TITLE: INCINERATION AND INCINERATOR ASH PROCESSING

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INCINERATION AND INCINERATOR ASH PROCESSING

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ABSTRACT

Parallel small-scale studies on the dissolution and anion exchange recovery of plutonium from Rocky Flats Plant incinerator ash were conducted at the Los Alamos National Laboratory and at the Rocky Flats Plant. Results from these two studies are discussed in context with incinerator design considerations that might help to mitigate ash processing related problems.

INTRODUCTION

Incineration has long been the preferred method for volume reduction of combustible waste contaminated with transuranic elements. Although incinerator ash has been successfully processed at production sites for many years, it has not been without difficulty. Problems that adversely affect actinide recovery process operations and efficiencies arise from complicated ash chemistries that in part can be attributed to poorly designed, highly inefficient incinerators.

In the early 1980's when processing off-site incinerator ash from Hanford at Los Alamos, a myriad of new, not previously encountered processing problems were observed. These included (a) excessive foaming during ash addition to the dissolver when using nitric/hydrofluoric acid mixtures, (b) poor filtration, (c) a viscous residue buildup on equipment, and (d) fouling of anion exchange columns. Ash analyses showed Hanford ash to have high concentrations of carbon. To resolve the process problems ascribed to unburned hydrocarbons in ash, Los Alamos developed and employed rotary calcination.1 This simple process proved so effective in removing residual ash carbonaceous material and in remedying the processing difficulties that were experienced that it was implemented in the Plutonium Finishing Plant at Hanford as a pretreatment prior to ash dissolution in the nitric/hydrofluoric acid system.

There exist other evidence of incomplete combustion of material during incineration. This is found in the literature and in support documentation where high levels of carbon are commonly reported in Rocky Flats Plant (RFP) ash,2,3 At RFP, feed to the incinerator includes such items as polyethylene bottles, plastic glovebox bags, paper towel wipes, rags, surgeons gloves, and plastic tape. Although the incinerator operating temperature is sufficiently high (approximately 850°C), the material residence time is not adequate for complete combustion of hydrocarbons. This was recognized by scientist and engineers from sites across the production complex that were assembled to assess the Plutonium Recovery Option Verification Exercise (PROVE) then under construction at RFP. (The future of PROVE remains unclear, however, it was to be the new aqueous incinerator ash processing line consisting of dissolution, anion exchange,
peroxide precipitation, and calcination capabilities.) Having knowledge of the problems associated with processing carbon-bearing ash, the committee strongly recommended that rotary calcination be added to the flowsheet and final design.4

Other processing problems result from high concentrations of silica in ash. In nitric/hydrofluoric acid (HF), silica reacts with HF and water to form fluorosilicic acid and silicon solids that plug offgas systems.5,6 When aluminum nitrate is added to dissolver filtrates to complex free fluoride (to minimize fluoride-induced corrosion of equipment), it complexes with silicon species present to form a troublesome gelatinous precipitate that readily plugs filters. If this gel is not completely removed, solids collect in storage tanks and diminished flow or plugging of ion-exchange systems occurs.

Following issuance of the PROVE committee's report, the Plutonium Technology Committee, a body organized to coordinate research activities between Los Alamos and Rocky Flats, formed and chartered the Incinerator Ash Processing Working Group (IAPWG) with investigating areas identified as important to RFP.

Four specific areas were identified as sufficiently important to warrant further investigation: (1) the optimal fluoride concentration needed for the dissolution of plutonium from incinerator ash, (2) the effect of free fluoride on anion exchange performance if aluminum nitrate is not added to the filtrate as a complexing agent, (3) possible equipment corrosion problems from potential large quantities of uncomplexed fluoride, and (4) the effects of ash carbonaceous material on anion exchange behavior.

Presented below is a compendium of results obtained from parallel small-scale dissolution and anion exchange studies at Los Alamos and Rocky Flats.7,8 I have limited the discussion to addressing only concerns 2 and 4 above because incineration system design changes could help to mitigate there effect.

EXPERIMENTAL

Six identical tests, with identical equipment and operating parameters were conducted. All incinerator ash used in this study originated from RFP. RFP used virgin ash feed (uncalcined, no treatment prior to experimentation), whereas Los Alamos rotary calcined the ash feed at 600°C for a minimum of 4 hours to remove as much ash carbonaceous material as possible. A comparison of the data from untreated and calcined ash feed experiments would provide the basis for determining the effect of unburned carbonaceous material on dissolution efficiencies and on anion exchange plutonium loading efficiencies. The test comparison could also aide in the decision to continue with or omit the addition of a fluoride complexing agent to avoid processing problems attributed to the presence of silicon in ash.

Dissolution was performed using a small-scale cascade dissolver system composed of three 2-in. diameter by 12-in. long glass-pipe dissolvers arranged in series. Cascade dissolver systems and their principle of operation are described elsewhere.9 Six runs were made using feed fluoride concentrations of 0.4, 0.1, 0.25, 0.35, 0.5, and 0.4 M respectively. With the exception of calcium fluoride, which was added to achieve the specific feed fluoride concentration, ash feed and solution flow rates were fixed at a predetermined value.

