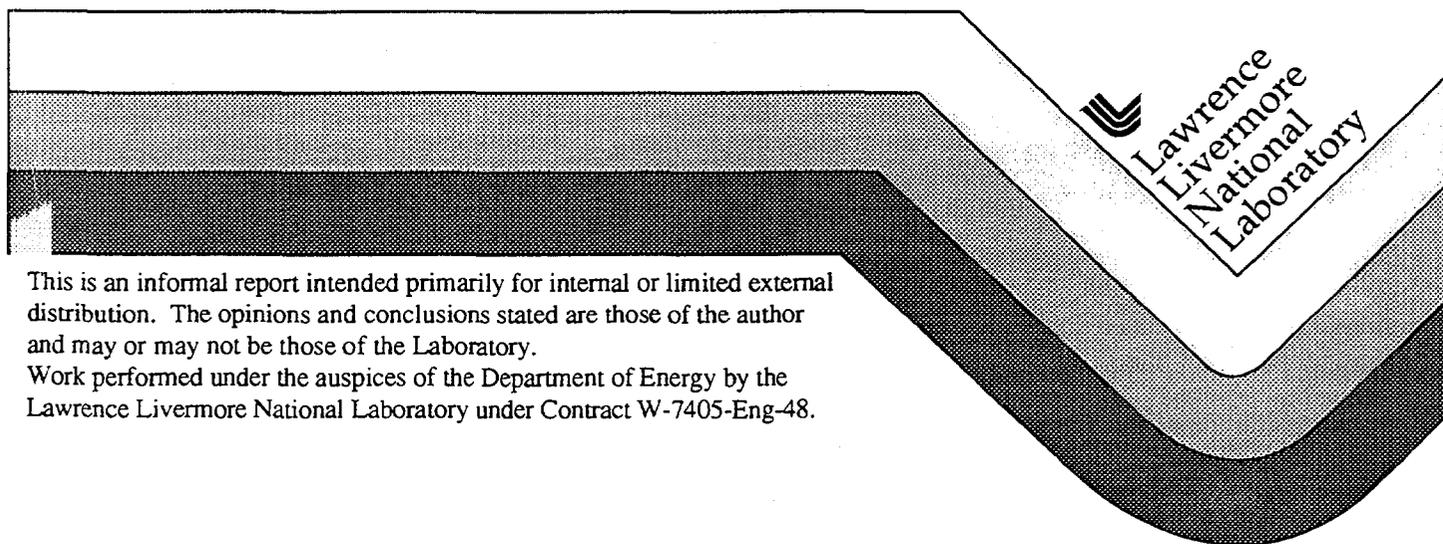# Bulging of Cans Containing Plutonium Residues— Summary Report

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March 1996

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Bulging of Cans Containing Plutonium Residues— Summary Report*

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Contents

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Abstract

In 1994, two cans in the Lawrence Livermore National Laboratory Plutonium Facility were found to be bulging as a result of the generation of gases from the plutonium ash residues contained in the cans. This report describes the chronology of this discovery, the response actions that revealed other pressurized cans, the analysis of the causes, the short-term remedial action, a followup inspection of the short-term storage packages, and a review of proposed long-term remedial options.

Bulging of Cans Containing Plutonium Residues— Summary Report

1.0 Introduction

In June 1994, during a routine surveillance of storage containers at the Lawrence Livermore National Laboratory (LLNL), two hermetically sealed packages—each consisting of concentric double (food-pack type) cans containing plutonium mixed-oxide residues—were discovered to have bulging lids. The packages were in storage in the LLNL Plutonium Facility. The mixed oxides included calcined precipitates from plutonium-containing solutions, other calcined material containing plutonium, off-gas duct scrapings, and some calcined box sweepings. Further investigation revealed that eight of the 111 packages containing similar material were bulged, either the outer can (observed visually) or the inner can (observed in radiographs) or both. This bulging indicated internal pressurization of the containers.

2.0 Background and Origins of the Material Stored

Small amounts of a wide variety of residues containing plutonium are inevitably generated at any plutonium facility in the course of research, development, and testing activities. At LLNL, these residues have included machine turnings, research and metallographic samples, residues from chemical analyses and solutions, crucible residues, wiping tissues, glovebox sweepings, and so on. They have contained mostly weapons-grade plutonium, but it is possible that small amounts of other plutonium isotopic mixes also have been present. When plutonium is present in quantities on the order of a gram or more in residues, the material is processed by dissolution in acid, and the plutonium is then precipitated and calcined to form "reacted ash" (RA). This processing eliminates pyrophoric materials, reduces the volume, and facilitates fissile materials control and accountability. In the 1970s and 1980s, this type of material was routinely calcined at about 450°C. This temperature was chosen apparently because it was thought to be high enough to decompose organic material and to produce a granular residue that could be made fairly homogeneous to permit accurate measurement of the plutonium inventory. This was a procedure generally followed at other sites at that time in processing pure plutonium compound precipitates (Ref. 1).

The plutonium residues in these batches had been stored since the 1970s in screw-top cans, and these in turn were packaged in outer cans that were not hermetically tight. This RA material was originally retained at LLNL with the intention of eventually recovering

the plutonium from it. However, as a result of changes in the supply/demand picture for plutonium, residue recovery is no longer performed.

2.1 Precipitation

During the period from the 1970s through 1992, the materials were first dissolved using hydrochloric acid solution. Some nitric and hydrofluoric acids were also used occasionally to facilitate the dissolution.

The plutonium-containing acid solution was then neutralized and rendered basic by the addition of excess sodium hydroxide. This caused the plutonium to precipitate as hydroxide. In the process, oxides and hydroxides of other metals (gallium, iron, tantalum, etc.) were also precipitated. The pH was not rigorously controlled, but exceeded pH 12, as indicated by using pH test paper. The solution was then filtered to remove the precipitate. The filter cake was not rinsed after filtering in order to minimize the amount of filtrate solution. The result of not rinsing was that some residual sodium hydroxide, together with chlorides, nitrates, and fluorides, probably remained in the filter cake.

2.2 Calcining

Calcining was carried out in an air-filled glovebox in which the materials were exposed to an atmosphere having the humidity of ambient air throughout the process. The filter cake, together with filter papers from the precipitation, was inserted into a stainless steel beaker, along with any cleaning tissues that were used and other residues such as glovebox sweepings. The beaker was placed into a vertical-axis electrical resistance clamshell furnace, also located in the air-atmosphere glovebox. Air was allowed to flow up through the furnace tube around the beaker.

The actual residue temperature was not monitored, but it is estimated to have risen to at least 400°C during this processing, and we believe that a reasonable estimate would be at least 450°C (Ref. 2). This is inferred from the temperature at the furnace heating element, which was monitored and controlled at 650°C. Higher furnace temperatures were thought to be undesirable because they would render the plutonium oxide more difficult to dissolve in recovery and reuse, which, it was expected at that time, would be performed at a later time.

The material was periodically stirred during a run, but this process is probably best characterized as distillation, pyrolysis, and partial calcining, rather than air roasting, because of the temperatures used and the diffusion-limited access of oxygen through the residue to the bottom of the beaker. It is likely that most organic species were decomposed or volatilized off, but some carbon would be expected to have remained as charcoal. Small amounts of oxyanions such as nitrates, if present initially, may have remained in the ash. The balance of the material after calcining would have consisted of plutonium oxide and other oxides, salts including chlorides, and residual sodium hydroxide.

2.3 Blending

After calcining, the material remained in the furnace as it cooled overnight. It can be expected that water would have adsorbed onto the ash from the glovebox air during and after cooling. It can also be expected that carbon dioxide would have adsorbed from the air and would have reacted with residual sodium hydroxide. Other atmospheric gases, such as nitrogen and oxygen, can also be expected to have adsorbed onto the ash.

