

## A MELT REFINING METHOD

### FOR URANIUM CONTAMINATED STEELS AND COPPER

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#### ABSTRACT

Melt refining was studied as a means of uranium decontamination of metallic wastes. Samples of mild steel, and copper, contaminated with uranium, were melted by adding  $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3$  system fluxes. Various contamination levels, and melting temperatures and times were used. Uranium concentration in the resulting ingots were determined. Flux composition and melting temperature were found to influence the level of decontamination, but melting time had little effect. For mild steel, the most effective flux composition was  $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3\text{-NiO}$  with a slag basicity 1.5, at a melting temperature of around  $1700^\circ\text{C}$ . For stainless steel and copper, the effective flux composition was  $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3\text{-CaF}_2$  and melting temperatures were  $1550$  and  $1600^\circ\text{C}$ , respectively. Using these melting conditions, each metal could be decontaminated to the same uranium concentration level as before contamination.

#### INTRODUCTION

In nuclear fuel processing plants, a variety of metal scraps contaminated with uranium or transuranic elements are produced. As more waste are being produced annually, it is increasingly necessary to provide better waste management technology. While effective decontamination technologies have been developed, a melting method offers high volume reduction and the possibility of decontamination by concentrating radionuclides in slag.<sup>1,2,3</sup> Substantial progress has been made at Oak Ridge National Laboratory in selecting effective flux compositions for many kind of metals.<sup>2</sup> However optimum melt refining conditions to obtain reusable metals in which radionuclide concentration levels are less than before contamination, have not been determined yet.

The aim of this study was to establish an optimized decontamination technology based on a proposed decontamination mechanism and its accompanying melting experiments. Using various uranium concentration levels, samples of mild steel, stainless steel (SUS 304) and copper, which are representative plant structural materials, were melted and some general conclusions were drawn. Then for mild steel, effect of flux composition, and melting temperature and time were examined. Based on the results, flux composition influence on the decontamination mechanism was discussed.

#### EXPERIMENTAL METHOD

##### Apparatus

Uranium contaminated samples were prepared as follows. Commercially available mild steel, stainless steel (SUS 304) and copper sticks (diameter: 5mm) were cut to about 60 mm length. These sticks were surface contaminated with uranyl nitrate solution for which the concentration was accurately know, so as to give a uniform contamination level. In the heating process, it may be considered that uranyl nitrate decomposes to  $\text{UO}_3$  between  $200$  and  $300^\circ\text{C}$  and  $\text{UO}_3$  loses oxygen to give  $\text{U}_3\text{O}_8$  or  $\text{UO}_2$  above  $800^\circ\text{C}$ .

The test equipment is shown in Fig. 1. It consisted of a resistance furnace and an evacuation system. The furnace was a vertical type equipped with 8 Lantane-Cromite rods for heaters. The maximum furnace temperature used was about  $1800^\circ\text{C}$ . The furnace core tube was made of corundum alumina ( $\alpha\text{-Al}_2\text{O}_3$ ) and was 50 mm in diameter and 800 mm long. The upper and lower sides of the tube were sealed by silicone packings, to allow evacuation to less than 0.1 mm Hg, even during heating. The heating rate was controlled to reach  $1800^\circ\text{C}$  ( $10^\circ\text{C}$ ) within 5 hours. The temperatures inside and outside the tube were measured by platinum rhodium 20-40 (PR 20-40) thermocouples.

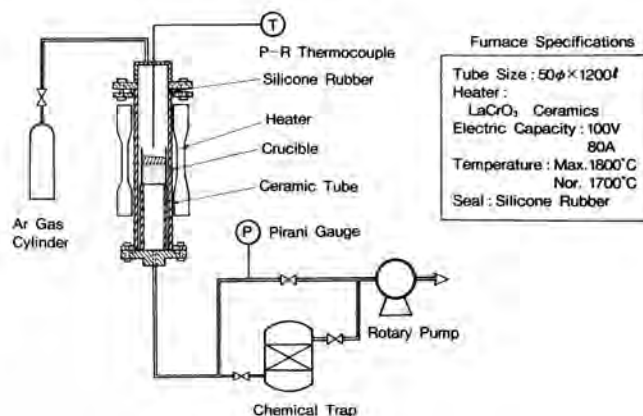


Fig. 1. Schematic Diagram of Melt-Refining Test Equipment.

