing. A recent sorting operation was performed on a limited sampling of INEL-furnished material and two pipe pieces out of 40 were found to be off chemistry and identified by the portable XRF device to be Nitronic 50. This mixing of metal alloys in as-received material stored for future use points up the

TABLE 4. Inventory of OGI Remelt Material.

Sample Identification				
Billet ID #	Description	Diameter (in.)	Flux	Remarks
OGI 1	Melted at OGI on ESR under DC conditions starting with assembled piping.	3.5	ESS 595	OGI ESR-DC Remelt
OGI 2	Melted at OGI on ESR under DC conditions starting with assembled piping.	3.5	Lincoln Bluemax 4000	OGI ESR-DC Remelt
OGI 3	Single pipe melted on DC ESR to an ingot. This chemistry shows that some starting stock was not 304L.	3.5	Lincoln Bluemax 4000	OGI ESR-DC Remelt
OGI 4	Assembled piping on large AC ESR.	9.5	Lincoln Bluemax 4000	OGI ESR-AC Remelt
OGI 5	Not important, just a stainless steel bar melted to test the AC ESR in small crucible.	3.5	Lincoln Bluemax 4000	OGI ESR-AC Remelt
OGI 6	ESR of plasma sprayed E1 (PSE1) using AC conditions.	3.5	Lincoln Bluemax 4000	OGI ESR-AC Remelt
ESCO 1	Induction melted starting material was scrap piping from WINCO. This is our starting material.	≈ 2.5	No flux	Melted at Esco

TABLE 4. (Cont.)

Sample Identification				
Billet ID #	Description	Diameter (in.)	Flux	Remarks
PSE1	These ingots were plasma sprayed with a 50-50 mix of lanthanum oxide and cerium oxide powders to yield about 0.1% of each oxide in the coatings.	≈ 2.5	NA	Part of the E1 heat was plasma sprayed
ESCO 2	Induction melted starting material was scrap piping from WINCO.	≈ 2.5	No flux	Melted at ESCO
ESCO 3	Induction melted starting material was scrap piping from WINCO.	≈ 2.5	No flux	Melted at ESCO
ESCO 4	ESCO induction melt of surrogate coated E1 (PSE1).	≈ 7	No flux	PSSE1 melted at ESCO
MTK	Plasma melted from WINCO scrap with surrogates added to the melt. Jack Devletian brought parts of this ingot back for further remelting.	≈ 8	No flux	Montana Tech ingot melted at Retech
Retek 1	Plasma melt at Retech starting with Plasma sprayed E1 (PSE1)	≈ 8	No flux	PSE1 melted at Retech
ESR AC	Electroslag AC melt at OGI of Plasma coated ESCO 1 billet material.	3.5	Lincoln Bluemax 4000	Crucible melt through
VAR	Vacuum arc melt at OGI starting with E1	4.5	No Flux	No problems

TABLE 5. Summary of Analysis Methods and Labs Used for Analysis of Samples and Dates of Analysis

Sample	Oregon State University/ INAA	Metallurgical Testing Corp./ D.C. Plasma Leco C/S	Teledyne Wah Chang/ ICP Mass Spec	Other Labs
OGI 1 ESR DC welded piping		O.E.S. Spark 9/21/93 Plasma/Leco 9/28/93		
OGI 2 ESR DC welded piping		O.E.S. Spark 9/21/93 Plasma/Leco 9/21/93		
OGI 3A single pipe before melt		9/28/93		
OGI 3B single pipe after melt DC		9/28/93		
OGI 4 large ESR AC assembled piping		10/7/93		
E1 Master Melt 1	12/23/93 2/4/94	11/17/93	2/1/94	Esco/ Spectrograph 9/93 INEL not back Newport News not back
E2 Master Melt 2	12/23/93	11/17/93		Esco/ Spectrograph 9/93
E3 Master Melt 3	12/23/93 2/4/94	11/17/93		Esco/ Spectrograph 9/ 93

TABLE 5. (Cont.)

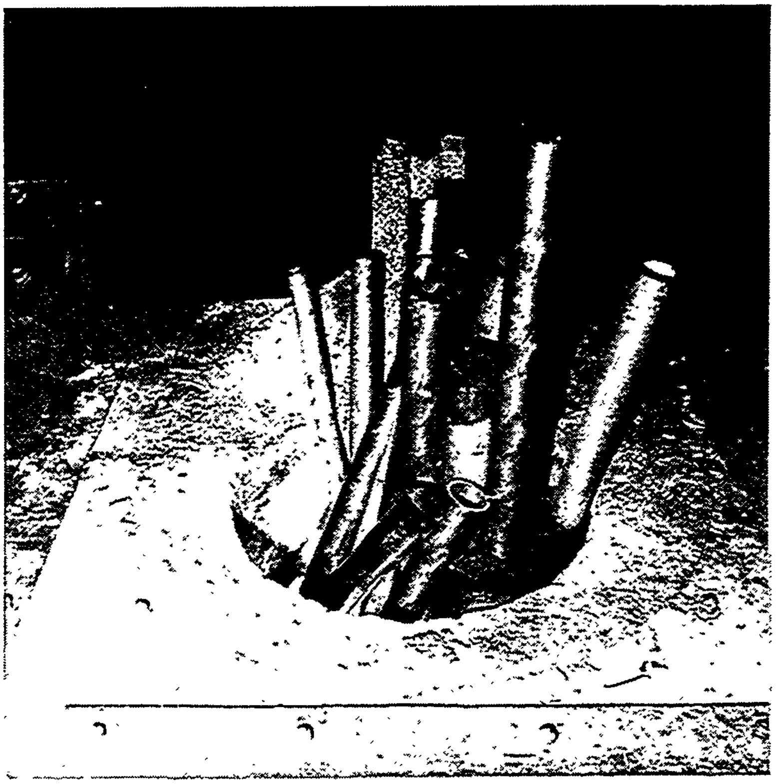
Sample	Oregon State University/ INAA	Metallurgical Testing Corp./ D.C. Plasma Leco C/S	Teledyne Wah Chang/ ICP Mass Spec	Other Labs
MTK Montana Master Melt	12/23/93	11/17/93	2/1/94	INEL: 5/16/94 Newport News not back
Reteck 1 - plasma melt of coated E1 material	12/23/93 2/4/94	11/17/93	2/1/94	INEL: 5/16/94 Newport News not back
Plasma Skull skull splash from Reteck 1	2/4/94			
ESR AC melt of coated E1	2/4/94	3/11/94		
E4 Induction of coated E1 material	2/4/94	3/11/94		Esco/Spectro Nov. 8, 1993
Slag before ESR AC	2/4/94		3/5/94	
Slag after ESR AC #1	2/4/94		3/5/94	
VAR melted coated E1	2/4/94	3/11/94	3/5/94	
304 before arc melter		3/11/94		
304 after arc melter		3/11/94		
Slag after ESR AC #2	Not back yet		3/14/94	
Slag after ESR AC #3	Not back yet		3/14/94	

problems associated with site material inventory and the apparent need for piece-by-piece alloy composition verification, if one desires to produce ASTM chemistry-controlled material out of site remelt material. WINCO is presently conducting a research study into methods for piece-by-piece metal characterization.

2.2 MASTER MELT BILLETS

It was decided that the majority of OGI remelting experiments would be carried out using "bar" stock cast from INEL-furnished 304L stainless steel. These Master Melt Billets were cast at ESCO in Portland, OR. Approximately 2,000 pounds of stainless steel scrap was melted in ESCO's 2,000 pound capacity air induction furnace, Figure 6. The chemistry of the molten metal was checked prior to pouring and needed alloying elements were added to reach a 304L chemistry compatible with the ASTM cast stainless steel specification. These additions were made just prior to the pouring of the molten metal into a transfer crucible in preparation for casting, Figure 7. The transfer crucible was pre-heated by a natural gas heater before the molten metal was poured into it to minimize/eliminate the formation of a solidified skull on the inside of the crucible that would have immediately formed if the crucible wall was at a lower temperature than the melting point of the metal alloy.

The molten metal was poured from the crucible into two sand casting molds to form the required bar stock, Figure 8. The bars were cast by a bottom pour method whereby the metal was poured into a large down-pipe that fed the molten metal into a bottom distribution system and then up into a series of ceramic tubes to form the bar stock, Figure 9. The castings were allowed to cool to room temperature and then the cast structures, consisting of the bar stock connected to the distribution system and the pouring spout was separated from the sand molding material on a shaker table. The bar stock was subsequently separated from the distribution system at OGI by plasma cutting. The bars were then surface cleaned by grit blasting at ESCO.



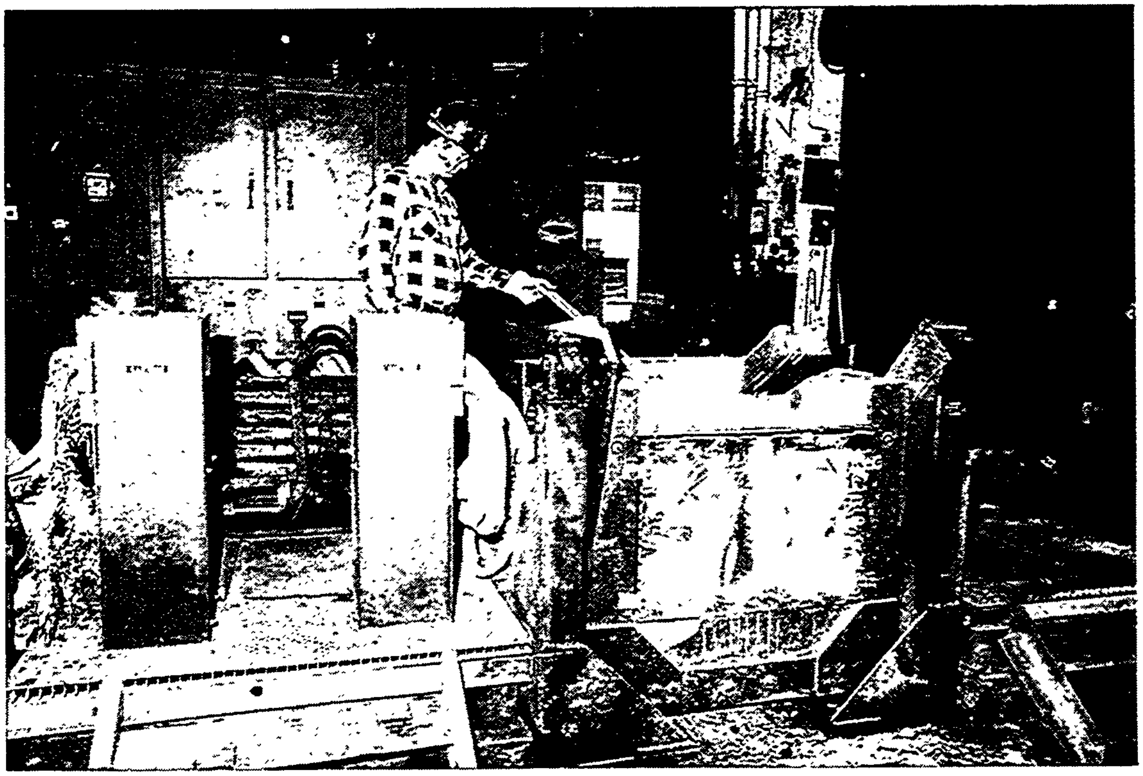


FIGURE 6. Melting of OGI Master Melt in ESCO 2000 pound air induction melting furnace.

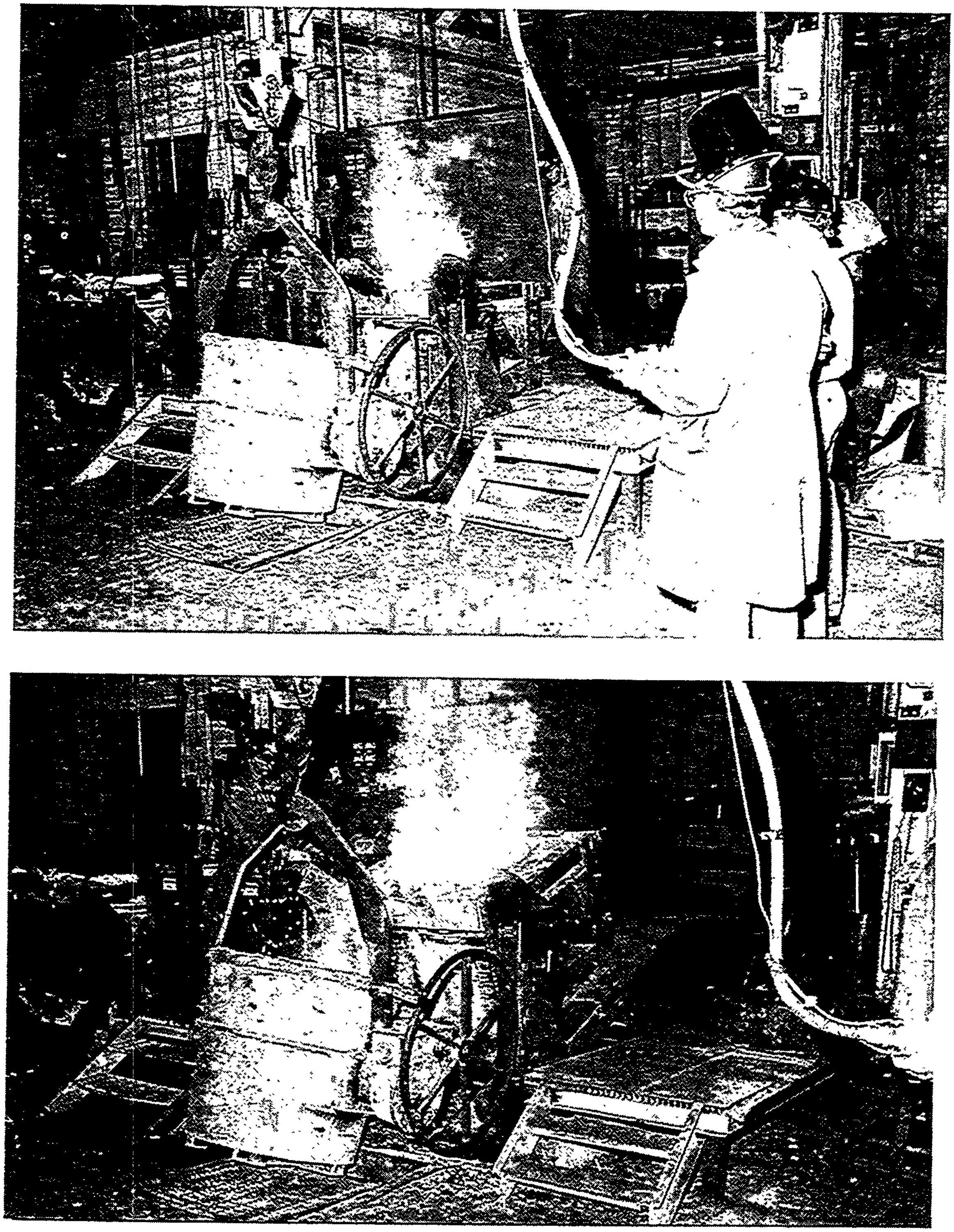


FIGURE 7. Pouring of molten stainless steel into a transfer crucible prior to pouring into mold.

FIGURE 8. Pouring of molten metal from transfer crucible into sand cast molds.

