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**The Effects of Slag Composition
and Process Variables on
Decontamination of Metallic
Wastes by Melt Refining**

B. Heshmatpour
G. L. Copeland

MASTER

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METALS AND CERAMICS DIVISION

THE EFFECTS OF SLAG COMPOSITION AND PROCESS VARIABLES ON
DECONTAMINATION OF METALLIC WASTES BY MELT REFINING

B. Heshmatpour and G. L. Copeland

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THE EFFECTS OF SLAG COMPOSITION AND PROCESS VARIABLES ON
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B. Heshmatpour and G. L. Copeland

ABSTRACT

Melt refining has been suggested as an alternative for decontamination and volume reduction of low-level-contaminated metallic wastes. Knowledge of metallurgical and thermochemical aspects of the process is essential for effective treatment of various metals. Variables such as slag type and composition, melting technique, and refractory materials need to be identified for each metal or alloy. Samples of contaminated metals were melted with fluxes by resistance furnace or induction heating. The resulting ingots as well as the slags were analyzed for their nuclide contents, and the corresponding partition ratios were calculated. Compatibility of slags and refractories was also investigated, and proper refractory materials were identified. Resistance furnace melting appeared to be a better melting technique for nonferrous scrap, while induction melting was more suitable for ferrous metals. In general uranium contents of the metals, except for aluminum, could be reduced to as low as 0.01 to 0.1 ppm by melt refining. Aluminum could be decontaminated to about 1 to 2 ppm U when certain fluoride slags were used. The extent of decontamination was not very sensitive to slag type and composition. However, borosilicate and basic oxidizing slags were more effective on ferrous metals and Cu; NaNO_3 - NaCl - NaOH type fluxes were desirable for Zn, Pb, and Sn; and fluoride type slags were effective for decontamination of Al. Recrystallized alumina proved to be the most compatible refractory for melt refining both ferrous and nonferrous metals, while graphite was suitable for nonferrous metal processing. In conclusion, melt refining is an effective technique for volume reduction and decontamination of contaminated metal scrap when proper slags, melting technique, and refractories are used.

INTRODUCTION

The extensive nuclear operations that involve work with transuranic (TRU) elements have resulted in accumulation of large quantities of contaminated waste. Metals constitute about 30% of the volume of such waste

and cannot be burned or otherwise treated as can the combustible material. Furthermore, detection of very low levels of contamination in complicated metallic forms is not feasible. Current Department of Energy (DOE) guidelines require retrievable storage of all DOE wastes containing TRU elements above 10 nCi/g (370 Bq/g). The high cost of this retrievable storage and ultimate disposal in a repository is a strong incentive to reduce the volume requiring storage. The purposes of the present study are to demonstrate the feasibility of cleaning and reducing the volume of contaminated metals and transforming them into readily assayed form.

Prior work in this area has shown that melting for volume reduction is a technically feasible approach for consolidating metal waste and that melting effectively removes uranium contamination from many metals.¹ The removal of TRU elements appears feasible also but has not been extensively demonstrated. Melt refining steels contaminated with plutonium has been suggested as a possible decontamination process that has the potential advantages of producing steel for reuse and simplifying analytical problems.² Results of laboratory-scale investigations have indicated a high degree of decontamination of plutonium- and americium-contaminated metals by pyrochemical methods.^{3,4} In general, these studies were limited to steel, and the effects of slag weight and composition were not extensively investigated. In this report the emphasis is on the effect of slag weight and composition on decontamination of both ferrous and nonferrous metals. Uranium oxide is used as the contaminant to simplify the experiments and minimize the health hazards. The results of this investigation are being presently applied and tested on TRU-contaminated metals.

THERMODYNAMICS

The thermodynamic treatment of the removal of TRU contaminants from a metal by melting assumes that the contaminant can combine with oxygen and enter a slag that acts as an inert solvent for the resulting oxides.¹ It also assumes a complete thermodynamic equilibrium between the liquid metal and the slag. Oxidation of a pure contaminant metal *i* can be expressed as

where

ΔG_1° = standard Gibbs free energy of formation of iO;

R = ideal gas constant;

T = absolute temperature, K;

P_{O_2} = oxygen partial pressure.

In practice, a very small quantity of contaminant metal is present in the solvent metal, and therefore the standard state must be changed from pure i to i in infinite dilution, $\underline{i}$; that is,

$$i \rightarrow \underline{i}, \quad \Delta G_2 = RT \ln a(i), \quad (2)$$

where ΔG_2 is the Gibbs free energy and $a(i)$ is the activity of i in the solvent metal.

Assuming that i obeys Henry's law in the solvent metal, then

$$a(i) = \gamma^\circ(i)X(i), \quad (3)$$

where $\gamma^\circ(i)$ and $X(i)$ are the thermodynamic activity coefficient and the atomic fraction of i, respectively, in the solvent in atomic fraction scale. Thus,

$$\Delta G_2 = RT \ln \gamma^\circ(i)X(i). \quad (4)$$

For convenience the weight percent scale is preferred over the atomic fraction scale and $X(i)$ is expressed as

$$X(i) = \frac{\text{wt \% } i}{(100 - \text{wt \% } i)M(i)/M(m) + \text{wt \% } i}, \quad (5)$$

where

wt % i = weight percent of i in the solvent metal m,

$M(i)$ = atomic weight of i,

$M(m)$ = atomic weight of m.

The solution is assumed to be composed of i and m only. At infinite dilution

$$a(i) \rightarrow \text{wt \% } i . \quad (6)$$

Taking 1 wt % i as the standard state for uranium in liquid iron, Eq. (5) results in

$$X(U) \approx 2.364 \times 10^{-3} \text{ (atomic fraction) } .$$

Substituting this value in Eq. (4) and combining Eqs. (1) and (2) and the corresponding ΔG_1° and ΔG_2 for uranium we obtain

$$\Delta G_7^\circ = \Delta G^\circ(UO_2) - RT \ln[(2.364 \times 10^{-3}) \gamma^\circ(U)] , \quad (8)$$

where $\Delta G^\circ(UO_2)$ is the standard Gibbs free energy of formation of UO_2 . Obviously, if uranium obeys Henry's law in liquid iron, the solvent will behave ideally in iron-uranium solutions. Therefore,

