VOLUME REDUCTION AND SALVAGE CONSIDERATIONS FOR
PLUTONIUM-CONTAMINATED FERROUS METAL

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I. Introduction

The extensive operations in facilities operated by the federal Energy Research and Development Administration (ERDA) which handle plutonium have resulted in the accumulation of large quantities of contaminated metal waste. Materials and equipment contaminated to varying degrees with plutonium originate in fabrication, reprocessing, and other operations, and from decommissioning, and include obsolete or failed process equipment, tools, materials from enclosures, and valuable metals. The nature and extent of the contamination prohibits normal disposal and presently requires exclusion procedures, among them, rather costly retrievable storage. Safety and economic advantages are likely if effective decontamination could result in salvage of valuable equipment and metals, and/or disposal procedures compatible with the handling of other low-level wastes, and recovery and concentration of the actinides.

Most facilities that carry out operations involving transuranium elements include some form of decontamination and waste handling, but there appear to be no systematic studies in progress dealing with decontamination of metals and equipment contaminated by alpha-emitting elements such as plutonium. In contrast, a program dealing with uranium-contaminated metal has been in progress at National Lead. The objectives of our program are to provide and evaluate decontamination techniques, both conventional and unconventional, for the decontamination of contaminated metals in light of criteria for release, reuse, or disposal. The present work is concerned mainly with contaminated steel.

The scope of the nature and magnitude of the overall problem was determined through visits to pertinent sites and review of literature; some aspects of the
problem that were identified are shown in Table 1. As an example of the
information obtained, it is reported\(^1\) that 2.3 million cubic feet of equipment
are stored at the Hanford site in eight different locations. The associated
plutonium inventory is about 15 kg. A single decommissioning operation\(^2\)
at the Mound Laboratory produced three times the annual quantity of waste, of
a given type, shipped from this site; this single job produced 150,000 ft\(^3\)
of type B waste (1.0 μCi to 20.0 Ci/package). Transuranic waste has been
generated at the Rocky Flats Plant in Colorado at a rate of about 185,000 ft\(^3\)/yr.\(^3\)
No detailed account of the total metal inventory associated with the transuranic
waste is available, however, a reported estimate is that 20 to 40% by volume of
the total waste produced is in metallic form.\(^3\)\(^4\) Furthermore, under current
Federal regulations material contaminated with transuranic elements in excess
of 10 nCi/g of waste cannot be disposed of in normal burial grounds and require
storage in a retrievable posture, possibly for periods to 20 yr.

**Information from the Literature on Decontamination**

Considerable information in the literature discuss removal of beta gamma
(β-γ) contamination, but much less deals with alpha decontamination.
Christensen\(^5\) reports his compilation of plutonium-decontamination techniques is
based on work with fission-product (β-γ) contamination. Applicability of these
techniques to removal of alpha-activity needs to be verified. Knowledge and
experience gained from the development of procedures and reagents for metal
cleaning in the non-nuclear field has provided the foundation for many of the
procedures currently in use. For our purposes it is assumed that contamination
is a surface (or near surface) phenomenon, rather than one involving grain
structure.

**Review of Current Assay Methods**

Assay for plutonium is a key problem area. Reliable assay infers
reliability in sampling, which is extremely problematic at the 10 nCi/g level.
TABLE 1

Problems Identified in Early Effort

1. Inventories of plutonium-contaminated metals are vast and are increasing at a substantial rate.
2. Contaminated materials are often of mixed metals.
3. Contaminated materials are often non-uniform in shape.
4. Decontamination methods for alpha (plutonium) contaminated metals vary from site-to-site, i.e., they are not systematized.
5. Monitoring capability for metal wastes by NDA techniques at the plutonium level of 10 nCi/g of matrix does not exist.
6. Criteria for unrestricted reuse of plutonium-contaminated metal have not been developed.
The most functional assay methods are those employing non-destructive assay (NDA) techniques. Desired features are simple equipment, speed, high sensitivity and precision. Use of the natural radiation of the material (passive methods) offers some simplicity, but often promoting emission (active methods) by subjecting the material to external radiation, e.g., neutron activation, becomes necessary. Unfortunately, commercial assay equipment is not yet developed to the levels of sensitivity needed for our purpose.

Facilities that deal with actinides employ a wide variety of quantitative analytical methods for determining plutonium at extremely low concentrations down to less than nanogram quantities; these usually require samples in the form of aqueous solutions. Whole body counting represents an NDA method with sensitivities in the range of a few micrograms but is not considered practical for waste containers. Gamma counting has been used successfully at low levels but not for high-Z (high density) materials. Passive gamma scanning is used for assay of finished products such as fuel plates and rods, but this involves a relatively high plutonium level; also, such material is well characterized and standards are available. Passive and active systems involving neutron counting are employed in areas other than waste monitoring, where plutonium levels are higher.