The material was removed from the furnace and sieved using a 65-mesh (200-μm) screen. Any material not passing the screen was ground and rescreened. The material was sometimes brownish, but mostly tended to be gray or blackish, sometimes pepper-like. The powder was then mixed for four hours in a V-blender in air having the humidity of the ambient air. The purpose of this mixing was to ensure that the material was homogeneous in order to make possible the accurate determination of the plutonium inventory by calorimetry and gamma spectrometry of the final package. It can be expected that if the residues were not already at sorption capacity at this point, further adsorption of water would have occurred, particularly if very hygroscopic salts were present.

3.0 Material Storage and Inventory Reduction

From the 1980s until 1992, the storage procedure remained unchanged. Then, in 1992, the material was repackaged in a new way with the intent of shipping it off-site.

3.1 Material Storage, 1980s until 1992

For many years, the next step after calcining and sieving was to place the reacted ash in what locally came to be called "Kaufman cans." These are tin-plated steel cans incorporating screw-on lids with neoprene rubber gaskets. The Kaufman cans were of convenient, criticality-safe size, were easy to use, and prevented dispersal of plutonium-containing particulate material. The rubber gasket limited exchange of gases between the interior and the environment but did not provide a completely hermetic seal to gases. This was not considered to be a problem, because no radioactive gases were to be contained. Indeed, the lack of gas-tightness was an advantage in storage, and no bulging of Kaufman cans was ever observed as the reacted ash was accumulated and stored.

Furthermore, when Kaufman cans were used as the primary containers, the second—outer—can was also not hermetically sealed. Thus, the intent in the past at LLNL was to use cans that would not pressurize, but instead would leak at a very slow rate, should gases be generated.

3.2 Inventory Reduction Starting in 1992

In late 1992, a Plutonium Inventory Reduction Program was initiated. As part of the program, all batches of reacted ash in the LLNL Plutonium Facility were removed from the Kaufman cans, and most batches were consolidated together in pairs into larger

batches. The batches were blended, loaded into larger food-pack cans, and analyzed for material control and accounting. The material was not recalcined during the consolidation. The intent was to reduce overall package volume to facilitate shipping to the Savannah River Site for reprocessing and reclamation of the plutonium. This repackaging started in November 1992 and continued through July 1993, and combined the Facility's ash inventory into a total of 111 food-pack cans. Also, material was included from a general cleanup of the glovebox following a furnace replacement. This material was not reheated in the furnace, but was simply milled, sieved, and packaged in cans. This material did not undergo any further calcining.

The double-containment standard for the storage of plutonium materials was met in the new packaging, which is shown in Figure 1 (figures at end of report). The inner can was surrounded by two plastic bags, namely an inner PVC bag within an outer polyethylene bag. Each was taped shut. The inner bag was used to bag the inner can out of the glovebox. There would likely have been some plutonium-containing particulate material in contact with the inside of this PVC bag. The outer bag provided reasonably good containment of any particulate material exposed at the taped end of the PVC bag. The double-bagged inner can was finally placed within an outer can, which was then sealed. Both of the cans were designed to be hermetically sealed, although leak checking was not performed to verify this for each can. The sealing was considered necessary to prevent contamination of the shipping casks during the planned transport to Savannah River.

These packages using food-pack cans provided larger volume and double containment as well as a tighter seal to gas permeation. *Because no pressurization problems had been encountered with the Kaufman cans, none were anticipated with the food-pack cans, and they were not intended for long-term storage in any case.* However, because policy changes brought about by the state government of South Carolina made shipping the material to the Savannah River Site impossible, the packages that were sealed and prepared for shipment were not actually sent out of the Plutonium Facility. Thus, the material remained in the Plutonium Facility vault at LLNL for longer than originally intended. This longer storage time, combined with the nature of the material contained and the sealing of the cans, led to the bulging that followed.

4.0 Discovery of the Bulged Cans and Response

On June 17, 1994, during a routine inspection of the inventory, a technician noticed that two packages containing reacted ash exhibited bulged outer can lids, as shown in Figure 2. The packages were transferred to a fume hood, and their outer surfaces were surveyed for contamination. None was found, and the packages were then bagged into a glovebox.

A project team was formed to take the steps necessary to ensure the health and safety of plutonium facility workers, to investigate the cause(s) of the can bulging, and to recommend corrective actions. The team initiated the following actions:

- All remaining packages containing RA material were placed in sealed plastic bags inside the vault. This would provide some additional

containment and would facilitate decontamination in the event of an outer can rupture in the vault.

- A weekly inspection of the packages was begun to ensure the detection of any additional can bulging at an early stage.

- Radiographs were taken of 22 packages of RA material, selected on the basis that their contents and history were similar to those of the packages that had exhibited bulging.

- The use of respirators and gloves was made a requirement for personnel entering the vault that contained the repackaged RA material.

- Eight of the packages were found to have bulged inner or outer cans. These packages were then punctured, using a gas-sampling system in a glovebox, and the gases within them were analyzed. The solid contents of the cans and the cans themselves were examined. Results of these studies are discussed below in Section 5.

- Finally, the rest of the packages were punctured in the glovebox to allow release of gases. The packages were then placed inside plastic bags, and each package was bagged out of the glovebox and placed inside an imperial-gallon paint can having a fritted carbon disk plug to allow the escape of any further gases generated, while preventing the escape of plutonium-containing particulates.

5.0 Characterization of Cans, Gas, and Reacted Ash

The 22 selected packages were first visually inspected and radiographed. Then the gases within the eight packages found to have bulged cans were sampled and analyzed. The eight packages were opened, and their interiors and contents were visually examined. A few chemical features of the solids were measured. It appears that there were two types of chemical behavior, corresponding to packages in Groups I and II as described in Section 5.4 below.

The pressures required to produce the observed bulging and to vent the outer juice cans were determined using juice cans from the same batch as those originally used for the RA materials. Venting occurred over a range from 9 to 103 psig, but the median venting pressure was between 30 and 60 psig (Ref. 3).

5.1 Gas Sampling

Sampling of gas was performed on the eight packages, taking separate samples of gas from the region between the inner and outer cans and from inside the inner cans. The technique involved the use of a "vampire valve," a hollow needle that punctured the cans and extracted gas into a previously evacuated container. By expanding the gas into known volumes and measuring the pressures, the initial volumes and pressures inside the cans could be calculated.

5.2 Visual Inspection of the Cans and Solid Contents

As noted above, eight of the inner cans were opened. The insides of these cans were examined visually for corrosion, and the contents were also examined. Portions of the reacted ash were screened through a 32-mesh (500-μm) sieve to separate out larger particles, with the thought that pieces of organic or charcoal materials might be found.

5.2.1 Appearance of Solids

The solids in some cans had a nearly black color. In others, the solids tended toward brownish in color. Light-colored lumps were sometimes present. In some cases, the powder had caked a little but could be broken up easily. Occasionally, screening revealed brush bristles and some plastic particles. No large particles of charcoal were seen, but some of the smaller particles may have included charcoal.

5.2.2 Can Corrosion

In most cases, the cans were observed to be corroded. In some cases, this was a blotchy attack; in others, a uniform etching. In some, there was corrosion only above the solids fill-line, while in others, the whole interior exhibited attack. In no case was the corrosion deep enough to penetrate the can wall or lid.