$$a(Fe) = X(Fe) = 1 - X(U) \approx 0.9976 . \quad (9)$$

The oxidation of iron also is expressed as

where $\Delta G^\circ(FeO)$ is the standard Gibbs free energy of formation of FeO . Both oxides FeO and UO_2 will be contained in the slag and could be safely assumed to behave ideally for a narrow range of composition. Therefore,

$$a(UO_2) \approx X(UO_2) , \quad (11)$$

and

$$a(FeO) \approx X(FeO) . \quad (12)$$

Assuming that the slag is composed of 50 CaO, 44 SiO₂, 5 FeO, and 1 UO₂ (wt %), then X(FeO) and X(UO₂) can be calculated from the following relations:

$$X(\text{FeO}) = (\text{wt \% FeO}) / \left[(\text{wt \% CaO}) \frac{M(\text{FeO})}{M(\text{CaO})} + (\text{wt \% SiO}_2) \frac{M(\text{FeO})}{M(\text{SiO}_2)} + (\text{wt \% UO}_2) \frac{M(\text{FeO})}{M(\text{UO}_2)} + (\text{wt \% FeO}) \right], \quad (13)$$

and

$$X(\text{UO}_2) = (\text{wt \% UO}_2) / \left[(\text{wt \% CaO}) \frac{M(\text{UO}_2)}{M(\text{CaO})} + (\text{wt \% SiO}_2) \frac{M(\text{UO}_2)}{M(\text{SiO}_2)} + (\text{wt \% FeO}) \frac{M(\text{UO}_2)}{M(\text{FeO})} + (\text{wt \% UO}_2) \right]. \quad (14)$$

Substituting the corresponding values we obtain

$$X(\text{FeO}) \cong 4.10 \times 10^{-2} \text{ (atomic fraction)},$$

and

$$X(\text{UO}_2) \cong 2.18 \times 10^{-3} \text{ (atomic fraction)}.$$

Combining Eqs. (7) and (10) results in

$$\underline{\text{U}} + 2\text{FeO}(\text{slag}) = \text{UO}_2(\text{slag}) + 2\text{Fe}(\text{L}), \quad (15)$$

$$\begin{aligned} \Delta G_{15}^\circ &= \Delta G^\circ(\text{UO}_2) - 2\Delta G^\circ(\text{FeO}) - RT \ln[(2.364 \times 10^{-3})\gamma^\circ(\text{U})] \\ &= -RT \ln \frac{X(\text{UO}_2)X^2(\text{Fe})}{X^2(\text{FeO})(\text{wt \% U})}, \end{aligned} \quad (16)$$

or

$$\ln(\text{wt \% U}) = \frac{\Delta G^\circ(\text{UO}_2) - 2\Delta G^\circ(\text{FeO})}{RT} + \ln \frac{X(\text{UO}_2)X^2(\text{Fe})}{(2.364 \times 10^{-3})\gamma^\circ(\text{U})X^2(\text{FeO})}. \quad (17)$$

Equations (15), (16), and (17) describe the thermodynamic equilibrium between the slag and the liquid metal. For 1900 K Glassner⁵ reported the following values for $\Delta G^\circ(\text{UO}_2)$ and $\Delta G^\circ(\text{FeO})$:

$$\Delta G^\circ(\text{FeO}) = -140.9 \text{ kJ/mol } (-33.670 \text{ kcal/mol}) ,$$

and

$$\Delta G^\circ(\text{UO}_2) = -738.7 \text{ kJ/mol } (-176.550 \text{ kcal/mol}) .$$

Substituting these and the corresponding other quantities in Eq. (17) we obtain

$$\text{wt \% U} = (1.5 \times 10^{-10})/\gamma^\circ(\text{U}) . \quad (18)$$

The partition ratio, λ , is defined as the amount of contaminant in the slag, $m(\text{U})(\text{slag})$, divided by the amount of contaminant in the melt, $m(\text{U})(\text{melt})$; that is,

$$\lambda = \frac{m(\text{U})(\text{slag})}{m(\text{U})(\text{melt})} . \quad (19)$$

Previously the weight of slag was assumed to be 10% the weight of the melt.¹ In practice, a portion of the slag is adsorbed on the crucible that contains the liquid metal and the slag; thus the final weight of the slag is considerably smaller than the original weight of the added flux. It is also desirable to have small slag volumes if the decontamination remains effective. Reducing the slag volume reduces the volume of highly contaminated material requiring disposal or storage. Thus we assume that the final slag weight is about 5 wt % of the liquid metal. Therefore, for 100 g metal the slag weight will be 5 g, which contains 1 wt % (i.e., 0.05 g) UO_2 , as discussed earlier. As a result

$$\begin{aligned} m(\text{U})(\text{slag}) &= \frac{M(\text{U})}{M(\text{UO}_2)} m(\text{UO}_2) = \left(\frac{238.07}{270.07} \right) 0.05 \\ &= 0.04408 \text{ g} . \end{aligned} \quad (20)$$

Similarly

$$\begin{aligned} m(\text{U})(\text{melt}) &= m(\text{metal})(\text{wt \% U}) \\ &= 100(\text{wt \% U}) . \end{aligned} \quad (21)$$

Substituting these values and the value of wt % U from Eq. (18) in Eq. (19), we obtain

$$\lambda = (2.95 \times 10^6) \gamma^\circ(\text{U}) . \quad (22)$$

We have not identified a reported value for $\gamma^\circ(\text{U})$ in liquid iron. Dealy and Pehlke⁶ reported values of γ° for infinitely dilute solutions of uranium and some other solutes in various solvents. These values are given in Table 1.

Table 1. Thermodynamic Activity Coefficient, γ° , at Infinite Dilution in Liquid Metals

Solvent	Solute	γ°	Temperature (°C)
Bi	U	1.6×10^{-5}	450
		2.5×10^{-5}	507
		4.6×10^{-5}	540
		7.8×10^{-5}	570
		5.5×10^{-5}	700
Cd	Na	0.01	350
		0.01	395
		6.58	467
		8.15	507
Fe	Al	0.063	1600
	B	0.022	1600
	Si	0.0072	1600
	Ti	0.011	1627
		0.048	1600
	Zr	0.0076	1600
Ni ^a	Ti	1.00×10^{-5}	1600
Pb	Na	0.0022	400

^aSource: D. J. Bradley, *The Thermodynamics of Carbon in Nickel-Based Multicomponent Solid Solutions*, ORNL/TM-6282 (April 1978) p. 144.