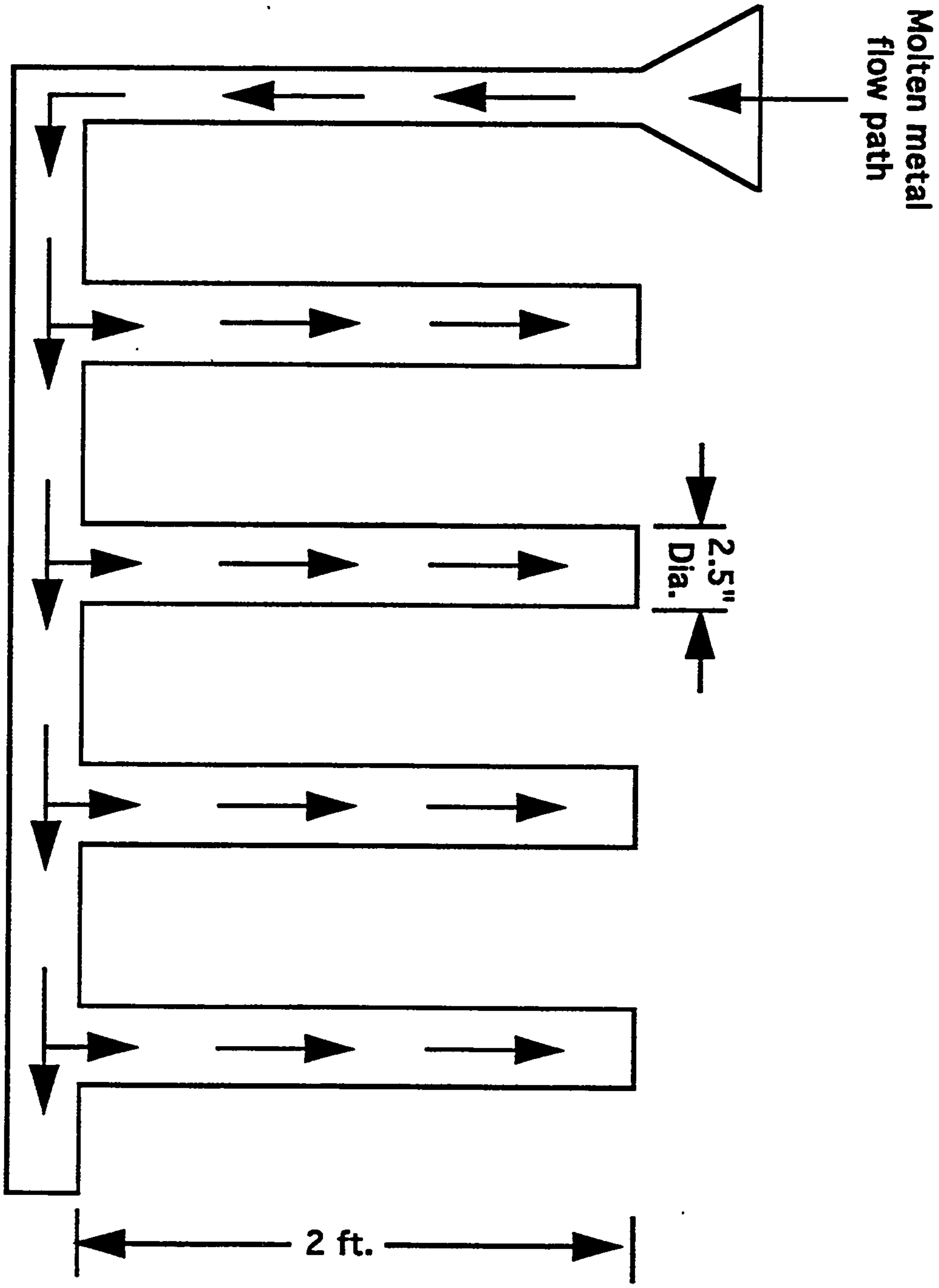


FIGURE 9. Schematic illustration of bottom feed pour.

Three Master Melts were cast at ESCO. The first melt of approximately 1,800 pounds was cast into forty 2.5 in. dia, 2 ft long "tubes" for subsequent (electroslag) remelting by OGI; twenty billets were two ft long and twenty were approximately one ft long. This melt was carried out in August 1993, and was witnessed by the WINCO Technical Monitor. Extra feed stock was added to the second and third melts which resulted in twenty billets two ft long and twenty billets one and one-half to two feet. These melts were completed by the end of September. This has resulted in a total of one hundred and twenty billets for subsequent remelting studies. Chemical analysis of the Master Melts, Table 6, indicates that all meet 304L casting material specifications and that their chemistries are essentially similar.

2.3 ESR REMELT BILLETS

A range of ESR-related work has taken place at OGI to date. This includes the fabrication of laboratory ESR melting facilities, use of the existing OGI pilot plant ESR unit, demonstration of the feasibility of making scrap metal ESR electrodes and removal of surrogate material by ESR.

2.3.1 Development of ESR Laboratory Scale Capabilities

The OGI already had an AC powered ESR pilot plant capable of up to 2,000 pound remelts. However, it was felt that the majority of programmatic ESR melts would be between 25 and 100 pounds. Thus it was decided to construct a laboratory ESR unit capable of this size melts. A zone melting furnace frame in OGI possession prior to program initiation was modified to fulfill this charter. Two direct current 750 amp welding power supplied owned by OGI were parallelled for use as the laboratory ESR power supply. Both the laboratory and pilot plant ESR units are shown in Figure 10.

TABLE 6. Chemistry Analysis of OGI Master Melt Base Metal (DC Plasma)

Element Percent	OGI Master Melts			304L ASTM Standard Required Max Chemistry	
	E1	E2	E3	Wrought	Cast
Cr	17.14	17.5	17.29	18-20	17-21
Ni	12.13	11.09	9.88	8-12	8-12
Mn	1.31	1.13	1.25	2.0	1.5
Si	0.69	0.41	0.63	0.75	2.0
Mo	1.12	0.94	0.55	NA	NA
Cu	0.22	0.25	0.16	NA	NA
S	0.011	0.011	0.012	0.030	0.04
P	0.005	0.005	0.005	0.045	0.04
C	0.025	0.034	0.030	0.03	0.03

Note: C and P analyzed by Leco Combustion.

The laboratory ESR system was completed in July and tested in August 1993. An existing 3.5" diameter water cooled mold was used to test the melting system and for the initial programmatic remelts, Figure 11. A second mold with a 5.5" diameter and a third with a 7.5" diameter were partially constructed in the last quarter of FY93. The design and construction of second and third water cooled molds was initiated for the use of repetitive remelt experiments. It is also possible to use the billet from the latter mold as a starting electrode for the present pilot plant remelter water cooled mold which has a diameter of 9". This allows a total of four billet remelts without having to section the various billets. Construction of a second remelter and a second set of water cooled molds was initiated in the last quarter of FY93 in anticipation of them being used for "hot" melts at a yet-to-be-determined site further on in the program.

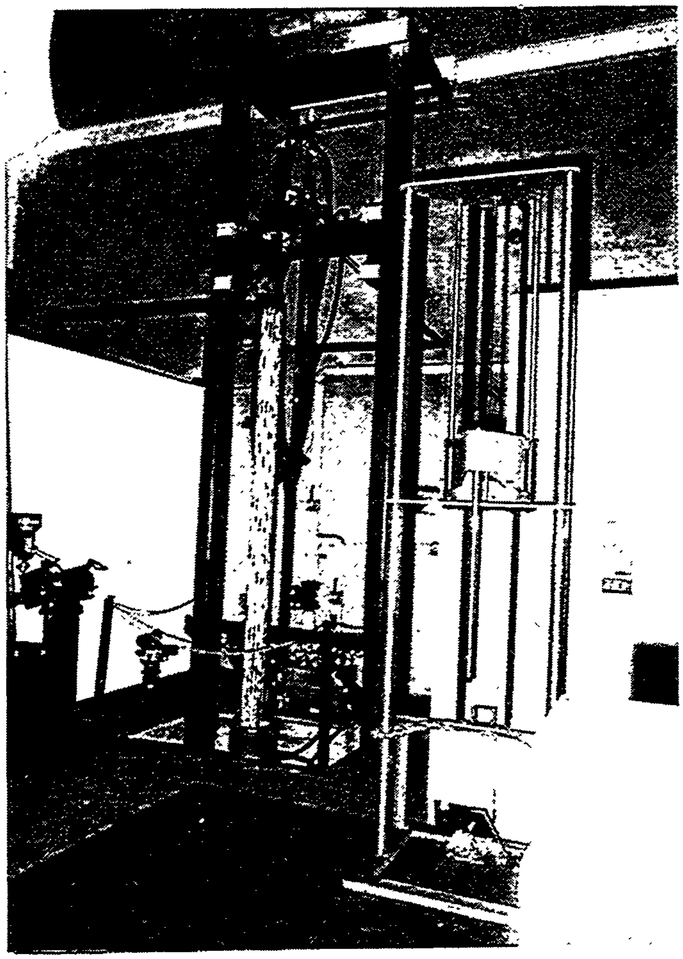


FIGURE 10. Comparison of the laboratory and pilot scale electroslag remelting systems.

A program of ESR furnace upgrade is underway and it includes design of a fume collection system, a hot starting capability for the laboratory and pilot scale ESR remelters and a control system for the pilot scale ESR unit. Fume collection system design was initiated in the last quarter of FY93 and generic components were purchased.

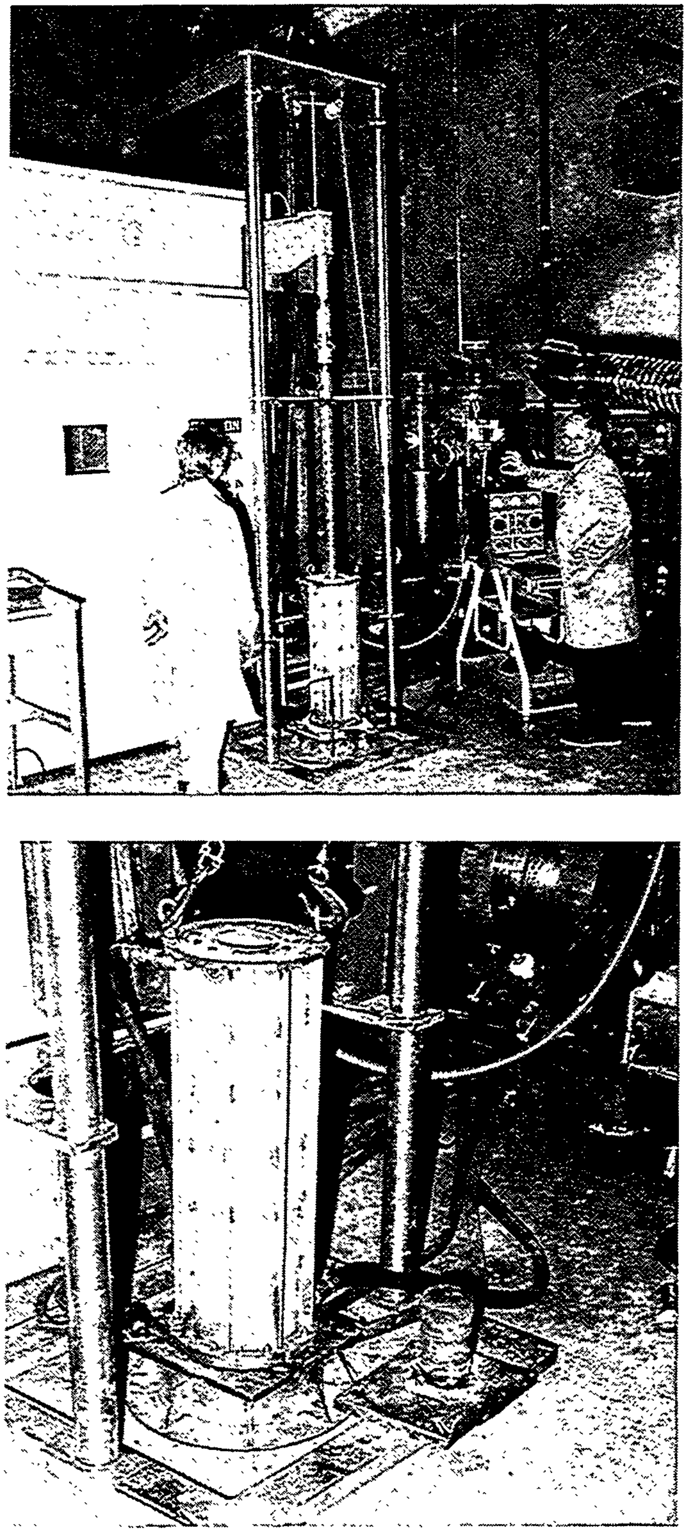


FIGURE 11. Electroslag remelt using the laboratory remelter.

2.3.2 Melting of Scrap Metal ESR Electrodes

Three laboratory ESR melts were completed by the end of September. All three were from WINCO furnished scrap metal. The feedstock for the first (OGI 1) consisted of a 304L stainless steel bar (1.25 in. diameter) slipped inside two other pipes to make up an electrode with a two and one-quarter outside diameter. The second remelt (OGI 2) consisted of a series of seven tubes/pipes slipped over the top of one another and resulted in an electrode with an outside diameter of 2.375 in. The third remelt (OGI 3) consisted of only one pipe, 2.375 in. in diameter with a 0.25 in. thick wall. The cross-sections of all three laboratory electrodes and a typical resultant billet cross-section are presented in Figure 12 and demonstrate the versatility of ESR in melting electrodes with a wide variance in effective density. This is further illustrated by a plot of OGI billet number versus normalized effective electrode density, Figure 13. All completed melts were made with the same fluxes OGI previously used for electroslag Inconel strip cladding applications, Table 4.

This demonstrates the use of direct ESR melting of pipes of various sizes without additional length reduction. This parallels work done in Japan (9) in which uranium contaminated metal cylinders were melted by electroslag refining without cutting them into smaller pieces. Uda and co-workers selected ESR because it was easy to scale up to the industrial level. Also, by reducing necessary scrap preparation, worker exposure will be reduced, as will scrap preparation costs.

The laboratory ESR unit was powered by two DC submerged arc welding power supplies, and it was noticed that they were running close to capacity for the multicomponent electrode melts. Thus it was decided that extra melting capacity would be needed for the 2.5 in. dia solid electrodes expected to be remelted for the major portion of the OGI study. Therefore a third welding power supply was added to power the laboratory ESR unit.

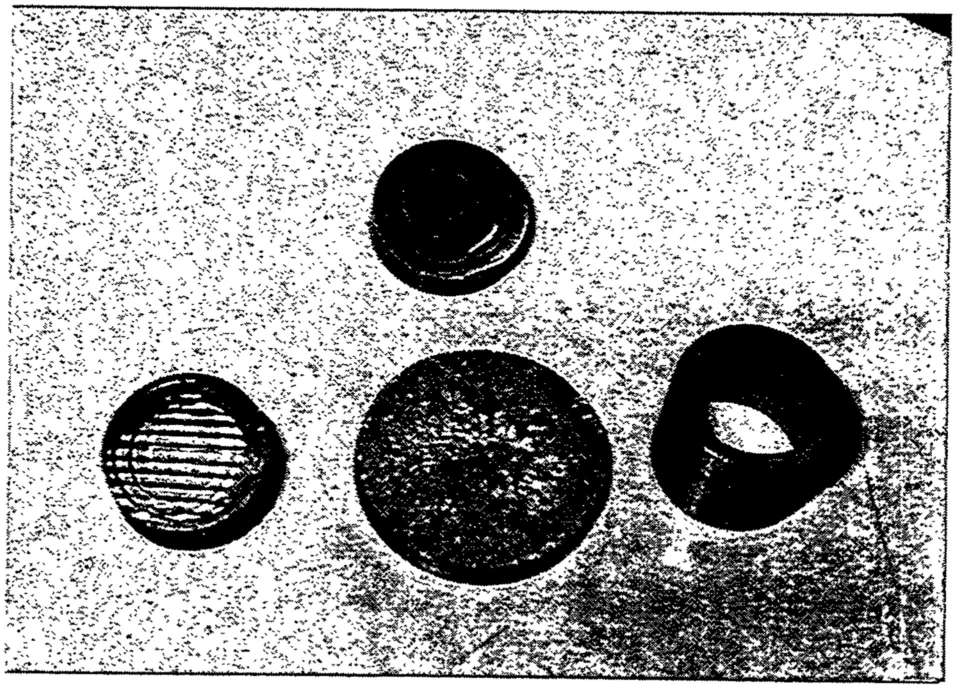


FIGURE 12. Cross section of laboratory remelt electrode billets fabricated from "scrap" metal and cross-section of typical remelt billet.

A 500 pound ESR pilot plant remelt (OGI 4) was also made. The electrode for this melt was fabricated from WINCO-furnished bar and pipe, Figures 10 and 14. It was melted using one of the same fluxes as used in the laboratory ESR melts, but was melted under AC conditions, Table 4. This demonstrates direct ESR melting of pipe up to 13 ft long and various sized without having to length reduce to the small sized generally required by induction and arc melting.

