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CORROSION OF PLUTONIUM METAL WHEN STORED
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CORROSION OF PLUTONIUM METAL WHEN STORED
IN CONTAINERS HAVING PLASTIC COMPONENTS

By

R. H. Bond

Plutonium Chemistry Laboratory
Research and Engineering Operation
Chemical Processing Department

March 6, 1964

HANFORD ATOMIC PRODUCTS OPERATION
RICHLAND, WASHINGTON

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CORROSION OF PLUTONIUM METAL WHEN STORED IN
CONTAINERS HAVING PLASTIC COMPONENTS

I. INTRODUCTION

The formation of "oxide" from plutonium metal during storage and shipment in normal HAPO storage containers has been recognized for many years and accepted as an unavoidable nuisance.

An evaluation of accumulated data was begun recently to determine the rate of oxidation of plutonium in the storage containers. The availability of data for corrosion of ingots under these storage conditions provided a sharp contrast to data for buttons, since the former were invariably accompanied by so much more "oxide" than the latter. The availability of this corrosion data for ingots provided the clue to solution of the corrosion problem.

Since no means could be found to explain the entry of air into a sealed container in sufficient quantity to form all the "oxide" found with ingots, the powder in the containers could not be PuO_2 .

The data evaluation was pursued to determine the nature of the powder and source of the corrosive agents. Reasons were sought for the marked difference of corrosion behavior of ingots and buttons. The ultimate goal was to determine and eliminate the cause of the corrosion.

II. SUMMARY AND CONCLUSIONS

Correlation of the small amount of available data, and combination of this data with a theoretical evaluation of the storage-container geometry and radiation phenomena, have provided an understanding of the problems involved of greater significance than was expected from so little data. The conclusions are as follows:

1. The formation of powder or "oxide" in the storage container is caused almost entirely by the packaging of the plutonium in plastic materials.
2. The corrosion of the plutonium follows degradation of the plastic due to the intense radiation to which the plastic is subjected.
3. The powder formed by this corrosion is not PuO_2 , but a mixture of oxides, hydrides, and chlorides in varying proportions, depending on the type and amount of plastic in the individual storage container.
4. The powder consists predominantly of hydrides. Hydrogen is considered the major cause of severe corrosion. The surface-disruptive nature of hydriding prevents formation of any protective

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film on the metal. Fresh surface is provided continuously for further attack.

5. The hydrides are pyrophoric. Spontaneous ignition of the powder and metal occurs occasionally, immediately following opening of the container. This effect may be more severe for ingots than for buttons because of unreacted- or only partially-reacted metal fines in the powder from ingots.
6. Metal loss of eight percent in 100 days of storage has been observed for unalloyed ingot metal of moderate purity under the storage conditions described in this report. Corrosion rate depends on purity of the metal. Impurities in unalloyed metal inhibit corrosion.
7. Corrosion rate increases exponentially with duration of storage. For a 2000 g ingot of moderate purity, the rate of weight loss per month, as percentage of initial weight, is about 2.0 percent at the end of one month, 2.8 percent at the end of three months.
8. The corrosion rate for buttons is less than that for ingot metal of moderate purity by a factor of 18- to 90-fold. Calcium (or calcium fluoride) as an impurity in buttons may be an important corrosion inhibitor under the conditions of the storage container. For specific rates, see Figure 5, Page 32.
9. Packaging of plutonium metal in all-metal containers--free of all organic materials--should permit storage indefinitely with formation of not more than a gram or two of PuO_2 .

III. DISCUSSION

The data for this report were obtained at HAPO, as related to the HAPO storage and shipping container. Most of the data were noted and recorded in relation to various investigations and operations in the Plutonium Chemistry Laboratory during the past three years. Data on the two well-aged buttons were requested from the Rocky Flats Plant after the latter expressed concern over the large amount of "oxide" contained with the buttons.