By inspecting these quantities one expects a value between 0.1 and 10^{-5} for $\gamma^\circ(\text{U})$ in liquid iron. Values of the uranium content, $\text{U}(\text{ppm})$, in liquid iron and the corresponding values of λ , which were calculated from Eqs. (18) and (22) for $\gamma^\circ(\text{U})$ between 0.1 and 10^{-5} , are presented in Table 2. These values are about five orders of magnitude smaller than the previous calculations.¹ The difference is attributed to errors in calculations and assumptions in previous studies. Starkey and co-workers⁷ reported values of 3 ppm U and 6×10^2 for λ for their experimental melt refining of uranium-contaminated scrap steel. Results of our melt refining experiments on uranium-contaminated mild steel showed that a sample of 100 g mild steel with 10 g $\text{CaO-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$ flux results in an average uranium concentration of 1 ppm in the steel and 1000 ppm in the slag. This represents a value of about 10^2 for λ . Thus it seems reasonable to assign a value of 10^{-3} to 10^{-4} for $\gamma^\circ(\text{U})$ in liquid iron, which results in a partition ratio on the order of 10^2 to 10^3 . In practice, not only are the equilibrium conditions not completely met, but also some UO_2 may be entrapped in the melt. As a result, the theoretically expected decontamination levels are not obtained. Further discussion of the sources of error and the limitations are given in the next sections.

Table 2. Calculated Uranium Concentrations and Partition Ratios for Corresponding Uranium Activity Coefficients, $\gamma^\circ(\text{U})$, in Liquid Iron

$\gamma^\circ(\text{U})$	Uranium (ppm)	Partition Ratio, ^a λ
10^{-1}	1.5×10^{-5}	2.95×10^5
10^{-2}	1.5×10^{-4}	2.95×10^4
10^{-3}	1.5×10^{-3}	2.95×10^3
10^{-4}	1.5×10^{-2}	2.95×10^2
10^{-5}	1.5×10^{-1}	2.95×10

^aDefined as the amount of contaminant in the slag divided by the amount of contaminant in the melt.

EXPERIMENTAL METHODS

Melt refining was used throughout this study to measure the degree of decontamination and the corresponding partition ratios for metals and alloys contaminated with UO_2 . This investigation included mild steel, stainless steel, Al, Pb, Sn, Cu, Zn, Ni, and Pb-Sn alloys. To contaminate a metal sample several parts per million UO_2 were thoroughly mixed with the flux and added to the metal in a crucible. The assembly was then melted in an induction or a resistance furnace and sufficient time was allowed for slag-metal separation and equilibration. The samples were then cooled to room temperature and samples were taken from the metal and the slag. Solidified slags were glassy and brittle and were easily separated from the metallic ingot and crushed into small fragments for sampling. Metallic ingots were drilled in the middle to a depth of about 5 mm and the chips were discarded. This was done to remove the slag from the surface of the ingot. Samples of the ingot were taken from the same hole by further drilling. Care was taken to minimize recontamination of the metal samples; however, some cross contamination does occur and leads to occasional scatter in the data. The samples of the metals and the slags were analyzed for their uranium content by fast-neutron activation analysis (FNAA). Details of the analytical technique are not discussed here and are given elsewhere.¹ Other aspects of the experimental technique are given in the next section. Compatibility of various crucible materials with various types of metallurgical slags was also studied and proper material selections were made for future melt refining applications.

RESULTS AND DISCUSSION

The results of melt refining for uranium decontamination of metals and alloys and the specific information on each sample are outlined below.

Mild Steel

Composition of the flux and, in some cases, the amount of UO_2 were varied for different experiments. Table 3 presents the metal and flux masses, UO_2 concentrations, and flux compositions for these experiments. The temperature was maintained at about 100°C above the melting point. Of the crucibles tried, quartz tubes performed best and worked better for resistance furnace heating than for induction heating. All other crucible materials were attacked moderately by the slags in resistance furnace melting and were severely corroded in induction melting. A considerable amount of flux was lost when it reacted with the crucible material, thus reducing the efficiency of the melt refining process. Results of the uranium analyses on the solidified metal and the corresponding slags are given in Table 4. In some cases the absorption of slag in crucible walls did not allow its subsequent sampling, and as a result the corresponding uranium contents could not be obtained and are not reported in Table 4.

The results indicated that the degree of decontamination is related to the extent of crucible attack. For example, for mild steel, alumina and zirconia crucibles were badly corroded by the slag, while quartz tubes worked well in resistance furnace melting; the corresponding partition ratios for quartz were also large. With a proper crucible material, less slag volume is required to achieve the desired degree of decontamination. Although induction melting reduces crucible life by accelerating slag attack, it provides sufficient contact between the slag and the metal and reduces the contamination to as low as 0.01 to 0.9 ppm U. On the contrary, resistance furnace melting provides somewhat better crucible life but allows less contaminant to enter the slag, which results in higher residual contamination.

The degree of decontamination was not highly sensitive to slag composition. However, borosilicate and highly fluid basic slags with relatively high Fe_2O_3 contents could reduce contamination to 0.01 to 1 ppm U. By using small volumes of these slags and properly choosing crucible material, uranium contents as low as 0.01 to 0.1 ppm could be achieved in the bulk for mild steel by induction melting.