2.4 PLASMA COATING OF MASTER MELT BILLETS

The original program concept was to simulate radioactive isotope material contamination by metallic additions of surrogate elements directly into the ESCO Master Melts, similar to the technique used by researchers at Montana Tech. Their technique involves sealing elemental surrogates in stainless steel envelopes which are then welded down the length of a section of pipe. This pipe is then melted in a plasma cold hearth furnace and surrogate elements are presumably distributed throughout the bulk of the steel. Discussions between OGI, ESCO and the WINCO Technical Monitor resulted in the decision to attempt to add surrogates through the use of a plasma sprayed coating to be applied at OGI versus direct metallic additions of additives into ESCO's induction melt. It was felt that the plasma coating

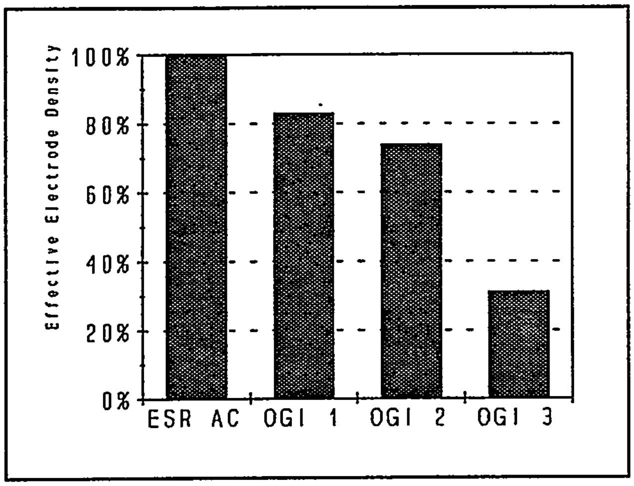


FIGURE 13. Illustration of electrode density versatility of electroslag remelting process.

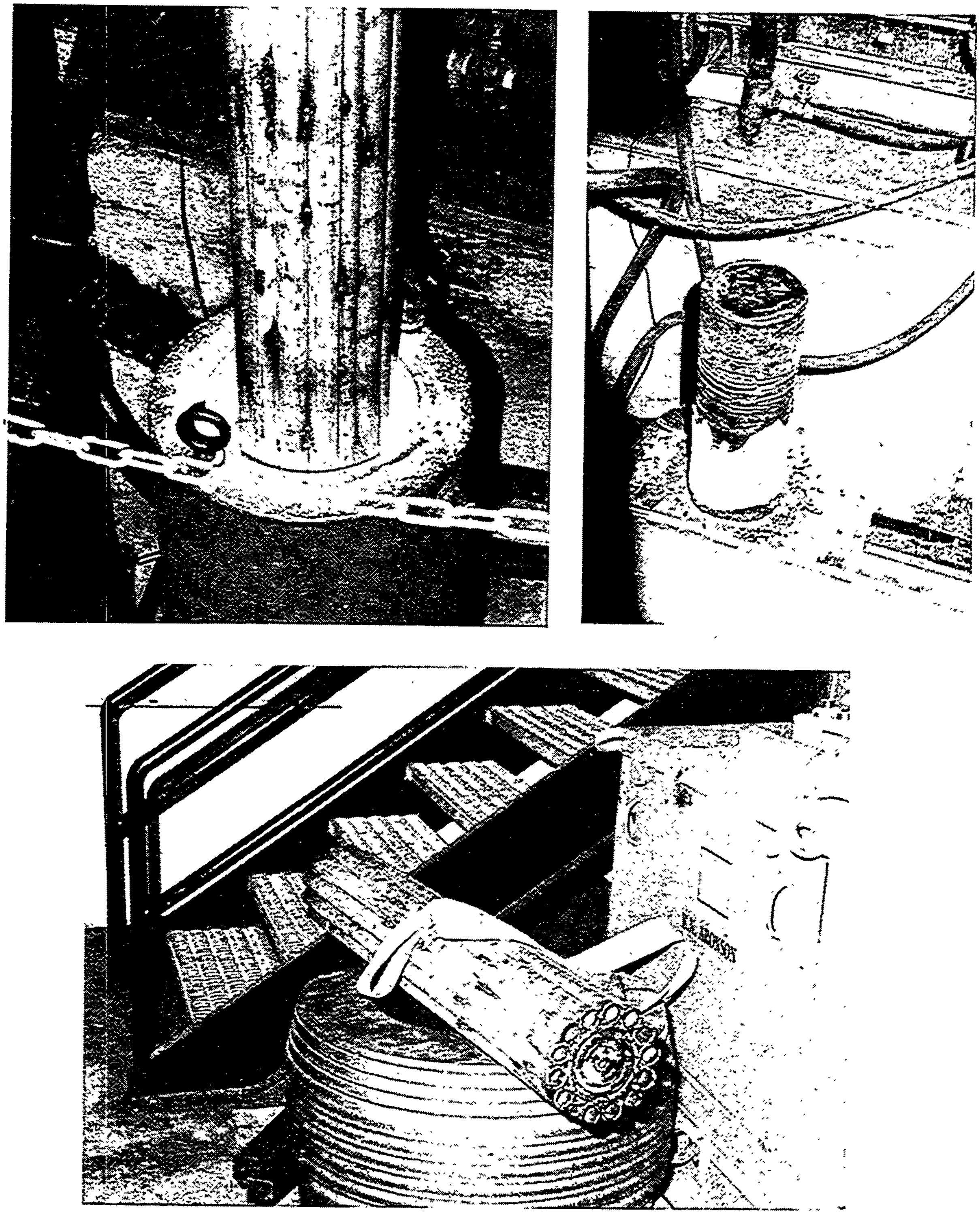


FIGURE 14. Pilot plant electrode fabricated from "scrap" stainless steel being melted and resultant billet.

approach was closer to reality and more cost effective, and that elemental surrogate losses during induction melting would be unacceptable. The OGI plasma spray equipment has the potential for co-depositing multiple element oxides at the same time, and thus OGI suggested that its plasma spray equipment be used on this program to simulate the actual oxide coating expected on surface contaminated material. Although this method has come under some criticism because the surrogates may be "too easy to remove by remelting", in reality, this method has several strong points:

1. Except for activated alloying elements, the majority of radioactive material is present on the inner surface of pipes as some form of oxidized crud. The plasma sprayed surrogate oxides mimic this crud deposition quite well.

2. The plasma spray process is inherently flexible. It is easy to increase the thickness of the surrogate layer, thus nicely simulating the difference in pipes with varying amounts of crud from various times in service.

3. In order to model the case when oxidized crud has seeped into cracks, plasma spray can be used to deposit surrogate oxides and deposit a layer of steel over the top.

4. By changing spray parameters, a number of types and quantities of waste can be easily modeled and tested for changes caused in remelting by initial waste type.

An overview of plasma spray systems and OGI equipment and planned upgrades is presented in Appendix I.

2.5 COATED MASTER MELT BILLET REMELTS

2.5.1 Plasma Coating Feasibility Studies

The surrogate elements that WINCO requested be added for subsequent removal by remelt and the radioactive isotopes/elements they substitute for are given below:

Surrogate Element	Radioactive Species
Cs	Cs
Ce	Ce, U, Pu
La	U, Am, Cm, Actinides
Nd	Pu
Sr	Sr

The OGI plasma spray equipment is capable of spraying (oxide) compounds of all the surrogate elements at one time, if desired. However, OGI decided to initiate surrogate plasma spraying feasibility studies with only La and Ce powder oxides, as these are readily available and low in cost. It was also expected that the other surrogates would be as active, or more active, in forming stable oxides and thus end up in remelt slags as easily as La and Ce, or would be removed by pre-melting vaporization. The OGI also decided to co-spray stainless steel along with the oxides to assure a coherent oxide-containing coating that would not spall off prior to emersion in the remelt bath. Note that the stainless steel feed stock was weld wire. Thus the plasma spray feedstock consisted of a 50/50 mixture of La and Ce oxide powders co-sprayed with a stainless steel wire, illustrating the versatility of the OGI plasma spray system.

Plasma spray studies orientated toward the goal of producing plasma sprayed Master Melt billet material for initial remelt studies were initiated in August 1993 and initial remelt plasma sprayed ingots were produced in September 1993. One foot long Master Melt billets from ESCO heat E1 were coated with a mixture of La and Ce surrogate oxides in association with stainless steel; the latter was added to assure coating adhesion during subsequent melting operations. One of the major reasons that OGI has been/is spraying the one ft bars is the present plasma gun travel limitation. The current system allows the gun to traverse about 18 inches horizontally with a separate manual control on the vertical motion and is not practical to use as the substrate size increases. This system is presently being upgraded to allow a 36 inch range of motion horizontally, and 12 inches vertically.

2.5.2 ESR Remelt Billet

The first ESR remelting experiment with coated E1 bar stock was done using the ESR-AC pilot plant. This was done to test the ESR-AC technique surrogate removal efficiency as well as to determine if small diameter electrodes could be used in the pilot plant. Preliminary test results with non-coated stainless steel bar stock indicated this was feasible. If so, this would allow direct comparison between AC- and DC-powered ESR units with comparable starting stock sizes.

The ESR-AC remelt was initiated and partially completed at which time a crucible wall meltdown occurred. It is felt that this was due to the use of an experimental crucible design, coupled with first time use of the ESR-AC pilot plant unit for small scale melts. Never-the-less, this meant that neither ESR-AC or ESR-DC melting could be continued due to lack of a remelt crucible. Construction of a replacement 3.5 in. dia. crucible will be completed by mid-year in FY94. Sufficient ESR-AC material was remelted to allow a sample of the melt to be sent out for analysis.

A comparison of the base chemistry of the Master Melt starter stock E1 and the resultant ESR-AC billet is given in Table 7. It indicates that the ESR slag used (Table 4) was essentially neutral in regards to the major alloying additions, with little or no composition change noted. Analysis for the surrogate elements, Tables 8 and 9, indicates that essentially all surrogates were removed by the ESR-AC process, as the original and remelt material have essentially the same baseline concentration of surrogate elements. A slag chemistry comparison between the ESR-DC melt produced slag associated with a non-coated stainless steel electrode and the ESR-AC melt produced slag from the coated electrode, Table 8, indicates that the ESR-AC slag is greatly increased in Cs and La, as expected; note that both ESR remelts were done using flux of the same composition, Table 4.

2.5.3 Plasma Remelt Billet

Three hundred pounds of bar stock from the ESCO Master Melt E1 was plasma coated with Ce and La oxide powder co-sprayed with stainless steel at OGI and subsequently plasma remelted. The material was remelted by RETECH in their plasma cold hearth melter equipped with a bottom withdraw ingot production unit in September 1993. A comparison of the base chemistry of the Master Melt starter stock E1 and the resultant plasma remelt billet is given in Table 7. It indicates that the plasma melting technique was essentially neutral in regards to the major alloying additions, with little or no composition change noted, similar to the ESR results. The surrogate chemical analysis results, Table 8, indicate that surrogate levels remaining in the remelt billet are comparable to those found in the starting stock and in the ESR-AC remelt billet. Note that these plasma remelt results are considerably different from the Montana Tech RETECH plasma remelt billet results. Montana Tech added metallic surrogate additions (La, Ce and Nd were added as elements, Cs and Sr were added as fluorides) placed in stainless steel "envelopes" sealed by welding in an inert gas glove box. These envelopes were welded periodically along a section of stainless steel pipe, which was subsequently inserted along with multiple other pipes into a larger diameter pipe to make up the Montana Tech furnace charge(10), Figure 16. The Montana Tech billet chemical analysis results, Tables 8 and 9, indicate a high retention of surrogate Ce, La and Nd.

TABLE 7. Chemistry of base metal of remelted OGI Master Melt E1 material after surrogate coating by plasma spray (DC Plasma analysis)

DC Plasma Analysis of Coated Steel Melted by Various Methods (Metallurgical Testing Corp.)					
Element %	E1 Starting Material	Reteck 1 Plasma Melt	ESR/AC	ESCO Induction	VAR
Mn	1.31	1.23	1.39	1.32	1.35
Si	0.69	0.65	0.69	0.64	0.75
P	<0.005	<0.005	0.027	0.024	0.018
Cr	17.14	17.29	16.94	18.59	18.64
Ni	12.13	12.05	11.71	12.51	12.74
Mo	1.12	1.11	0.90	0.99	0.98
Cu	0.22	0.22	--	--	--
Co	0.14	0.13	--	--	--
C*	0.027	0.015	0.038	0.030	0.023
S*	0.011	0.011	0.010	0.011	0.010

* Note: Carbon and Sulfur Analysis by LECO Combustion

TABLE 8. Instrumented Neutron Activation Analysis of Various Metal and Slag Samples Showing Duplicate Analysis Where Available.

Instrumental Neutron Activation Analysis (INAA) of Metal Filings & Slags				
Sample	Cs (ppm)	La (ppm)	Ce (ppm)	Nd (ppm)
Montana Tech Master Plasma Melt - MTK	<4.2	398	640	440
Starting Material E1	<5.1/<5.4	0.11/0.12	<81/<78	<100/<140
Electroslag AC of Coated E1	<11	0.25	<120	<230
Induction Melt of Coated E1	<9.9	0.17	<120	<230
Plasma Melt of coated E1 - Reteck 1	<4.8/<8.4	0.02/0.32	<84/<120	<110/<230
Reteck 1 Skull	<6	0.39	<78	<150
Vacuum Arc Remelt of Coated E1	<7.5	230	159	<150
Slag after ESR/AC	<17	1570	1010	<220
Slag before ESR/AC	<8.4	7.3	22	<75
E2 - Master Melt 2	<4.5	0.13	<75	<100
E3 - Master Melt 3	<6.6/<5.1	0.14/0.2	<75/<78	<100/<130

Note: / indicates duplicate readings. (X) indicates reading taken after six weeks of decay time; original numbers are preliminary reading after two seeks of decay time.

TABLE 9. Surrogate element analysis by Inductively Coupled Plasma Mass Spectroscopy Analysis.

Surrogate Element	Starting Material E1 for Retch 1	Reteck 1 - Remelt of Coated E1	Montana Tech Master Melt
Ce (ppm)	<1.0	<1.0	1,000
Cs (ppm)	<1.0	<1.0	<1.0
La (ppm)	<1.0	<1.0	670
Nd (ppm)	<1.0	<1.0	840
Sr (ppm)	<1.0	<1.0	<1.0

Both the Montana Tech and OGI RETECH plasma remelts were made in the same research two-gun plasma melter, Figure 17. The electrode material was loaded through a port in the side of the melting chamber, Figure 18. The melting chamber consisted of a cold hearth that the electrode material was first melted into and an ingot bottom withdraw system that the molten metal accumulated on the cold hearth was pour into; each of these units had a dedicated plasma torch associated with it (10), Figure 19. A photograph of the resultant Montana Tech remelt billet, essentially similar to the OGI plasma remelt billet, is shown in Figure 20.

2.5.4 Induction Remelt Billet

Three hundred pounds of bar stock from the ESCO Master Melt E1 was plasma coated with Ce and La oxide powder co-sprayed with stainless steel at OGI and sent to ESCO for subsequent induction melting; this melt was completed in October. A comparison of the base chemistry of the Master Melt starter stock E1 and the resultant induction remelt billet is given in Table 7. It indicates that the induction melting technique was essentially neutral in regards to the major alloying additions, with little or no composition change noted. The

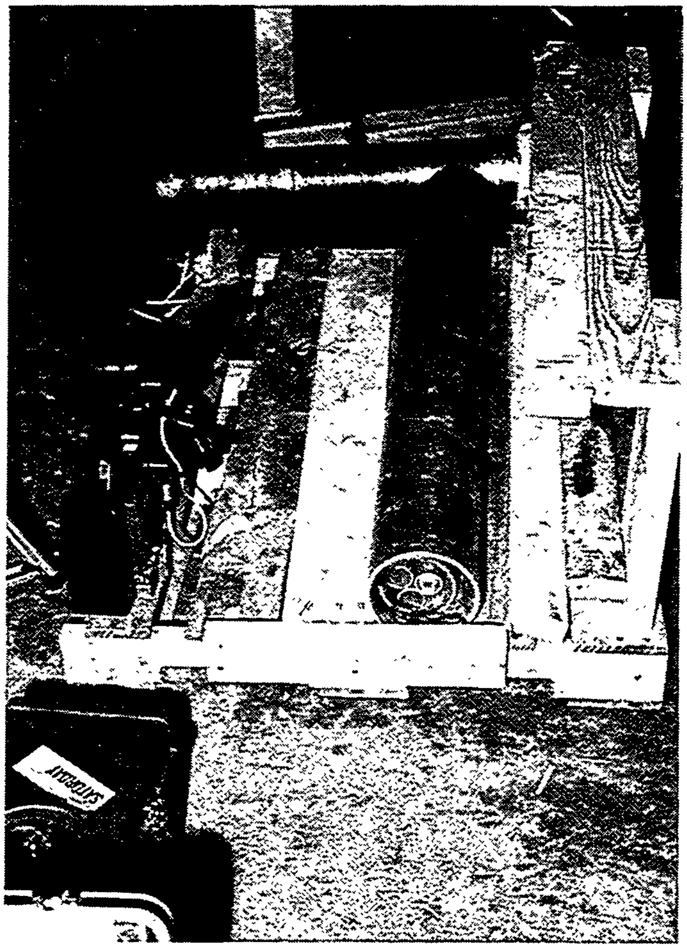


FIGURE 16. Montana Tech Plasma furnace charge.

surrogate chemical analysis results, Table 8, indicate that surrogate levels remaining in the remelt billet are comparable to those found in the starting stock, the ESR-AC remelt billet and the OGI plasma remelt billet.

