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Electroslag Remelting (ESR) Slags for Removal of Radioactive Oxide Contaminants from Stainless Steel

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ELECTROSLAG REMELTING (ESR) SLAGS FOR REMOVAL OF RADIOACTIVE OXIDE CONTAMINANTS FROM STAINLESS STEEL*

Annual Report (1998-1999)

March 30, 1999

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ABSTRACT

Decontamination of radioactive contaminated stainless steel using the ESR process is investigated by conducting thermophysical and thermochemical laboratory studies on the slag. The ESR base slag investigated in this research project is 60wt%CaF₂-20wt%CaO-20wt%Al₂O₃. In this report, we present the data obtained to date on relevant slag properties, capacity to incorporate the radioactive contaminant (using CeO₂ as surrogate, simulant for PuO₂ and UO₂), slag-metal partition coefficient, volatilization rate and volatile species, viscosity, electrical conductivity and surface tension as a function of temperature. The impact of these properties on the ESR decontamination process is presented.

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1.0 INTRODUCTION

1.1 Purpose

Downsizing and decommissioning of nuclear facility operations is increasing the stockpile of Radioactive Scrap Metal (RSM). The annual generation of RSM for the entire DOE complex is estimated to be approximately 120,000 metric tons, of which contaminated stainless steel with high chromium and nickel contents constitutes 25-30 % by weight [1]. Disposal of this material not only represents significant resources and value lost, but also necessitates long term monitoring for environmental compliance. The latter results in additional recurring expense. It is desirable to be able to decontaminate the radioactive stainless steel to a very low level that can be recycled or at least used for fabrication of containers for RSM disposal instead of using virgin stainless steel.

1.2 Decontamination Processes

The goal of the RSM decontamination process is to reduce the radioactive contaminant to a sufficiently low level so that the metal can be handled safely or reused. Melt decontamination provides an effective means for both consolidation and removing the contaminants from the bulk in a kinetically favorable manner. Various methods of melt decontamination evaluated are Electric Arc Melting, Air and Vacuum Induction Melting, Plasma Melting and Electroslag Remelting (ESR). In this research program, the ESR process with some of its inherent advantages is the subject of the investigation.

1.3 ESR Process

In the ESR process (see Figure 1), the RSM forms one of the two electrodes. Joule heating through a molten slag layer maintains the slag temperature between 1700-2000°C and melts one end of that consumable electrode. The molten metal droplets from the consumable (RSM) electrode fall through the slag layer. While the metal is in contact

with the slag, most of the radioactive contaminants from the metal are preferentially incorporated into the slag. The metal droplets are solidified in a water-cooled copper mold and form part of the consolidated and decontaminated ingot underneath the slag layer. This can be easily formed into a useful product by mechanical processes such as rolling, forging etc. The ingot also serves as the other electrode in the process. The slag containing the contaminants is removed as a solid and can be reused or appropriately disposed.

FIGURE 1: SCHEMATIC OF THE ESR FURNACE

1.4 Importance of Slag in the ESR Process

The slag in the ESR process is crucial for its success [2]. For instance, it must have a high capacity for incorporating the contaminants with a high partition coefficient between the slag and the metal. Its interfacial properties must be such that it wets the metal for effective removal of the contaminants, but it must not facilitate formation of slag skin over the ingot. Along with surface tension its density and viscosity must be such that it provides sufficient residence time for the metal droplets without adversely affecting slag fluidity and mass transfer properties. The electrical conductivity must be such that it

provides efficient joule heating while still permitting a reasonable melt rate. The volatilization rate and the volatile species must be known for determining effective means of capture. The solid-state slag structure must be such that the phases formed are stable and non leachable for ease of handling and disposal. It is also desirable to minimize the slag skin around the ingot and concentrate the radioactive contaminants in the slag cap over the ingot.