Filtrate from the dissolution of ash was processed through a 3-in. by 12-in. ion exchange column loaded with Lewatit MP-500-FK, 40-70 mesh, macroporous resin converted from the chloride to the nitrate form. As a final step in preparing feed solutions for anion exchange, acid and plutonium concentrations were adjusted to approximately 7.5 M and 1.5 g/L respectively, and fed to the column at a rate of approximately 650 ml/min. No fluoride complexing agent (aluminum
nitrate) was added before anion exchange. The plutonium loading capacity of the anion exchange resin was based on a plutonium breakthrough point arbitrarily set at 5% of the feed concentration.

**EXPERIMENTAL RESULTS**

Table 1 gives the relative concentration of plutonium and impurities (important to this discussion) found in the uncalcined and calcined ash feeds. From the data, two points can be made: (1) it is readily seen that rotary calcination is an effective method for removing cabonaceous material, and (2) certain impurities are found in excess of 1% of the total mass of the ash feed.

![Table 1. Composition of virgin and calcined ash feeds.](image)

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>CALCINED (Wt %)</th>
<th>UNCALCINED* (Wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pu</td>
<td>9.0 - 14.5</td>
<td>6.0</td>
</tr>
<tr>
<td>C</td>
<td>0.26 - 0.32</td>
<td>15.0</td>
</tr>
<tr>
<td>Cl</td>
<td>2.9 - 3.3</td>
<td>1.2</td>
</tr>
<tr>
<td>Al</td>
<td>5.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Si</td>
<td>7.0 - 10.0</td>
<td>&gt; 1.0</td>
</tr>
<tr>
<td>Ca</td>
<td>6.0 - 8.0</td>
<td>&gt; 1.0</td>
</tr>
</tbody>
</table>

*Analytical data available for only 1 of 6 ash feeds used.

In all tests, the fluoride complexing agent was omitted prior to anion exchange. The gelatinous precipitate that normally forms was not observed.

Figure 1 shows the plutonium and bulk dissolution efficiencies as a function of fluoride concentration for both uncalcined and calcined incinerator ash feeds. In all cases, the dissolution efficiencies were higher in the calcined ash.

It should be noted that in the Los Alamos tests, offgas plugging was not observed until the feed fluoride concentration was increased to 0.5 M. In this study, the percent of plutonium dissolved either did not improve, or did not significantly improve at the higher feed fluoride concentration of 0.5 M. As a rule of thumb, however, plutonium dissolution is often enhanced at feed fluoride concentrations in excess of 0.4 M. Thus, less than optimum plutonium dissolution is the trade off for minimizing the effects of silicon in ash feed.

Figure 2 shows the resin plutonium loading capacity when processing filtrate from both the uncalcined ash and calcined ash feeds at various fluoride concentrations. The capacity was greater with filtrate from calcined incinerator ash at all feed fluoride concentrations. It should be noted that the resin plutonium loading capacity was not calculated for calcined ash runs 1 and 2 because all of the feed filtrate was processed before the 5% breakthrough point was reached. Thus, the resin plutonium loading capacity was arbitrarily set as (and graphically shown in Figure 2 as) the quantity of plutonium loaded on the column at the time the run was terminated.

**DISCUSSION**

The ash dissolution data show improved plutonium and bulk dissolution efficiencies...
Figure 1. Dissolution Comparison

![Bulk Dissolution and Plutonium Dissolution Graphs]

In all tests, the addition of a fluoride complexing agent to the dissolution filtrate was omitted in order to circumvent the ill-effects of silicon. Although the appearance of a troublesome gelatinous precipitate was avoided, offgas plugging was still observed in the Los Alamos tests. Thus, there is still a high price for optimizing plutonium dissolution. Also, Marsh has shown that uncomplexed fluoride effects the anion exchange of plutonium from nitric acid. \(^{(11)}\)

It is clear that the plutonium loading capacity of the resin is adversely affected when processing incinerator ash with a high carbon content. At all feed fluoride concentrations the resin plutonium loading capacity when processing filtrate from the calcined incinerator ash was significantly greater than the capacity found when processing filtrate from the uncalcined ash.

RECOMMENDATIONS

From the data above, it is evident that (1) the concentration of bad actors such as carbon and silicon and quite possibly aluminum in incinerator ash should be kept to minimum, and (2) ash from the incinerator at RFP is high in these impurities.

During the PROVE assessment, it was found that the firebrick liner in the RFP

with calcined ash. Although this observation can be attributed to the absence of carbonaceous material that would compete for the fluoride ion present and needed for plutonium dissolution, the improved dissolution realized could also be attributed to the higher level of plutonium found in the calcined starting material.

Recently at Los Alamos, researchers working on new methods for recovering plutonium from ash found that simple water washing produced a discardable filtrate while reducing the ash weight by as much as 39%. This is not only an attractive and simple method for high-grading plutonium, but has significance where scrap storage is limited.\(^{(10)}\)
incinerator was principally composed of oxides of aluminum and silicon. Because of deterioration, the liner had to be replaced on about 5 year intervals. The deterioration of the firebrick most certainly was a contributor to the high levels of aluminum and silicon characteristically found in RFP ash. Also, the floor of the incinerator was constructed such that the ash material fell from the "hot" zone as soon as it was sized to less than that of the holes in the grated floor; resulting in incomplete combustion of the material.

In the future, new and improved liners should be evaluated and incorporated into incinerator designs. Also, system operating temperature and material residence time must be taken into account and be sufficient to remove excess carbon.

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REFERENCES


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