Table 3. Details of Mild Steel Experiments

Sample	Metal (g)	Flux (g)	UO ₂ (ppm)	Flux Composition (wt %)
1	100	10	500	50 CaO, 50 Fe ₂ O ₃
2	100	10	500	40 CaO, 60 Fe ₂ O ₃
3	100	10	500	30 CaO, 70 Fe ₂ O ₃
4	100	10	500	20 CaO, 80 Fe ₂ O ₃
5	100	10	500	10 CaO, 90 Fe ₂ O ₃
6	100	10	1000	30 CaO, 70 Al ₂ O ₃
7	100	10	1000	20 CaO, 80 Al ₂ O ₃
8	50	5	1000	60 CaO, 10 SiO ₂ , 30 Fe ₂ O ₃
9	50	5	1000	55 CaO, 15 SiO ₂ , 30 Fe ₂ O ₃
10	50	5	1000	40 CaO, 30 SiO ₂ , 30 Fe ₂ O ₃
11	50	5	1000	30 CaO, 40 SiO ₂ , 30 Fe ₂ O ₃
12	50	5	1000	50 CaO, 25 SiO ₂ , 25 Fe ₂ O ₃
13	100	10	500	70 CaO, 10 SiO ₂ , 20 Fe ₂ O ₃
14	100	10	500	40 CaO, 40 SiO ₂ , 20 Fe ₂ O ₃
15	100	10	500	70 CaO, 20 SiO ₂ , 10 Fe ₂ O ₃
16	100	10	500	50 CaO, 40 SiO ₂ , 10 Fe ₂ O ₃
17	100	10	500	65 CaO, 35 SiO ₂
18	100	10	500	25 CaO, 75 SiO ₂
19	100	10	500	60 SiO ₂ , 40 Al ₂ O ₃
20	500	50	500	60 CaO, 25 Al ₂ O ₃ , 10 SiO ₂ , 5 CaF ₂
21	500	50	500	60 CaO, 10 Al ₂ O ₃ , 25 SiO ₂ , 5 CaF ₂
22	500	50	500	50 CaO, 25 Al ₂ O ₃ , 10 SiO ₂ , 10 CaF ₂ , 5 Fe ₂ O ₃
23	500	50	500	50 CaO, 10 Al ₂ O ₃ , 25 SiO ₂ , 10 CaF ₂ , 5 Fe ₂ O ₃
24	500	50	500	60 CaO, 35 SiO ₂ , 5 CaF ₂
25	100	10	500	Borosilicate glass ^a
26	160		500	No flux

^aNominal composition is 80 SiO₂, 13 B₂O₃, 4 Na₂O, 2 Al₂O₃, 1 K₂O (wt %).

Table 4. Results of Uranium Analyses in Mild Steel Experiments

Sample	Uranium, ppm		Partition Ratio, ^a λ	Melting Technique	Crucible Material
	Metal	Slag			
1	0.45			Induction	Quartz tube
2	0.42			Induction	Quartz tube
3	0.47			Induction	Quartz tube
4	0.36			Induction	Quartz tube
5	0.51			Induction	Quartz tube
6	0.31			Induction	Quartz tube
7	0.20			Induction	Quartz tube
8	0.04	233	5.83×10^2	Resistance	Recrystallized alumina
9	2.04	234	0.12	Resistance	Recrystallized alumina
10	3.90	231	0.06	Resistance	Recrystallized alumina
11	5.23	184	0.04	Resistance	Recrystallized alumina
12	0.05	398	7.96	Resistance	Recrystallized alumina
13	0.84	1210	1.44	Resistance	Quartz tube
14	0.70	322	0.46	Resistance	Quartz tube
15	1.08	1640	1.52	Resistance	Quartz tube
16	0.14	1780	12.71	Resistance	Quartz tube
17	2.72	1440	0.53	Resistance	Quartz tube
18	0.21	162	0.77	Resistance	Quartz tube
19	4.60	303	0.07	Resistance	Quartz tube
20	0.44	1290	2.92	Induction	Zirconia
21	0.03	150	5.00	Induction	Zirconia
22	<0.01	3710	>371	Induction	Zirconia
23	0.91	1090	1.20	Induction	Zirconia
24	0.16	715	4.50	Induction	Zirconia
25	<0.10	1400	>14	Resistance	Zirconia
26	0.52			Induction	Zirconia

^aDefined as the amount of contaminant in the slag divided by the amount of contaminant in the melt.

Stainless Steel

Induction melting was used for all stainless steel experiments. To reduce slag attack on crucibles, fluxes were added after the metal samples were melted. In spite of this precautionary step, crucible attack was severe. The temperatures of the melts were approximately 1600°C. Table 5 presents the metal and flux masses, UO₂ concentrations, and flux composition for these experiments. The results of uranium analyses on the solidified metals and the slags, as well as the partition ratios, the melting techniques, and the crucible materials, are given in Table 6.

Table 5. Details of Stainless Steel Experiments

Sample	Metal (g)	Flux (g)	UO ₂ (ppm)	Flux Composition (wt %)
1	500	50	500	60 SiO ₂ , 40 Al ₂ O ₃
2	500	50	500	60 CaO, 25 Al ₂ O ₃ , 10 SiO ₂ , 5 CaF ₂
3	500	50	500	65 CaO, 35 SiO ₂
4	500	50	500	25 CaO, 75 SiO ₂
5	500	25	500	50 CaO, 30 SiO ₂ , 10 Al ₂ O ₃ , 5 Fe ₂ O ₃ , 5 CaF ₂
6	160		500	No flux

Table 6. Results of Uranium Analyses in Stainless Steel Experiments

Sample	Uranium, ppm		Partition Ratio, ^a λ	Melting Technique	Crucible Material
	Metal	Slag			
1	2.53	346	0.13×10^2	Induction	Zirconia
2	2.39	231	0.10	Induction	Zirconia
3	0.28	73	0.26	Induction	Zirconia
4	≤0.01	2260	>226	Induction	Zirconia
5	0.05	507	5.07	Induction	Magnesia
6	0.65			Induction	Zirconia

^aDefined as the amount of contaminant in the slag divided by the amount of contaminant in the melt.

For stainless steel experiments the degree of decontamination was also inversely proportional to the extent of crucible attack. Both zirconia and magnesia crucibles were severely attacked by the slags. The decontamination factor was not highly dependent on the slag composition, although low efficiencies were associated with high-silica slags. This probably resulted from the highly corrosive action of SiO_2 on zirconia crucibles. In general, highly fluid basic oxidizing slags are more effective and result in decontamination of the metal to as low as 0.01 to 0.05 ppm U even with 5 wt % slag, as in sample 5.

Nickel

The nickel samples were melted in both resistance and induction furnaces. Magnesia and zirconia crucibles were used and were moderately attacked by the slags. The temperature was held at 1550°C for 0.5 h after the sample was melted. Table 7 summarizes the metal and flux masses, UO_2 concentrations, and flux compositions for the nickel experiments. The results of uranium analyses on the solidified metal and slag, as well as the partition ratios, melting techniques, and crucible materials, are given in Table 8 for each experiment.