The development of NDA methods for assay of small quantities of plutonium, distributed heterogeneously in a poorly characterized, relatively dense matrix having a relatively high atomic number is expected to be receiving increased attention with time, but little work specific to this area of waste management is in progress.

Work on a program (unrelated to waste management) at ANL-CEN with liquid scintillators may have application to low-level plutonium assay in metals but the work is not very far advanced. The method is based on the detection of
neutrons from the spontaneous fission of $^{239}$Pu. The liquids give good pulse shape discrimination for neutrons and gammas and thereby lend themselves to correlation techniques. Sensitivity of the system can be increased with multiple detectors. It will be necessary to have the system well characterized, i.e., to know the isotopic content of the plutonium and neutron contribution from the $\alpha$, $n$ reaction. Overall, initial results show good potential for the system, compared to other methods (e.g., use of plastic scintillators in a commercial machine).

The Generalized Approach to the Problem

The main feature of the problem which represented the focal point for our experimental program is that equipment or structures (e.g., glove boxes) are difficult to assay for plutonium contamination levels because of size and shape. One solution appeared to lie in transforming the material to such a form that current assay methods can be applied. Reducing the material to a standard shape such as a cylindrical ingot or slab by melting was selected as the method to be explored. In effect this precludes salvage of the original usable form, but does not preclude salvage of the metal.

The process scheme under investigation is referred to as melt refining of steel, generically, a pyrochemical process. The process is intended to permit reliable sampling of a standard shape, provide decontamination of the metal, and volume reduction of the plutonium fraction, as well as some overall volume reduction. The main containing species is assumed to be PuO$_2$. Slags are expected to be needed to achieve the desired levels of decontamination. Past work$^6$ with molten iron and fission products employed excessive amounts of molten salts and oxide slags. The latter is an area of concern in the present work, which will attempt to minimize slag/salt requirements.
The technology for melting and casting steel is well established so a good base of knowledge is available. The chemistry of plutonium is fairly well understood to allow preliminary estimates to be made of the potential of various melt-refining systems. For any scheme that is selected, recycle of materials will be stressed to reduce the overall waste burden.

The Experimental Program

The purpose of the experimental program is to investigate the chemical feasibility of the melt refining of steel to achieve a separation of plutonium to a residual level of 10 nCi/g of matrix. Melting with and without slags has started, and screening tests on candidate slag materials are in progress. Similarly crucible materials are undergoing testing. Compatibility of slag-crucible combinations will be evaluated as the work proceeds. The main features of the program are listed in Table 2.

Work with plutonium-contaminated steel is being done in a newly-installed glove box facility, while support studies with non-contaminated or stand-in materials are being done in direct-access equipment. The glove box is the type widely used in the Chemical Engineering Division at Argonne, and is referred to as a 1 1/2-by 3-module unit, a module being essentially a 3.5 ft (1.15 m) cube. The glove box is equipped with a helium atmosphere for added flexibility. The key item of equipment is a modified Brew furnace with tungsten mesh heating elements, capable of temperatures near 3000°C; modifications largely concerned changes in heating element design to make furnace operation more compatible with glove box work.

A small arc melter has also been installed in the glove box; this unit has about a 50 g capacity.

Shakedown test melts of about 200 g of steel have started in the Brew furnace, as of this writing. Startup of work with plutonium is expected in
TABLE 2. **Features of the Steel Melt-Refining Experimental Program**

1. Examine effect of slag material/composition on residual PuO$_2$ level in the product ingot.
2. Examine effect of crucible material on residual PuO$_2$ level in the product ingot.
3. Study kinetic factors.
4. Study phase separation problems.
5. Determine homogeneity of PuO$_2$ distribution in the steel after melt-refining.
6. Establish operating procedures.
July, and initial results will be presented orally.

Support studies have involved test melts with UO₂ added as a stand-in for PuO₂. Initial tests involved 450g of mild steel (m.p. ~1425°C). Initial melts were made in slip-cast magnesia crucibles (2.5 in. OD x 2.25 in. ID x 5.275 in. high). The charge was heated to a nominal 1500°C, and held at temperature for one to two hours. In initial experiments the melt was allowed to solidify in the crucible, which cracked as the metal solidified. In later experiments, the molten metal was poured into a mold, permitting better evaluation of crucible behavior (resistance). Samples were obtained from the ingots by machining (turnings) and drillings. Conditions and early results are summarized in Table 3.