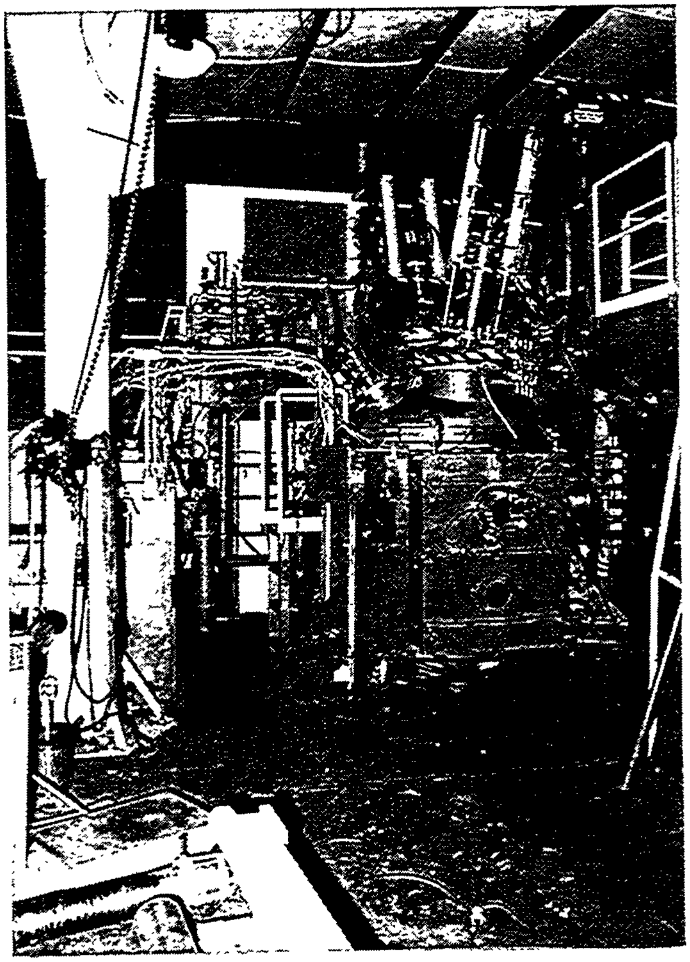


FIGURE 17. RETECH research plasma remelter used for Montana Tech and OGI feedstock remelts.

FIGURE 18. Loading of the Montana Tech feedstock into the plasma remelter.

2.5.5 VAR Remelt Billet

An electrode fabricated from ESCO Master Melt E1 bar stock plasma coated with Ce and La oxide powder co-sprayed with stainless steel was remelted in the OGI VAR pilot plant unit in December 1993, Figure 21. A comparison of the base chemistry of the Master Melt starter stock E1 and the resultant VAR remelt billet is given in Table 7. It indicates that the VAR melting technique was essentially neutral in regards to the major alloying additions, with little or no composition change noted. This result actually came as somewhat of a surprise, as it was expected that the high vapor pressure elements such as Cr and Mn would

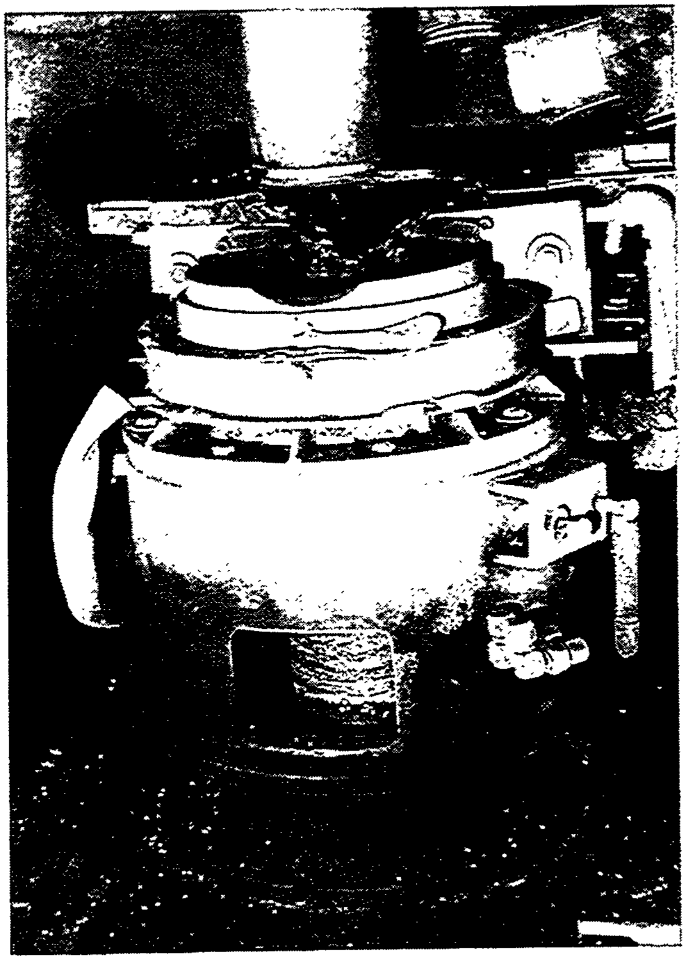


FIGURE 19. Plasma remelter chamber showing duel torches. The back torch for feedstock melting and the front torch for heating of the billet top.

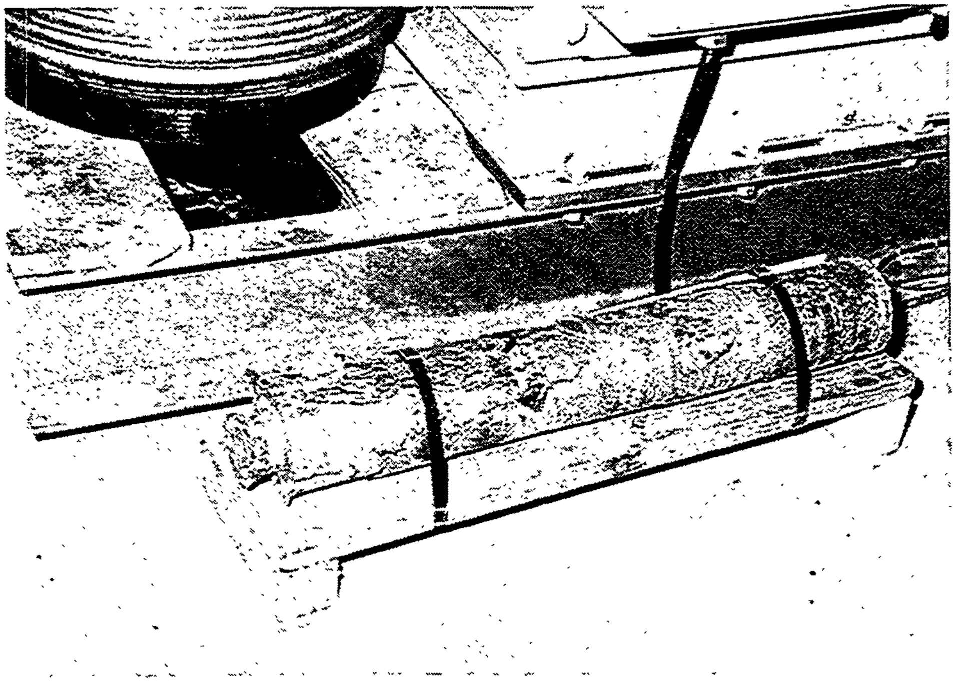


FIGURE 20. Montana Tech Plasma remelt billet.

be selectively removed. Subsequent surrogate chemical analysis results, Table 8, indicate that a substantial amount of Ce and La surrogate material was retained in the remelt billet. Note the various retained concentrations are the same order as found in the Montana Tech Plasma remelt concentrations, but are about half the magnitude of the concentrations retained by the Montana Tech remelt.

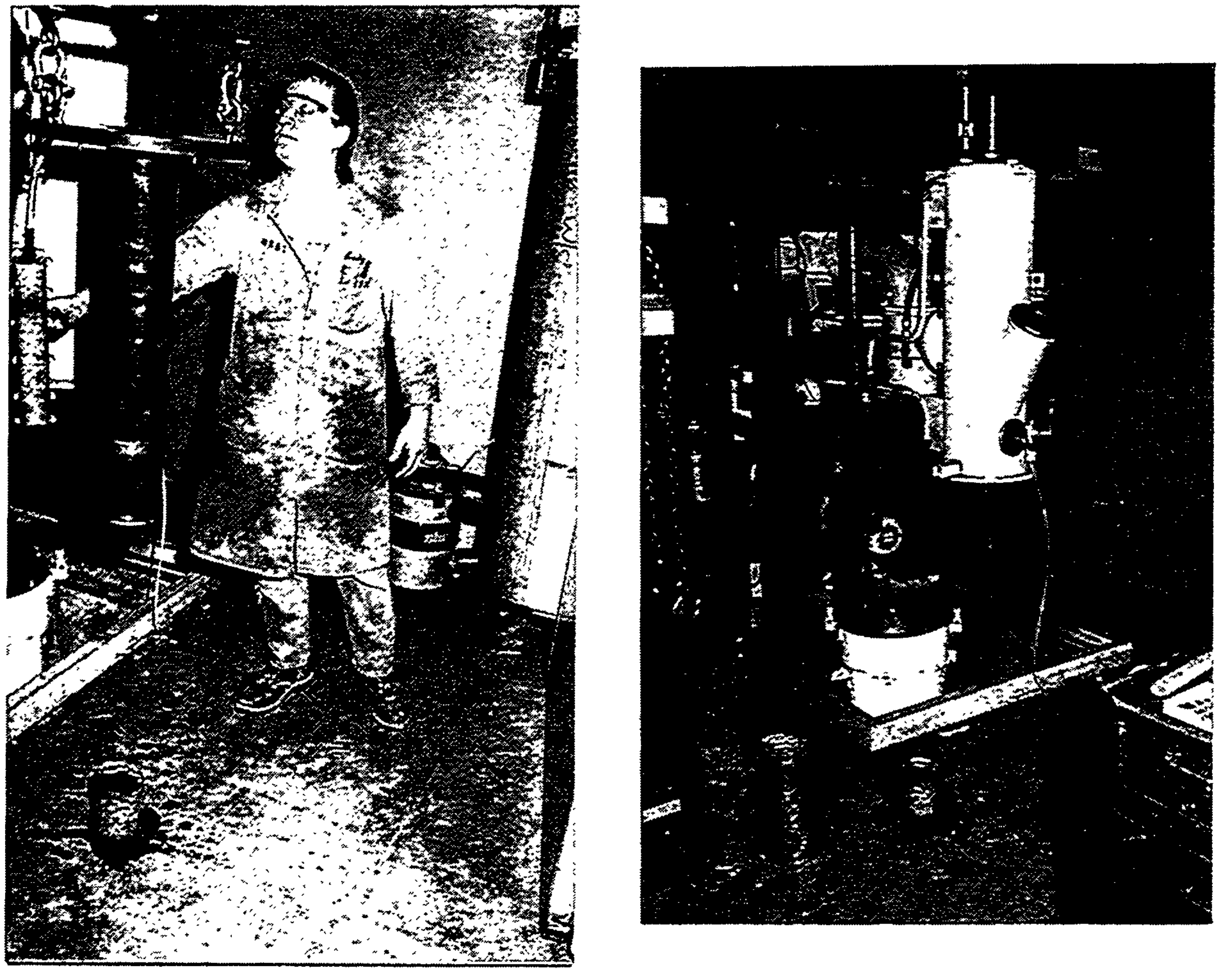


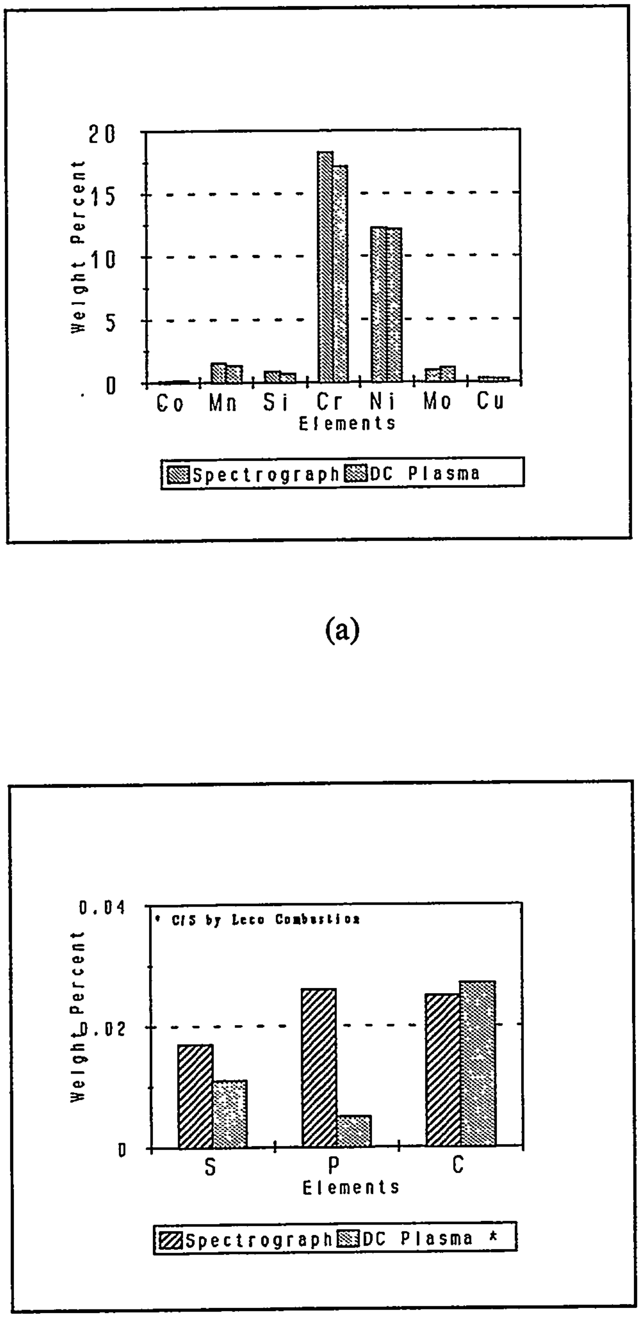
FIGURE 21. Vacuum Arc Remelt system with resultant stainless steel billet.

3.0 CHEMICAL ANALYSIS RESULTS

The work reported below not only consists of analysis of the base chemistry of various billets, as well as residual surrogate concentrations in both billets and companion slags, where applicable, but a comparison between various analytical techniques used to assess these quantities. The purpose of the latter work was to assess which method(s) were most applicable to the various analysis criteria required to successfully complete this program. A detailed description and overview of technique attributes and detriments are presented in Appendix I.