Only 10 data items were found that appeared reliable in terms of completeness of records, accuracy of weighing, and consistency of material balances. These consisted of three moderate-to-low-quality quadrant ingots, one single-piece ingot of known high impurity content and of a shape similar to buttons, and six buttons of assorted age and quality. The data are evaluated and discussed in the Appendix (p. 19).

Also contained in the Appendix (p. 9) is a theoretical evaluation of the container, its contents, and the probable affects of plutonium radia-

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tion on the container items.

The theoretical evaluation was developed on the assumption that neutron and gamma radiation would probably be more significant causes of plastic degradation than alpha radiation. This would imply relatively uniform degradation throughout the container. The overall findings of this report appear to indicate that alpha radiation is the most important cause of degradation.

This finding implies that most of the degradation of the plastic and gas evolution occur at the innermost surface of plastic in contact with plutonium. Hence, all gases released are available to react with the plutonium. If the plutonium is contained in a polyethylene bag, the release of hydrogen should be more serious than the theoretical evaluation would indicate. Also, since hydrogen appears to be the most corrosive substance available, the use of polyethylene inside the container is definitely undesirable.

The theoretical evaluation was based on two possible mechanisms of PVC degradation: either chlorine would be released in direct proportion to its distribution in the plastic, or chlorine would not be released at all--hydrogen would be released in place of chlorine. The findings indicate that the former mechanism is the more probable of the two. The more likely situation is that chlorine will be released in less than strict proportionality to chlorine content of the plastic, but chlorine will certainly be released to some extent.

Hence, the powder will contain some chlorine. The chlorine content of the powder may be expected to cause corrosion problems in equipment used for reprocessing the powder, depending on amount of this powder processed relative to other materials being processed.

The severe corrosion of plutonium, when packaged in plastic, constitutes a serious fire hazard. Ingots, so packaged, represent the more serious source of hazard because of the greater volume of powder formed and the possibility that some of this powder is unreacted- or incompletely-reacted metal fines. A package of this sort ignited recently when opened in a partially-inert atmosphere in the Plutonium Chemistry Laboratory. The metal continued to burn until consumed.

Buttons may also ignite under similar circumstances, as occurred recently in the HAPO Foundry. In the latter case, the can and contents were dumped immediately into a container of dry ice present in the glove box, which cooled and quenched the metal. Similar spontaneous ignitions have occurred at the Rocky Flats Plant, according to unofficial sources, but have not been confirmed officially.

This fire hazard is undoubtedly a result of the presence of pyrophoric plutonium hydride. Packaging in all-metal containers--free of any organic materials--should eliminate this hazard.

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Processing of plastic materials from containers for recovery of plutonium is a complicated procedure. Elimination of the plastic should provide an appreciable savings.

Recent information from the United Kingdom⁽¹⁾ indicates that plutonium is packaged by double canning. The metal is sealed in an organic-free can, then sealed out of the glove box in plastic, and sealed in a second, larger can.

Plutonium is never packaged in contact with PVC under any circumstance in British installations. Corrosion can be initiated by even brief contact, due to plasticizers in the PVC. When packaging in plastic is required (as for radiograph), polyethylene is used.

IV. FURTHER EVALUATIONS SUGGESTED

Complete elimination of plastics and organic substances from contact with plutonium during storage should be undertaken as soon as possible.

A possible container system for buttons or ingots would consist of the following items:

1. Inner can, of size used commercially for tuna canning, free of lacquer or other interior finish.
2. Seal-out in plastic; PVC should be satisfactory.
3. Plastic-sealed can would fit inside of can of size used commercially for salmon or pineapple (flat).

The use of this system will require a suitable can sealer inside the glove box. Ease of canning may require the development of a different plastic-sealing bar than now used. One would be required that is capable of sealing the plastic quite close to the inner can.