2.0 ESR SLAG AND SYSTEM USED

The ESR base slag investigated in this research is 60wt%CaF₂-20wt%CaO-20wt%Al₂O₃. The ternary plot of the system is shown in Figure 2 [3]. Preliminary ESR trials have shown that this slag can be used to decontaminate radionuclides and chemical surrogates from contaminated stainless steel [2,4]. In this program, the potential radioactive contaminants of interest to be removed from the stainless steel are uranium (U), plutonium (Pu), cesium (Cs), strontium (Sr) and technetium (Tc). Due to high oxygen affinity of U, Pu, Cs, Sr and Tc, these radioactive contaminants are expected to be present as oxides in decommissioned nuclear processing, fabrication or in nuclear reactor facilities either as surface contaminants or lodged in cracks and crevices of piping or other components. The nonradioactive surrogates used to simulate and test these radioactive contaminants are oxides of Ce and Hf (for U and Pu oxides), Re (for Tc oxide) and Cs and Sr (for their radioactive counterparts). The properties used for surrogate selection are reported in Table I.

FIG. 1707.—System CaF₂-CaO-5CaO·3Al₂O₃.
W. Eitel, *Zement*, 27, 30 (1938).

FIGURE 2: EQUILIBRIUM PHASE DIAGRAM

Table I: Radioactive and Surrogate Compound Properties

Solid Compound	Molecular Weight (g/mol)	Density (g/cm ³)	Melting Point (°C)	Boiling Point (°C)	Oxidation States	Electron Affinity	$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ (kJ/mol)	ΔG° Temperature Range (°C)
U	238	198.05	1132	3818	3 ⁺ ,4 ⁺ ,5 ⁺ ,6 ⁺	1.38	-	-
UO ₂	270	10.96	2878	NA			-1084.91 - .077822T	25 - 1227
U ₃ O ₈	842	8.3	d. 1300	NA			NA	NA
Pu	239.1	16.5-17.7	122-639	NA	3 ⁺ ,4 ⁺ ,5 ⁺ ,6 ⁺	1.28	-	-
PuO ₂	271.1	11.46	2400	NA			-1055.83 - .066128T	25 - 2442
Ce	140.1	6.66	799	3426	3 ⁺ ,4 ⁺	1.12	-	-
CeO ₂	172.1	7.13	2600	NA			-1088.68 - .0623T	25 - 1727
Ce ₂ O ₃	328.4	6.86	1692	NA			-1796.19 - .150582T	25 - 927
Hf	178.5	13.31	2227	4602	4 ⁺	1.3	-	-
HfO ₂	210.5	9.68	2812	NA			10.46 - .005301T	1700 - 2900
Tc	98	11.5	2200	5027	4 ⁺ ,6 ⁺ ,7 ⁺	NA	-	-
TcO ₂	130	NA	2127	NA			-433.044 - .054392T	25 - 927
TcO ₃	146	NA	927	NA			-539.736 - .077404T	25 - 127
Sr	87.6	2.6	769	1384	2 ⁺	0.95	-	-
SrO	103.6	4.7	2430	NA			-592.036 - .055522T	25 - 727
Cs	132.9	1.88	28.4	669	1 ⁺	0.79	-	-
Cs ₂ O	281.8	4.25	NA	NA			-345.975 - .146858T	25 - 490
Re	186.2	20.53	3180	5627	4 ⁺ ,6 ⁺ ,7 ⁺	1.9	-	-
ReO ₂	218.2	11.4	NA	NA			-448.943 - .047827T	25 - 1127
Re ₂ O ₇	484.4	6.1	297	Subl. 250			0.084 - .000205T	140 - 327

This paper reports the results of an ongoing research effort. The ESR slag that is investigated here is 60wt%CaF₂-20wt%CaO-20wt%Al₂O₃ with and without xCeO₂ (CeO₂ is the nonradioactive surrogate for U and Pu oxides); 'x' varying from 250ppm to 25wt%. The investigation conducted included measurements of CeO₂ solubility in the slag, slag-metal partition coefficient for Ce, slag volatilization, viscosity, electrical conductivity and surface tension. The measurements were made primarily between 1400-1650°C and were extrapolated to higher temperatures by utilizing the Arrhenius relationship.