##### Procedure

Uranium contaminated mild steel, stainless steel, and copper, in the form of sticks (90-100 g/batch) and 10 wt% of flux were put into an alumina crucible (diameter : 24 mm, length : 120 mm). The crucible was set in the furnace, then the metal and flux were melted in an argon atmosphere of 200 mmHg. After melt

refining was completed, the sample was cooled to room temperature in the furnace, the crucible was removed and broken down to release the slag and an ingot. Uranium concentration in the ingot was determined by epithermal neutron activation analysis in the Musashi Institute of Technology Research Reactor (TRIGA-II). The activated samples were subjected to  $\gamma$ -ray spectrometry. For determination of uranium via  $^{239}\text{Np}$ , the 106, 228 and 278 KeV peaks were used. Then the decontamination factor (DF) was defined as uranium contamination level/uranium content in the ingot ratio, by assuming that all the uranium except that contained in the ingot was incorporated into the slag.

## RESULTS

### Contamination Level Effect

Figure 2 shows variation of uranium concentration in ingots and contamination level for mild steel, stainless steel and copper. In these experiments flux composition ( $40\text{SiO}_2\text{-}40\text{CaO-}20\text{Al}_2\text{O}_3$ ), melting time (1.0 hr) and temperature ( $1650^\circ\text{C}$  for mild steel and stainless steel, and  $1550^\circ\text{C}$  for copper respectively) were fixed and only the contamination level was varied

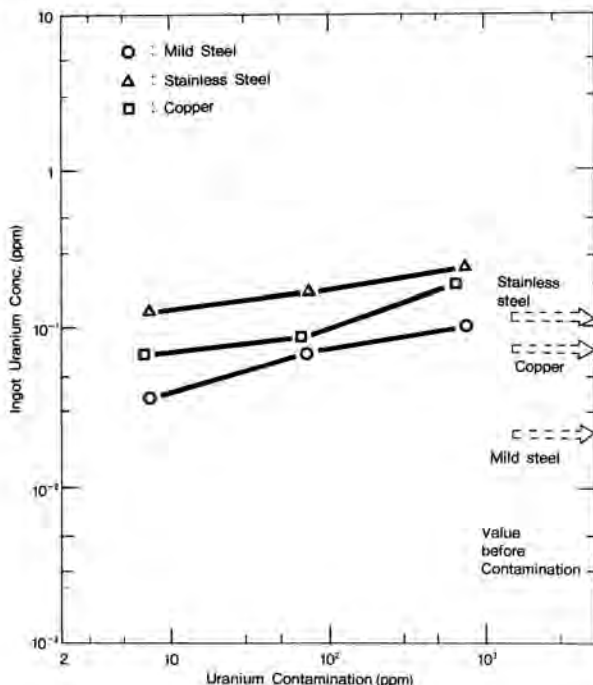


Fig. 2. Effect of Uranium Contamination Level to an Ingot Uranium Concentration. (Melting Temperature,  $1550\text{-}1650^\circ\text{C}$ ; Melting Time, 1h; and Flux Composition  $40\text{SiO}_2\text{-}40\text{CaO-}20\text{Al}_2\text{O}_3$ )

over the range of 9-900 ppm. Figure 3 shows variation of decontamination factor (DF) and contamination level as obtained from Fig. 2. These figures indicated that uranium concentrations in the ingots were nearly constant and the DF values increased in proportion to the contamination level. By using the above mentioned flux composition and melting conditions, stainless steel and copper could be decontaminated to a level near that before contamination. While the DF value of mild steel was higher than the other metals, it could not be decontaminated to a uranium concentration lower than that before contamination. Therefore it was decided to select the optimum flux composition and melting conditions for mild steel based on systematic experiments.

