Optimization of Thermochemical, Kinetic, and Electrochemical Factors Governing Partitioning of Radionuclides during Melt Decontamination of Radioactively Contaminated Stainless Steel

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Research Objectives

The goal of this project is to characterize and optimize the use of molten slags to melt decontaminate radioactive stainless steel scrap metal. The major focus is on optimizing the electroslag remelting (ESR) process, a widely used industrial process for stainless steels and other alloys, which can produce high quality ingots directly suitable for forging, rolling, and parts fabrication. It is our goal to have a melting process ready for a DOE D&D demonstration at the end of the third year of EMSP sponsorship, and this technology could be applied to effective stainless steel scrap recycle for internal DOE applications. It also has potential international applications.

The technical approach has several elements: 1) characterize the thermodynamics and kinetics of slag/metal/contaminate reactions by models and experiments, 2) determine the capacity of slags for radioactive containment, 3) characterize the minimum levels of residual slags and contaminates in processed metal, and 4) create an experimental and model-based database on achievable levels of decontamination to support recycle applications. Much of the experimental work on this project is necessarily focussed on reactions of slags with surrogate compounds which behave similar to radioactive transuranic and actinide species.

This work is being conducted at three locations. At Boston University, Prof. Uday Pal's group conducts fundamental studies on electrochemical and thermochemical reactions among slags, metal, and surrogate contaminate compounds. The purpose of this work is to develop a detailed understanding of reactions in slags through small laboratory scale experiments and modeling. At Sandia, this fundamental information is applied to the design of electroslag melting experiments with surrogates to produce and characterize metal ingots. In addition, ESR furnace conditions are characterized, and both thermodynamic and ESR process models are utilized to optimize the process. To complete the process development, ESR melting experiments, which include actual radioactive contaminates as well as surrogates, are being conducted at the Mining & Chemical Combine in Zheleznogorsk, Russia. These experiments measure decontamination efficiencies in ingots for uranium and plutonium in stainless steel, as well as correlate removal of radioactive and surrogate compounds in the same melts. This will "close the loop" and allow us to use measured surrogate behaviors to model removal of radioactive species.

Research Progress and Implications

At Boston University, experiments were conducted to measure the dissolution of cerium oxide, as a surrogate for uranium and plutonium compounds, into the baseline ESR slag (60wt%CaF_2-20wt%CaO-

$20wt\%Al_2O_3$). It was found that CeO_2 is very highly soluble into the slag, with the implication that the Ce concentration in the metal will be below the detection limit. This was experimentally seen in earlier ESR experiments. A volatilization study was conducted to determine the rate which the base slag with dissolved CeO_2 volatilizes as a function of temperature. The slag volatilization followed an Arrhenius behavior with temperature, and analyses of the volatile species showed them to be species generated from the base slag, with no ceria present. Physical property measurements on the molten baseline slag were performed. These data are needed for process characterization and modeling. These included slag viscosity, surface tension, and electrical conductivity from 1300 to 1700°C. Each of these properties showed Arrhenius behavior as a function of temperature.

At Sandia, several ESR experiments using nested pipe electrodes, which simulate scrap piping, were completed to determine the optimum furnace control strategy. This geometry of electrodes, made of reactor coolant piping, is used in the Russian furnace. Surrogate compounds and their concentrations were selected for the Sandia and Russian experiments. Surrogates include CeO_2, (to represent uranium and plutonium oxides), CsF, and SrO (non-radioactive forms of radioactive fission products), HfO2 (oxide with density similar to uranium oxide), and ReO_2 (surrogate for ^{99}Tc)

A series of six ESR experiments was begun to assess the influence of melt rate, slag composition, and slag additives. These melts used the surrogates listed above and were highly instrumented to measure slag temperatures, thermal performance, and furnace electrical characteristics. Chemical analysis of the slag samples and metal ingots is underway to determine chemical partitioning efficiency.

Thermodynamic modeling at Sandia using the commercial software MTDATA predicts that all surrogates should strongly partition to the slag, except for Re, which should end up in the metal phase. All Cs compounds should vaporize, and uranium compounds should not. Tc and Co would also go into the metal.

Under a Sandia project funded by another DOE program (IPP), two ESR melting experiments using plutonium contaminated pipe electrodes were run at the Mining & Chemical Combine in Russia. Analyses of ingot material and slag showed very effective partitioning of the Pu to the slag and decontamination of the metal. Under EMSP, we are funding two additional experiments this summer to determine slag reactions with plutonium and uranium oxides, as well as the surrogates. Results of these experiments will allow us to directly correlate the behaviors of radioactive species with their surrogates. This should validate our ability to predict decontamination efficiencies at different furnace operating conditions and allow us to optimize the process using surrogates.

Planned Activities

These are the planned activities during the final year of this EMSP project:

Boston University

1. Measure the dissolution kinetics of cerium oxide surrogate compound in the baseline slag (60% CaF, 20% Al2O3, 20% CaO) and measure the partitioning of cerium between the molten slag and molten metal in equilibrium at elevated temperatures.
2. Measure the electrical conductivity of baseline slag with additions of titanium oxide to 4, 8, and 12 wt. % and addition of cerium oxide to 4 wt. % (no titanium oxide).
3. Measure the solubility of hafnium oxide and strontium oxide at 100 to 5000 ppm initial quantity in baseline slag.
4. Measure baseline slag volatility with strontium oxide surrogate additive (5000 ppm).
5. Perform thermodynamic modeling of slag-metal (stainless steel)-surrogate/contaminate systems and coordinate with modeling activities at Sandia. Surrogate/contaminate species of interest include Ce, U, Pu, Cs, Sr, and Tc.
6. Measure slag physical properties including contact angle, surface tension, and viscosity of slags with surrogate additives .

Sandia:

1. Perform thermodynamic modeling of slag/surrogate/metal systems.
2. Complete ESR furnace experiments and analyses of chemical, temperature, and electrical data.
3. Analyze results of ESR melting experiments performed at M&CC in Russia and correlate with laboratory experiments with surrogates.
4. Define optimum ESR furnace design and operation to propose for D&D demonstration.

Mining & Chemical Combine:

1. Conduct two ESR furnace experiments using pipe electrodes contaminated with Pu, U, and surrogates. Two slag chemistries will be tested.
2. Analyze the stainless steel ingots at bottom, middle, and top to measure concentrations of contaminates, surrogates, and alloy content. Also analyze the slag skin and slag cap from each melting experiment.