Melt Decontamination of Radioactively Contaminated Stainless Steel
Project #60363

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Process Studies for Decontamination of Stainless Steels: Current Results

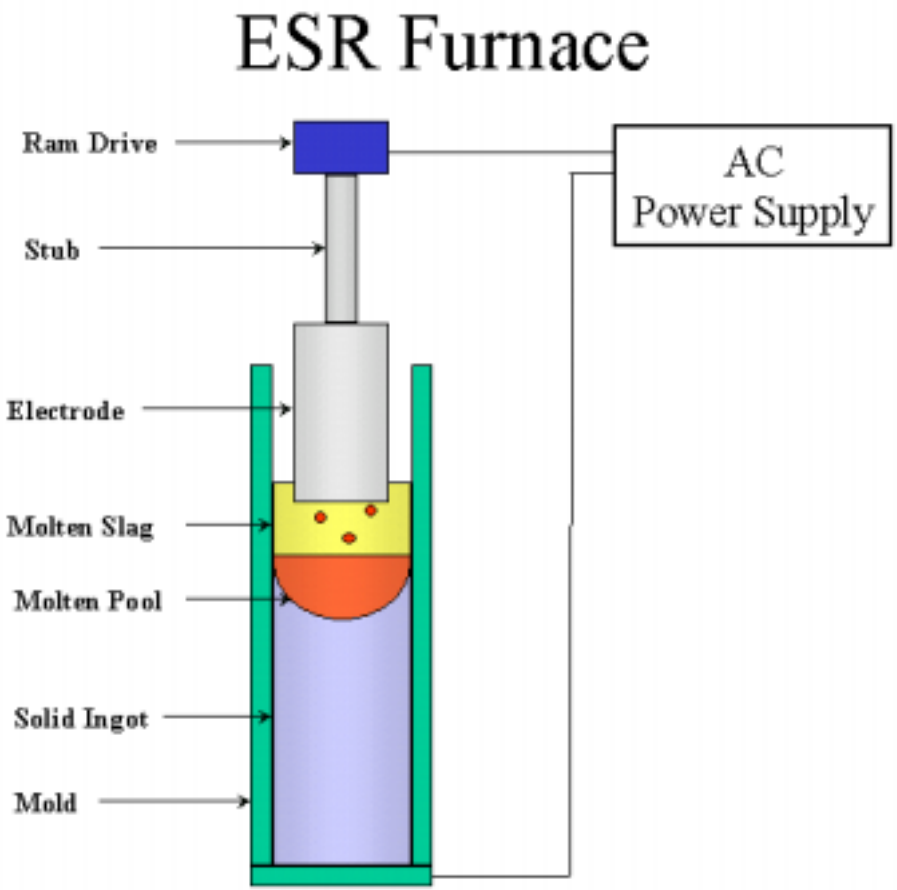
ABSTRACT

Ongoing, coordinated studies on an electroslag remelting (ESR) process for decontamination of radioactive scrap stainless steels has yielded appreciable progres. Melt decontamination can convert a metals disposal liability into a product that can be recycled for use in nuclear-related applications, with a significant decrease in overall materials cost. At Sandia, an industrial pilot-scale ESR furnace has been instrumented and used for several test melts to measure and characterize the partitioning of surrogate contaminants (Ce and Hf for Pu and U; Re for Tc; Cs and Sr) between the stainless steel and slag (CaF_2-CaO-Al_2O_3, optimized at about 60-20-20 wt.%). The slag is used to control the chemistry of the resultant ingot; slag additions, as well as changes in melt rate, are being evaluated for optimizing the ingot surface quality (with minimal slag entrapment). The ESR furnace, with a vertically split ingot mold, allows detailed examination of slag skin and slag cap structure, thickness, and chemistry. Furnace control studies are in process to optimize the melting of nested-pipe stainless steel electrodes as well as solid electrodes. At Boston University, relevant slag thermochemical and thermophysical laboratory studies are being conducted to quantify the slag-metal partition coefficient, dissolution capacity, and kinetics for various surrogate contaminants (250 ppm to 23 %) as a function of temperature (~1300 to ~1700°C). Molten slag viscosity, surface tension, electrical conductivity, volatilization rates, and volatilized species have been measured. Thermodynamic modeling of the slag-metal-surrogate system has started, in coordination with similar modeling at Sandia. At the Mining & Chemical Combine, in Zheleznogorsk (Krasnoyarsk), Russia, a similar ESR furnace test system has been set up. This study is funded by the DOE's Initiatives for Proliferation Prevention program, in cooperation with Sandia. Several radioactive contaminated, stainless steel, nested-pipe electrodes have been melted. These were doped with known amounts of ^{239}Pu, U, and surrogate elements; two slag compositions also have been tested. High stainless steel purification/decontamination factors for ^{239}Pu and ^{238}U were achieved. M&CC has designed a commercial scrap reprocessing facility utilizing a consolidation/purification gaslift furnace and an ESR for final ingot production. The intent is to prepare for scale-up to an industrial-scale facility with materials cutting and handling, first-melt consolidation, and final melt by ESR to produce high quality ingots.