5.3 Analyses of the Solids

The residues from five of the cans were analyzed for total carbon, total sulfur, and the pH of a small amount of water after mixing it with the solids. Weight loss upon heating in air was measured for temperatures in steps up to 1000°C in platinum crucibles in a dry argon atmosphere. The total losses ranged between 11% and 44%. Such large numbers are possible if the RA contained charcoal and hygroscopic materials such as NaOH.

5.4 Results of Analyses

In cases where little carbon was present in the initial residue in a particular can, the conditions in the gas phase remained relatively oxidizing, radiolysis gases were found to contain oxygen and nitrogen but little carbon dioxide and no detectable carbon monoxide, and the pH of the solids upon redissolution was found to be about 10. Where a large amount of carbon was present in the initial material, the final conditions were reducing, the gas was found to be rich in carbon monoxide, hydrogen, and carbon dioxide, and the solids gave solutions with a pH near 4.

Analysis of these data suggests that it is possible to divide the eight packages into two groups:

- **Group I** had <u>oxidizing conditions</u> in the final gas and pH 10 in the ash (where measured), and the can pressurization resulted primarily from nitrogen and oxygen.

- **Group II** had <u>reducing conditions</u> in the final gas and pH 4 in the ash (where measured), and can pressurization resulted primarily from carbon dioxide and hydrogen. This second group also had higher carbon and water content in the ash (where measured) and higher final gas pressures, corrected for can leakage. All cans in this group contained at least some material that had not received a final calcining treatment.

6.0 Discussion of the Causes of Pressure Buildup

Given the nature of the material and the circumstances, the prime suspect in this case was radiolysis, which is a combination of physical and chemical processes. The following is a summary of these processes:

- The solids contained water-soluble material that might have been washed out if they had been thoroughly rinsed. Rinsing was not done in order to limit resulting liquid waste volumes. As a consequence of not being washed, the solids are believed to have contained sodium hydroxides and smaller amounts of chlorides, nitrates, and possibly other soluble materials.

- Most of the batches of solids were calcined, but this was done at temperatures and under air-flow conditions that permitted the retention of carbon char and perhaps even some organic material. At 450°C—the estimated calcining temperature—these materials would not have been completely oxidized or perhaps not even completely pyrolyzed.

- After calcining, the solids were handled in such a way that they could have adsorbed moisture, carbon dioxide, nitrogen, and oxygen. The box atmosphere was derived from room air, the materials were exposed to it for hours and perhaps days, and some of the salts suspected to be present are hygroscopic.

- The dose rate from plutonium alpha-radiation in the powder is of the order of a megarad per hour. This is sufficient to decompose many organic materials within a few days to weeks. In addition, adsorbed water would have been radiolyzed to give hydrogen and oxygen. Therefore, gases would have been evolved that initially contained hydrogen, oxygen, and perhaps oxides of carbon.

- Radiolysis of carbon char when exposed to air would have initially yielded carbon monoxide.

- In those cans having a relatively small amount of carbon (Group I), the gas remained relatively oxidizing, and the carbon monoxide would have been further oxidized to carbon dioxide under irradiation. Much of this would have reacted with the sodium hydroxide to form sodium carbonate. The residual gas would be expected to contain some oxygen and only small amounts of carbon dioxide. The added nitrogen observed in the gas phase cannot be accounted for by radiolysis. Radiolysis of nitrates, if present, would give mostly nitrites. The added nitrogen probably originated as sorbed gas on the solids and was replaced by carbon dioxide when it was sorbed in turn. The fact that water had pH 10 when mixed with samples of these solids is to be expected for a $NaHCO_3$ - Na_2CO_3 mixture,

which would result from the reaction of CO_2, NaOH, and water, since it would buffer the pH at this value.

- In those cans having a relatively large amount of carbon (Group II), oxygen was used up, the gas became reducing, and the carbon would not all have been oxidized. The gases present would have included hydrogen, carbon monoxide, and some hydrocarbons, and some carbon dioxide would initially have formed solid carbonate. Under radiolysis conditions, the water-carbon monoxide mixture would have yielded formic and oxalic acids, which are stronger acids than carbonic acid and would have dropped the pH to 4, liberating the carbon dioxide back to the gas phase from any solid carbonates present.

7.0 Puncturing of All Suspect Packages and Overpacking in Frit-Vented Cans

Radiolysis of the plastic bags between the inner and outer cans would not have produced the amounts of gas observed. Therefore, the outer can would have bulged only if the inner can had released at least some of its gas. Because radiography had revealed bulging of some inner cans without visible bulging of the outer cans, it could not be ruled out that any one of the entire lot of 111 cans could eventually develop internal pressurization. As mentioned above, pressurization tests indicated that an occasional outer juice can might release gas upon pressurization to as little as 9 psig. It was further determined that sudden gas release from a juice can that was inside an imperial-gallon paint can with a carbon frit vent could sometimes pop the lid off the latter. Therefore, it appeared necessary to first puncture the juice and inner cans before overpacking them in the gallon cans.

An apparatus and procedure were therefore developed to puncture all the packages containing reacted ash. This was done inside a glovebox. The packages were bagged-out with double bags and were overpacked in imperial-gallon paint cans, the lids of which were fitted in advance with carbon frits (Nuc Fil 013 filters).

These filters would allow gas-flow in and out but would prevent release of particulates from the can. The spike used for puncturing the cans was made of alumina ceramic, an insulator, to guard against sparking. The puncturing and overpacking were completed in mid-September 1994, and the cans were returned to the vault.

It is recognized that this procedure is not the final solution. While it prevents the buildup of gas pressure, it also allows unlimited access of air of ambient humidity to the reacted ash. The plastic bags would be permeable to air and moisture. Thus, further radiolysis remains probable, producing corrosive species as well as additional gas. Indeed, radiolysis of humid air could be expected to generate appreciable amounts of nitric acid along with the hydrochloric acid known to be formed from the salts. However, further action was intended to be carried out within a few years, as soon as an appropriate storage procedure was decided upon and could be implemented.

8.0 Surveillance of Overpacked Storage Containers

Two storage packages from the former bulged-can batches were opened and inspected on December 4, 1995. All three cans in each package (the inner quart can, the outer juice can, and the imperial-gallon can) were in good condition and appeared capable of continued safe storage until the planned reprocessing is completed within several years.

The two packages examined were the following:

- #1: This was one of the "oldest" of the batches of RA materials. It had been sealed on November 20, 1992. It had never exhibited any bulging. It was vented in 1994 at the same time the other packages were vented as described in Section 7.0. It had then been bagged-out in new double plastic bags and placed into an imperial-gallon paint container with a carbon frit vent in the lid.

- #2: This batch had been found to be bulged in 1994 and was among the packages analyzed in the subsequent study. It had the highest carbon content of the materials examined, and the cans exhibited appreciable corrosion. The material was repackaged at that time into new cans. The repackaging duplicated the original packaging (inner quart can and outer juice can, separated by double plastic bags). This was placed inside a second set of double bags and a vented imperial-gallon can, in that order. However, the lid of each of the two innermost cans had been pre-punctured and lightly taped in order to provide ventilation.

The outer surfaces of all of the cans were in excellent condition. Both inner containers exhibited light corrosion on the inside of the lid, and the older package, which had been vented but not repackaged, contained some light browning of the innermost plastic bag where it was in direct contact with oxide/ash that had escaped from the vent.

The inner can from the newer package also had some light black corrosion on either side of the seam weld above the oxide fill-line. The tape sealing this inner can exhibited an outward dimple, indicating the presence of slight inner gas pressure.

The conclusion from this followup examination was that the rate of any deterioration was not great enough be of concern for periods of a few years, even in the case of the #2 sample, which was among the most chemically active originally. Nevertheless, careful monitoring of all packages will continue, and selected packages will be opened periodically, inspected, and repackaged.