Table 7. Details of Nickel Experiments

Sample	Metal (g)	Flux (g)	UO_2 (ppm)	Flux Composition (wt %)
1	100	10	500	Borosilicate glass ^a
2	100	10	500	75 SiO_2 , 20 CaO , 5 Fe_2O_3
3	100		500	No Flux
4	100	10	500	40 CaO , 40 SiO_2 , 20 Fe_2O_3
5	100	10	500	70 CaO , 10 SiO_2 , 10 Fe_2O_3
6	100	10	500	50 CaO , 40 SiO_2 , 10 Fe_2O_3
7	100	10	500	60 CaO , 35 SiO_2
8	250	25	500	50 CaO , 30 SiO_2 , Al_2O_3 , 5 Fe_2O_3 , 5 CaF_2

^aNominal composition is 80 SiO_2 , 13 B_2O_3 , 4 Na_2O , 2 Al_2O_3 , 1 K_2O (wt %).

Table 8. Results of the Study with Nickel

Sample	Uranium, ppm		Partition Ratio, ^a λ	Melting Technique	Crucible Material
	Metal	Slag			
1	0.78	599	0.77×10^2	Resistance	Magnesia
2	<0.01	116	>11	Resistance	Magnesia
3	2.17			Resistance	Zirconia
4	0.16	973	5.08	Resistance	Zirconia
5	0.33	383	1.16	Resistance	Zirconia
6	0.12	4530	4.04	Resistance	Zirconia
7	1.94	812	0.42	Resistance	Zirconia
8	0.61	3000	4.92	Induction	Zirconia

^aDefined as the amount of contaminant in the slag divided by the amount of contaminant in the melt.

Generally nickel behaves similarly to mild steel, and induction melting probably will be preferred over resistance furnace melting. Again slag attack on the crucible is a significant factor and it sharply decreases the efficiency of the melt refining technique as in the case of sample 7. Higher temperatures and fluid slags are also essential for better results. The slag composition does not seem very important, although basic oxidizing slags are preferable and can result in reducing the contamination to 0.1 to 0.5 ppm U. High uranium content in some nickel samples correlates with slag attack on the crucible.

Copper

Copper samples were contained in recrystallized alumina crucibles and were melted by resistance heating. The samples were held at about 1250°C after melting. No significant crucible attack was observed in any of the samples. Some of the copper samples were melted in zirconia crucibles by induction melting. Table 9 shows the metal and flux masses, UO₂ concentrations, and flux compositions for these experiments. The results of uranium analyses for the solidified metal and the slag are presented in Table 10 along with the corresponding partition ratios, melting techniques, and crucible materials for these experiments.

Table 9. Details of Copper Experiments

Sample	Metal (g)	Flux (g)	UO ₂ (ppm)	Flux Composition (wt %)
1	100	10	500	50 SiO ₂ , 25 CaO, 25 Al ₂ O ₃
2	100	10	500	60 SiO ₂ , 20 CaO, 20 Al ₂ O ₃
3	100	10	500	70 SiO ₂ , 15 CaO, 15 Al ₂ O ₃
4	100	10	500	65 SiO ₂ , 5 CuO, 35 CaO
5	100	10	500	65 SiO ₂ , 5 CuO, 20 CaO, 10 Al ₂ O ₃
6	100	10	500	55 SiO ₂ , 5 CuO, 30 CaO, 10 Al ₂ O ₃
7	100	10	500	75 SiO ₂ , 5 Fe ₂ O ₃ , 10 CaO, 10 Al ₂ O ₃
8	100	10	500	65 SiO ₂ , 5 Fe ₂ O ₃ , 10 CaO, 10 Al ₂ O ₃
9	100	10	500	55 SiO ₂ , 5 Fe ₂ O ₃ , 30 CaO, 10 Al ₂ O ₃
10	250	25	500	Borosilicate glass ^a
11	250	25	500	50 CaO, 30 SiO ₂ , 10 Al ₂ O ₃ , 5 Fe ₂ O ₃ , 5 CaF ₂
12	170		500	No flux

^aNominal composition is 80 SiO₂, 13 B₂O₃, 4 Na₂O, 2 Al₂O₃, 1 K₂O (wt %).

In general, copper responded very well to the melt refining technique and uranium was effectively removed, regardless of the flux composition. Fluxes with no CuO showed a slightly better partition ratio, perhaps because CuO enhances the crucible-slag reactions. In fact, some crucible attack was observed for crucibles with CuO-containing flux. Residual uranium concentrations well below 0.5 ppm are expected for the melt-refined copper. Although melting in both induction and resistance furnaces was successful in reducing the contamination to 0.1 to 2 ppm U and 0.1 to 0.8 ppm U, respectively, the mixing action by induction is expected to result in higher partition ratios. One drawback is that more contaminant could be dissolved or trapped in the melt unless sufficient time is allowed for phase separation and the temperature is decreased slowly after the power is turned off. The degree of decontamination was again not too sensitive to the slag composition, although fluid basic slags with high silica content and borosilicate slags were effective in reducing the contamination to 0.1 to 0.8 ppm U and 1.3 ppm U, respectively.

Table 10. Results of Uranium Analyses in Copper Experiments

Sample	Uranium, ppm		Partition Ratio, ^a λ	Melting Technique	Crucible Material
	Metal	Slag			
1	0.13	934	7.18×10^2	Resistance	Recrystallized alumina
2	0.37	341	0.92	Resistance	Recrystallized alumina
3	0.11	411	3.74	Resistance	Recrystallized alumina
4	0.14	213	1.52	Resistance	Recrystallized alumina
5	0.54	265	0.49	Resistance	Recrystallized alumina
6	0.45	390	0.87	Resistance	Recrystallized alumina
7	0.83	1813	2.18	Resistance	Recrystallized alumina
8	0.04	1273	31.82	Resistance	Recrystallized alumina
9	0.25	943	3.77	Resistance	Recrystallized alumina
10	1.36	1590	1.17	Induction	Zirconia
11	0.14	1650	11.79	Induction	Zirconia
12	1.96			Induction	Zirconia

^aDefined as the amount of contaminant in the slag divided by the amount of contaminant in the melt.

Aluminum

Samples of pure aluminum were melted in a resistance or an induction furnace. Zirconia crucibles or quartz tubes were used, and no serious crucible-slag reaction was observed. The temperature was held at about 1300°C after melting. Table 11 summarizes the metal and flux masses, UO₂ concentrations, and flux compositions for these experiments. Samples 10 through 16 were prepared from the solidified aluminum ingot of sample 9 and the corresponding fluxes. The results of the uranium analyses of the metal and the slag, as well as the partition ratios, melting techniques, and crucible materials, are given in Table 12 for these experiments.