Melt Processing Description & Goals

- Optimize ElectroSlag Remelting (ESR) process for radioactive decontamination of stainless steel scrap and production of high quality ingots
- Use molten slags, CaF_2-CaO-Al_2O_3 to remove radionuclides, control metal ingot chemistry
- Utilize chemical surrogates for baseline melt, partitioning tests: Ce & Hf - for Pu & U , Re - for ^{99}Tc , $^{natural}Cs$ - for ^{137}Cs , ^{nat}Sr - for ^{90}Sr
- Characterize thermochemical and thermophysical properties of slag/contaminate reactions
- Have melt process ready for DOE D&D demonstration at end of EMSP project
- Lead to $$ cost-effective stainless steel scrap recycle for internal DOE or nuclear industry reuse applications

Advantages of Melt Decontamination



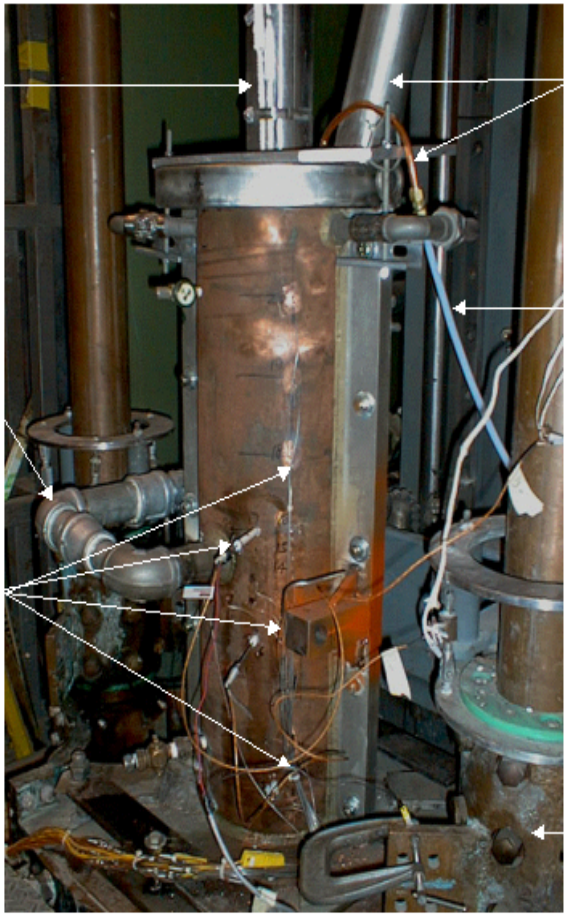
- **Potential to decontaminate 1000's of tons of stainless steel to levels low enough for internal DOE or other reuse**
  - **our cooperative project in Russia has demonstrated effective Pu and U removal from metal to slag**
- **Produce *high quality* ingots suitable for forming into needed shapes**
- **Minimize waste of: valuable metals resources, disposal costs, long-term environmental monitoring**

Benefits of Electroslag Remelting

- Maintains the pedigree of the high value metals
- Produces an ingot suitable for direct forming
  - Reduced contamination
  - No shrinkage porosity
- Captures and concentrates radionuclides in a stable, solid slag mass
- Furnaces are easily enclosed and use no refractories

Test Resources

Instrumented ESR Crucible



Sandia National Laboratories

ESR Process Validation Experiments

- **Highly instrumented, pilot-scale, split mold ESR furnace**
- **Optimize process controls** (for solid and pipes feed electrodes)
- **Slag, additive, & ingot finish optimization**
- **Assess partitioning efficiency of surrogates separations**
- **Measure thermal environment during melting**