9.0 Options for Making the Material Stable for Long Periods

There appear to be several options for stabilizing the RA material for storage times of decades or longer, as described in the following subsections.

9.1 Chemical Separation of the PuO_2

Stabilization of the residue material could be achieved by complete chemical reprocessing, in effect a recovery of the plutonium, with its conversion to pure oxide,

PuO_2. The purpose of this reprocessing would not be to recover the plutonium per se, but rather to put it into a form that has well-characterized behavior during storage instead of the complex behavior of poorly defined residues. There is an existing body of knowledge about the properties of plutonium oxide, its rate of adsorption of gases, its adsorption capacity, and its loss of water on ignition, so that its storage behavior is more predictable. However, this option would involve considerable chemical processing.

9.2 Partial Processing

Partial chemical processing, rather than the complete separation of the plutonium from the residues, might be satisfactory. The objective would be to remove those constituents that would lead to the generation of gases. The formation of pressurizing gases and corrosive substances depends on the radiolysis of adsorbed water, organic material or incompletely pyrolyzed organics, sodium hydroxide, and salts. Some of the constituents—for example, NaOH and $NaNO_3$—can combine to form low-melting eutectics that could inhibit the pyrolysis of some organic materials by forming a protective film over them. If these were removed from the residues by washing, the remaining mix of metal oxides and compounds, once calcined, would be much less likely to outgas. Also, the tendency for such washed and calcined material to readsorb water would probably be less than for the original reacted ash.

The washed material would have to be calcined to drive off adsorbed water, to pyrolyze the organics, and to burn off the carbon. This would probably require a temperature of at least 850°C. The calcined material would then have to be removed from the calcining furnace and packaged with special care to avoid the readsorption of moisture, although the material would be less hygroscopic than the original RA.

The disadvantages of this option would be (1) the production of large volumes of wash water, which would have to be incorporated into cementing material for storage and eventual disposition as low-level transuranic waste and (2) the need for higher calcining temperatures than previously used and possibly new equipment to achieve these temperatures.

9.3 Direct Incorporation of Residual Ash Materials into Glass or Ceramic

Another option is to directly incorporate the residues into glass or ceramic. This would decompose the unstable components during the course of the processing and would place the residue metal oxides into a monolithic form that is less likely to adsorb water. Rare earth borosilicate and alkali tin silicate (ATS) glasses have been studied for plutonium immobilization. Ceramic formulations have also been studied, and the residues discussed in this report would probably be well suited to incorporation in mineral phase assemblages similar to that of Synroc-D.

The procedures developed for making glass would involve mixing residue materials with glass-forming materials and neutron absorbers to ensure criticality control. This mixture would then be calcined and melted. It could then be poured into canisters or formed into

small monoliths and placed in cans. The product would be in the form of fairly large ingots, and, since the surface area of such ingots would be small, the adsorption of moisture would be small, even if there were some moist air in the containers.

The incorporation of plutonium into glass and ceramics is the subject of ongoing development in the Plutonium Immobilization Project sponsored by the Surplus Fissile Materials Disposition (MD) program of the U.S. Department of Energy. Those efforts, however, have been focused primarily on plutonium having smaller amounts of impurities. More development would be required for incorporation of reacted ash material, so this option would involve development and some equipment costs.

10.0 Possible Courses of Action at this Time

There are several possible courses of action that could be taken now to cope with the unattractive features of the RA materials. The following are believed to span the options available, and each is evaluated briefly:

- **Leave the material in its current configuration**, i.e., in storage in the overpacked cans having porous vents.

  — Advantages: This involves minimum work in the short run. There would probably be no significant change in the status of the material or the cans over a few years, as indicated by the surveillance inspection of containers after one year of storage (see Section 8.0). This course of action would provide time for the MD program to reach decisions about final disposition of surplus weapons-grade plutonium.

  — Disadvantages: Continuing radiolysis of the reacted ash material and humid air inside the cans will produce nitric, hydrochloric, formic, and oxalic acids as well as hydrogen peroxide. These will promote corrosion of the cans. Corrosion will limit the time that materials can be stored in the present configuration. However, periodic sampling of the cans for examination will allow the monitoring of their condition.

- **Add a check valve** outside the vent on each can of the current overpack (gallon cans) to limit the access of reactant gases (humid air), and continue storing.

  — Advantages: A check valve would be designed to allow the escape of excess gas within the cans while limiting the access of additional air and humidity. Limiting such access should enable the control of the formation of corrosive substances. Thus, corrosion of the cans and the formation of other undesirable species such as nitrates would be limited. A check valve should extend the length of time the material could be stored without further processing.

  — Disadvantages: Even though the cans would not suffer pressurization, they would still experience corrosion. Enough radiolytically vulnerable materials are already present in the ash material to produce significant amounts of reactive materials such as HCl and HNO_3, and other radiolysis products such as oxalic acid would tend to complex metal cations and thereby assist corrosion. The bulged cans that have been examined in this study include

several cases in which corrosion of the cans, if allowed to proceed unhindered, appears capable of leading eventually to the breaching of containment. The valve itself would be subject to corrosion. Thus, a check valve could not be relied upon to increase the storage life expectancy by a significant factor.

- **Arrange to ship the material to another DOE site for processing,** and do the minimum amount of work necessary to satisfy the requirements for shipping. This amounts to a repeat of the previously planned approach, and would require a policy decision in addition to a technical decision, but the technical factors can be still be considered briefly.

  — Advantages: The processing could be handled at a site that already has a large amount of residue materials, making for greater efficiency.

  — Disadvantages: It seems probable that the material would still have to receive some processing before shipment in order to avoid a repeat of past history, i.e., a policy change after packaging, which could further extend the storage time, resulting in repressurization. Storage at the receiving site before processing also might turn out to be longer than planned. The transportation regulations and agreement with the recipient would determine the details of the requirements.

- **Process (wash and calcine) and repackage the material so that it will be stable in vault storage** for a longer period of time. As described in Section 9.2 above, this involves washing and calcining at a temperature of at least 850°C.

  — Advantages: This would put the material into a form that should be entirely safe to store for many years. This approach could be tailored to meet DOE Standard 94-1, which currently does not apply to dilute plutonium residues. This approach seems to be the minimal chemical processing needed if the material is to be put into a form suitable for decades-long storage.

  — Disadvantages: While the processing would convert the RA material to a form suitable for storage, the material would still be in powder form. Therefore, it would easily adsorb moisture and other gases if exposed to them. Special care would be required after calcining and before packaging to prevent exposure to moisture. The technology for ensuring acceptable adsorption of unwanted gases might require some development. An inert-gas box might be required, with special attention to furnaces and other components that would not themselves pick up moisture during standby conditions only to release this moisture upon being heated. Assured gas-tight packages would be needed.

- **Process and repackage the material in conformance with DOE Standard 94-1,** which applies to relatively pure PuO_2. This option would be quite similar to the option discussed immediately above, although the Standard calls for a higher calcining temperature than suggested above.

  —Advantages: The material should be storable for many years. The process of developing the procedures to meet these goals at LLNL would contribute to DOE-wide research on residue processing.

— Disadvantages: Drawbacks are similar to those listed under the preceding option. An important detail is the fact that mixed oxide materials might be expected to sinter and form clinkers more readily than pure PuO_2 at the required calcining temperature. In addition, the furnace and containers would be more costly than for the preceding option.

- **Convert the material to a glass or a ceramic** and store it pending final disposition.

    — Advantages: This could put the material into a form suitable for final disposition and thereby eliminate further processing.