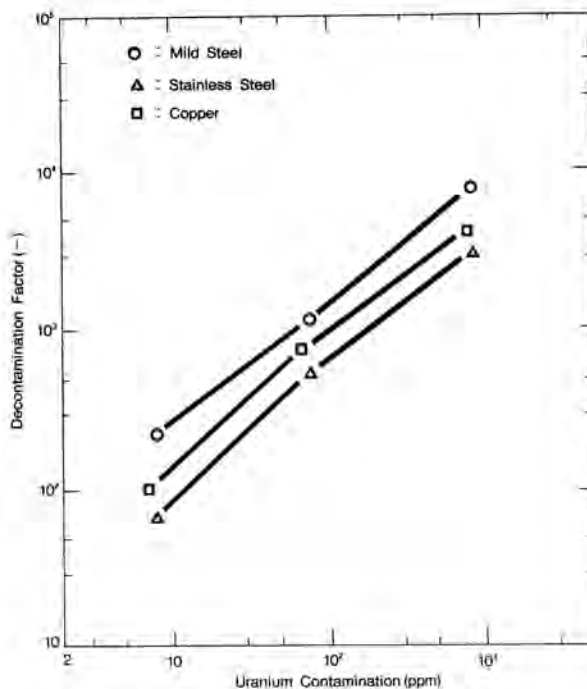


Fig. 3. Effect of Uranium Contamination Level to Decontamination Factor. (Melting Temperature,  $1550\text{-}1650^\circ\text{C}$ ; Melting Time, 1h; and Flux Composition,  $40\text{SiO}_2\text{-}40\text{CaO-}20\text{Al}_2\text{O}_3$ )

### Effective Melting Conditions for Mild Steel

Slag basicity effect. Melting conditions of temperature ( $1650^\circ\text{C}$ ), time (0.5 hr) and sample contamination level (500 ppm) were fixed and only flux composition was varied. Figure 4 shows the effect of slag basicity on ingot uranium concentration. The slag basicity which could represent the ionic

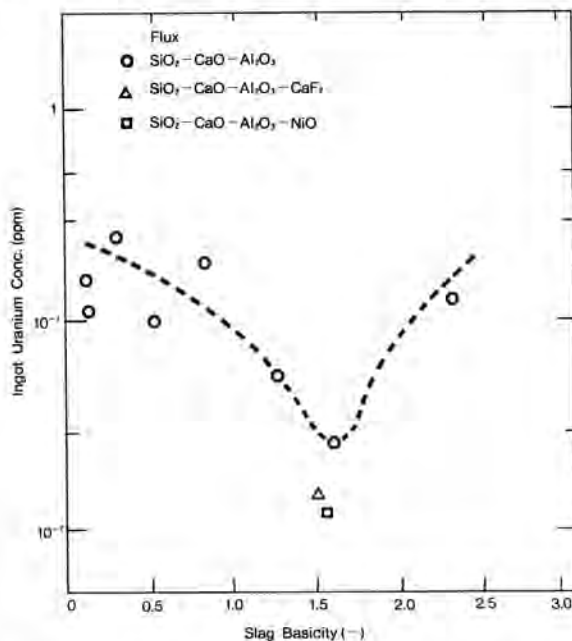


Fig. 4. Effect of Slag Basicity. ( $\text{CaO}+\text{NiO}$  or  $\text{CaF}_2/\text{SiO}_2+\text{Al}_2\text{O}_3$  Mole Ratio) on Uranium Concentration in a Mild Steel Ingot

characteristic of the slag was defined as the mole ratio of basic oxide (CaO) to acidic oxide (SiO<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub>)<sup>4</sup>. The maximum decontamination effect was obtained around a basicity of 1.5. It was proposed that this maximum was due to production of acidic oxide ions like SiO<sub>4</sub><sup>4-</sup> or Al<sub>2</sub>O<sub>5</sub><sup>4-</sup>, which combined with uranyl ions at the interface between the slag and metal<sup>5</sup>. For the same basicity, flux containing NiO or CaF<sub>2</sub> had a better decontamination effect. In these cases, as shown in Fig. 4, uranium concentration in the ingots decreased to less than 0.02 ppm which was its before contamination. Thus effects of slag basicity and flux elements NiO or CaF<sub>2</sub> were considered to relate to the decontamination mechanism at slag-metal interface. These points are discussed later.