3.0 EXPERIMENTAL

3.1 Solubility Studies

Experiments were conducted in an open-air induction furnace by melting and equilibrating 10g of either base slag (60wt%CaF₂-20wt%CaO-20wt%Al₂O₃) or 10g of base slag mixed with different amounts of ceria (Table II). The experimental setup is schematically shown in Figure 3. The base slag was prepared by self-milling the constituent powders. The ceria (produced by sol-gel) was sintered in air at 1695°C to a theoretical density of over 90% as a 3/4" closed-porosity pellet. Portions of the ceria pellet were broken and added to the slag as needed. The slag samples were all isothermally held at 1500°C for 15 minutes and air quenched. This process was determined to be adequate for equilibrating the molten slag.

The quenched graphite crucible was sectioned along the central axis with a low speed diamond saw using an oil lubricant. The sample was cleaned with methanol and mounted either in an acrylic or epoxy medium. The sample was polished with diamond paste and cleaned during the process with methanol.

Table II: Details of the Solubility Experiments

Mass of Base Slag (g)	Mass of CeO ₂ (g)	Weight Percent of CeO ₂	Results of Air Quenched (from 1500°C)
10.000	0.000	0.00	2-phase structure
10.155	0.0025	0.025	2-phase structure
9.973	0.010	0.10	2-phase structure
10.065	0.051	0.50	2-phase structure
10.010	0.105	1.00	2-phase structure
10.000	0.254	2.50	2-phase structure
10.060	0.495	4.70	2-phase structure
10.907	0.990	8.30	3-phase structure
10.028	1.510	13.10	3-phase structure
10.031	2.996	23.00	3-phase structure

The polished samples were analyzed with Electron Micro Probe (EMP) JEOL SuperProbe 7300. Wavelength Dispersed Spectroscopy was used for the chemical analysis; the standards used are shown in Table III. A light element detector was used for

the fluorine and oxygen analysis. Image analysis was used to determine the fraction of each type of phase present. By combining the image analysis with the composition analysis of the phases, a comparison was made between the analyzed and theoretical composition of the slag.

FIGURE 3: EXPERIMENTAL SET UP FOR CeO_2 SOLUBILITY STUDY

Table III: Standards Used in EMP Analysis

Element	F	Ce	Al	Ca	O
Standard	CaF_2	CePO_4	Al_2O_3	$\text{CaAl}_2\text{SiO}_8$	Al_2O_3

EMP analyses showed that the air-quenched base slag is homogeneous and has a two-phase structure, one is darker than the other. The backscattered electron image (BEI) and the composition of the two phases are shown in Figure 4 and Table IV, respectively. The dark phase contained Al-Ca-O-F. If we assume that the fluorine is associated with Ca as CaF_2 , then the remaining Al-Ca-O had a composition that closely matched $5\text{CaO}-3\text{Al}_2\text{O}_3$. The lighter phase contained Ca-F and its composition matched CaF_2 . The dark-colored phase (Al-Ca-O-F), solidified first, and the Ca-F phase which is the light colored phase solidified later. These observations agree with the expected crystallization path of the

slag (Figure 2). When CeO_2 was added to the slag up to 4.7wt%, the air-quenched slag still had the same two-phase structure. The higher melting Al-Ca-O-F phase had a higher concentration of Ce in solid solution and the Ca-F phase had a much lower concentration of Ce. These observations are shown in Figures 5-10 and Tables V-X. It is interesting to note that when the CeO_2 content is 2.5wt% or more in the base slag, the BEI of the Al-Ca-O-F phase with Ce in solid solution changes from dark to light. This is due to the variable Ce content. When the CeO_2 content was 8.3wt% or more, there appeared a third crystalline Ce-rich phase that grew in size as the CeO_2 content increased. This is shown in Figures 11-13 and the composition of the phases are listed in Tables XI-XIII. However, these high CeO_2 levels may not be interest to the ESR decontamination process, because the level of CeO_2 in the slag phase is not expected to exceed a couple 1000ppm.