    —Disadvantages: Such processing would require development and construction of some new equipment at this time. In addition, the acceptance standards for immobilization forms for the final disposition have not yet been established.

11.0 Summary and Conclusions

The bulging-can phenomenon is not new. It has been reported several times at other sites. As has been described in this report, the phenomenon results from radiolysis with the formation of gases that pressurize the containers. The circumstances that led to the storage of radiolysis-sensitive residues in sealed containers at LLNL in the 1992 period were (1) an imperative to reduce inventory, i.e., to ship as much plutonium-containing material off-site as possible, including poorly characterized material, (2) the absence of any previous experiences at LLNL that might have alerted the staff to a potential problem, since previous residue packaging had not used hermetically tight cans, and (3) the absence because of retirement or transfer to other work areas of personnel having a broader knowledge of or experience in the radiolytic behavior of materials contained in the reacted ash.

This analysis of the bulged cans at LLNL does, however, carry forward the general understanding of what can happen in the storage of plutonium residues, as discussed in the appendices to this report. Radiolysis of water might have been expected, but the presence of residual carbon also has been found to play an important part in the generation of gas pressures.

12.0 Acknowledgments

13.0 References

1. Jerry Stakebake, SAIC, Rock Flats Environmental Technology Center, personal communication, March 1995.

2. William Kuhl, LLNL, personal communication, November, 1994.

3. Memorandum from K. D. Stickle to Larry Walkley, "Imperial gallon and juice can test," LLNL, August 23, 1994.

14.0 Glossary

Can, food-pack: This can is like those used for canned foods. It has a double roll-bonded lid that is intended to be hermetically sealed. It is made of tin-plated carbon steel.

Can, gallon: This is the overpack can used in this project. These 1-imperial-gallon paint cans have pressed-on lids and have been fitted with a porous carbon frit, Nuc Fil 013, to allow venting of gas generated in RA material. The original packages containing reacted ash were punctured, bagged, and placed inside these cans.

Can, juice (outer): This is a food-pack can having an inside diameter of 10.5 cm (4.13 in.) and an inside height of 17.4 cm (6.85 in.). The metal wall thickness is 0.46 mm (0.018 in.). The inside volume of the can is about 1.5 liters.

Can, quart (inner): This is a food-pack can having an inside diameter of 9.8 cm (3.84 in.) and an inside height of 13.4 cm (5.28 in.). The metal wall thickness is 0.25 mm (0.010 in.). The inside volume of the can is about 1.0 liter. Its outside volume is about 1.025 liters.

Group I RA: These cans had oxidizing conditions in the final gas and pH 10 in the ash (where measured), and can pressurization resulting primarily from nitrogen and oxygen.

Group II RA: These cans had reducing conditions in the final gas and pH 4 in the ash (where measured), and can pressurization resulting primarily from carbon dioxide and hydrogen. This second group also had higher carbon and water content in the ash (where measured) and higher final gas pressures.

RA: Reacted ash material, the material stored in the cans after calcining and grinding.

Appendices

Introduction to Appendices on Radiolysis

The scientific problem with the bulging cans is to explain how the extra gas was generated, how the chemical conditions changed from the initial to the final states, and why the final states fall into two discrete groups so different from each other. The pH values present an interesting puzzle—why pH 4 and pH 10, and why only these values? Also, why the correlation between ash pH and gas redox conditions?

The appendices review literature data on the radiolysis of (A) water, (B) air-water vapor mixtures (with the production of nitric acid), and (C) carbon-water vapor-air combinations.

Appendix A: Radiolysis of Water

Making use of past work (Refs. 1-4), our calculations suggest, to the accuracy of the approximation, that the pressurization of the cans might be explained by the radiolysis of water alone. However, other processes are known to occur and are discussed in Appendices B and C.

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Appendix B: Radiolysis of Humid Air and the Production of Nitric Acid

The effect of ionizing radiation on moist air systems has been reviewed (Ref. 5) in connection with the disposal of high-level nuclear waste in geologic repositories (Ref. 6). Many intermediate molecular and radical species are formed during reaction, but the overall reaction that produces nitric acid may be expressed

$$N_2 + H_2O + 5/2\,O_2 \rightarrow 2HNO_3.$$
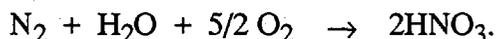
Early experimental evidence for this was reported (Ref. 7) for an irradiation experiment in which nickel wire was exposed to dry air, to water vapor excluding air, and finally to moist air. A nitrate was formed only in the moist-air experiment. The authors' analysis suggests that the G value for nitrogen fixation followed by its reaction with the nickel is about 1.0 molecules per 100 eV absorbed. This paper also reviews briefly the corrosion of other metals in the radiation field of a nuclear reactor in the presence of humid air. The reactor radiation fields resulting from fast neutrons, gamma rays, and induced nuclear reactions in air were about 400 rads per second, or 1.4 megarads per hour, not greatly different from the alpha-radiation field near the surface of plutonium oxide.

In another study in dry air with gamma irradiation at 1-atmosphere pressure and $40^\circ C$, the equilibrium concentrations of nitrous oxide and nitrogen dioxide each reached about 25 torr (Ref. 8). Reed and Bowers (Ref. 9) showed that nitrogen fixation to nitrate in alpha radiolysis of water in contact with air occurs as a result of ionization of nitrogen in the air rather than when dissolved in the water.

The overall products of nitrogen oxidation produced by the radiolysis of air include nitrous oxide (N_2O), which is relatively stable, and other oxides, such as the dioxide (NO_2), which react with water to produce nitrous acid (HNO_2) and nitric acid (HNO_3). The yields of N_2O and of total acid are comparable when air is irradiated. In the storage cans, the N_2O would appear in the gas analysis, but the acids would be expected to condense onto surfaces of the ash or the wall of the can. They would tend to lower the pH of the ash and to promote corrosion of the can. N_2O was observed in the inner can gas analyses for all the cans in the first group, which apparently maintained oxidizing conditions to the end. The pH in the first group of cans was reduced from a probable pH 11.5 or greater (assumed for a carbonate) down to pH 10. Some corrosion was observed on the inner surfaces of the cans of the first group.

This analysis can also be applied to the issue of residues being stored in cans vented to the air through a filter, which is the present situation for the vented cans being overpacked in a vented gallon paint can. In this case, air would have access to the high-radiation field above the residues. We can estimate the rate of nitric acid production.

The amount of radiation product equals the radiation exposure times the sensitivity of the material to that radiation. The equation becomes:

Radiolysis product (moles/year) in a radiation field of 1.0×10^6 rads per hour (the alpha radiation intensity over PuO_2) = $G \times 9.3 \times 10^{-3}$ moles/year/gram.

The G value for the reaction has been found to be 1.9 molecules per 100 eV absorbed (Ref. 5) for the consumption of N_2 (2×1.9, or 3.8 for the production of HNO_3) (Ref. 10). We will assume that humid air can circulate through a free space above the solids. If the free space in a can is 0.5 liter, the air is 80% nitrogen, and the density of pure nitrogen is 1.25 grams/liter (STP), then there would be 0.5 grams of nitrogen being exposed to the radiation at any given time. If we take G = 3.8, then the amount of product acid per year for HNO_3 will be

$$= 3.8 \times 9.3 \times 10^{-3} \text{ moles of } HNO_3/\text{year}$$

$$= 0.035 \text{ moles of } HNO_3/\text{year}$$

$$= 2 \text{ grams of } HNO_3/\text{year.}$$

This value is greater than the initial amount of nitrogen within the can, but the assumption is that the nitrogen can be replaced continually by circulation through the filtered vent. This result does not mean that the molecules of nitric acid produced at the beginning of the year will continue to exist at the end of the year. Any molecule produced will eventually be decomposed by the radiation or will react chemically. If the rate of chemical reaction is greater than the rate of radiolytic decomposition, then most of the acid will go toward promoting corrosion of the can or reaction with other materials in the can. For this to happen, a molecule only need circulate from the point of production in the gas to a reactive surface, a process that might be expected to take no more than a few seconds.