The results of this study indicated that for aluminum induction melting is a less efficient decontamination technique than resistance

Table 11. Details of Aluminum Experiments

Sample	Metal (g)	Flux (g)	UO ₂ (ppm)	Flux Composition (wt %)
1	76	7.6	500	CaF ₂
2	81	8.1	500	NaF
3	81	8.1	500	60 CaF ₂ , 40 NaF
4	80	8.0	500	40 CaF ₂ , 60 NaF
5	78	7.8	500	20 CaF ₂ , 80 NaF
6	50		500	No flux
7	50		500	No flux
8	166	8.3	500	55 NaF, 35 AlF ₃ , 10 Al ₂ O ₃
9	503	25.15	500	55 NaF, 35 AlF ₃ , 10 Al ₂ O ₃
10	36	0.4		C
11	36	0.4		B
12	36	0.4		S
13	36	0.4		Sb
14	36	0.4		Si
15	36	0.5		Hexachloroethane degasser ^a
16	30	3		50 NaOH, 45 NaCl, 5 Fe ₂ O ₃
17	250	25	500	Borosilicate glass ^b
18	250	25	500	50 CaO, 30 SiO ₂ , 10 Al ₂ O ₃ , 5 Fe ₂ O ₃ , 5 CaF ₂
19	200		500	No flux

^aCl₃CCl₃ or perchloroethane.

^bNominal composition is 80 SiO₂, 13 B₂O₃, 4 Na₂O, 2 Al₂O₃, 1 K₂O (wt %).

furnace melting. Since aluminum is a reactive metal, the mixing action helps dissolve more contaminant in the melt. Although resistance furnace melting is preferred over induction melting, the residual contaminant in the melt is still likely to be high, even with resistance furnace melting. The presence of slags reduces the amount of uranium in the melt to 1 to 30 ppm U. In particular CaF₂, cryolite, and other low-melting fluoride type slags (CaF₂-NaF-AlF₃-Al₂O₃) were effective in reducing the

Table 12. Results of Uranium Analyses in Aluminum Experiments

Sample	Uranium, ppm		Partition Ratio, ^a λ	Melting Technique	Crucible Material
	Metal	Slag			
1	1.2	9610	8.01×10^2	Resistance	Zirconia
2	111.0	1360	0.01	Resistance	Zirconia
3	0.9	405	0.45	Resistance	Zirconia
4	2.4	570	0.24	Resistance	Zirconia
5	315.0	150		Resistance	Zirconia
6	469.0			Resistance	Zirconia
7	430.0			Resistance	Zirconia
8	31.4	1760	0.03	Resistance	Zirconia
9	81.1	4190	0.03	Induction	Zirconia
10	87.9			Resistance	Quartz tube
11	95.3			Resistance	Quartz tube
12	66.4			Resistance	Quartz tube
13	91.3			Resistance	Quartz tube
14	82.3			Resistance	Quartz tube
15	88.7			Resistance	Quartz tube
16	70.5			Resistance	Quartz tube
17	50.6			Induction	Zirconia
18	308.0	255		Induction	Zirconia
19	447.0			Induction	Zirconia

^aDefined as the amount of contaminant in the slag divided by the amount of contaminant in the melt.

contamination to 1 ppm U. Addition of metals and nonmetals that form high-melting compounds with U (C, B, S, Sb, Si, as well as hexachloroethane degasser) did not appear to be effective in decontaminating liquid Al. With fluoride slag treatment of aluminum melts in a resistance furnace, residual contaminant concentrations as low as 1 ppm could be achieved.

Lead

The lead samples were contained in quartz tubes or zirconia crucibles and were melted in a resistance or an induction furnace. The temperature was held at about 1200°C after melting. Higher temperatures are required to maintain homogeneous and fluid slags when resistance furnace melting is used. Generally, lead was readily decontaminated and residual uranium contents as low as 0.1 ppm were achieved. Table 13 presents the metal and flux masses, UO₂ concentrations, and flux compositions for these experiments. The results of uranium analyses on the metal and the slag, as well as the partition ratios, melting techniques, and crucible materials, are given in Table 14 for these experiments.

Table 13. Details of Lead Experiments

Sample	Metal (g)	Flux (g)	UO ₂ (ppm)	Flux Composition (wt %)
1	100	10	500	80 Na ₂ CO ₃ , 10 NaNO ₃ , 10 PbO
2	100	10	500	60 Na ₂ CO ₃ , 30 NaNO ₃ , 10 PbO
3	100	10	500	40 Na ₂ CO ₃ , 50 NaNO ₃ , 10 PbO
4	100	10	500	45 NaCl, 35 NaOH, 10 NaNO ₃ , 10 PbO
5	100	10	500	35 NaCl, 25 NaOH, 30 NaNO ₃ , 10 PbO
6	100	10	500	50 NaNO ₃ , 20 NaCl, 20 NaOH, 10 PbO
7	100	10	500	70 NaNO ₃ , 10 NaCl, 10 NaOH, 10 PbO
8	100	10	500	40 SiO ₂ , 25 Al ₂ O ₃ , 20 CaO, 15 Fe ₂ O ₃
9	50		500	No flux
10	200		500	No flux
11	100	10	500	40 NaNO ₃ , 30 NaCl, 30 NaOH
12	100	10	500	Borosilicate glass ^a
13	100	10	500	50 CaO, 30 SiO ₂ , 10 Al ₂ O ₃ , 5 Fe ₂ O ₃ , 5 CaF ₂

^aNominal composition is 80 SiO₂, 13 B₂O₃, 4 Na₂O, 2 Al₂O₃, 1 K₂O (wt %).

Table 14. Results of Uranium Analyses in Lead Experiments

Sample	Uranium, ppm		Partition Ratio, ^a λ	Melting Technique	Crucible Material
	Metal	Slag			
1	1.03	4460	4.33×10^2	Resistance	Quartz tube
2	0.49	3060	6.24	Resistance	Quartz tube
3	0.26	3710	14.27	Resistance	Quartz tube
4	0.24	4360	18.17	Resistance	Quartz tube
5	0.35	250	0.71	Resistance	Quartz tube
6	0.31	184	0.59	Resistance	Quartz tube
7	0.06	260	4.33	Resistance	Quartz tube
8	0.48	2610	5.44	Resistance	Quartz tube
9	0.11			Resistance	Zirconia
10	0.23			Induction	Zirconia
11	0.99	1530	1.54	Induction	Quartz tube
12	3.16	4410	1.42	Induction	Quartz tube
13	0.72	1250	1.73	Induction	Quartz tube

^aDefined as the amount of contaminant in the slag divided by the amount of contaminant in the melt.