Examination of the MgO crucibles showed undercutting, evidence of corrosive attack; also the crucible adhered to the ingot in some areas. Tests with commercial fire-brick materials supplied by Harbison-Walker showed generally good resistance, particularly the "Ruby" material; see Table 3 for composition. The UO₂, added as powder as a stand-in for PuO₂, does not appear to be wetted by the molten steel, and the bulk of it remains behind in the crucible. A survey of a dross on one ingot after solidification in the mold showed a very low radiation source indicative of traces of uranium. Quantitative results from samples of the dross and various metal sections are pending.

Work with slags has also begun. The initial test involved cryolite (3NaF·AlF₃). The cryolite completely penetrated the MgO crucible in this case. On the basis of literature information and discussions with steel industry personnel, empirical testing of slags appears necessary. Slags selected for study include CaO·SiO₂ and CaO·MgO·SiO₂. Basic slags (e.g., CaO/SiO₂ >1) were recommended for initial testing.
<table>
<thead>
<tr>
<th>Test No.</th>
<th>Crucible</th>
<th>Charge</th>
<th>Conditions</th>
<th>Preliminary Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>MgO</td>
<td>Steel</td>
<td>1475°C, 1 hr</td>
<td>Crucible cracked.</td>
</tr>
<tr>
<td></td>
<td>(2.5 in. OD x 2.25 in. ID x 5.275 in. high)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>Same as 1</td>
<td>Steel</td>
<td>1515°C, 2 hr</td>
<td>Crucible cracked.</td>
</tr>
<tr>
<td>3.</td>
<td>Same as 1</td>
<td>Steel +</td>
<td>1515°C, 2 hr</td>
<td>Crucible severely attacked by cryolite.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>cryolite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>Same as 1</td>
<td>Steel</td>
<td>1400°C, 2 hr</td>
<td>Crucible cracked.</td>
</tr>
<tr>
<td>5.</td>
<td>Same as 1</td>
<td>Steel</td>
<td>1545°C, 2 hr</td>
<td>Molten metal poured into mold, crucible intact.</td>
</tr>
<tr>
<td>6.</td>
<td>H-W Ruby</td>
<td>0.5 kg steel</td>
<td>1525°C, 1.3 hr</td>
<td>Melt poured into SiC mold, crucible appears to be unattacked, UO₂ found in crucible.</td>
</tr>
<tr>
<td></td>
<td>a, c</td>
<td>0.5 g UO₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(2.75 in. OD x 1.5 in. ID x 4.5 in. high)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.</td>
<td>H-W COPUR</td>
<td>0.5 kg steel</td>
<td>1525°C, 1.3 hr</td>
<td>Melt poured into mold, crucible appears unattacked, UO₂ found in crucible.</td>
</tr>
<tr>
<td></td>
<td>b, c</td>
<td>0.5 g UO₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(Dimensions as in test 6)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.</td>
<td>H-W GUIDON</td>
<td>0.5 kg steel</td>
<td>1525°C, 1.3 hr</td>
<td>Melt poured into mold, some attack of crucible evident, UO₂ found in crucible.</td>
</tr>
<tr>
<td></td>
<td>d</td>
<td>0.5 g UO₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(Dimensions as in 6)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9.</td>
<td>H-W Ruby</td>
<td>0.5 kg steel</td>
<td>1535°C, 2 hr</td>
<td>Re-used crucible from Test 6; material seems satisfactory after pour of melt; UO₂</td>
</tr>
<tr>
<td></td>
<td>a</td>
<td>0.5 g UO₂</td>
<td></td>
<td>appears intact in crucible.</td>
</tr>
<tr>
<td>10.</td>
<td>H-W Ruby</td>
<td>0.5 kg steel</td>
<td>1525°C, 2 hr</td>
<td></td>
</tr>
<tr>
<td></td>
<td>a</td>
<td>0.5 g UO₂</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

^a Product of Harbison-Walker, 89.7% Al₂O₃, 10% Cr₂O₃, apparent porosity 16.5-19.5%.

^b Product of Harbison-Walker, 33.5% MgO, 32.5% Cr₂O₃, 20.3% Al₂O₃, apparent porosity 16-20%.

^c Crucibles outgassed for 1 hr at 1600°C prior to melting test. Crucibles showed weight loss of 1.7%.

^d Product of Harbison-Walker, 62.7% MgO, 18.1% Cr₂O₃, 5.4% SiC₂, 1% JiO₂, 12% Fe₂O₃, 0.8% CaO, apparent porosity 13-16%.
Summary and Conclusions

A survey of the literature and discussions at pertinent sites operated for ERDA disclosed an inventory exists of plutonium-contaminated metal. Furthermore, this type of waste continues to accumulate at a substantial rate. The burden of storage is of increasing concern.