It appears plausible that a significant amount of chemical action by nitric acid can take place. This might occur as a corrosion of metal parts and possibly as the addition of nitrates to the materials present. The concentrations of acid and the pH of the solids might not always be appropriate for driving nitration reactions, but as seen in Appendix C below, the presence of organic residues tends to favor the creation of acidic conditions.

This has serious implications for those storage configurations in which air can freely circulate into a space directly above an intense radioactive source such as a plutonium alpha-emitter. Eventual corrosion of the can appears probable, and the formation of chemically unstable species by nitration appears possible. Nevertheless, actual experience (see Section 8.0 of this report) suggests that—for most cans—at least several years would be required before corrosion would impair the integrity of the cans.

References

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10. W. G. Burns, A. E. Hughes, J. A. Marples, R. S. Nelson, and M. Calvin, "Effects of radiation on the leach rates of vitrified radioactive waste," *J. Nucl. Mater.* **107**, 245–270 (1982).

Appendix C: Radiolysis Involving Carbon

It is to be expected that the alpha radiation would have produced radiolysis reactions involving the adsorbed water and adsorbed atmospheric gases on the ash, the charcoal in the ash, organic material (if any is present), and the air initially in the can, since they were packed in an air-atmosphere glovebox. The net products from the radiolysis of water are hydrogen (H_2) and hydrogen peroxide (H_2O_2), which decomposes to yield water and oxygen (O_2). Generally speaking, if the redox conditions are oxidizing (as was the case for all the cans initially, and apparently for the first group of cans throughout their history), such conditions will dominate the radiation chemistry of the system. The species available to be oxidized include nitrogen (both adsorbed and in the air), carbon (in the charcoal and in organic material, if present), and possibly hydrogen, if organic compounds are present.

Initially, most of the cans likely contained residual sodium hydroxide and, considering the small amount of adsorbed water, likely started with a high pH. If this material had come into equilibrium with the normal concentration of carbon dioxide in the air during the cooling, sieving, and blending operations to produce Na_2CO_3, the pH would not have fallen below about pH 11.5 when the cans were sealed.

We now turn attention to the radiolytic behavior of carbon in contact with air. This was studied in connection with the use of graphite in nuclear reactors (Refs.11, 12). The initial product of carbon oxidation by radiolysis is carbon monoxide (CO). If excess oxygen is available, CO will be further oxidized to carbon dioxide (CO_2). CO did not appear in the final gas of the first group of packages, which did have excess oxygen. In contact with ash incorporating adsorbed water with a basic pH, most of the CO_2 will be adsorbed and will react with the hydroxide to produce carbonate ions, CO_3^{2-}:

$$CO_2 + 2OH^- \rightarrow CO_3^{2-} + H_2O.$$
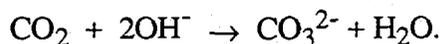
This would remove CO_2 from the gas phase and would also lower the pH of the ash. The amounts of CO_2 observed in the final atmospheres of the first group of packages were small, and as noted above, the pH was reduced only to pH 10. It is likely that the pH stopped at approximately pH 10 because the carbonate-bicarbonate pH buffer at pH 10.4 could not be overcome by the amounts of the combined production of the nitrogen acids and the CO_2:

$$CO_3^{2-} + H^+ \rightarrow HCO_3^- \quad \text{and}$$

$$CO_3^{2-} + CO_2 + H_2O \rightarrow 2HCO_3^{2-}.$$
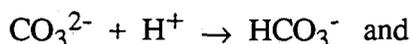
The products of radiation-chemical oxidation of organic materials are primarily CO_2 and water, if excess oxygen is present. The CO_2 would have adsorbed on the surfaces of the solids.

When the CO_2 was adsorbed onto the ash, it is likely that it would have displaced adsorbed gases that are less tightly bound, such as nitrogen. This probably accounts for the increase in N_2 content of the final atmosphere in the cans of the first group. Thus, part of the pressurization of this group of cans appears to be an indirect effect of the production of carbon dioxide from oxidizable carbon and water radiolysis.

The cans in the second group ended up with reducing conditions in the gas phase and pH 4 in the ash. It is necessary to explain how they dropped to pH 4. The most likely explanation is that the radiation chemistry in this group of cans started out the same as in the first group, but that the larger amounts of carbon caused the oxygen to be depleted in forming CO and CO_2. When this occurred, CO was able to coexist in the gas phase with CO_2. It has been reported that when CO dissolved in water at basic pH is irradiated, a high-yield chain reaction occurs to produce formate ion (Ref. 13) with the following net reaction:

$$CO + OH^- \rightarrow HCOO^-.$$
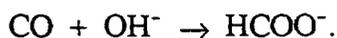
If enough formic acid were produced, the pH 10.4 buffer would be overcome, and the pH would then drop rapidly to the CO_2-bicarbonate buffer at pH 6.4. This would be accompanied by the conversion of CO_3^{2-} in the ash to HCO_3^- and then to CO_2 in the gas, which would permit resorption of the nitrogen gas on the ash.

Further production of formic acid would cause the buffer at pH 6.4 to be overcome, thus allowing a continued, rapid drop in pH. It has also been reported that at low pH in the absence of oxygen, irradiation of CO_2 dissolved in water produces carboxyl radicals (CO_2^-), which dimerize to form oxalate ($C_2O_4^{2-}$). The pH would drop to the vicinity of pK_2 for oxalic acid at 4.27. In this pH range, the production of both formic and oxalic acids would continue.

The large increase in gaseous hydrogen (H_2) may have originated from radiolysis of organic species, if present in the absence of oxygen, or from radiolysis of water accompanied by consumption of oxygen by production of CO and CO_2.

The presence of light hydrocarbons and methyl chloride observed in the Group II packages may have resulted either from radiolysis of heavier hydrocarbons or by radiation-induced reaction of hydrogen with carbon and chloride.

The major features observed in both groups of cans can thus be accounted for in a qualitative way by known reactions. It is not possible to be more quantitative because of the lack of a detailed chemical analysis of the ash and the lack of a quantitative, coupled model of the radiation chemistry of solid-gas systems incorporating adsorption.

