DP-MS-86-4

# FLUORINATION BY FUSION

by

J. H. Gray

E. I. du Pont de Nemours & Company
Savannah River Laboratory
Aiken, S. C. 29808

A paper for presentation at the
Tenth Annual Actinide Workshop
Los Alamos, NM
May 12-15, 1986



This paper was prepared in connection with work done under Contract No. DE-AC09-76SR00001 with the U.S. Department of Energy. 

DP-MS-86-4

# FLUORINATION BY FUSION

by

J. H. Gray

E. I. du Pont de Nemours & Company
Savannah River Laboratory
Aiken, S. C. 29808

## ABSTRACT

LECO crucibles and incinerator ash are two waste categories that cannot be discarded due to the presence of insoluble transuranics. Current chemical processing methods are not too effective, requiring a number of repeated operations in order to dissolve more than half the transuranics. An alternate dissolution approach has been developed involving the use of ammonium bifluoride. Low temperature fusion of the waste with ammonium bifluoride is followed by dissolution of the fused material in boiling nitric acid solutions. Greater than 60% of the transuranics contained in LECO crucibles and greater than 95% of the transuranics mixed with the incinerator ash are dissolved after a single fusion and dissolution step. Fluorination of the transuranics along with other impurities appears to render the waste material soluble in nitric acid.

* The information contained in this article was developed during the course of work under Contract No. DE-AC09-76SR00001 with the U.S. Department of Energy.

ACKNOWLEDGMENT

The information contained in this paper was developed during the course of work performed at the Savannah River Laboratory (SRL) under Contract No. DE-AC09-76SR00001 with the U. S. Department of Energy (DOE) (Slide 1).

INTRODUCTION

An improved chemical process has been developed for removal of transuranics from incinerator ash and LECO crucibles. The process involves both pyrochemical heat treatment and aqueous dissolution steps. By first using a low temperature fusion step, insoluble refractories were converted to soluble fluorides. Residues remaining after dissolution contain only trace quantities of the transuranics and can now be classified as discardable waste (Slide 2).

Incinerator ash and LECO crucibles are the two low-level waste categories investigated using the fusion step. Because of the transuranic content, none of the waste categories listed in Slide 3 can be classified as discardable waste. However, after chemical processing, conversion from nondiscardable to discardable waste was demonstrated.

LABORATORY STUDY

The flowsheet developed for removal of transuranics from incinerator ash and LECO crucibles has two basic process steps (Slide 4). The first step involves low temperature fusion with ammonium bifluoride ($NH_4HF_2$) for 4 hours at 140-170°C.

The fused material was then dissolved in boiling 14 M $HNO_3$ solutions for an additional 4 hours. Centrifugation of the production solutions easily separated solids from the liquid phase.

By careful addition of $NH_4HF_2$ to each of the whole LECO crucibles, efficient removal of the transuranics was possible. However, complete mixing of $NH_4HF_2$ with crushed LECO crucibles was not demonstrated. After dissolution, the inside bowl section of the whole LECO crucible was clean, whereas some of the original black transuranic crust material can still be seen attached to crushed LECO fragments (Slide 5).

Good mixing of the incinerator ash with the $NH_4HF_2$ was demonstrated. Using equal weights of the two solids, essentially complete removal of the transuranics was accomplished. Good mixing also was shown by the "crust-like" texture of the fused incinerator ash (Slide 6). Without suitable mixing, some loose incinerator ash remained after fusion.

## EXPERIMENTAL RESULTS

During fusion of the incinerator ash (Slide 7), approximately 10 wt % of the mixture vaporized into the off-gas system. However, all of the transuranics remained in the fused material. After dissolution, 10-20 wt % of the incinerator ash remained as undissolved solids. Only trace quantities of transuranics were detected in these solids. The remaining solids were difficult to filter but were easily centrifuged. Under all test conditions examined, greater than 95% of the transuranics were removed from the incinerator ash.

The whole LECO crucibles lost less weight during fusion and retained more of their initial mass after dissolution than the crushed sections (Slide 8). This was attributed to the smaller surface area of the whole LECO crucibles in contact with the $NH_4HF_2$. Solids remaining after dissolution were easy to filter and centrifuge. Although greater than 95% of the transuranics were removed from whole LECO crucibles, the quantity removed from crushed sections depended on the degree of mixing with the $NH_4HF_2$. Even with incomplete mixing, greater than 60% of the transuranics were removed after a single fusion and dissolution step.