3.1 TUBING RECEIVED FROM WINCO

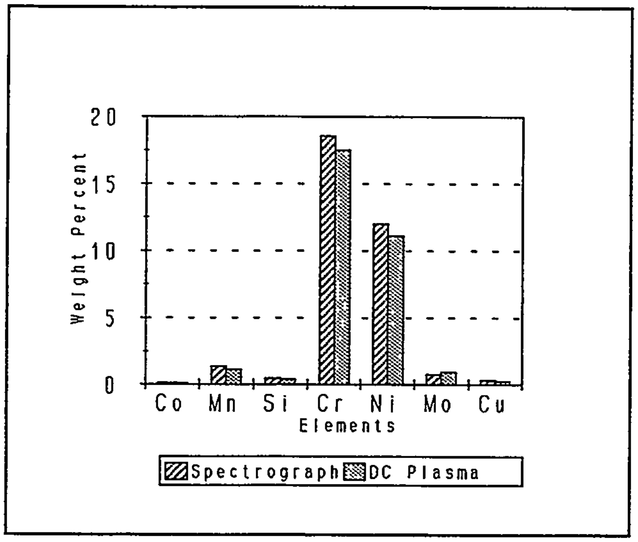
The tubing received from WINCO was subsequently melted at ESCO in three heats and cast into ingots of one foot and two foot lengths. These heats have been called E1, E2, and E3. At the time of melting, spectrographic analysis was performed by ESCO. Later, samples of each heat were sent out for DC Plasma analysis. Figure 22a shows a comparison of the chemistry results for the first heat (E1). The results compare very well, considering that the spectrographic analysis was done on the last ladle sample of the melt and the DC Plasma analysis was done on turnings taken from one billet. In most cases, the results for the major alloying elements, Figure 22a, obtained by spectrographic analysis are higher than those obtained by DC Plasma. Figure 22b shows the differences in carbon, sulfur, and phosphorous chemistries reported by ESCO and those obtained by use of a Leco carbon/sulfur analysis and DC Plasma phosphorous analysis. Again, the results compare very well, with sulfur and phosphorous numbers being higher when reported by spectrographic analysis than by the other techniques. The carbon was slightly higher when analyzed by the Leco instrument. Figures 23a and b and 24a and b show the same types of comparisons for heats E2 and E3. The most obvious discrepancy between the test methods is that the chrome content is consistently reported higher by spectrographic methods than by the DC plasma technique. Sulfur and phosphorous are consistently reported to be higher when analyzed by spectrography and carbon is reported to be lower.



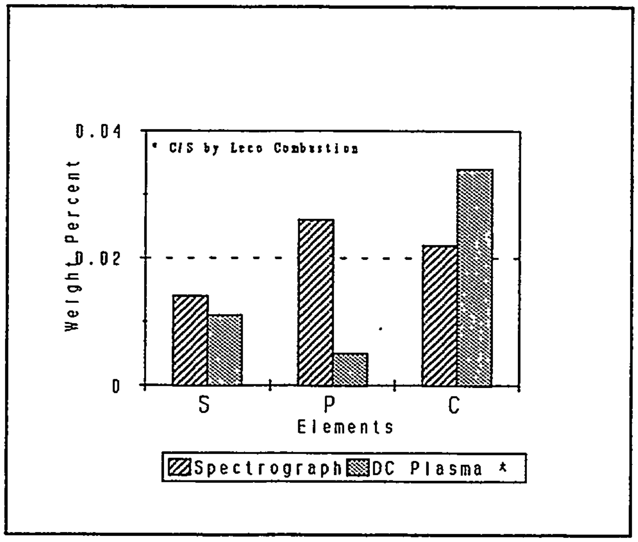
(a)

(b)

FIGURE 22. Comparison of chemistry results by two techniques; (a) for major alloying elements in E1 starting stock material, and (b) for minor elements in E1 starting stock material.

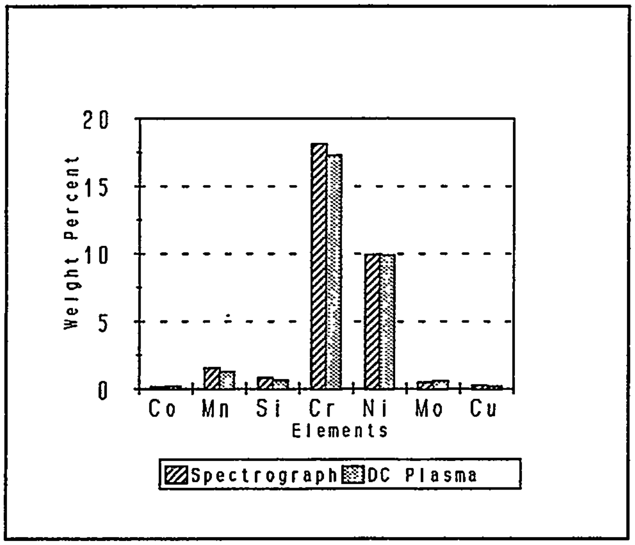


(a)

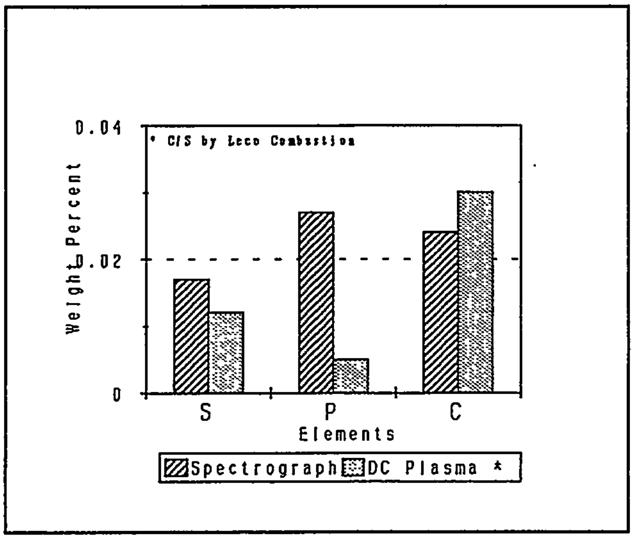


(b)

FIGURE 23 Comparison of chemistry results by two techniques; (a) for major alloying elements in E2 starting stock material, and (b) for minor elements in E2 starting stock material.



(a)



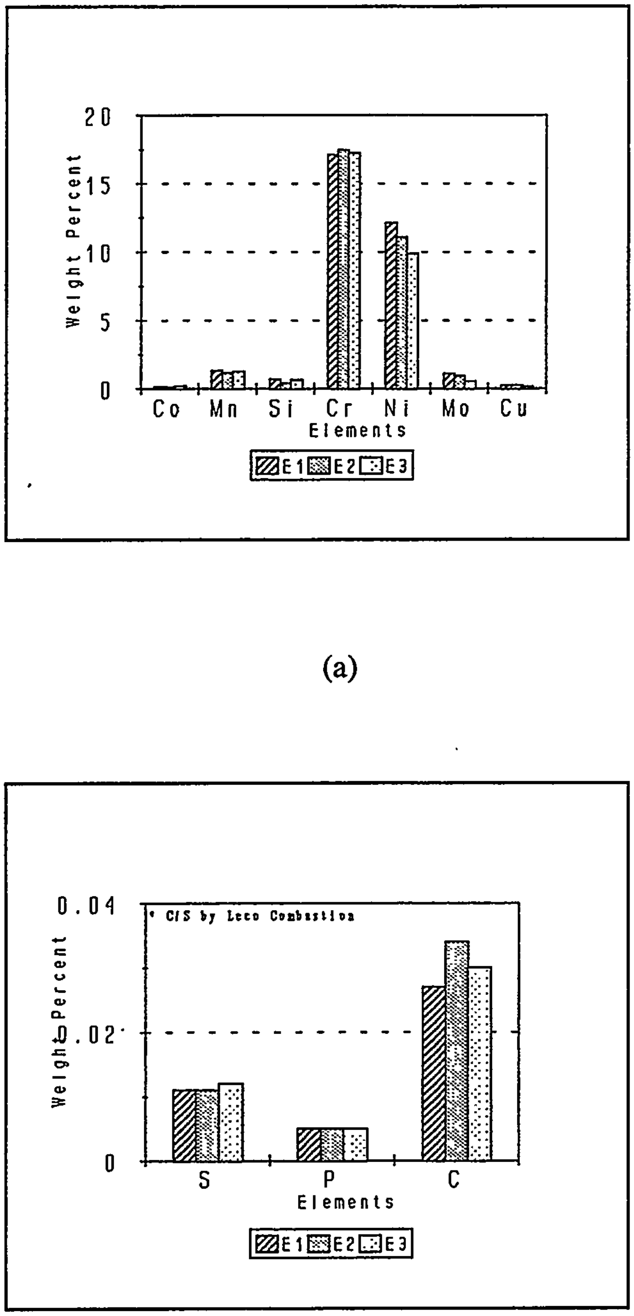
(b)

FIGURE 24. A comparison of chemistry results by two techniques; (a) for major alloying elements in E3 starting stock material, and (b) for minor alloying elements in E3 starting stock.

Figure 25 shows how the chemistries of each of the three master melts compare. Values for Ni and Mo varied the most, with the weight percent of Ni being slightly higher in the E1 melt than is called out in the standard for 304L stainless steel wrought material. The percentage of carbon in heat E2 also exceeds the ASTM 0.03 standard. These discrepancies are shown in Figure 26. The percentages of Mo were also shown to be higher than is usual in 304L. A comparison of the chemistries on master melts E1, E2, and E3 along with the ASTM standards for both maximum and minimum requirements for wrought 304L stainless steel are shown in Figure 27; note, however, that the melt chemistries do meet 304L cast material chemistry requirements, except for carbon in E2, (Table 6).

3.2 MELTS OF TUBING AT OGI

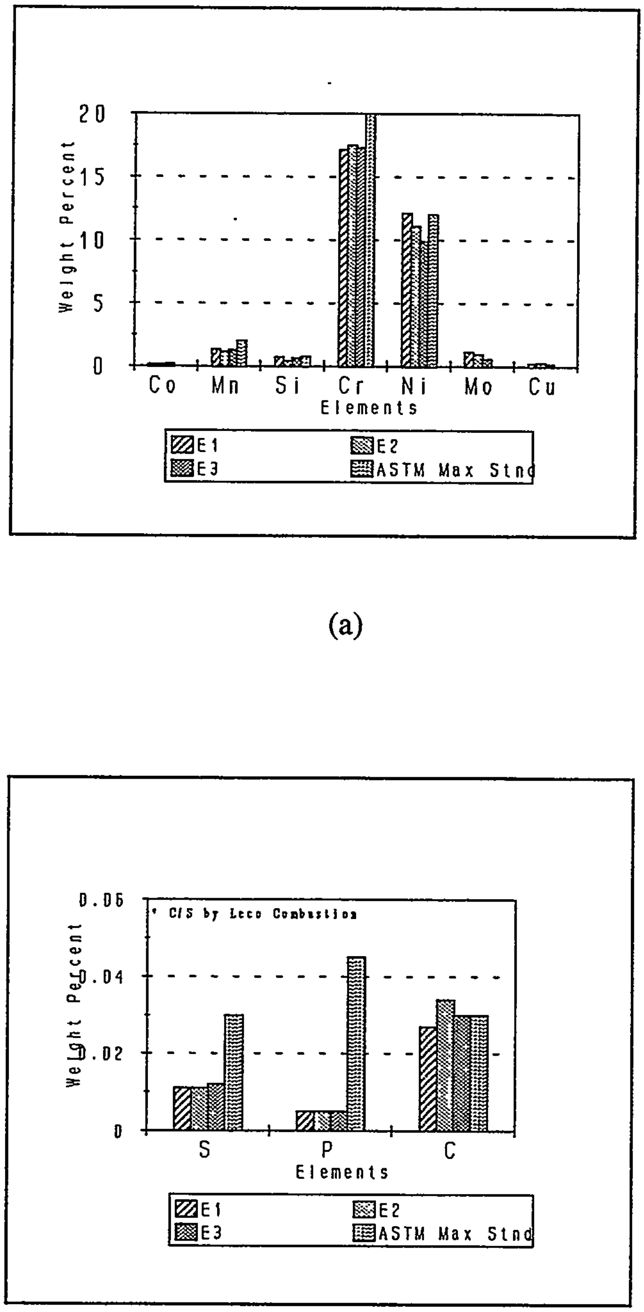
Of the tubing received from WINCO, several melts were made at OGI to show that assembled piping could be electroslag remelted to yield a sound ingot. A single pipe was melted using the ESR DC unit. The slag used was an industrial flux manufactured by Lincoln Electric, Bluemax 4000. Chemical analysis was performed before and after melting. These results are shown in Figure 28. This figure shows only small changes in chemistry between the material before and after melting. The figures show that chromium was retained in the steel. Interestingly, both Cr and Mn are out of specification for wrought 304L, and Mo is considerably higher than expected. However, this composition is well within the Nitronic 50 specification, see Table 10. The single pipe melted in this test was a piece of the mixed steel received from INEL along with the 304L. WINCO has subsequently informed OGI that Nitronic 50 alloy was also purchased for processing plant fabrication, but different alloys were supposed to be segregated. Pieces of such steel, when unknowingly incorporated into master melts can result in chemistries (slightly) different from typical 304L stainless steel, and could end up making remelt heats unusable if strict specification requirements are imposed.



(a)

(b)

FIGURE 25. Comparison of (a) major element amounts and (b) minor element amounts in three starting stock materials.



(a)

(b)

FIGURE 26. Comparison of (a) major element chemistries and (b) minor element chemistries in three starting stock materials with the ASTM maximum standard for wrought material.

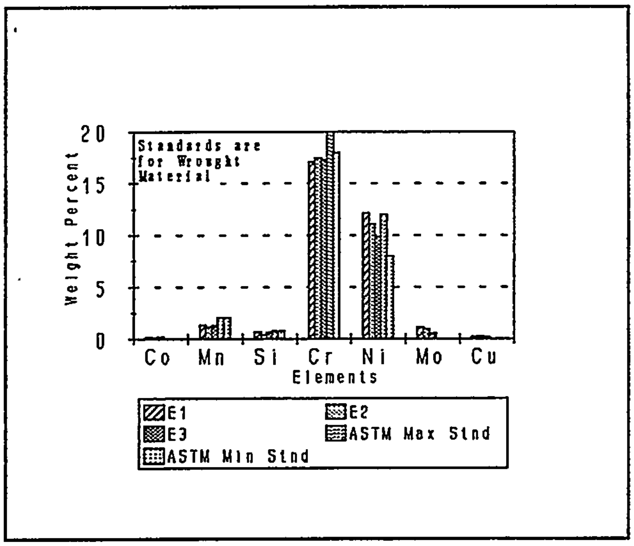
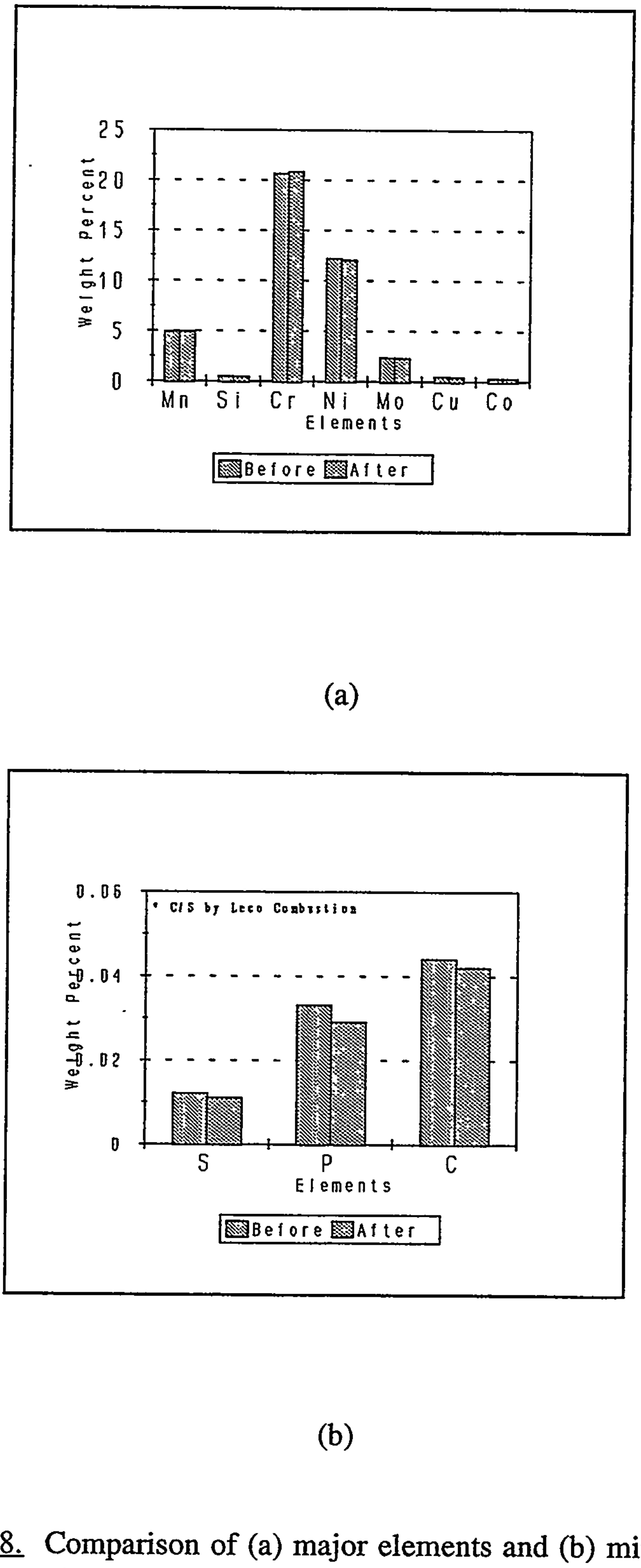


FIGURE 27. Comparison of major element chemistries in three starting stock materials with the ASTM maximum and minimum standards.