FIGURE 4: BEI OF PURE BASE SLAG

Table IV: EMP Analysis of Base Slag

Phase	Weight%						Atomic%					
	Ca	Al	Ce	O	F	Total	Ca	Al	Ce	O	F	Total
Dark	40.2	18.76	0.048	33.09	9.47	101.56	23.514	16.298	0.008	48.49	11.69	100
Light	54.9	0.409	0.063	0	47.02	102.4	35.483	0.3922	0.012	0	64.11	100

Composition	47.77413	9.304	0.055	16.04	28.82	101.99
Theoretical	45.1	10.6	0	15.1	29.2

FIGURE 5: BEI OF BASE SLAG WITH 0.025WT% CEO2

Table V: EMP Analysis of Base Slag with 0.025wt% CeO₂

Phase	Weight%						Atomic%					
	Ca	Al	Ce	O	F	Total	Ca	Al	Ce	O	F	Total
Top Light	57.57	0.021	0.036	0	48.08	105.7	36.1844	0.0195	0.007	0	63.79	100
Top Dark	36.89	22.55	0.063	35.2	7.51	102.22	21.1427	19.208	0.01	50.55	9.088	100
Bottom Light	57.55	0.036	0.047	0	47.96	105.59	36.2311	0.0336	0.008	0	63.73	100
Bottom Dark	36.73	22.99	0.009	35.39	6.75	101.87	21.1306	19.648	0.001	51.02	8.2	100

Composition Top	45.142	13.56	0.052	21.15	23.7	103.61
Composition Bottom	45.3356	13.5	0.024	20.76	23.78	103.41
Theoretical	45.1	10.58	0.02	15.12	29.2

FIGURE 6: BEI OF BASE SLAG WITH 0.10WT% CEO2

Table VI: EMP Analysis of Base Slag with 0.10wt% CeO₂

Phase	Weight%						Atomic%					
	Ca	Al	Ce	O	F	Total	Ca	Al	Ce	O	F	Total
Top Light	57.7	0.025	0.037	0	47.43	105.2	36.5523	0.0235	0.007	0	63.42	100
Top Dark	36.91	23	0.262	35.85	6.97	103	21.0042	19.45	0.043	51.13	8.374	100
Bottom Light	56.7	0.018	0.039	0	47.58	104.34	36.0783	0.0173	0.007	0	63.9	100
Bottom Dark	39.89	19.79	0.165	35.86	7.78	103.49	22.7111	16.751	0.027	51.16	9.35	100

Composition Top	45.5824	13.42	0.168	20.90	23.85	103.91
Composition Bottom	46.84251	11.61	0.113	21.03	24.24	103.84
Theoretical	45.1	10.58	0.081	15.12	29.2

FIGURE 7: BEI OF BASE SLAG WITH 0.50WT% CEO2

Table VII: EMP Analysis of Base Slag with 0.50wt% CeO₂

Phase	Weight%						Atomic%					
	Ca	Al	Ce	O	F	Total	Ca	Al	Ce	O	F	Total
Top Light	56.28	0.054	0.193	0	48.43	140.96	35.4797	0.0505	0.035	0	64.43	100
Top Dark	36.36	22.41	0.736	36.55	6.27	102.32	20.8087	19.063	0.12	52.43	7.577	100
Bottom Light	55	0.486	0.149	0.73	47.5	103.86	34.8506	0.4577	0.027	1.153	63.51	100
Bottom Dark	36.12	22.85	0.779	35.3	7.11	102.17	20.787	19.546	0.128	50.9	8.635	100

Composition Top	44.83883	12.89	0.505	20.99	24.22	103.45
Composition Bottom	43.60199	13.99	0.529	21.6	23.12	102.83
Theoretical	44.8745	10.53	0.415	15.05	29.05