Test Resources

- **Coordinate overall ESR project study teams:**
  - **Sandia Nat. Labs, Boston University, Mining and Chemical Combine**

- **Equilibrium Thermodynamic Modeling**
  - **Enumerate possible stable compounds and phases in system**
  - **Components in: Stainless steel, slag, radionuclides, surrogates**
  - **Predict nuclide separation efficiencies** (slag:stainless steel:volatiles)
  - **Evaluate how components are distributed in the phases**
  - **Benchmark to fundamental slag measurements at BU, ESR surrogate experiments at SNL, and radioactive ESR tests at M&CC**
  - **Thermodynamic Modeling Tool: MTDATA™**

Current Status

Ingot Slag Skin

Split Mold allows accurate correlation between melt conditions (melt rate, voltage, current, slag temperatures) and slag skin properties including thickness, solidifying phases, and cross sectional and bulk composition.

- CaF_2-CaO-Al_2O_3 baseline slag (~60-20-20 wt%) + TiO_2
- Pipe-electrode melt experiments completed, multiple solid-electrode melts in progress
- ESR controls experiments underway
- Slag factor-space melt experiments ongoing

Current Status

Typical Three-Layer Slag Skin Structure

First Vitreous Layer
Rapid Solidification

Middle Layer
Steady State
Crystal Growth

Final Layer
Ingot causes remelting
Lower Temperature Phases

Crucible Side

Ingot Side

Thermodynamic Calculation Results

- All surrogates partition to the slag phase except Re, which ends up in liquid metal phase
- All radionuclides partition to the slag phase, except Tc and Co, which go into the liquid metal, and Cs, which vaporizes
- U is not lost from the system as volatile fluoride in any appreciable amount