**Melting temperature effect.** Experimental results for a temperature versus mild steel ingot uranium concentration plot are shown in Fig. 5. In these experiments, flux composition, sample contamination level (500 ppm), and melting time (0.5 hr) were fixed and only melting temperature was varied. The minimum uranium concentration was obtained at 1700°C. It was considered that decontamination proceeded with increasing temperature, but at too high a temperature, the uranium compound which was extracted from the metal phase would return to the metal. Therefore melting temperature should be kept at around 1700°C, a value 200°C higher than the melting point of mild steel.

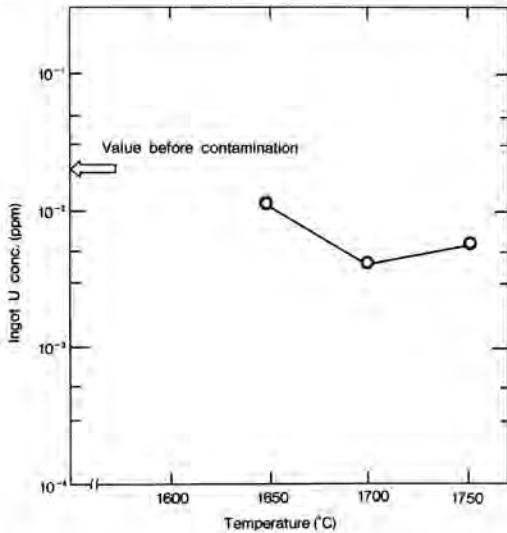


Fig. 5. Effect of Mild Steel Melting Temperature on Ingot Uranium Concentration.

**Melting time effect.** Figure 6 shows the effect of melting time on mild steel ingot uranium concentration. In these experiments, the flux composition, sample contamination level (500 ppm), and temperature (1700°C) were fixed and only melting time was varied. Uranium concentrations in the resultant ingots were constant over the melting times of 0.1 - 1.0 hours. This indicated that the decontamination reaction was over in at least 0.1 hours. Therefore a melting time of 0.1 hours at 1700°C was sufficient.

Effective Melting Conditions for Stainless Steel and Copper

From the results of experiments for mild steel, the most effective flux composition was obtained as SiO<sub>2</sub>-CaO-Al<sub>2</sub>O<sub>3</sub>-NiO for which slag basicity was 1.5. However melting point of the flux was higher than that of stainless and copper was 40SiO<sub>2</sub>-30CaO-20Al<sub>2</sub>O<sub>3</sub>-10CaF<sub>2</sub> of which melting point was estimated from a phase

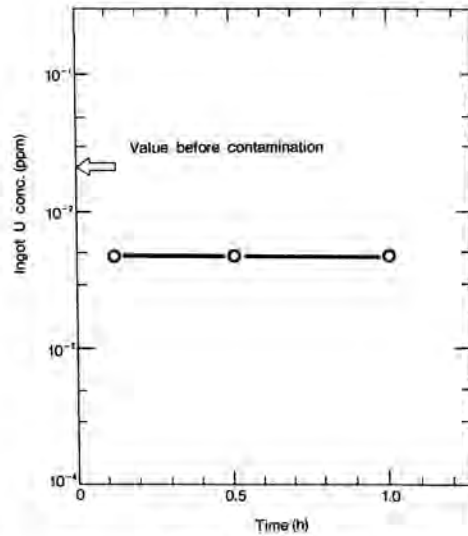


Fig. 6. Effect of Mild Steel Melting Time on Ingot Uranium Concentration.

diagram to be lower than 1300°C. Optimized melting temperatures were up to 200°C of the melting points of metals, i.e. 1600°C for stainless steel and 1300°C for copper. However, in the case of copper, the melting temperature should be at least 1400°C to melting the flux. The effective melting conditions are summarized in Table I.

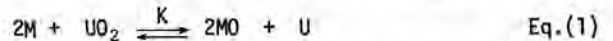
TABLE I

Results of Melt Refining Experiments for Uranium Contaminated (500ppm) Mild Steel, Stainless Steel and Copper.