FIGURE 8: BEI OF BASE SLAG WITH 1.0WT% CEO2

Table VIII: EMP Analysis of Base Slag with 1.0wt% CeO₂

Phase	Weight%						Atomic%					
	Ca	Al	Ce	O	F	Total	Ca	Al	Ce	O	F	Total
Top Light	54.54	0.054	0.281	0	48.89	103.77	34.5419	0.051	0.051	0	65.36	100
Top Dark	35.29	22.8	1.518	36.01	6.56	102.17	20.3154	19.503	0.25	51.96	7.969	100
Bottom Light	55.82	0.056	0.262	0	46.97	103.11	35.9907	0.0535	0.048	0	63.91	100
Bottom Dark	35.32	22.84	1.545	35.4	6.48	101.59	20.5254	19.724	0.257	51.55	7.949	100

Composition Top	41.95525	14.92	1.09	23.54	21.22	102.73
Composition Bottom	42.81487	14.51	1.076	22.46	21.28	102.14
Theoretical	44.63096	10.47	0.855	14.98	28.9

FIGURE 9: BEI OF BASE SLAG WITH 2.5WT% CEO2

Table IX: EMP Analysis of Base Slag with 2.5wt% CeO₂

Phase	Weight%						Atomic%					
	Ca	Al	Ce	O	F	Total	Ca	Al	Ce	O	F	Total
Top Light	34.8	22.06	3.63	35.54	6.51	102.54	20.2983	19.129	0.606	51.95	8.015	100
Top Dark	52.52	0.023	0.574	0	51.5	104.63	32.5361	0.0207	0.102	0	67.34	100
Bottom Light	52.07	0.035	0.565	0	51.7	104.38	32.2599	0.0322	0.1	0	67.61	100
Bottom Dark	34.46	22.26	3.55	35.47	6.98	102.73	20.0156	19.215	0.591	51.63	8.549	100

Composition Top	43.81416	10.85	2.076	17.46	29.4	103.6
Composition Bottom	43.03607	11.44	2.096	18.2	28.76	103.52
Theoretical	43.98152	10.29	2.01	14.79	28.4

FIGURE 10: BEI OF BASE SLAG WITH 4.7WT% CEO2

Table X: EMP Analysis of Base Slag with 4.7wt% CeO₂

Phase	Weight%						Atomic%					
	Ca	Al	Ce	O	F	Total	Ca	Al	Ce	O	F	Total
Top Light	32.75	21.24	6.84	34.70	5.40	100.93	19.8921	19.179	1.188	52.82	6.922	100
Top Dark	48.43	0.044	1.065	0.00	52.88	102.42	30.1946	0.0404	0.19	0	69.58	100
Bottom Light	32.82	21.25	6.79	34.61	6.90	102.37	19.5788	18.843	1.159	51.73	8.687	100
Bottom Dark	48.85	0.028	1.067	0.00	53.06	103	30.306	0.0262	0.189	0	69.48	100

Composition Top	40.4332	10.85	4.01	17.7	28.67	101.66
Composition Bottom	41.35002	9.957	3.745	16.19	31.46	102.71
Theoretical	42.9803	10.08	4.032	14.5	27.83

FIGURE 11: BEI OF BASE SLAG WITH 8.3WT% CEO2

Table XI: EMP Analysis of Base Slag with 8.3wt% CeO_2

Phase	Weight%						Atomic%					
	Ca	Al	Ce	O	F	Total	Ca	Al	Ce	O	F	Total
Top Light	30.36	21.25	12.45	35.54	7.84	107.44	17.749	18.451	2.082	52.04	9.674	100
Top Dark	46.46	1.223	2.663	3.18	39.79	93.32	32.964	1.289	0.54	5.644	59.56	100
Top Very Light	8.09	16.12	52.2	23.91	2.287	102.6	7.242	21.441	13.37	53.63	4.32	100
Bottom Light	30.94	20.01	12.42	30.57	6.09	100.02	20.136	19.343	2.313	49.85	8.356	100
Bottom Dark	46.11	3.06	3.65	11.08	39.85	103.75	28.198	2.7797	0.638	16.97	51.41	100
Overall Composition	39.11035	10.37	7.131	17.95	25.2	99.763						
Theoretical	41.07	9.63	8.94	13.77	26.59