Two other ESR/DC melts were made at OGI using assembled piping as the electrode. In both cases, sound melts were made. Chemical analysis was performed by emission spectrometry at the core of the ingot, at mid-radius, and at the edge. These results were compared with analysis performed by DC Plasma Spectrographic analysis from turnings taken from mid-radius of the samples. Figures 29a and b and 30a and b show that edge to center variation of the ingots is minimal, which would be expected with ESR. These figures also show that, while there is some variation in results when different analysis techniques are used, the chemical trends observed are verified by both analysis methods.

3.3 MELTING OF COATED MATERIAL

Half of the master melt heat E1 was coated with a 50/50 mixture of lanthanum and cerium oxides. The goal of this surrogate coating was to deposit enough oxide on the surface of the bars to result in approximately 1000 ppm of La and 1000 ppm of Ce on an as



(a)

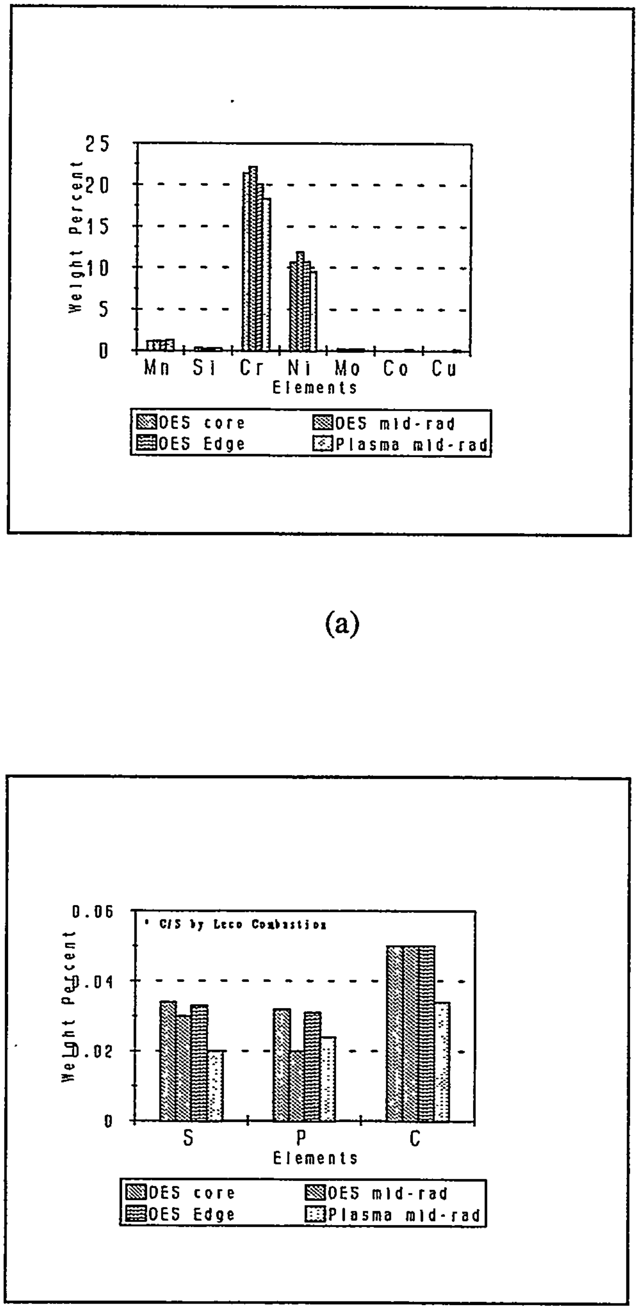
(b)

FIGURE 28. Comparison of (a) major elements and (b) minor elements in a single tube before and after melting by ESR/DC.

TABLE 10. Chemical Analysis of ESR-DC Remelts Made From INEL Scrap Metal Electrodes (DC Plasma).

Element	OGI 1	OGI 2	OGI 3	OGI 3	304L	Nitronic50
Cr	18.34	19.27	20.67	20.85	18-20	20.5-23.5
Ni	9.52	15.27	12.19	12.02	8-12	11-13.5
Mn	1.28	2.27	4.9	4.9	<2	4-6
Si	0.26	0.47	0.49	0.43	<0.75	<1
Mo	0.22	1.18	2.35	2.3	NA	1.5-3
Cu	0.17	0.79	0.47	0.46	NA	
Co	0.13	0.11	0.27	0.27	NA	
S	0.02	0.0086	0.012	0.011	<0.030	0.03
P	0.024	0.019	0.033	0.029	<0.045	0.04
C	0.04	0.026	0.044	0.042	<0.03	0.06
Nb+Ta						0.1-0.3
N						0.2-0.4
V						0.1-0.4

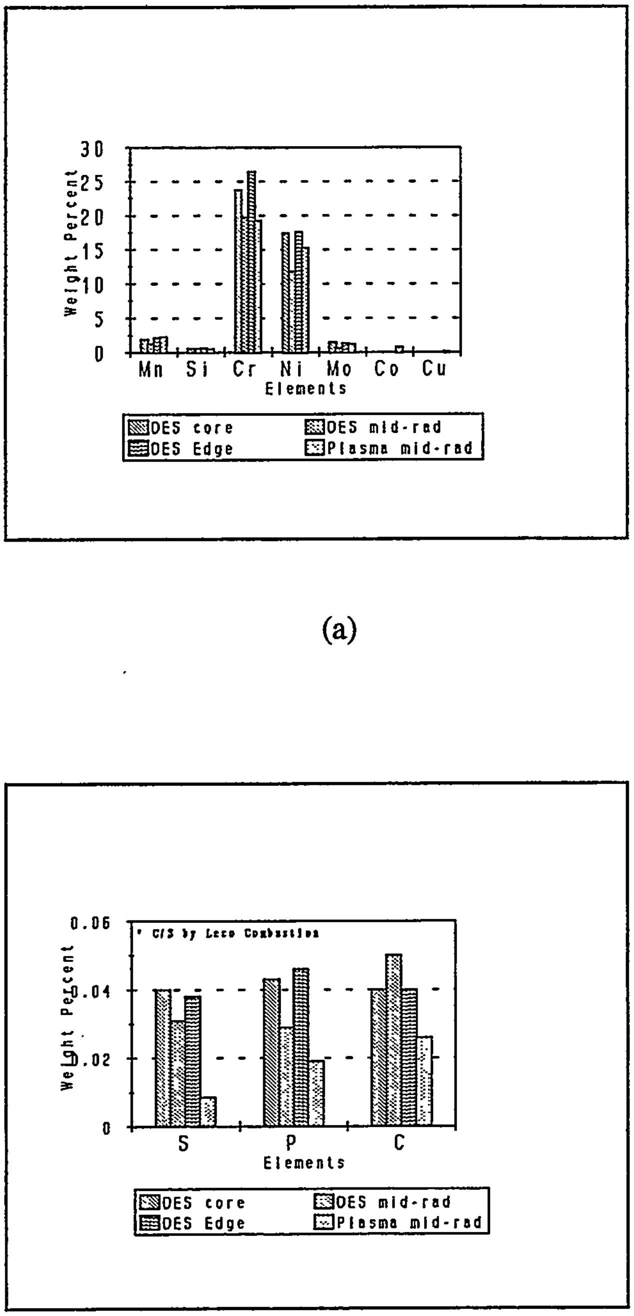
metal basis. This coated master melt was melted several ways. Several sections of the coated bar stock were sent to Retech to be plasma melted. The resulting plasma melt weighed approximately three hundred pounds. It was returned to OGI where it was sectioned and samples sent for analysis. Other sections of coated master melt were induction melted at ESCO and a three hundred pound ingot was received by OGI, sectioned, and sampled. Additional melts performed on the surrogate coated master melt included a VAR melt and an ESR/AC melt, both performed at OGI.



(a)

(b)

FIGURE 29. Comparison of chemistry results; for (a) major elements and (b) for minor elements in OGI pipe melt 1. Optical emission spectrophotometry (spark) was done at three locations and compared with DC Plasma results at mid-radius.



(a)

(b)

FIGURE 30. Comparison of chemistry results; for (a) major elements and (b) for minor elements in OGI pipe melt 2. Optical emission spectrophotometry (spark) was done at three locations and compared with DC Plasma results at mid-radius.

3.4 ANALYTICAL ANALYSIS OF REMELT BILLETS AND SLAGS

In December 1993, OGI began receiving analysis from the neutron activation lab at Oregon State University. Two problems became immediately apparent. The first problem was the long (6 week) turnaround time required by OSU to irradiate and obtain the counts necessary for sample analysis. The second problem was more serious. Mr. Art Johnson, at Oregon State, reported that the stainless steel matrix of our samples was interfering with the sample counts. The INAA lab uses standards made up of clays and minerals and the OGI materials presented samples dramatically different from the standards. Questions arose regarding the confidence that should place in any one set of analysis results. It was decided that other techniques should be investigated.

After discussion of the problem with a substantial number of chemists, it was decided to try the Inductively coupled plasma mass spectrometry technique (ICP MS) available from Teledyne Wah Chang, Albany. This technique has proven to be much faster than INAA for our steel samples and the lower analysis limits much more acceptable for our studies of surrogate partitioning. Figure 31 shows the lower analysis limits for steels when analysis is performed by INAA and ICP MS. This figure shows that for steels, ICP MS is a much more sensitive analysis tool. Another factor must be considered, however, that being accuracy. A test was done to get an idea of how closely the two analytical techniques were when the samples were within the analysis limits of the technique. Figure 32 shows the resulting chemistries when samples of the same piece of steel were sent out for INAA and ICP MS analysis. The figure shows that the values given by ICP MS are in all cases much higher than the values given by INAA. It is not presently obvious to OGI which technique yields the more accurate absolute value of retained surrogates. Table 11 lists the elements which have been analyzed for OGI by each technique currently being used. By using various techniques and comparing results for common elements, one may obtain data about the confidence limits of various analysis techniques.

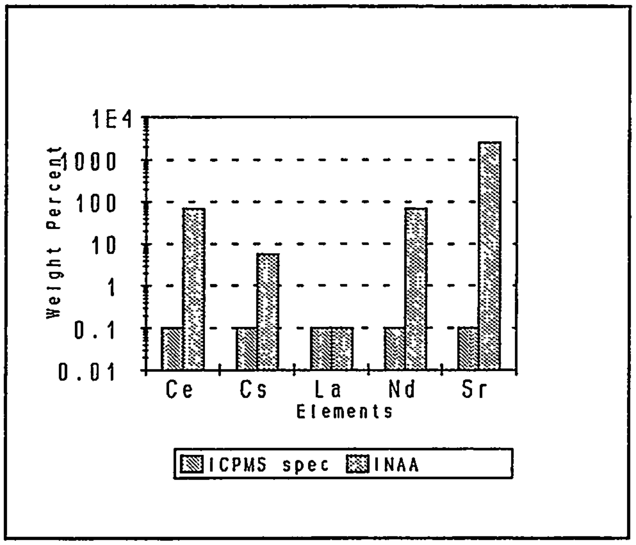


FIGURE 31. Comparison of lower analysis limits attainable for surrogate elements in steel by two techniques.

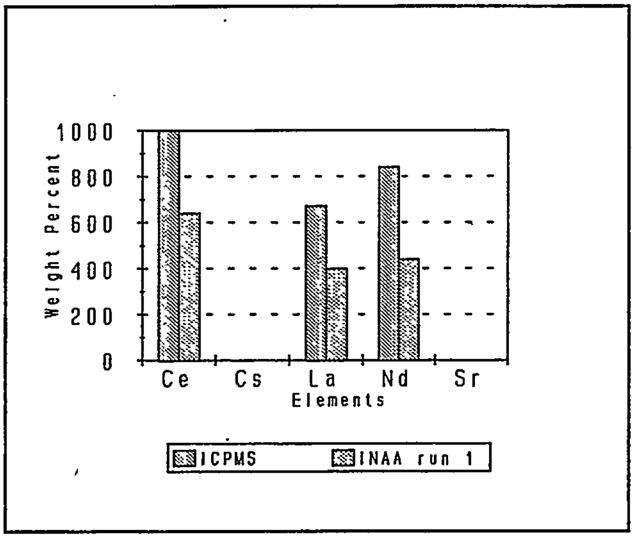


FIGURE 32. Comparison of Montana Tech starting stock chemistry by two techniques.

TABLE 11. Elements Analyzed for OGI Using a Variety of Techniques.

Element	Spectro	INAA	DC Plasma	Leco Com	ICP Mass
Mn	X		X		
Si	X		X		
P	X		X		
Cr	X	X	X		
Ni	X		X		
Mo	X		X		
Cu	X		X		
Co	X	X	X		
C	X			X	
S	X			X	
P	X				
Al	X				
Ti	X				
Zr	X				
Nb	X				
V	X				
B	X				
Pb	X				
Sn	X				
Ce		X			
La		X			X
Cs		X			X
Nd		X			X

TABLE 11. (Cont.)

Element	Spectro	INAA	DC Plasma	Leco Com	ICP Mass
Sr					X
As					X
Sb		X			
Ba		X			
Sc		X			
Zn		X			
W	X	X			
Th		X			
U		X			
Rb		X			
Eu		X			
Tb		X			
Yb		X			
Lu		X			
Hf		X			
Ta		X			

Because the standards used by the INAA lab at Oregon State are mineral samples, and because slags are synthetic minerals, samples of slags were sent for INAA analysis. Analysis limits proved to be lower for slags than for steels. This is important because it underscores the fact that matrix interference may be substantial. Analysis limits for ICP MS were still lower than the lower limits for INAA, as shown in Figure 33. However, because of the high concentration of surrogates initially found in our slags, the lower analysis limits may not be as important as the accuracy and precision of the analysis. Analysis of slags by ICP MS requires that the slags be prepared by fusion, which can introduce errors due to the use of fluxes and crucibles. Further work will be done to determine which technique will provide the best accuracy for analysis of slags. Accuracy of analysis will become a greater factor once thermodynamic modeling work gets further underway. The extent to which elemental distribution between slag and steel can be modeled and calculated will only be as meaningful as the actual distribution can be analyzed. It will become imperative to demonstrate the most accurate mass balance possible when it comes time to begin verification of various slag models. In order to accomplish this, proper mixing, splitting, and sampling techniques will be performed each time a slag sample is sent out for analysis.

3.5 ANALYSIS RESULTS

Figures 34 shows how the background chemistry of the steel changed by melting it in various ways. Initially, it had been thought that chromium would be lost during melting due to its low vapor pressure. This did not prove to be the case, however. In some cases, a higher analysis was obtained after melting than before. This demonstrates that sampling may be a problem and that the degree of uncertainty in analytical results is important and should be quantified.