Metals	Flux Composition (wt%)	Melting		Decontamination Factor	Ingot Uranium Concentration (ppm)	Before Contamination (ppm)
		Temperature (°C)	Time (hr)			
Mild Steel	10SiO <sub>2</sub> -40CaO-40Al <sub>2</sub> O <sub>3</sub> -10NiO	1700	0.1	10 <sup>4</sup>	0.005	0.02
Stainless Steel	40SiO <sub>2</sub> -30CaO-20Al <sub>2</sub> O <sub>3</sub> -10CaF <sub>2</sub>	1600	0.5	5×10 <sup>3</sup>	0.10	0.11
Copper	40SiO <sub>2</sub> -30CaO-20Al <sub>2</sub> O <sub>3</sub> -10CaF <sub>2</sub>	1500	0.5	8×10 <sup>3</sup>	0.083	0.075

DISCUSSION

Based on metallurgical thermodynamics, the decontamination level in melt refining of uranium contaminated metals depends particularly on their reactivity, i.e. free energies of metal oxide formation. Figure 7 compares free energies of formation for some representative metal oxides. The oxidation-reduction reaction of metal and uranium oxide occurs as



Where M : metal (valence is assumed as + 2);  
MO : metal oxide ; and  
K : equilibrium constant.

$$K = \frac{a_M^2 a_U}{a_{MO}^2 a_{UO_2}} = \exp \left\{ -\frac{(2\Delta G_{MO} - \Delta G_{UO_2})}{RT} \right\} \quad \text{Eq. (2)}$$

Where a : activity ;  
ΔG : free energy of formation (cal/ mol);  
R : gas constant (1.98 × 10<sup>3</sup> cal/mol K); and  
T : temperature (K).

When the K value is larger than 1, the reaction Eq. (1) proceeds to the right and reduction of UO<sub>2</sub> is promoted which prevents uranium from being extracted into the slag phase. On the other hand, when the K

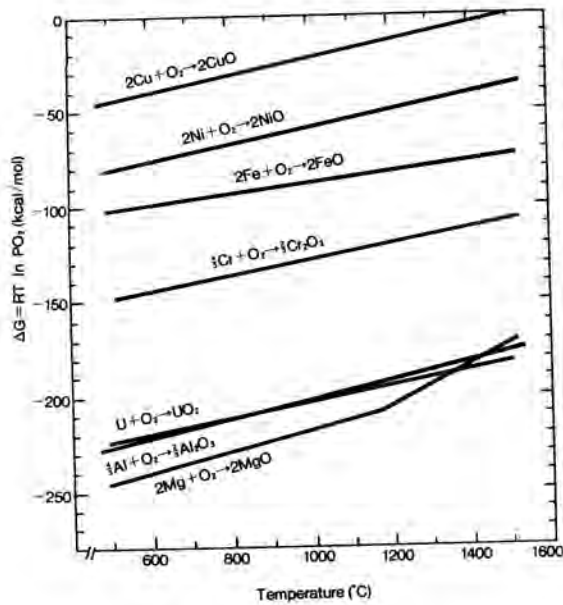
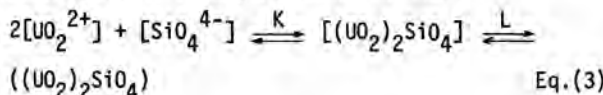


Fig. 7. Free Energies of Metal Oxide Formation ( $\Delta G = RT \ln PO_2$ ) as a Function of Temperature.

value is less than 1, most of the uranium remains as its oxide which can be extracted to the slag. In the case of iron, copper, nickel and chromium, the K values are so small that uranium must be extracted into the slag phase as  $UO_2$ . However it was found that a little uranium was contained in the melt refined ingots. This was because uranium oxide and the slag elements caused some reaction at the melting metal/slag interface. Therefore we proposed the decontamination model as summarized in Fig. 8. Silicate (or alumina) anions generated in the slag and uranyl cations in the metal combined to form a complex at the interface.<sup>5</sup> Then the ionic reaction is expressed as follows.