FIGURE 12: BEI OF BASE SLAG WITH 13.1WT% CEO2

Table XII: EMP Analysis of Base Slag with 13.1wt% CeO₂

Phase	Weight%						Atomic%					
	Ca	Al	Ce	O	F	Total	Ca	Al	Ce	O	F	Total
Top Light	30.15	16.38	16.46	28.59	9.7	101.28	19.932	16.086	3.112	47.35	13.52	100
Top Dark	47.92	0	3.68	0.377	47.81	99.79	31.785	0	0.698	0.626	66.89	100
Top Very Light	9.03	16.11	50.55	25.44	2.237	103.36	7.791	20.653	12.48	55	4.073	100
Bottom Light	29.59	18.93	17.36	29.45	5.57	100.89	19.971	18.972	3.351	49.78	7.925	100
Bottom Dark	48.72	0	3.62	0.126	48.97	101.44	31.765	0	0.675	0.206	67.35	100
Bottom Very Light	30.29	16.6	19.42	32.55	0.895	99.75	21.047	17.13	3.859	56.65	1.311	100
Overall Composition	37.68135	9.053	11.41	15.92	26.59	100.65						
Theoretical	39.12	9.19	13.1	13.14	29.37

FIGURE 13: BEI OF BASE SLAG WITH 23WT% CEO2

Table XIII: EMP Analysis of Base Slag with 23wt% CeO₂

Phase	Weight%						Atomic%					
	Ca	Al	Ce	O	F	Total	Ca	Al	Ce	O	F	Total
Top Dark	42.5	14.63	3.02	37.05	1.587	98.78	26.358	13.475	0.535	57.56	2.076	100
Top Very Light	11.14	16.86	47.37	26.17	2.169	103.71	9.296	20.898	11.3	54.68	3.818	100
Top Crust Very Light	8.78	16.09	50.22	25.64	2.186	102.91	7.573	20.624	12.4	55.43	3.980	100
Bottom Dark	37.07	20.53	3.25	32.64	4.70	98.18	23.146	19.038	0.581	51.05	6.185	100
Bottom Very Light	23.97	11.74	38.46	24.54	4.65	103.35	19.379	14.096	8.896	49.7	7.928	100
Bottom Very Light 1	2.9608	14.21	62.2	21.89	2.997	104.26	2.8738	20.493	17.270	53.23	6.136	100
Overall Composition	37.0904	15.01	10.67	35.17	1.687	99.636						
Theoretical	34.73	8.15	23	11.6	22.5							

3.2 Slag-Metal Partition Coefficient

The foregoing observations have profound implication on the slag-metal partition coefficient. Since the CeO_2 is completely soluble in the ESR slag (60wt% CaF_2 -20wt% CaO -20wt% Al_2O_3), it implies that the CeO_2 activity in the ESR slag will be extremely small since its concentration is not expected to exceed 2000 ppm. Therefore, from the Ce/CeO_2 equilibrium (Table 1), it is reasonable to expect that the Ce concentration in the metal phase will be below the detection limit (<1ppm). This has been observed experimentally.

The solidification behavior (crystallization path) of the slag system, as discussed in the previous section, suggests that it is possible for the slag skin over the ingot to have a higher ceria concentration than the slag cap; this is undesirable. This will be verified in future experiments. If high ceria partitioning between the slag skin and the cap is found to occur then the slag properties need to be tailored by changing its composition in order to avoid such partitioning.

3.3 Volatilization Study

The purpose of the study is to determine the rate at which the base slag and the base slag mixed with different amounts of ceria volatilizes as a function of temperature and the chemical nature of the volatile species. This is accomplished using a thermogravimetric (TG) balance and a quadrupole mass analyzer. Also, the volatile species were condensed and chemically analyzed.