No severe crucible attack was observed for lead melts except when borosilicate or basic slags were used at high temperatures. Induction melting results in 0.2 to 3 ppm U residual contaminant concentration in liquid lead compared with 0.06 to 1 ppm U in resistance furnace melting. Both borosilicate and basic slags were similar in their effect, although the former attacked the quartz tube and resulted in higher uranium contents in the samples. The best flux appeared to be NaNO_3 - NaCl - NaOH mixtures with high NaCl and NaOH contents. Residual contaminant levels as low as 0.1 ppm are achieved for melt refining of the contaminated lead scrap.

Tin

Samples of tin were melted by resistance furnace or induction melting in quartz tubes or zirconia crucibles. The temperature was held at about

1200°C after the sample was melted with resistance heating. Tin was readily decontaminated by melt refining, and products were produced that contained less than 0.1 ppm U. Table 15 presents the metal and flux masses, UO₂ concentrations, and flux compositions for these experiments. The results of uranium analyses on the melt-refined metal and slag are given in Table 16 along with the partition ratios, melting techniques, and crucible materials.

Table 15. Details of Tin Experiments

Sample	Metal (g)	Flux (g)	UO ₂ (ppm)	Flux Composition (wt %)
1	50		500	No flux
2	50	5	500	45 SiO ₂ , 30 CaO, 20 Al ₂ O ₃ , 5 Fe ₂ O ₃
3	50	5	500	50 NaNO ₃ , 45 Na ₂ CO ₃ , 5 Fe ₂ O ₃
4	50	5	500	50 NaOH, 45 NaCl, 5 Fe ₂ O ₃
5	50	5	500	25 NaNO ₃ , 25 NaOH, 25 NaCl, 25 Na ₂ CO ₃
6	150		500	No flux
7	100	10	500	40 NaNO ₃ , 30 NaCl, 30 NaOH
8	100	10	500	50 CaO, 30 SiO ₂ , 10 Al ₂ O ₃ , 5 Fe ₂ O ₃ , 5 CaF ₂

No crucible attack was observed except when borosilicate and basic slags were used at high temperatures. Again induction melting resulted in 0.5 to 7 ppm U residual contamination in the melt compared with the 0.06 to 0.1 ppm U in resistance furnace melting. The NaNO₃-NaCl-NaOH type flux appears to be an efficient melt refining slag, although borosilicate and blast furnace type slags can also be used with proper choice of crucibles. Residual contamination below 0.1 ppm is achieved for melt refining tin by resistance furnace melting.

Table 16. Results of Uranium Analyses in Tin Experiments

Sample	Uranium, ppm		Partition Ratio, ^a λ	Melting Technique	Crucible Material
	Metal	Slag			
1	0.08			Resistance	Quartz tube
2	0.09	356	3.96×10^2	Resistance	Quartz tube
3	0.51	710	1.39	Resistance	Quartz tube
4	<0.10	2640	>26	Resistance	Quartz tube
5	0.06	1390	23.17	Resistance	Quartz tube
6	19.00			Induction	Zirconia
7	7.13	666	0.09	Induction	Quartz tube
8	0.48	1860	3.88	Induction	Quartz tube

^aDefined as the amount of contaminant in the slag divided by the amount of contaminant in the melt.

Zinc

Samples of pure zinc were melted in a resistance furnace and quartz tubes were used as crucibles. No severe crucible attack was observed. The temperature was held at 800°C for a few minutes after the samples were melted. Because of the high vapor pressure of zinc, some of the liquid metal was vaporized and oxidized to zinc oxide. For this reason the samples could not be held in the furnace for longer times. Generally, zinc responds well to melt refining, provided that an inert atmosphere is used. Table 17 summarizes the metal and flux masses, UO₂ concentrations, and flux compositions for these experiments. The results of uranium analyses for both solidified metal and slag are given in Table 18 along with the partition ratios, melting techniques, and crucible materials for these experiments. Except for sample 2, which has a slightly higher residual uranium content, the samples show uranium contents much lower than 0.5 ppm. The reason for the slightly higher value for sample 2 probably was the severe oxidation of the metal, which virtually carried away the surface slag.

Table 17. Details of Zinc Experiments

Sample	Metal (g)	Flux (g)	UO ₂ (ppm)	Flux Composition (wt %)
1	50		500	No flux
2	50	5	500	50 NaNO ₃ , 45 Na ₂ CO ₃ , 5 Fe ₂ O ₃
3	50	5	500	50 NaNO ₃ , 45 NaCl, 5 Fe ₂ O ₃
4	50	5	500	50 NaNO ₃ , 25 NaOH, 25 NaCl, 25 Na ₂ CO ₃ , 5 Fe ₂ O ₃

Table 18. Results of Uranium Analysis in Zinc Experiments

Sample	Uranium, ppm		Partition Ratio, ^a λ	Melting Technique	Crucible Material
	Metal	Slag			
1	0.07			Resistance	Quartz tube
2	2.10	1650	0.8×10^2	Resistance	Quartz tube
3	0.14	1110	7.9	Resistance	Quartz tube
4	0.54	2470	4.6	Resistance	Quartz tube

^aDefined as the amount of contaminant in the slag divided by the amount of contaminant in the melt.

Lead-Tin Alloys

Two sets of lead-tin alloys [80 Pb-20 Sn and 50 Pb-50 Sn (wt %)] were studied. The samples were melted in a resistance or an induction melting furnace and were held at 1300°C for about 1 h after melting. Quartz tubes or zirconia crucibles were used, and no severe crucible attack was observed except when borosilicate or blast furnace type slags were used. Table 19 presents the metal and flux masses, UO₂ concentrations, and flux compositions for these experiments. The results of uranium analyses on solidified metal and slag are given in Table 20 along with the partition ratios, melting techniques, and crucible materials for these experiments. The results show that residual contamination is 0.5 to 3 ppm U in induction melting compared with 0.01 to 1.5 ppm U in resistance furnace melting.