This canning system would be evaluated most definitely by packaging of ingots of the highest-grade metal available. This metal would corrode most rapidly, if corrosive conditions existed to any degree. If the ingot metal shows no more than a gram or two of powder formation in two or three months, as is expected, then storage of buttons in this manner should result in negligible powder formation, regardless of duration of storage.

Analysis of powder samples for chlorine should provide further verification of the hypothetical findings of this report. For this purpose, samples should be obtained from packages containing only PVC, and from packages containing PE as well as PVC. Chlorine content may be expected to vary from about 1 w/o in the latter case to 5 w/o in the former case.

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APPENDIX AVI. ESTIMATE OF COMPOSITION OF CONTAINER ATMOSPHERE AND COMPOSITION OF POWDER FORMED DURING PROLONGED STORAGE - A THEORETICAL EVALUATIONA. Container Geometry And Constituents

Each button or ingot is sealed in a plastic envelope, then packed into a metal can and sealed. Some buttons or ingots are placed inside polyethylene freezer bags, before sealing in plastic, to prevent possible puncturing of the plastic or to facilitate loading into the envelope material.

1. Can

A commercial lacquered sheet steel can is used for this purpose. The can is 3.90" inside diameter, 2.41" inside height, and weighs 88.0 grams. The lacquer interior finish of the can is assumed to be of typical alkyd composition (glycerol-phthalic anhydride). The lacquer measures only 0.0001" thickness, hence could not represent a total of more than 0.150 g of lacquer, nor contain more than 0.05 g oxygen or 0.005 g hydrogen. No detectable radiation damage of the lacquer has been observed.

2. Plastic Envelope Composition

The plastic envelope is made of Bakelite "Krene" sheeting. Composition of this material is a trade secret, hence is not available. Federal specifications (L-P-375a) covering the type of material used for this purpose designate "suitably formulated chlorine-bearing vinyl resin with phosphate and phthalate plasticizers".

A typical formulation (Bennett's Formulary, Vol. IX, pp. 475) for extrusion as sheeting and tubing should contain about 2/3 polyvinyl chloride (PVC) resin and 1/3 plasticizer. Typical plasticizers used for this purpose are of quite similar molecular weights (360 - 390) and compositions (17.1 ± 0.15 percent oxygen and 7.5 ± 0.25 percent hydrogen). No chlorinated plasticizers are used for this purpose.

Hence, the envelope plastic should analyze 5.7 ± 0.1 percent oxygen, 5.7 ± 0.1 percent hydrogen, 37.8 percent chlorine, remainder carbon.

3. Plastic Envelope Weight

A recent batch of 44 canned buttons was evaluated for package weight. Gross canned weight less net button weight varied from 98 to 108 g with an average of 103.0 g (essentially normal distribution). The can alone weighs 88.0 g (no change of can specification within the time dealt with in this report). Hence, the plastic

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envelope (including masking tape) weighs 15.0 ± 5.0 g. The envelope from button X-21-5-55 weighed 14.25 g after brushing free of powder. Envelope weight for other buttons discussed in this report was generally smaller (12.9 g) than recent envelope weight. No canned weights or envelope weights were recorded for ingots, but should be about the same as for buttons.

4. Use Of Polyethylene

At the present time, some buttons are being placed in polyethylene (PE) pint-size freezer bags before sealing in plastic envelopes. The quadrant ingots described in Table VI were so packaged. These bags weigh 3.29 g and contain 14.37 percent hydrogen (0.47 g).

5. Initial Can Atmosphere

At the time of sealing, the can contains about 0.10 g of oxygen, as air, based on 1800 g of metal at 19.0 density, and allowing for volume of the plastic. The envelope plastic may contain as much as 3 percent moisture (0.45 ± 0.15 g) (Federal specification L-P-375a).