This waste comprises a wide variety of metal forms and in many cases is of mixed metals. Salvage of the metal for storage as a non-alpha-bearing waste or possibly for re-use and consolidation of the plutonium fraction offer significant economic and safety benefits if these goals can be achieved.

Reliable assay of much of the waste for plutonium content requires reliable sampling and is virtually impossible because of its heterogeneous nature (size, shape, configuration). Furthermore, reliable methods for assaying to the presently required plutonium level of 10 nCi/g of matrix are not commercially available: this level is the present criterion for designation as non-alpha-bearing waste and permits ordinary storage (as opposed to rather costly retrievable storage), but not necessarily unrestricted distribution (re-use) of the metal. Work on assay methods, particularly non-destructive assay (NDA) techniques, continues to be monitored. Recent work with liquid scintillators for monitoring neutrons appears to have some potential for our application and is being pursued.

Transforming the metal waste to a standard form such as an ingot or slab by melting (melt-refining) should facilitate both sampling and assay and has been selected for exploratory study. Present emphasis of work is on ferrous materials.

Small-scale studies on the melt-refining of steel contaminated with plutonium are just getting started in a glove box facility. Support work on
non-contaminated steel is in progress using UO$_2$ as a stand-in for PuO$_2$. The initial phase of work in the support studies is concerned with establishing operating procedures and finding crucible and slagging materials that are compatible. Preliminary results in steel-melting tests without slags indicate some of the commercial fire-brick materials may be satisfactory as crucibles. UO$_2$, added as a stand-in for PuO$_2$ in the support work, appears to be not wetted by the molten steel and remains in the crucible when the molten steel is poured into a mold. Quantitative information on the final distribution of uranium is being developed for presentation orally.

Crucible-slag combinations are undergoing compatibility testing in the support studies. Initial work with cryolite as a slag proved very corrosive to a MgO crucible.

Work with plutonium will focus on establishing the distribution of plutonium (oxide) in the various materials, i.e., ingot, slag crucible.

An ultimate goal of this work is the decontamination of plutonium-contaminated metal in the light of criteria for re-use release, or disposal.
THE BASIC PROBLEM

• Large Inventories of Plutonium-Contaminated Metal Wastes Exist at ERDA-Contractor Sites, and Represent an On-Going Burden.

• Production of Such Wastes is Continuing as Equipment is Repaired, Replaced, or Updated, or When Plutonium-Handling Facilities are Decommissioned
SCOPE OF WORK


3. Emphasis of Work to be on PuO$_2$-Contaminated Ferrous Metals.
THE APPROACH

Evaluate the Techniques of Melting Steel with and without Slagging Materials as a Means of Separating the Plutonium and Consolidating the Metal Waste.
THE NATURE OF THE PROBLEM

• The contaminated materials are

(A) Often bulky
(B) Heterogeneous in shape and composition
(C) Difficult to sample to establish the level of contamination or the level of decontamination
Current regulations require that waste containing more than 10 nCi of long-lived alpha-emitters per gram be given special storage considerations with retrievability capability, which is expensive.
SUPPORT STUDIES

• Procure and Test Suitability of Crucible Materials for Steel Melting with and without Slags.

• Test Melting Procedures.

• Determine the Distribution of Pu Stand-Ins (U, Ce) with and without Slags.
<table>
<thead>
<tr>
<th>Type of Crucible</th>
<th>Cerium Distribution, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Crucible</td>
</tr>
<tr>
<td>SLIP-CAST MgO</td>
<td>3300</td>
</tr>
<tr>
<td>SLIP-CAST MgO with Cryolite</td>
<td>--</td>
</tr>
<tr>
<td>Type of Crucible</td>
<td>Dross in Crucible</td>
</tr>
<tr>
<td>------------------</td>
<td>-------------------</td>
</tr>
<tr>
<td>Slip-Cast MgO</td>
<td>0.02 g</td>
</tr>
<tr>
<td>Ruby</td>
<td>0.4 g</td>
</tr>
<tr>
<td>Ruby w/ SiC and B$_4$C</td>
<td>0.4 g</td>
</tr>
<tr>
<td>Copur</td>
<td>0.4 g</td>
</tr>
<tr>
<td>Guidon</td>
<td>0.4 g</td>
</tr>
</tbody>
</table>
GLOVE BOX WORK

* Set Up a Suitable Glove Box Facility,

* Conduct Steel-Melting Experiments on PuO$_2$-Contaminated Metal Sections, with and without Slags,

* Determine the Distribution of Plutonium in the Various Phases Using Existing and Innovative Sampling and Analytical Procedures.