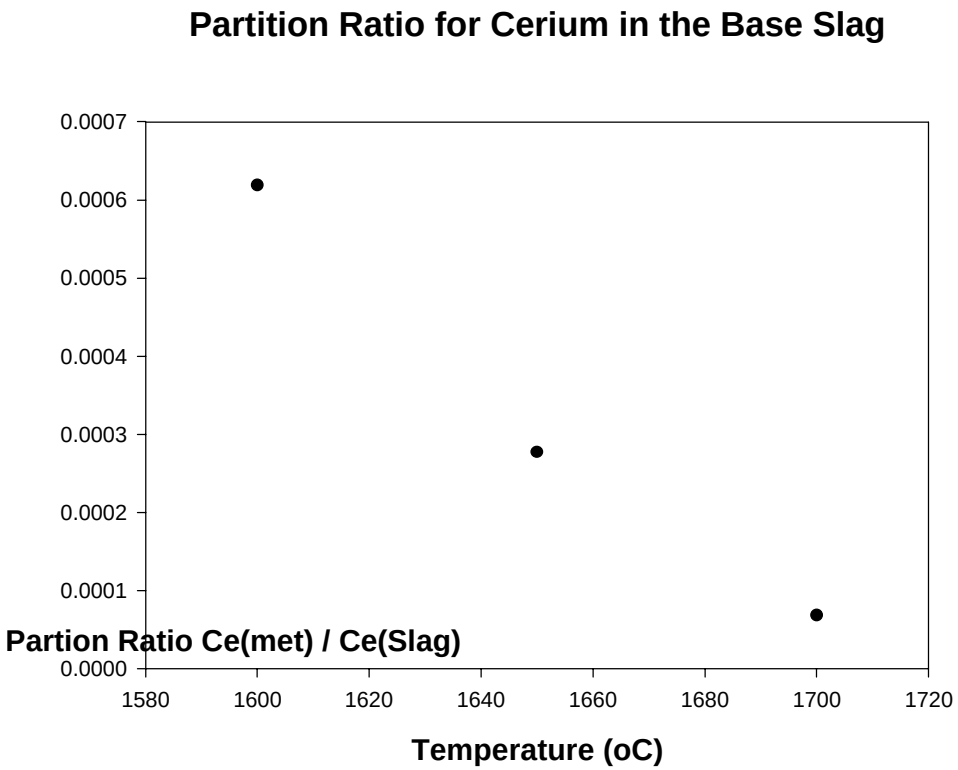
Test Resources

- **Boston University**

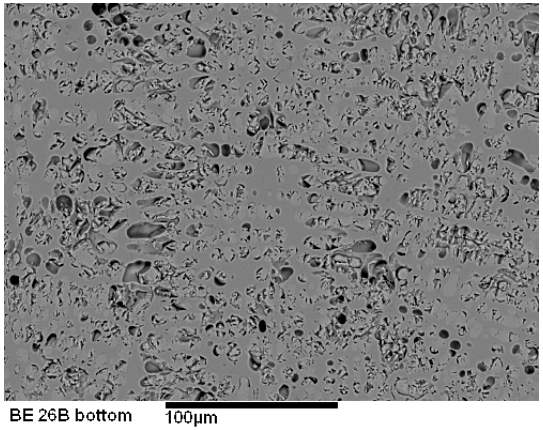
  High Temperature Materials Process Technology Laboratory,
  Dept. Of Manufacturing Engineering

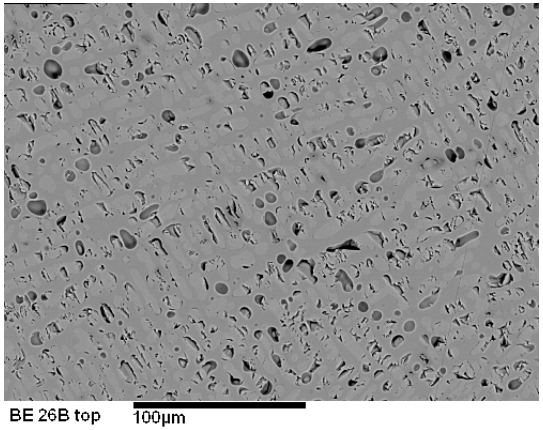
  - **As a function of temperature (1300-1700 °C):**
  - **Detailed molten slag/surrogate thermochemical measurements**
    - **Partitioning kinetics of surrogate dissolution (CeO, HfO, SrO)**
    - **Perform additional surrogate partition coefficient studies**
    - **Quantify slag-surrogates interactions, phase formation**
    - **Measure volatilization species and rates**
    - **Provide project analytical services, slag chemistry**
  - **Thermodynamic and kinetic modeling initiated (co-op w/Sandia)**
  - **Participate in analyses of Sandia ESR furnace melt/slag studies**

Ce partitioning to slag increases at higher temperatures



Atomic %						
Label	Ca	Al	Ce	O	F	% Tot.
Ce-top (light phase)	20.30	19.12	0.61	51.95	8.01	100.00
Ce-top (dark phase)	32.55	0.02	0.10	0.00	67.33	100.00
Ce-bottom (light phase)	20.02	19.21	0.59	51.62	8.55	100.00
Ce-bottom (dark phase)	36.00	0.05	0.05	0.00	63.90	100.00





Back scatter electron image of air-quenched ESR base slag homogenized at 1500 °C with 1w% ceria

Summary of Surrogate/Slag Equilibrium Partitioning Study

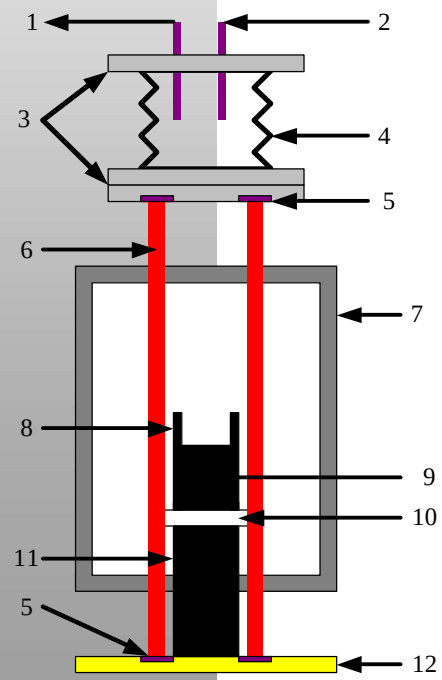
- Partitioning ratio of Ce between metal and slag is ~10^{-4}, decreasing with increasing temperature.

- Sr has a limited solubility in the metal ~1 ppm; it has high solubility in the slag.