6. Summary Of Can Contents

TABLE I

Material	Weight g	Weight Percent				Weight, g			
		C	H	O	Cl	C	H	O	Cl
Lacquer on can	0.150 (est.)	60	4	36	-	0.090	0.006	0.054	-
Air (initial)	361 (cc vol)			21 v/o				0.100	
PVC Envelope	15.0 ± 5.0	50.8	5.7 ± 0.1	5.7 ± 0.1	37.8	7.62 ± 2.54	0.85 ± 0.29	0.85 ± 0.29	5.67 ± 1.89
Moisture in PVC	0.45 ± 0.15	-	11.1	88.9	-	-	0.050 ± 0.017	0.40 ± 0.133	-
PE bag (if used)	3.29	85.6	14.4	-	-	2.82	0.47	-	-
Total from all sources						10.53 ± 2.54	1.38 ± 0.31	1.40 ± 0.42	5.67 ± 1.89

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B. General Evaluation

Consideration of the oxygen contained in the can initially in all forms shows that complete degradation of the plastic could not yield more than 1.82 g oxygen/0.1191 g oxygen per g $\text{PuO}_2 = 15.3 \text{ g PuO}_2$. Such complete degradation does not occur: the plastic does not appear appreciably degraded after prolonged storage. Air initially in the can and moisture in the plastic could not produce more than 5.3 g PuO_2 . How, then, can 150 g of "oxide" powder be found with a stored ingot?

The powder obviously contains compounds other than PuO_2 . Since no increase of total canned weight has been observed, the powder must have been formed from substances already in the can. The plastic envelope is the only material available to provide such reactants. Hence, the powder must also contain plutonium compounds of carbon, hydrogen, or chlorine.

From the summary of can contents above, complete degradation of the plastic could yield as much as 1.69 g hydrogen/0.01126 g hydrogen per g $\text{PuH}_{2.7} = 150 \text{ g PuH}_{2.7}$ ($\text{PuH}_{2.7}$ is representative of a mixture of PuH_2 and PuH_3 , frequently found in hydrided plutonium). By the same logic, as much as 24 g PuCl_3 could be formed. The formation of carbon compounds of plutonium is unlikely under such conditions. Since degradation of the plastic is not severe enough to release all of these materials to this extent, the "oxide" powder must consist of a mixture of oxide, hydride, and chloride.

The release of these substances from the plastic is caused by the intense radiation to which the plastic is subjected during storage.

C. Radiation-Induced Degradation Of Plastic

High-energy radiation of organic materials causes degradation to occur due to breakage of chemical bonds in the material.⁽²⁾ Plastics are covalent organic compounds which are subject to degradation in proportion to the total radiation dose received. In the absence of chemical effects, the different types of bonds in the substance are broken in a purely statistical manner; i.e., in proportion to the percentage of such bonds in the substance.⁽³⁾ However, chemical effects are seldom absent. Saturated compounds are more severely attacked than unsaturates, causing unsaturation.

In general, for the storage container, radiation from the plutonium will cause breakage of chemical bonds in the organic materials in proportion to the number of each type bond in the plastic materials present.

The breakage of carbon-to-carbon bonds will cause shortening of polymer chain length and release of low molecular weight hydrocarbons. This affect will be limited at first, but cumulative with time. Since hydrogen, oxygen, and chlorine are side-chain attachments, these substances should be released at a rate proportional to the radiation intensity.

Radiation intensity for buttons varies with time for individual buttons (decreases with duration of storage). It also varies randomly for different

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buttons, depending on impurities present.

Radiation intensity for ingots, as treated in this report, should be quite uniform for all ingots and constant with time because of the similarity of purity and age of the metal.

From the above considerations, the probable distribution of reactive materials from the plastic can be estimated.

D. Distribution Of Reactive Substances Released From Storage-Container Constituents By Irradiation

1. Bases

The summary of can contents (Table I) provides a basis for estimating the distribution of reactive substances released from the plastic and available for reaction with the plutonium.

Alpha radiation from the plutonium will cause severe degradation of the plastic in direct contact with the plutonium. If the metal is placed in a PE bag before sealing in the PVC envelope, the PE will be most severely damaged, and the principle substance released will be hydrogen. If the metal is sealed directly in PVC, the substances released will be hydrogen, oxygen, and chlorine in direct proportion to their atomic percent distribution in the PVC.