Insoluble residues remaining after dissolution contained trace quantities of the transuranics (Slide 9). Transuranics detected were only in pieces of crushed LECO crucibles that had not fused with the $NH_4HF_2$. The major constituents remaining in both types of residues were silicon and aluminum.

**CONCLUSIONS**

Results from the laboratory program have shown that low temperature fusion followed by dissolution can remove most of the transuranics from incinerator ash and LECO crucibles. Residues remaining after dissolution contain only trace quantities of the transuranics and are considered as discardable waste.

Although the chemistry of the solubilization process has been demonstrated, additional work with both incinerator ash and LECO crucibles is required (Slide 10). Two additional types of incinerator ash are available for future studies. These include a high transuranic content ash, and ash generated at alternate plant sites. LECO crucibles using copper as the accelerator are available for additional investigation. Those using iron and tin accelerators have already been examined.

Corrosion due to the high fluoride content will require investigation. Minimizing the quantity of $NH_4HF_2$ needed and/or complexing the fluoride are possible solutions. Both fusion and dissolver off-gas systems need to be studied. Potential plugging of the off-gas system due to $SiF_4$ hydrolysis is possible. Methods to improve filtration or the use of a centrifuge for dissolver solution clarification have not been examined. Efficient LECO crucible crushing techniques and optimization of the $NH_4HF_2$ mixing step will also require a significant development effort.

| | |
|---|---|
| Slide 1 | Fluorination by Fusion |
| Slide 2 | Transuranic Removal from Incinerator Ash and LECO Crucibles |
| Slide 3 | Waste Compositions |
| Slide 4 | Fluorinating by Fusion |
| Slide 5 | LECO Crucible Fusion |
| Slide 6 | Incinerator Ash Fusion |
| Slide 7 | Incinerator Ash Results |
| Slide 8 | LECO Crucible Results |
| Slide 9 | Residue Compositions (SEM) |
| Slide 10 | Future Studies |

# FLUORINATION BY FUSION

by

J. H. GRAY

SAVANNAH RIVER LABORATORY

CONTRACT WITH U. S. DEPARTMENT OF ENERGY

## TRANSURANIC REMOVAL

## FROM

## INCINERATOR ASH AND LECO CRUCIBLES

- Both pyrochemical and aqueous process
- Efficient transuranic removal
- Low temperature
- Insoluble refractories to soluble fluorides

**WASTE COMPOSITIONS***

| Waste Category | Backlog, % | Annual Generation, % |
|---|---|---|
| Salts | 36.8 | 15.3 |
| Ash | 13.1 | 28.8 |
| Heels (filter) | 11.1 | 3.2 |
| Graphite | 9.9 | 2.1 |
| SSC | 9.8 | 21.2 |
| Combustibles | 6.1 | --- |
| Ceramics (LECO) | 5.5 | 4.9 |
| Aluminum alloy | 2.7 | 12.3 |
| Others | 4.9 | 12.2 |

*Low Level

## FLUORINATING BY FUSION

Two process steps:

- Fusion with ammonium bifluoride
  - $NH_4HF_2$
  - 4 hours at 140-170°C
- Dissolution in 14 M $HNO_3$
  - Boiling for 4 hours

# LECO CRUCIBLE FUSION

# INCINERATOR ASH FUSION

**INCINERATOR ASH RESULTS**

- Lose 10 wt % during fusion
- 10-20 wt % solids remain
- Difficult to filter
- Easy to centrifuge
- 95-99% transuranics removed

**LECO CRUCIBLE RESULTS**

- Lose during fusion
  - 4-6 wt % (whole)
  - 10-13 wt % (crushed)
- Crucibles remaining after dissolution
  - 91-92 wt % (whole)
  - 69-76 wt % (crushed)
- Solids easier to filter
- Solids easy to centrifuge
- 65-70% transuranics removed

## RESIDUE COMPOSITIONS (SEM)

### Incinerator Ash

- Major - Si, Al, O, (Cr), (Fe), (Ti)
- Minor - Ti, Fe, Ni, Cr, Ta
- Trace - Pb, Ta, (TU)*, (Ni)

### LECO Crucibles

- Major - Si, Al, O, (Sn)
- Minor - Zr, Fe, Ni, (Al), (Si)
- Trace - (TU), (Cr)

*TU - Transuranics

## FUTURE STUDIES

### Incinerator Ash

- Process demonstration
  - Two types complete
  - Two types to be investigated

### LECO Crucibles

- Process demonstration
  - Two types complete
  - Third type to be investigated

### Problem Areas

- Corrosion
  - High fluoride content
- Crucible crushing
- Bifluoride mixing
- Solids handling during dissolution
- Off-gas system
- Slurry clarification