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Plastic bags

Outer Container

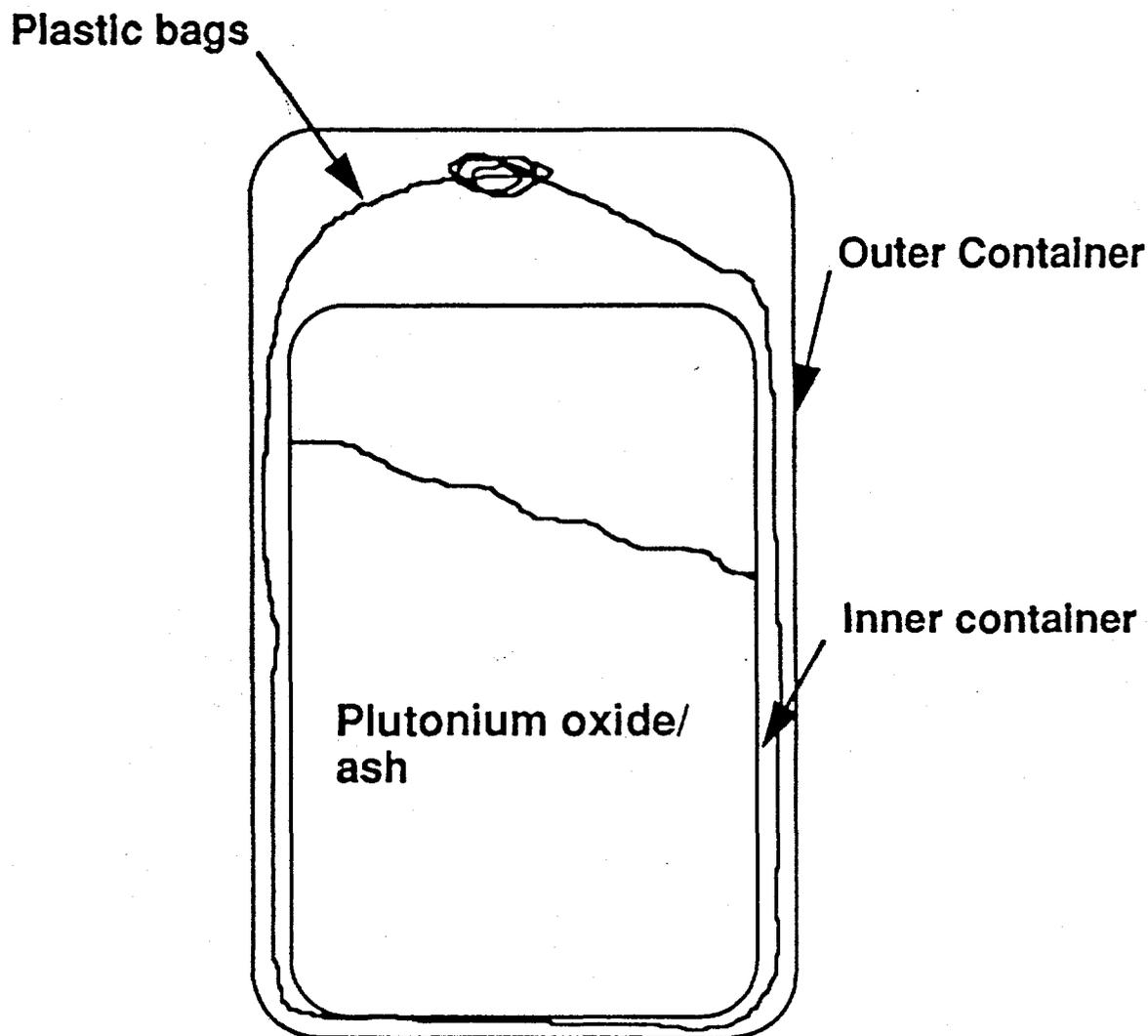**Inner container**

Plutonium oxide/ ash

Figure 1. Plutonium oxide/ash packaging configuration.

This is a schematic diagram of the package configuration. Plutonium oxide/ash residues were contained in an inner (quart) food-pack can. This was double-bagged in plastic bags, although only one bag is shown here. The bag was then placed inside an outer (juice) food-pack can. Both the inner and outer cans were sealed using a double roll-bonded seal.
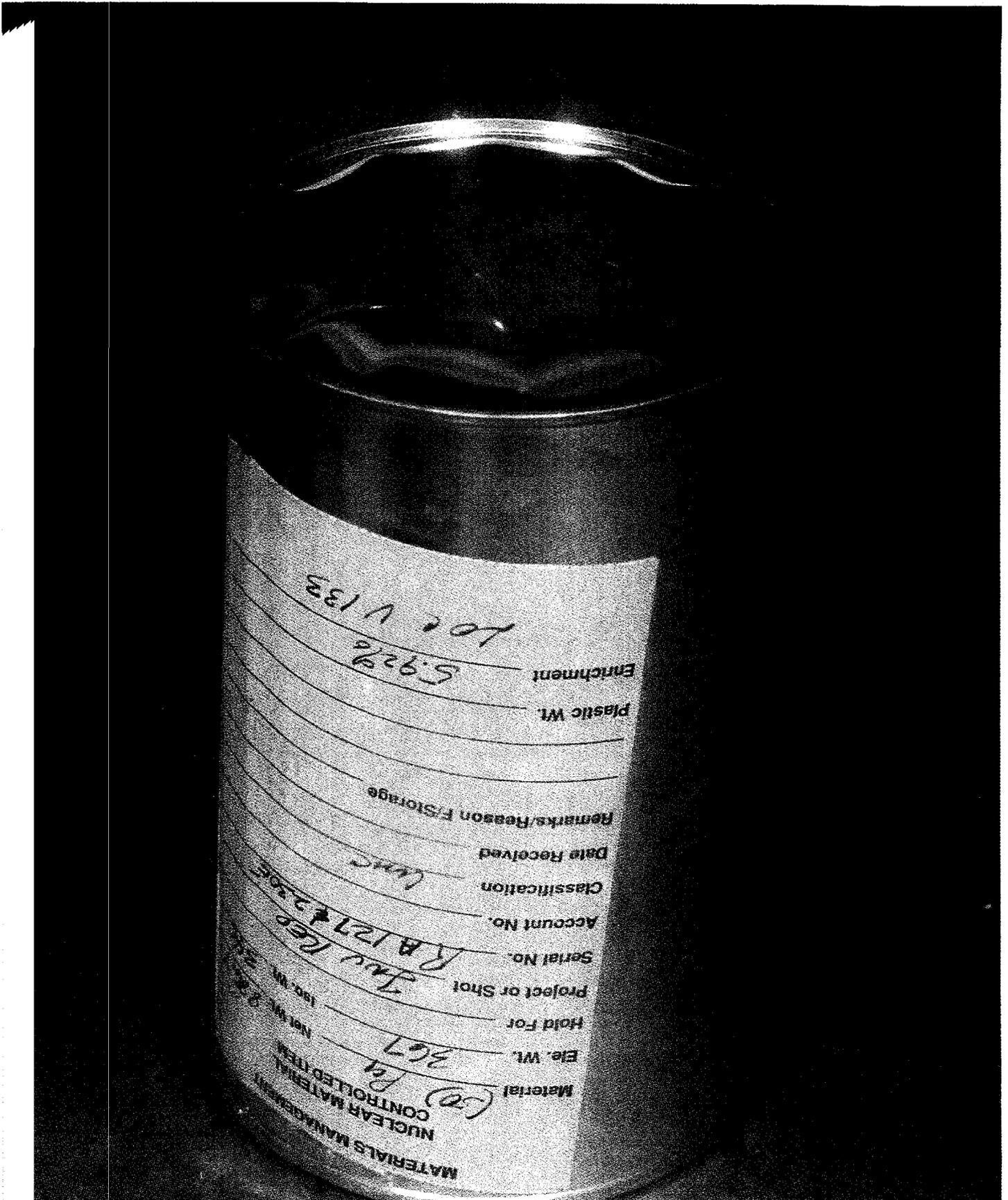
Figure 2. Photograph of bulged can.

The can is shown upside down to reveal the bulging at its base.