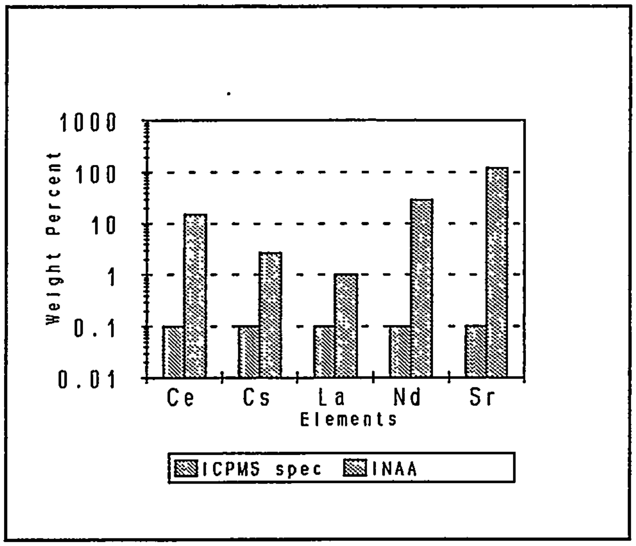
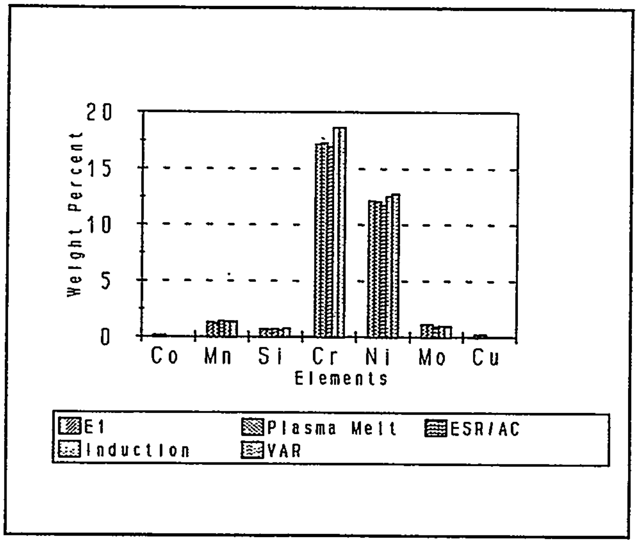


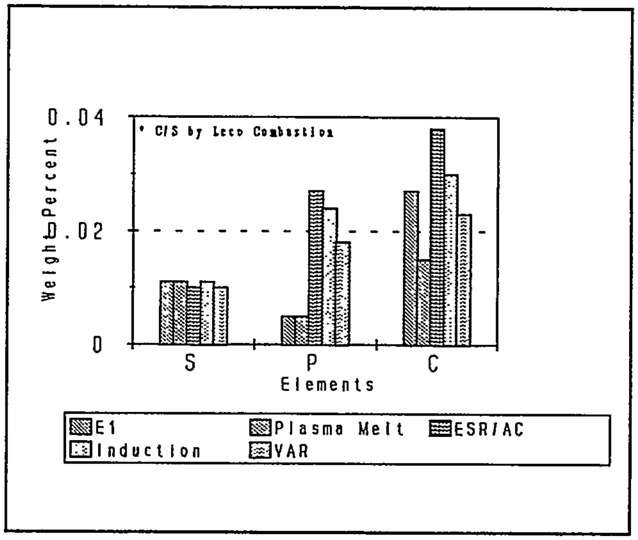
FIGURE 33. Comparison of lower analysis limits attainable for surrogate elements in slags by two techniques.

Figure 35 shows how the lanthanum concentration in the steel varied with melting process. The most lanthanum was retained in the VAR melt, while other melting methods effectively removed this surrogate material. Figure 36 shows how analysis of the steel from the VAR melt was different when analysis was performed by two different methods. In each case, the neutron activation results are higher than those obtained by ICP MS.

When the coated E1 master melt was remelted by AC/ESR samples of slag were collected before and after the melt. These samples were analyzed by INAA as well as by ICP MS. The INAA results are plotted in Figure 37 on a log scale. Lanthanum and cerium have a great tendency to partition to the slag. ICP MS results are plotted in Figure 38 and a similar trend is seen. Three samples of the same slag were sent for analysis and the agreement between the results is very encouraging both in terms of confidence in analytical results and confidence in sampling techniques currently being used for the slags.



(a)



(b)

FIGURE 34. Final steel chemistries for (a) major elements and (b) for minor elements attained after surrogate coated E1 was melted by various methods.

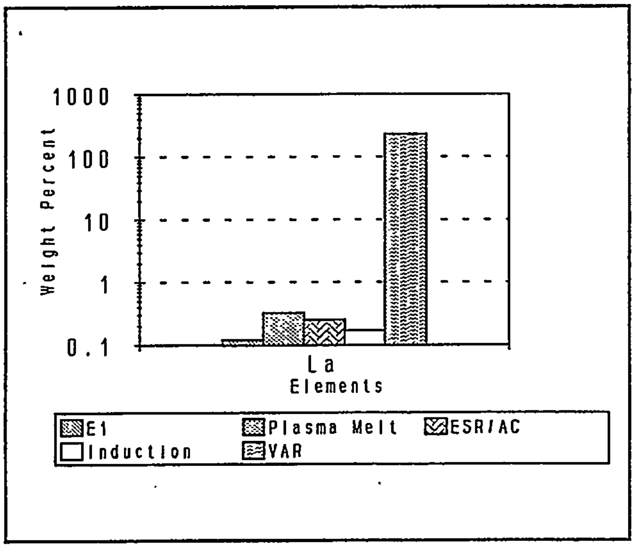


FIGURE 35. Distribution of lanthanum in steel resulting from melting coated E1 by various techniques.

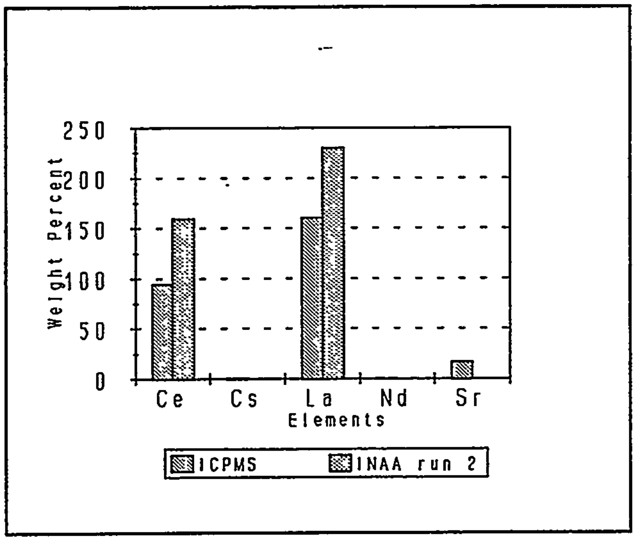


FIGURE 36. Comparison of VAR remelt material chemistry by two techniques.

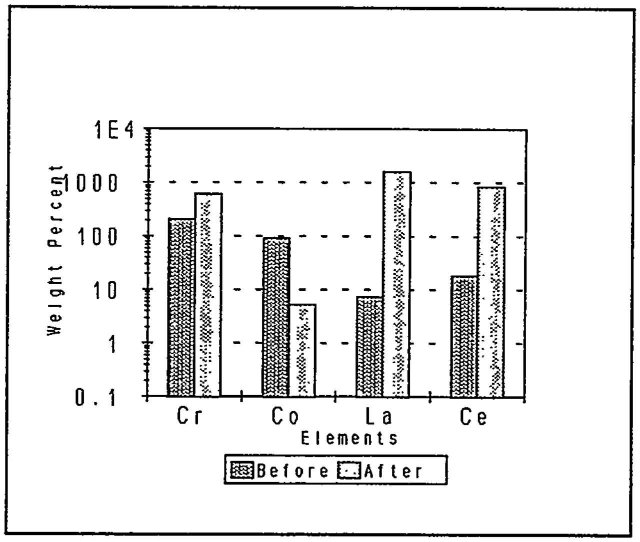


FIGURE 37. Comparison of ESR/AC slag chemistry before and after melt.

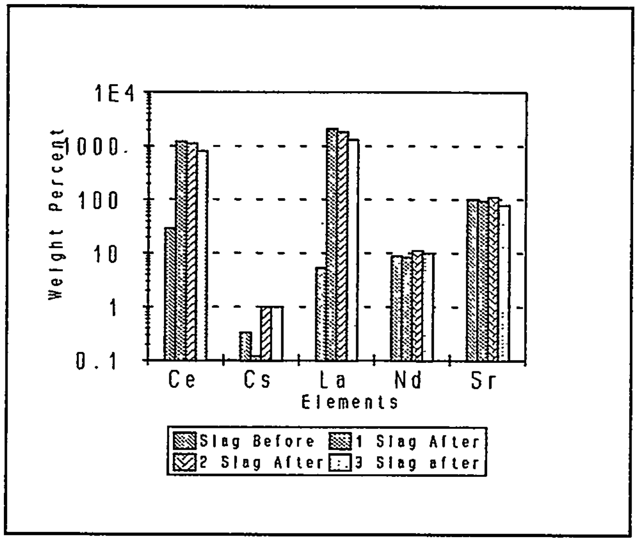


FIGURE 38. Comparison of slag chemistry and sampling accuracy.

4.0 CONCLUSIONS

From our literature studies, research experience and experimental data, the following conclusions may be drawn:

1) Stainless steel bars onto which approximately 1000 ppm of surrogate oxides had been plasma sprayed were melted by various techniques including VAR, ESR/AC, induction, and plasma. It was found that VAR left substantial amounts of surrogates in the resulting ingot while the other methods reduced the level of surrogates in the steel to below 1ppm. In the case of the ESR melt, the surrogates were found to be substantially concentrated in the slag.
2) Each melting technique has advantages and disadvantages. It is felt that the advantages of ESR are significant and merit its further comparison with other techniques in terms of process economics and design considerations. This is especially important since ESR is being given serious consideration by the Japanese as a melt refining method for RSM.
3) Thermodynamic studies show that the surrogates used in this study, Ce and La, are suitable for mimicking the oxide forming behavior of the radionuclides Pu, U, and Th.
4) ESR was successfully used to melt long pieces of stainless tubing and tubing assemblies of various electrode densities. This demonstrates an important advantage of ESR for the melting of RSM, namely the elimination of worker exposure necessary to reduce the size of scrap for charging into an induction furnace.
5) The plasma spray method of applying surrogates is realistic and flexible. It can be used to simulate the presence of various types and amounts of surface contamination.
6) After much evaluation, it was decided that, for the surrogate elements, the analysis method of choice would be ICP mass spec. Neutron activation analysis suffered from interference from other elements present in our samples, namely chromium. With the exception of lanthanum, the lower analysis limits of INAA were too high for the purposes of metallic experiment analysis for this study.

5.0 RECOMMENDATIONS FOR FUTURE WORK

Based on the experience gained and the results achieved in the preliminary phase of this study, it is recommended that future research should include the following tasks.

a) Depending on the degree and type of contamination and the starting size and shape of the RSM, it may be necessary to perform a primary consolidation melt followed by a refining melt. It is, therefore, recommended that a study be undertaken which will address the problems and benefits of performing the various melting methods in sequence. Such a study is necessary before the design of such a process is initiated.

b) The thermochemical models included in the FACT computer software should be used to their fullest extent to make predictions about both surrogate elements and radionuclides partitioning between molten slag and steel. These predictions need to be substantiated through development of a validation data base.

c) Work should be initiated on the characterization of surrogate containing inclusions in ingots melted by various techniques. This study will provide valuable data on the actual behavior of surrogate elements in the melt. Also, it will allow process comparison in terms of surrogate removal by inclusion flotation and capture. This will go hand-in-hand with a literature review to be performed comparing inclusion removal mechanisms in each melt method.

d) Development of an interactive, multilaboratory, multiuniversity database for compiling and analyzing experimental conditions and results in a timely fashion should be initiated. This will initially allow researchers at OGI, MT and CSM to interact more productively, as well as allow "instantaneous" data oversite and analysis by WINCO. Upon completion, this database will allow design engineers and melting metallurgists to have access to valuable information.

e) A variety of ESR melts need to be completed to allow quantification of the differences between ESR/DC and ESR/AC or combination of the two, surrogate removal as a function of flux composition, surrogate removal as a function of initial surrogate concentration, surrogate removal as a function of surrogate incorporation technique. Comparable studies of ESR surrogate removal efficiency from carbon steel alloys also need to be performed.

f) A kinetic study oriented towards surrogate removal as a function of melt time should be done on at least one of the above melts. To perform this study, a slag sample would need to be taken at various times during the melt. These samples would then be analyzed for surrogate content, which would be analyzed as a function of time.

APPENDIX I

ASSESSMENT OF CHEMICAL ANALYSIS TECHNIQUES

The choice of a method for determining the composition of samples is important for several reasons. Analytical methods may differ in the accuracy and precision which may be obtained as well as in the lower limits of detectability. The scatter of values for repetitive determinations is a measure of the precision. Accuracy is the agreement between the true value and the obtained result. Techniques may also differ in the types of errors and interferences to which they may be subject. Hence, a background study has been carried out with the goal of selecting the best possible analysis method as well as its limits of accuracy. A knowledge of such limits is necessary in order to determine real chemistry differences obtained in subsequent remelting studies. Also, the limits of chemical analysis techniques determine the precision necessary for any thermochemical model which may be employed.

Analytical methods may be classified into absolute methods and comparative methods. Absolute methods are usually based on a stoichiometric chemical reaction. Examples of absolute methods are titrimetry and gravimetry. Such methods are usually quite accurate and precise, but are usually not suitable for the determination of trace elements. Comparative methods require calibration against known standards to obtain accurate quantitative results. Most comparative methods are physical or instrumental techniques whereby a single property of the analyte is measured. Examples of comparative methods are spectrometric or electrochemical methods.

A-II.1 SAMPLE PREPARATION

In any technique, the preparation of samples is a vital step in sample analysis. The first criteria of samples is that they must be representative of the ingot or batch of interest. Unrepresentative samples can cause errors in mass balances as well as unrealistic and unrepeatable results.

Preparation techniques prior to actual analysis are also critical. When decomposition in necessary, care must be taken to insure that it is complete. This can be a problem when samples consist of more than one phase as in the case of metals containing refractory carbides or nonmetallic inclusions. Second phase particles may dissolve more slowly and under somewhat different conditions than the matrix. If such particles are not accounted for, subsequent analysis results will not be representative of the sample as a whole.

A-II.1.1 Representative Sampling

In order to insure that samples are representative some knowledge of theoretical chemistry changes as a function of sample geometry is useful. While sampling may not be a problem for solid, homogenous samples, the chemistry of cast parts may differ with location, based on solidification mechanics. Sampling of powdered samples may be done by mixing and splitting to obtain a sample representative of the whole.

A-II.1.2 Decomposition Methods

Decomposition of samples is an important part of several analytical techniques. Although some analytical methods such as X-ray fluorescence and electrothermal atomization can be applied directly to solid samples, most of the highly sensitive methods of analysis are performed on a solution of the sample. Decomposition may be done by wet methods such as bomb decomposition or by fusion. Most inorganic materials will dissolve in acids, but materials such as minerals and silicates must be brought into solution by fusion.

Modern wet decomposition techniques are performed in closed vessels made of inert and pure materials at high temperature and pressure. A recent development in wet decomposition is based upon microwave heating. Wet chemical decomposition in a closed system is done by a mixture of acids which may include nitric, hydrochloric, perchloric, and hydrofluoric. Temperatures are usually kept below 240°C, as teflon and other inert bomb materials lose their mechanical strength above these temperatures. Low pressure systems can be used up to a pressure of 1.6 MPa.

A number of substances such as silicates and some mineral oxides are attacked slowly, if at all, by the usual liquid reagents. In these cases it is necessary to use fused salt media or fluxes. Fluxes will decompose most substances at the high temperature required for their use (300-1000°C) and the high concentration of reagent which must be brought into contact with the sample.

The sample, in the form of a fine powder, is mixed with approximately a tenfold excess of the flux in a graphite or platinum crucible. The crucible is then placed in a muffle furnace at 300-1000°C for a specified time to give a "melt", which is dissolved after cooling. The selection of a flux is determined by the sample to be dissolved. Basic fluxes employed for the attack of acidic materials include carbonates, hydroxides, peroxides, and borates. Pyrosulphates are used as acidic fluxes. Sodium peroxide is an oxidizing flux useful for dissolving rock samples.

The addition of fluxes increases the risk of analytical error due to the amount of flux required for successful fusion. In addition, the final aqueous solution obtained from fusion will have a high salt content which may cause difficulties in the subsequent steps of analysis. The high temperatures required for fusion increase the possibility of vaporization losses.

A-II.2 USE OF STANDARDS

One factor which determines the reliability of any comparative method of analysis is the choice of standard materials. Several choices are available for standards and the selection of a standard is important to the final results.

A-II.2.1 Pure Materials

For most metallic elements, high purity metals are the best standards available. Standard solutions of high accuracy can be prepared starting from the pure metal. The use of a pure element instead of a compound eliminates stoichiometry as a factor in calculating the concentration of the standard solution. When pure metals are not available, compounds such as salts or oxides are used. Most compounds are non-stoichiometric to some degree, however. High purity, pedigree samples for both melts of compounds are available from the National Institute of Standards and Technology.

A-II.1.2 Matrix Matching Methods

Some analytical methods require the standard to be prepared in a matrix form that simulates the sample insofar as the major constituents are concerned. This can complicate matters because of impurities in the major constituents. In this method, in order to avoid matrix or multiplicative interferences, standards are prepared to match as closely as possible the sample matrix . For simple samples, such as metals, matrix matching is not difficult, for complex matrices, however, or matrices with an unknown composition, complete matrix matching is not possible. The purity of the matrix compounds used for preparing the matched standards is quite important.(11)

A-II.3 CALIBRATION

In all comparative methods there exists a mathematical relationship which relates the measured physical parameter to the analyte concentration:

$$y = f(x)$$

where y is the measured parameter and x is the analyte concentration. In the simplest case, the relationship between the measured parameter and the analyte concentration is linear:

$$y = a + bx$$

where b is the proportionality factor or sensitivity and a is the blank value. The blank value is defined as the signal from the sample which is identical in principle to the sample of interest except that the substance to be determined is absent.