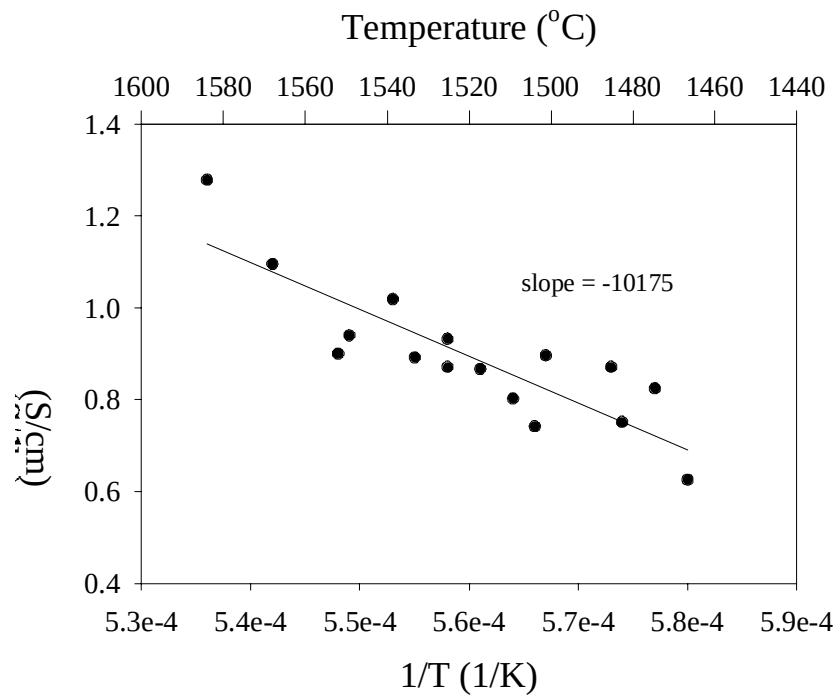
- Hf is soluble in the metal approaching ~100 ppm at 1700°C with isolated Hf rich phases in metal and slag.

Base Slag Thermophysical Results

High-Accuracy-Differential-Height Technique Developed to Measure Slag Conductivity



1: Argon Outlet
2: Argon Inlet
3: Aluminum Cover Plate
4: Bellow
5: Gasket
6: Reaction OBE Tube
7: Vertical Furnace
8: Crucible
9: Slag
10: Platform Disk
11: Insulation Brick
12: Brass Cover Plate



Ionic Slag Conductivity

Arrhenius Plot

Test Resources

- **Mining & Chemical Combine**

  Scientific Technology Center, Zheleznogorsk, Russia

  (Initiatives for Proliferation Prevention program)

  - **Constructed, demonstrated pilot-scale ESR furnace (FY 98-99) with dust and gas-handling radioactive capacity**
  - **Excellent chemical and radiochemical analysis facilities**
  - **Have 1000's of tons of radioactive contaminated stainless steels, with Pu, fission and activation products**
  - **Desire to commercially decontaminate and reuse the metal in Russia**

Current Status at M&CC

- Performed several pilot-scale ESR melts on contaminated stainless steel reactor pipes, to demonstrate process
  - Achieved high separation factors for ^{239}Pu, ^{241}Am, ^{137}Cs, ^{152}Eu
- Conducted two contaminated stainless steel piping ESR melts, w/ full analysis of ingots and slag
  - ^{239}Pu (1ppm), ^{238}U (1000 ppm) dopants to pipe electrodes
  - added chemical surrogates (to match Sandia and Boston Univ.)
    - Cs (100 ppm), Ce (1000 ppm), Sr (100 ppm)
- Performed engineering design of facility for commercial recycling of radioactive scrap stainless steel
  - Primary scrap melter is molten slag gaslift design
  - Final high quality ingot produced by ESR

ESR Decontaminated Stainless Steel

- ESR ingot produced from Pu-contaminated stainless steel reactor-coolant piping at M&CC, in Russia