Table 19. Details of Lead-Tin Alloy Experiments

Sample	Metal (g)	Flux (g)	UO ₂ (ppm)	Flux Composition (wt %)
<u>80 Pb-20 Sn (wt %)</u>				
1	50		500	No flux
2	50	5	500	45 SiO ₂ , 30 CaO, 20 Al ₂ O ₃ , 5 Fe ₂ O ₃
3	50	5	500	40 NaNO ₃ , 40 NaOH, 20 NaCl
<u>50 Pb-50 Sn (wt %)</u>				
4	50		500	No flux
5	50	5	500	45 SiO ₂ , 30 CaO, 20 Al ₂ O ₃ , 5 Fe ₂ O ₃
6	150		500	No flux
7	100	10	500	40 NaNO ₃ , 30 NaCl, 30 NaOH
8	100	10	500	Borosilicate glass ^a
9	100	10	500	50 CaO, 30 SiO ₂ , 10 Al ₂ O ₃ , 5 Fe ₂ O ₃ , 5 CaF ₂

^aNominal composition is 80 SiO₂, 13 B₂O₃, 4 Na₂O, 2 Al₂O₃, 1 K₂O (wt %).

Table 20. Results of Uranium Analyses on Lead-Tin Alloys

Sample	Uranium, ppm		Partition Ratio, ^a λ	Melting Technique	Crucible Material
	Metal	Slag			
<u>80 Pb-20 Sn (wt %)</u>					
1	<0.01			Resistance	Quartz tube
2	0.06	926	15.43 × 10 ²	Resistance	Quartz tube
3	1.35	570	0.42	Resistance	Quartz tube
<u>50 Pb-50 Sn (wt %)</u>					
4	1.66			Resistance	Quartz tube
5	1.04	416	0.40	Resistance	Quartz tube
6	2.56			Induction	Zirconia
7	1.44	445	0.31	Induction	Quartz tube
8	3.02	725	0.24	Induction	Quartz tube
9	0.54	624	1.16	Induction	Quartz tube

^aDefined as the amount of contaminant in the slag divided by the amount of contaminant in the melt.

The degree of decontamination was not sensitive to flux composition, and it appeared that any of the low-melting, borosilicate, or basic slags could be used.

Compatibility of Slags and Refractories

Various types of crucible materials were studied for their compatibility with borosilicate, basic blast furnace [40 CaO, 30 SiO₂, 15 Fe₂O₃, 10 Al₂O₃, 5 CaF₂ (wt %)], high silica [60 SiO₂, 30 CaO, 10 Al₂O₃ (wt %)], low-melting [(40 NaNO₃, 30 NaCl, 30 NaOH (wt %)], and cryolite [55 NaF, 35 AlF₃, 10 Al₂O₃ (wt %)] slags as well as with pure liquid metals at high temperatures. The temperature was 1600°C for the first three and 1200°C for the last two slags, and the effects of both resistance furnace and induction melting were examined. The results indicated that high-purity recrystallized alumina and graphite were the most compatible refractories, while quartz was moderately compatible and the others were compatible only with low-melting slags and pure liquid metals. The primary limitation of graphite was that it would dissolve in or react with ferrous metals, rendering the final ingot very hard and brittle and making the sampling very difficult. Recrystallized alumina proved to be the only refractory to be used where severe slag attack is expected. The slag attack was greater with induction melting. The results of this investigation are summarized in Table 21.

Table 21. Compatibility^a of Slags and Refractories

Refractory	Slags					
	Pure Metal	Borosilicate	Low Melting	Cryolite	Basic Blast Furnace	High Silica
Recrystallized alumina	C	C	C	C**	C	C
Quartz	C	MC	C	X	X	MC
Magnesia	C	X	MC	X	X	X
Graphite	C*	C	C	C	C	C
Zirconia	C	X	MC	MC	X	X
Alundum ^b	C	X	MC	MC	X	X

^aC = compatible; MC = moderately compatible; X = not compatible; C* = compatible only with nonferrous metals; C** = compatible when cryolite contains relatively high alumina (about 20%).

^bFireclay-bonded Al₂O₃. Product of Norton Company, Worcester, Mass.

SUMMARY AND CONCLUSIONS

The residual uranium composition and the partition ratios were determined for melt refining metals and alloys contaminated with UO_2 . Mild steel, stainless steel, Ni, Al, Cu, Pb, Sn, Zn, and Pb-Sn alloys were studied by using various fluxes. Melt refining techniques with resistance furnace and induction melting were investigated. The results indicate that the contaminant can be removed from the liquid metal successfully to a very low level provided that certain conditions are met. These conditions require that the nonferrous metals and alloys be processed by resistance furnace melting and the ferrous metals preferably by induction melting. This consideration is particularly critical for scrap aluminum. A major problem is crucible attack by the slags. In particular, borosilicate and basic blast furnace slags are highly corrosive at high temperatures. Recrystallized alumina was compatible with both borosilicate and basic blast furnace slags at temperatures below 1600°C . Quartz could be used for short-time application and preferably lower temperatures, while magnesite and zirconia were compatible with neither of the slags. However, quartz, magnesite, and zirconia refractories could be used for melting some metals and for their treatment with low-melting slags. High density and smooth surface are essential for longer refractory life.

The uranium contents of the melt-refined metals were as low as 0.01 to 0.1 ppm for mild steel, 0.01 to 0.05 ppm for stainless steel, 0.1 to 0.5 ppm for nickel, 0.1 to 0.8 ppm for copper, 1 to 2 ppm for aluminum, 0.1 to 0.3 ppm for lead and tin, 0.05 to 0.5 ppm for zinc, and 0.7 to 0.5 ppm for lead-tin alloys.

The slag volume must be as small as possible to increase the refractory life and to minimize the amount of the contaminated waste. It is desirable to add the fluxes after the solid scrap is melted. This in turn decreases the attack to refractories and minimizes the loss of slag and thus increases the efficiency of decontamination. The results indicated that the degree of decontamination is relatively insensitive to the flux type and composition. However, borosilicate and basic blast furnace slags with high Fe_2O_3 contents are preferable for ferrous metals and copper. Low-melting NaNO_3 - NaCl - NaOH type slags are suitable for Zn, Pb,

Sn, and Pb-Sn alloys, while fluoride type slags are desirable for Al. Melting the scrap without any slag lowers the contamination level, especially in resistance furnace melting. This suggests that the removal of dross after resistance furnace melting of the metal and its further treatment with a small volume of slag will be more efficient than a single treatment with large amounts of slag. This is particularly important in aluminum decontamination.

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