A-II.3.1 Calibration Curves

A calibration curve or line is obtained by measuring the parameter y for a number of standards with increasing analyte concentration and plotting these values against the respective concentrations. Ideally, the standards and the blank should contain the same concentration of all components except the analyte element, as the sample. The concentration of the standards usually spans the concentration range of the standards and enough standards must be measured to make sure the calibration line is well established.

A-II.3.2 Calibration Errors

When a calibration line is plotted, the results may not fall on a straight line. This is caused by indeterminate or random errors. Indeterminate errors arise from uncertainties in the measurements and will produce a scatter of results for replicate measurements which must be assessed by statistical methods. The linearity of calibration curves is often limited on the high concentration side, which may show a negative deviation. Curvature in calibration plots often occurs in spectrometric methods involving emission or absorption of radiation.

As blank values are also subject to random errors, the blank is best considered as a point with coordinates (0, blank) on the calibration line. It is usually not good practice to subtract the blank from every signal before establishing the calibration line.

If systematic errors are made in preparing the standards, in presenting the standards to the instrument, in measuring the standards, or in fitting the calibration curve, the calibration curve will be determined incorrectly which will cause systematic errors in the final analytical result. The determination of the analyte cannot be more accurate than the accuracy with which the analyte concentrations within the standards are known. It is sometimes required that the chemical form of the standard be identical to that of the sample, since the state of oxidation, complexation, isomerization of the analyte could influence the analytical signal. Systematic errors can also result from bias or improper fitting of the calibration curve to the data as can occur when a straight line least squares program is used to fit nonlinear data.

A-II.4 INTERFERENCES

Interferences arise due to differences in the composition of the analytical sample and the external standards and blanks used for calibration. The analytical sample matrix can be different from that of the standards because of the matrix of the original bulk sample or because of species added or removed during sample preparation. Interferences can be subdivided into blank or additive interferences and matrix or multiplicative interferences.(12) The former interfere with the analysis in an additive way (the same absolute error for every analyte concentration) and the latter in a proportional way (the absolute error is proportional to the concentration of the analyte or the relative error is constant.)

A-II.4.1 Blank Interferences

A blank or additive interference is due to a species or material which produces an uncompensated signal independent of the analyte concentration. A blank interference causes an error in the determination if the blank component of the total signal measured for the sample differs from the blank component of the total signal measured for the standards.

A-II.4.2 Matrix Interferences

Matrix or multiplicative interferences are caused by species or substances which alter the magnitude or the analyte component of the total signal in a way proportional to the signal. Even if the blank signal is negligible, a matrix interference may affect the measured analytical signal and cause an error in the determination if the interferant is present in the sample but not in the standards. If the interferant is added to the standard solutions, it will affect the calibration function by changing the shape of the calibration curve.

A-II.5 DETECTION LIMIT

The detection limit of an analytical method is defined as the smallest concentration that can be reported as present in a sample with a specified level of confidence. When the concentration of a component is decreased, the measured physical parameter will become so small that at a certain concentration level that it cannot be distinguished from the random fluctuations of the background or blank.(13)

The detection limit is an important criterion in the choice of analytical method. The values obtained are related to the sample as it was introduced into the analytical equipment, and they must be corrected for preconcentration or dilution steps. The detection limit can be decreased in two ways. The sensitivity can be improved by using a more sensitive detector or measuring at a more intense spectral line for spectrometric methods. If this is not possible, the standard deviation of the background may be optimally reduced by selecting the best instrumental conditions.

A-II.6 CROSS CHECKING

The accuracy of analytical methods relative to each other may be checked by analyzing a set of samples using two different methods. Results obtained with one method are plotted on the y axis and those obtained with the other method are plotted on the x axis. The correlation coefficient and the regression line are than calculated. If, for all the samples, the two results are identical ($r=1$, $a=0$, $b=1$ for $y = mx + b$) the techniques are ideally the same. If the slope is 1 but the intercept is not zero, one method gives results which are systematically higher than those of the other method. This may happen if the background is not corrected properly. If the slope is less than one, there is a systematic error on the slope of the calibration lines of one of the methods.

A-II.7 COMPARISON OF ANALYTICAL TECHNIQUES

The ideal analytical technique would be totally selective. The presence of contaminants would not affect the measured analytical signal. This is rarely the case especially for complex samples where the analyte is present in a concentration many orders of magnitude lower than that of matrix elements. The discussion below overviews various commercially available analytical techniques.

A-II.7.1 Spectrochemical Measurements

All spectrochemical techniques depend on the emission or absorption of electrochemical radiation, which accompanies certain energy changes within an atomic or molecular system. The energy changes are associated with a series of discrete energy levels in which atoms and molecules exist. When a substance is irradiated with electromagnetic radiation, the energy of the incident photons may be transferred to the atoms or molecules, raising them from their ground state to a higher energy one. This process is known as *absorption*, and is accompanied by the production of a beam of diminished transmitted power if the frequency of the incident beam corresponds to the energy difference necessary for specific excitation. The absorbed energy may be re-emitted discretely, a process known as *fluorescence.* The frequencies emitted correspond to the energy differences between levels. In *emission* spectrochemical methods, the radiation emitted by the analyte following non-radiational (thermal, electrical, or chemical) excitation is measured. Thermal excitation may occur in a flame or a plasma, or electrical excitation may occur using a direct current arc or a high voltage spark.

Spectroscopic instruments contain up to five typical components, a stable source of radiant energy, an atom reservoir, a wavelength selector, a radiation detector or transducer which converts the energy to a useful signal, and a signal processor and readout.(14)

Atomic emission spectroscopy (AES) is the oldest atomic spectrometric multi-element technique. All elements can be made to emit characteristic spectra by appropriate energization. AES is divided into categories according to the source of energy that causes the element excitation. In the past, the most widely used sources have been flame, arc and spark. During the last two decades, new radiation sources, such as ICP and DCP have become commercially available.

At present, flame emission photometry is used only for the determination of easily excited elements like Na, K, Li and Ca. Arc and spark discharge have been used as excitation sources for both qualitative and quantitative emission spectrometry. With the DC arc, 70-80 elements can be excited. The major use of the arc is qualitative and semi-quantitative because of its limited precision and accuracy. The spark is capable of higher precision and accuracy and is applied mainly in quantitative determinations, especially for rapid multi-element analysis of solid samples.

Arcs and sparks are less than ideal in many characteristics. Matrix effects are severe, which limit reproducibility. Plasma sources were developed for emission spectrometric analysis in the late 1960's. Inductively coupled and DC plasma spectrometers were introduced in the mid-1970's.

A plasma is an electrically neutral, highly ionized gas composed of ions, electrons and neutral particles. Commonly used plasmas have higher gas temperatures and less reactive chemical environments than flames. The plasma gas is usually a stream of argon which is energized with high frequency electromagnetic fields or with direct current. When combined with a high quality spectrometer, plasma sources provide great accuracy and precision.(15)

A-II.7.2 Mass Spectrometry

A mass spectrometer can be defined as an instrument that produces ions (positively or negatively charged), separates them according to their mass or their mass to charge ratio, and detects them. It consists of an ion source, a mass analyzer, and a detector.

Inorganic mass spectrometry originated in 1934 when Dempster introduced the spark source.(16) Hannay constructed the first spark source mass spectrometer in 1954. In spark source mass spectrometry the atoms of the sample are converted to gaseous ions by a high voltage spark in a vacuum chamber. The gaseous positively charged ions formed are accelerated into the mass spectrometer by a DC potential where they are focused and detected photographically. The use of SSMS has been limited over the last 30 years for inorganic samples because more powerful sources are needed to ionize them. Developments in the last decade have made it possible to use other ion sources for MS, such as inductively coupled plasma (ICP) and the glow discharge (GD). The ICP operates at atmospheric pressure while glow discharge requires a slight vacuum. These sources have been combined with modern quadruple or magnetic mass spectrometers, allowing rapid determination with low detection limits.

A-II.7.3 Inductively Coupled Plasma Mass Spectrometry

Inductively coupled plasma mass spectrometry (ICP MS) developed from the work of Gray who showed in 1975 that good detection limits can be obtained and isotope ratios can be determined when a solution is introduced into a D.C. plasma (DCP) at atmospheric pressure and the ions formed are extracted into a mass spectrometer. In a DCP, interferences

occur and for elements with an ionization energy above 9 eV the ion yield is low. Research into the possibilities if ICP MS was begun by Houk and coworkers in 1975.(17) ICP is a source of singly charged ions which may be used for analysis by mass spectrometry. The sample is usually introduced into the plasma in a stream of argon as an aerosol obtained by pneumatic nebulization of a solution. The argon stream punctures the plasma forming a central channel where atomization and ionization take place.
The inductively coupled plasma efficiently ionizes most elements to single charged positive ions (M+) so that the plasma can be used as an ion source for the mass spectrometer.

When the sample is dissolved in a mixture of acids, additional polyatomic ions are formed and detected in the blank. When nitric acid is used, only the concentration of nitrogen in the plasma is increased. Other acids such as hydrochloric, sulfuric, and phosphoric, cause much more serious problems because the species produced by these acids may interfere with the elements which must be detected. An important limitation of ICP MS is the occurrence of matrix effects or matrix induced charges. Matrix effects in the form of acid presence have been reported to cause both signal suppression and signal enhancement.(18) Matrix matching techniques may be of some use in eliminating these problems. The detection limits for ICP MS are <0.001 to 0.1 ug/l. The precision is 2-3% and accuracy depends on the quality of standards , the presence of interferences, and the extent of contamination.(19)

A-II.7.4 Nuclear Activation Analysis

In nuclear activation analysis, the production of a radionuclide from an analyte element is used for the identification and quantitative determination of the element. In neutron activation analysis, thermal neutrons in a nuclear reactor are used to irradiate the sample. As a result of a nuclear reaction between an activating projectile and the isotopes of the elements of interest, radionuclides are produced. The radiation emitted by these radionuclides is measured with a suitable detector after a variable decay time based on the half life of the nuclide. The elements present are identified by the energies and relative intensities of the gamma ray lines in the spectrum. The area of the appropriate photopeak is related to the amount of the element. When the measurement is carried out without prior chemical separation, the method is called instrumental neutron activation analysis. If it is necessary to separate the radionuclide produced, the term radiochemical neutron activation analysis (RNAA) is used.

Atomic nuclei are made up of protons and neutrons (nucleons). The atomic number Z of an atom is the number of protons in the nucleus, the mass number A is the sum of the number of protons (Z) and the number of neutrons (N). Atoms with the same Z and different A are isotopes and have virtually the same chemical properties. Elements may have two kinds of isotopes, stable isotopes and radioisotopes, which spontaneously disintegrate. The stability of isotopes is dependant upon the number of protons and neutrons in the nucleus. When a sample is irradiated in a nuclear reactor, reactions take place between the neutrons and the nuclides present in the sample. The rate of a nuclear reaction depends on three parameters: the number of target atoms present, the reaction cross section, and the neutron flux. The cross section depends on the target nuclide and the neutron energy.

The gamma ray detector will detect only a fraction of the emitted gamma rays having a given energy. In addition the abundance of gamma rays of a given energy emitted per disintegration must be taken into account. In practice, a comparative method is used whereby a reference with a known content of the element of interest is also irradiated. If the sample and the reference are irradiated with the same neutron flux and are measured with the same detection efficiency the mass of the element can be deduced. A high resolution gamma ray spectrometer is built around a high purity germanium or lithium drifted germanium detector. When a gamma ray enters the detector, it may interact and give an energetic electron which loses its kinetic energy by elevating thousands of electrons in the germanium from the valence band to the conduction band. The conductivity thus increases and a current pulse occurs each time a photon is absorbed.

Limitations of neutron activation analysis arise from reactions which may interfere with detection of events from the decay of radioisotopes of interest. In such cases, a chemical separation may be performed in order to eliminate the interfering element or elements. Chromium is usually considered to fall outside the scope of NAA, especially when it is present with iron.(20) Activation analysis is best suited for the analysis of solid samples, which may be irradiated with no need for a dissolution step. Sensitivities and detection limits in NAA are determined by several factors including nuclear constants, experimental parameters and the presence of easily activated elements in the sample. The sensitivities and detection limits vary in an irregular way from element to element and several elements are difficult or impossible to determine by standard instrumental NAA. These are Li, Be, B, C, N, O, P, S, Sn, T, and Pb.(21) In principle, NAA can provide very accurate results. Although in some cases interfering reactions may occur, they can usually be recognized and accounted for. For many elements the turn-around time is long which may be a drawback for routine analysis.

APPENDIX II

PLASMA SPRAYED COATINGS

Plasma-sprayed coatings are formed by the accumulation of molten and semi-molten particles on a substrate surface. In plasma-spraying, feedstocks are injected into a hot gas plasma where they are heated and accelerated towards the substrate. Bonding to the substrate, and to other impacted particles, is a function of both temperature and velocity of the particle. Plasma temperatures (8000 - 20,000°K) are sufficient to melt all materials and consequently plasma-spray systems are used routinely to deposit oxide based coatings. The supersonic plasma gas jet accelerates the particles to high velocities. Plasma jet velocities are above sonic velocities, yielding near-sonic or sonic particle velocities with particles of 50 µm diameter or less.

The plasma spray facility of the Materials Science and Engineering Department of the Oregon Graduate Institute consists of a Plazjet II 200KW plasma spray system with an associated three channel mass flow control, powder feeder, wire feeder, and various fixtures for holding and manipulating samples. This is housed in a 300 square foot acoustic room fitted with a six foot water curtain. The Plazjet II plasma-spray system uses a gun which is quite different in design from the traditional plasma-spray gun. The Plazjet works at high voltages, 300-450V, and low currents, 200-500A, yielding up to 225 kilowatts of power. Most plasma-spraying systems, i.e. 'conventional' systems, operate at nominally 40-75 volts and up to 2500 amps, yielding power levels of 40 to 100 KW. Most research on plasma gun dynamics and behavior has been performed using a "conventional" gun designed to operate at the lower voltages and high currents. The high working voltage of the Plazjet gun design increases the electric arc length within the body of the gun. This allows greater heating of the plasma forming gases. The long dwell time of the gas within the arc, coupled with high gas flow rates, generates hot plasma gas exit velocities which greatly exceed sonic velocities. Shock waves can be observed in the plasma plume. The power conversion efficiency of this gun is also quite high, having been measured at over 75 percent. In practical terms, this means that there is more thermal energy available at the gun exit than in a conventional gun, which in turn means that greater quantities of material can be melted and sprayed. The high gas exit velocities and the high gas mass flow rates mean that melted materials can also be accelerated to higher velocities. Thus this gun design can increase both the thermal energy and the kinetic energy of sprayed materials. The high power level also means that multiple feed-stocks of powder, wire, or both, can be utilized efficiently. One of the greatest advantages of this system lies in this versatility.

As currently configured, the system will perform an adequate job for feasibility studies on the WINCO program. However there will be limitations on the type of materials to be sprayed and on the quantity (i.e. the deposition rate). Some of the materials which are proposed to be used for coatings are quite expensive and recycling of the overspray would be advantageous. However the current water curtain does not allow this. Thus a high efficiency particulate filter, equipped with a HEPA after-filter, was purchased and is ready for installation.

A second limitation is the powder feed capability. The system currently uses a commercial wheel-type powder feeder which is sized for conventional plasma guns. The OGI 200 KW system is, however, capable of much higher deposition rates, up to 10 kg/hr of alumina. Standard wheel-type powder feeders are not available for these deposition rates unless multiple feeders are used. To overcome the limited powder delivery, a screw-type feeder has been ordered. Screw-type feeders are capable of very high deposition rates over a wide range of materials - from polymers to tungsten carbide. In order to accommodate the added equipment, the acoustic spray room needs to be expanded. It is modular in design and the addition of an expansion section having an area 4 by 16 feet is underway.

As the program grows beyond a feasibility study, gun manipulation capabilities will need to be expanded. The current system allows the gun to traverse about 18 inches horizontally with a separate manual control on the vertical motion. This system will need to be upgraded as the substrate size increases. A simple, in-house built manipulation system with a 36 inch range of motion horizontally and 12 inches vertically is essentially complete.

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