Where ( ) : concentration in slag ;  
 [ ] : concentration in metal ;  
 K : equilibrium constant; and  
 L : partition ratio of  $(UO_2)_2SiO_4$  complex.

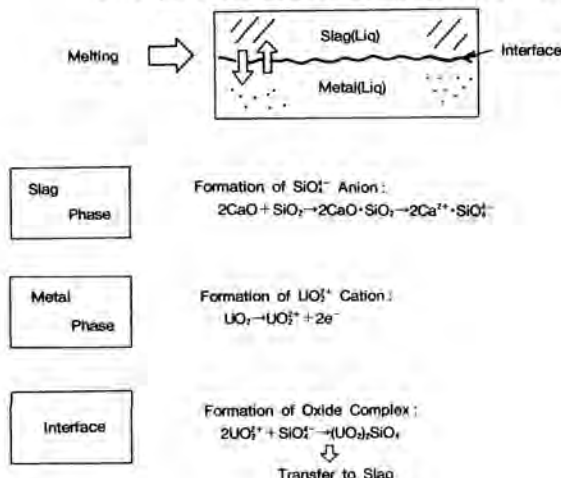


Fig. 8. Melting Decontamination Mechanism.

If equation (3) occurs quickly and has a very large K value, DF would depend on only the partition ratio L as follows.

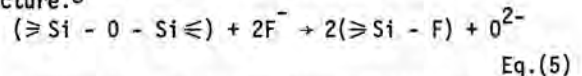
$$DF = \frac{W_S}{W_M} \frac{(\% (UO_2)_2SiO_4)}{[\% (UO_2)_2SiO_4]} + 1 = \frac{W_S}{W_M} \cdot L + 1 \quad \text{Eq.(4)}$$

Where  $W_S$  : weight of slag, and

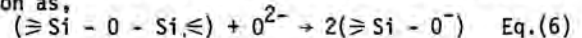
$W_M$  : weight of metal.

The L value is generally constant. However Fig.3 shows that the DF values have a proportional relation to uranium contamination level. The reason is given as follows : the  $UO_2^{2+}$  content was so dilute that a representative quantity of uranium could dissolve in the metal phase, although the DF value may become constant with increases in the contamination level.

Next the effect of fluoride or nickel oxide containing fluxes was considered to verify the proposed decontamination model. Fluorides have a tendency to brake the chemical bond of silicate polymer<sup>7</sup> which is known to form a three-dimensional network structure.<sup>8</sup>



Free oxygen ions may bring about further depolymerization as,



While the ionic potential of NiO is less than CaO, the flux containing NiO gave a higher decontaminations effect. The reason was proposed as due to the free energy of formation of its oxide which is so small that it prevents the reduction of uranium oxide.

## CONCLUSIONS

Experimental studies were done on obtaining reusable, decontaminated metals with melt refining of uranium contaminated mild steel, stainless steel and copper. In particular, for mild steel, the most appropriate melt refining conditions were determined and effects of slag basicity, flux composition, and melting temperature and time were examined. The results are summarized as follows.

- (1) The most effective slag basicity (= mole ratio of basic oxides/acid oxides) was around 1.5 and fluxes containing NiO or  $CaF_2$  were more effective. This was attribute to acid slag anions like  $SiO_4^{4-}$  and  $Al_2O_5^{4-}$ , which could be combined with uranyl cations at the slag-metal interface, being produced in maximum amounts.
- (2) In the case of mild steel, the melting time showed little effect on decontamination, but melting temperature should be kept at around  $1700^\circ C$ . When the uranium contamination level was 500 ppm, by using the appropriate flux composition of 10  $SiO_2$ -40  $CaO$ -40  $Al_2O_3$ -10 NiO, an ingot uranium concentration of 0.005 ppm was obtained which was less than before contamination.
- (3) For stainless steel and copper, the appropriate flux composition was 40  $SiO_2$ -30  $CaO$ -20  $Al_2O_3$ -10  $CaF_2$ , and melting temperatures were  $1600^\circ C$  and  $1500^\circ C$  respectively. When uranium contamination level was 500 ppm, ingots with concentrations of 0.1 and 0.083 ppm respectively were obtained. These were levels near that before contamination.

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