A sealed dust control and gas purification system has been installed

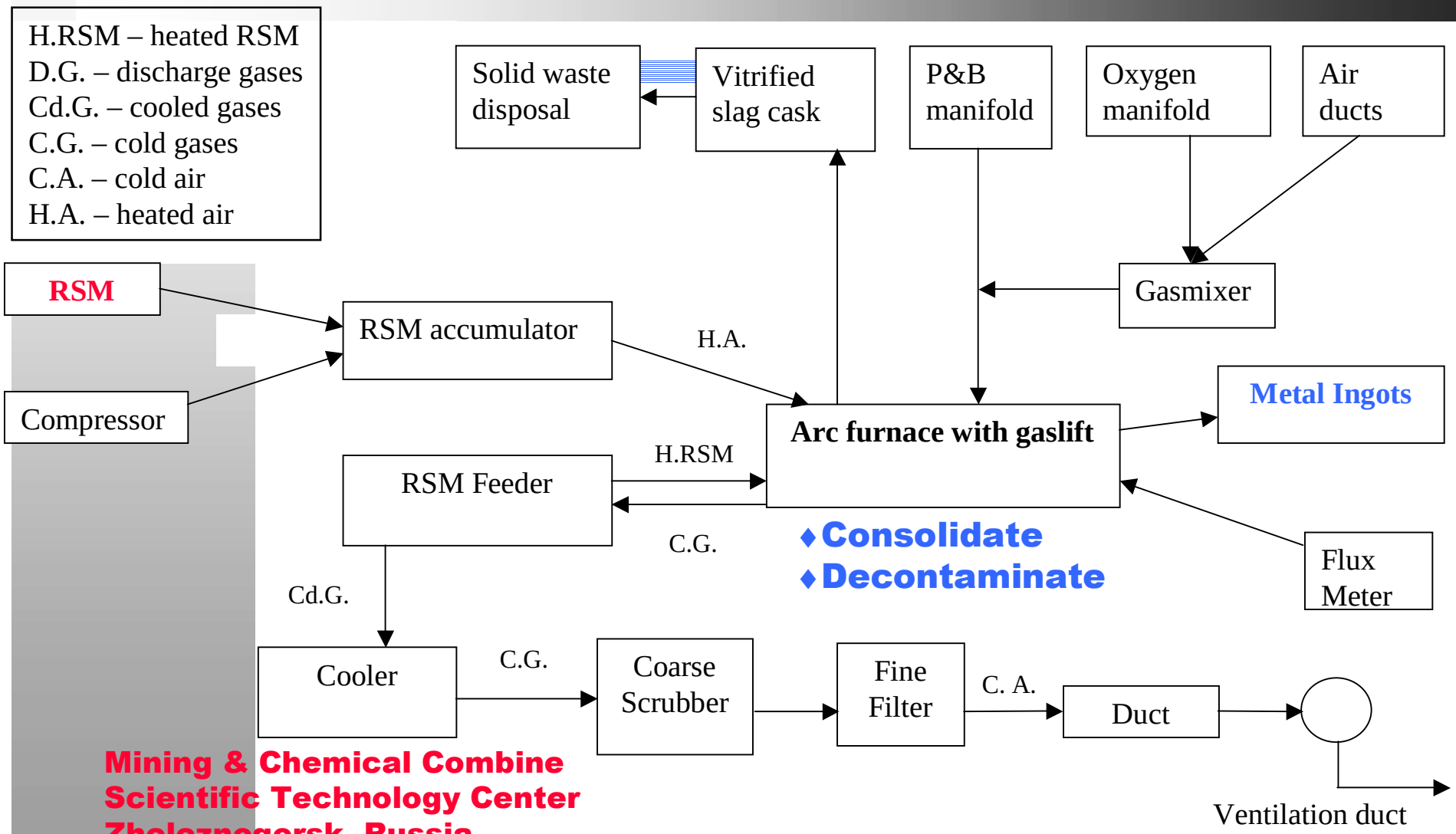
Mining & Chemical Combine
Scientific Technology Center
Zheleznogorsk, Russia

- Aerosol filters for furnace gas fine purification to remove radionuclides

- Protective box, equipped with a hatch and flaps to reload electrodes and ingots, operates under partial vacuum

- Stationary air sampling system located at 3 points to determine alpha aerosols content in operating area and ventilation flue.

Proposed Gas-lift Primary Melt Furnace for Radioactive Scrap Metal (RSM)



Mining & Chemical Combine
Scientific Technology Center
Zheleznogorsk, Russia

ESR Decontamination Summary

- Three project thrusts:
  - Fundamental slag/surrogate/metal reaction studies at Boston University
  - Melt process research at Sandia
  - Pilot decontamination tests at M&CC in Russia
- Experimental verification of thermodynamic and process models
- Experiments at M&CC showed Pu, U, and surrogates removal from contaminated stainless steel piping.