Filter:
Certified for
use with plutonium

Retaining
Clip
(8 each)

Cans punctured
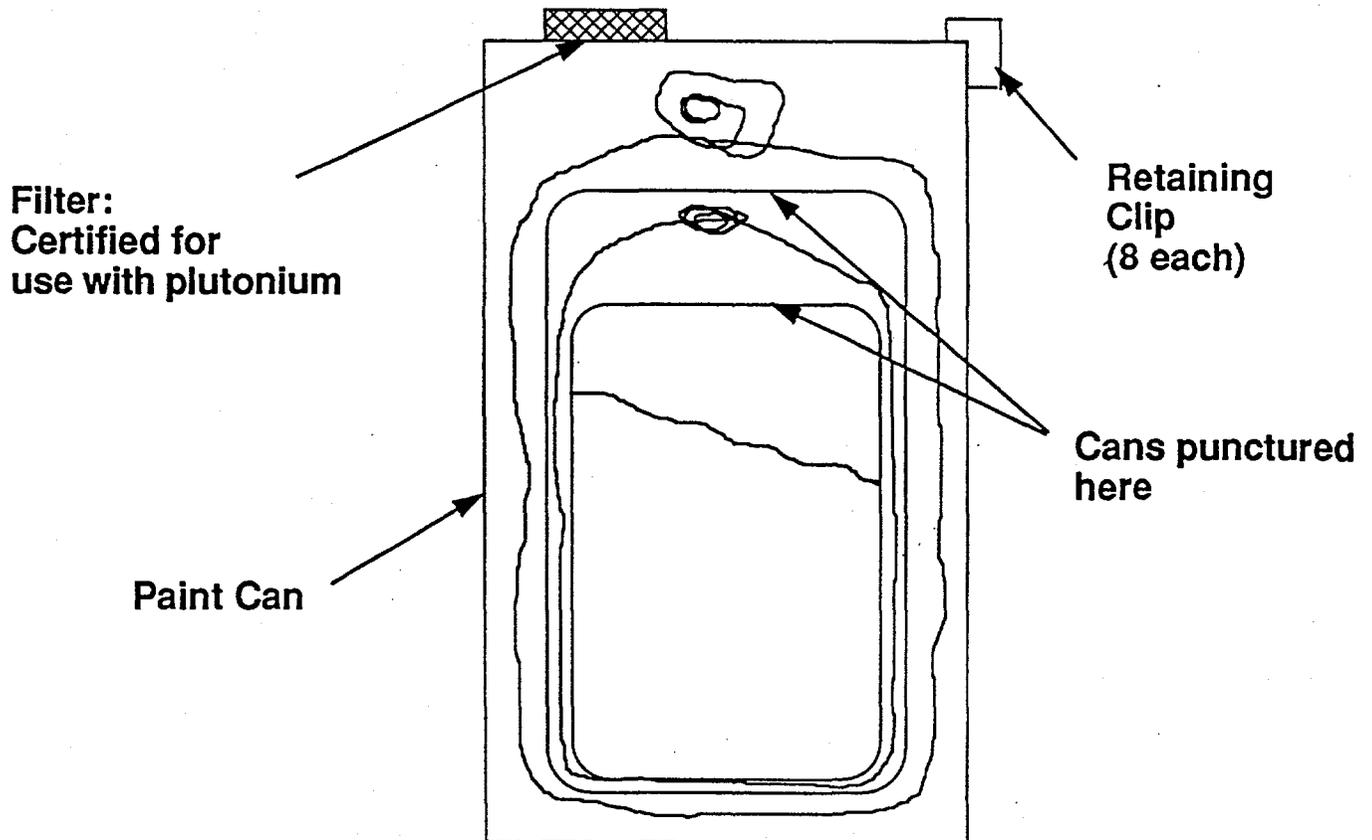**here**

Paint Can

Figure 3. Schematic diagram of overpack can.

To avoid the pressurization, all 111 inner and outer cans of plutonium residue oxide/ash in the inventory were punctured in a glovebox and bagged-out into an imperial-gallon paint can. This figure shows the inner can holding the residues, the double-bagging of this can, and the outer can. The outer can has been double-bagged and placed within the paint can. Retaining clips hold the lid on this paint can. The lid is provided with a carbon frit to allow the release of any pressure inside the can.
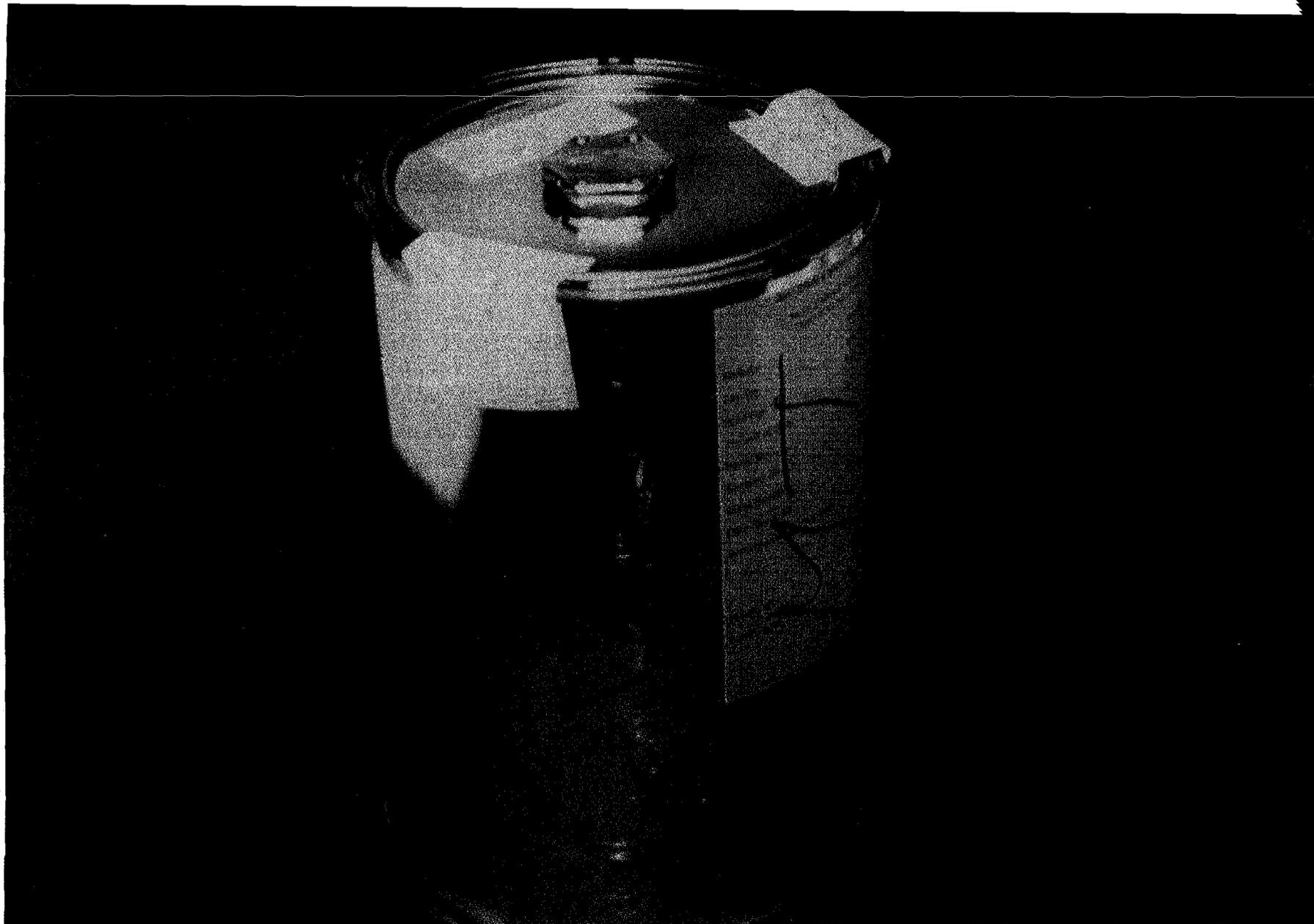
Figure 4. Photograph of overpack can.

This is an imperial-gallon paint can with a vent on the top consisting of a carbon frit to allow the release of any pressure inside the can.