The TG balance used was a CAHN D-100 Series system that is run with CAHN D-100 Series software version 2.0. The experiments are conducted in a graphite crucible suspended in a purified argon atmosphere to prevent oxidation of the crucible material. The arrangement is schematically shown in Figure 14. In order to measure the volatilization rate of the slag with CeO_2 , it was necessary to reduce the CeO_2 to Ce_2O_3 prior to melting the slag, so that the vaporization rate could be attributed to slag volatilization instead of to CeO_2 reduction. Under the experimental conditions maintained in the TG experiments, Ce_2O_3 was the stable phase (Figure 15). Typical TG results with

base slag and base slag with ceria are shown in Figures 16 and 17. The important runs to date and the calculated evaporation rates are listed in Table XIV. The natural logarithm of the evaporation rate as a function of inverse temperature for the runs reported in Table XIV are shown in Figure 18. From Figure 18, it can be seen that the volatilization rate of the base slag and the base slag with ceria did not differ much and followed an Arrhenius behavior. The volatilization rate of the base slag as a function of temperature can be expressed as:

$$R = 3445.26 \exp\left(-\frac{37955.09}{T}\right)$$

FIGURE 14: THERMOGRAVIMETRY EXPERIMENTAL SET UP TO STUDY VOLATILIZATION

FIGURE 15: PHASE DIAGRAM OF CE-C-O SYSTEM

FIGURE 16: THERMOGRAVIMETRIC
EXPERIMENT WITH BASE SLAG

FIGURE 17: THERMOGRAVIMETRIC
EXPERIMENT OF BASE SLAG WITH
100PPM CeO_2

Table XIV: Thermogravimetric Experiments and Results

Experiment Type	Base Slag Mass (g)	CeO ₂ Mass (g)	Temperature (°C)	Volatilization Rate (g/cm ² -sec.)
Pure Base Slag	37.687		1450	1.010E-06
Pure Base Slag	37.687		1500	1.500E-06
Pure Base Slag	37.687		1550	3.280E-06
Pure Base Slag	37.687		1600	5.560E-06
100ppm Ceria	38.017	0.00382	1450	1.378E-06
100ppm Ceria	38.017	0.00382	1500	1.892E-06
100ppm Ceria	38.017	0.00382	1550	3.313E-06
100ppm Ceria	38.017	0.00382	1600	4.958E-06
40000ppm Ceria	36.009	1.440	1450	7.006E-07
40000ppm Ceria	36.009	1.440	1500	2.193E-06
40000ppm Ceria	36.009	1.440	1550	4.001E-06
40000ppm Ceria	36.009	1.440	1600	6.286E-06
100000ppm Ceria	34.896	3.4896	1450	8.921E-07
100000ppm Ceria	34.896	3.4896	1500	2.318E-06
100000ppm Ceria	34.896	3.4896	1550	4.002E-06
100000ppm Ceria	34.896	3.4896	1590	5.965E-06

FIGURE 18: COMPARISON OF RESULT OF VOLATILIZATION EXPERIMENTS

3.4 Volatile Species

The experimental setup used to condense the volatile slag species onto a water-cooled copper coil is shown in Figure 19. The condensed vapor was an amorphous powder. Therefore, in order to analyze by X-ray diffraction, an attempt was made to crystallize the powder by annealing at 1000°C. The diffraction pattern showed the presence of CaF_2 (Figure 20). In order to determine the uncondensed volatile species, the volatile gas from the base slag was passed through a quadrupole mass analyzer as shown in Figure 21. The spectra from the mass analyzer (Figure 22) showed presence of AlF_3 among the volatile species.

FIGURE 19: EXPERIMENTAL SETUP FOR IDENTIFICATION OF VOLATILE SPECIES

FIGURE 20: X-RAY DIFFRACTION RESULT

- ⇒ Base slag 141.5 g
- ⇒ Graphite Tray
 - Length 13.335cm
 - Width 3.81cm
 - Depth 25.4cm
- ⇒ Helium flow rate 0.2 l/min.
- ⇒ Held at 1500C for 6 hr
- ⇒ Mass Spectrometer used for vapor specie analysis

FIGURE 21: EXPERIMENTAL SETUP FOR IDENTIFICATION OF VOLATILE SPECIES

FIGURE 22: MASS SPECTROSCOPY ANALYSIS OF THE VOLATILE SPECIES

3.5 Viscosity Studies

The viscosity of the base slag was measured using an inner cylinder rotation technique. The schematic of the set up is shown in Figure 23. The viscosity measurements were conducted as a function of temperature. The results are shown in Table XV and plotted in Figure 24. From Figure 24, it is apparent that there is a drastic increase in the viscosity of the base slag as the temperature decreases from 1400°C to 1390°C. This means that the base slag does not remain as a single phase below 1390°C. This conclusion is consistent with the liquidus temperature of the base slag as suggested in Figure 2. Furthermore, above 1400°C the viscosity is not a strong function of the temperature indicating that the slag is fluid and does not have long polymeric chains. The measured volatilization rate is not significant to change the fluorine content of the slag during the ESR process and therefore the slag viscosity is not expected to change.

Table XV: Base Slag Viscosity Data as a Function of Temperature

Temperature (k)	Viscosity (dPa.s)
1500	0.868
1500	0.707
1450	0.748
1400	0.708
1390	7.461
1380	6.806
1370	19.301

FIGURE 23: SET UP FOR VISCOSITY MEASUREMENT

FIGURE 24: ARRHENIUS PLOT OF BASE SLAG VISCOSITY

3.6 Surface Tension Measurements

The surface tension measurements were made using the maximum bubble pressure method. The schematic of the set up is shown in Figure 25. The measurements were made as a function of temperature. The results are shown in Table XVI and plotted in Figure 26. Figure 26 shows that the surface tension of the molten slag follows an Arrhenius behavior.

FIGURE 25: SET UP FOR SURFACE TENSION

FIGURE 26: ARRHENIUS PLOT OF BASE SLAG SURFACE TENSION

Table XVI: Surface Tension Data of Base Slag as a Function of Temperature

Temperature (k)	Surface Tension (dyne/cm)
1673	336
1683	322
1693	316
1703	311
1713	313
1723	306
1723	294

3.7 Electrical Conductivity Study

The electrical conductivity was measured using an AC impedance method with 2 point electrodes, as shown in Figure 27. The cell constant was determined by measuring the electrical conductivity of a KCl standard solution at 25°C. The electrical conductivity of

the base slag was measured as a function of temperature (Table XVII). The single Arrhenius behavior (Figure 28) above and below the single-phase region (around 1390°C) indicates that the conduction mechanism remains primarily unchanged, probably dominated by the F ions.

FIGURE 27: SET UP OF ELECTRICAL CONDUCTIVITY

FIGURE 28: ARRHENIUS PLOT OF CONDUCTIVITY

Table XVII: Conductivity Data of Base Slag as a Function of Temperature

Temperature	Conductivity
1583	1.15
1603	1.24
1653	1.49
1673	1.60
1693	1.71
1723	1.83

A novel calibration free conductivity cell has been developed that measures the molten slag impedance as a function of electrode height. The electrodes are coaxial and symmetrical as shown in Figure 29. From the slope of the linear plot of slag impedance as a function of the depth of electrode immersed, the slag conductivity is calculated. The technique has been successfully developed and it will be used to measure the slag conductivity in the future.

FIGURE 29: CALIBRATION FREE CONDUCTIVITY CELL

4.0 Concluding Remarks

The ESR base slag (60wt%CaF₂-20wt%CaO-20wt%Al₂O₃) has a high capacity for incorporating CeO₂ (surrogate for Pu and U oxides) and results in excellent slag-metal separation of the contaminant. However, it is also desirable to minimize the slag skin around the ingot, concentrate the radioactive contaminants in the slag cap over the ingot, and improve the surface quality of the ingot. In order to address these issues, the interfacial tension, viscosity, and solidification behavior were determined. Future experiments will attempt to alter these properties by adding varying amounts of TiO₂ and deoxidants and study the effect on the slag skin over the ingot and the slag cap. The measured slag volatilization followed Arrhenius behavior. Volatilization rates of the base slag were low, and ceria impurity incorporated in the slag does not significantly alter the volatilization rate. The volatile species were primarily CaF₂ and AlF₃. The electrical conductivity of the slag follows an Arrhenius behavior and provides efficient Joule Heating during the ESR process. Our ESR melt decontamination studies are continuing, and further results will be reported later.

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