Neutron and gamma radiation will cause release of substances on a statistical basis throughout the can contents. These sources of irradiation should provide a smaller contribution to the release of reactive substances than the contribution of alpha irradiation.

Any substances within the envelope will have access to the plutonium in the presence or absence of a PE bag. Most of the reactive substances will be released at or near the interior surfaces of the envelope. Some will be released outside the envelope, but may diffuse through the envelope.

2. Permeability Of PVC Plastic

Permeabilities of water vapor and various gases through PVC-type plastic sheeting are given in the tabulation below. The first set^(a) has units of

$$\text{g/24 hr/sq meter} / \left(\frac{\text{cm Hg partial pressure difference}}{\text{mm thickness of plastic}} \right).$$

$$\text{Units for the second set are g/24 hr/in}^2 / \left(\frac{\text{atm. pp difference}}{\text{mil thickness}} \right).$$

(a) Modern Plastics Encyclopedia, 1964, pp. 20 - 21.

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	Permeability Coefficients		Relative To Water Vapor
	Set 1	Set 2	
H ₂ O(b)	0.35 - 2.0	0.68 - 3.9 (2.29 + 1.61)	2.29 = 1.000
H ₂ (c)	0.00511	0.00986	0.0043
CO ₂	0.00097	0.00187	0.00082
N ₂	0.000024	0.000046	0.00013
HCl, Cl ₂	No data available		

3. Diffusion Through PVC Plastic - Estimated

- a. After a few days' storage, all the oxygen (ca. 0.10 g) contained in the can initially as air should have diffused through the plastic and reacted with the plutonium. Diffusion may be as oxygen gas, or as moisture formed in the presence of hydrogen (released from the plastic) and the intensely radioactive field. The atmosphere outside the envelope could then consist of the original nitrogen, and hydrogen in about the same proportion as the original air. Hydrogen and oxygen within the envelope should react with plutonium about as fast as it is available, hence the partial pressure of these gases within the envelope should be essentially zero.

On these assumptions, and with other variables as follows:

$$\text{coeff. for hydrogen} = (0.00986 \text{ g/24 hr})(\text{in}^2) \left(\frac{\text{atm. pp. diff.}}{\text{mil thickness}} \right)$$

$$\text{area of plastic} = 55 + 18 \text{ in}^2$$

$$\text{thickness of plastic} = 0.012 + 0.0012 \text{ mils}$$

$$\text{partial pressure difference} = \approx 0.21 \text{ atm.}$$

the rate of hydrogen diffusion should be about 9.5 g/day, or much more than the entire hydrogen supply available; hence, on this basis, diffusivity of hydrogen is more than adequate to permit diffusion of all hydrogen through the plastic.

Alternatively, if all the powder formed in the most severe case treated in this report (ingot FAD-22-5-187, ca. 150 g powder formed in 100 days) were entirely PuH_{2.7}, and all of this hydrogen were required to diffuse through the plastic, the hydrogen diffusion rate would be (1.5 g/day)(2.7)(at. wt. hydrogen)/(at. wt. PuH_{2.7}) = 0.0169 g hydrogen/day. This would permit a partial difference of only 0.037 atmosphere.

Since most of the hydrogen will be formed at or near the interior surface of the envelope, the rate of hydrogen diffusion is more than adequate to permit all hydrogen released anywhere in the container to diffuse through the plastic, and react with the plutonium.

- (b) Dependent on relative humidity.
(c) Estimated by comparison with PVF and polystyrene.

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- b. By similar logic, the lesser amount of oxygen formed anywhere in the container is available for reaction with the plutonium.
- c. The behavior of chlorine under the conditions of storage is less predictable than that of hydrogen or oxygen. If it were released on a strictly statistical basis (proportional to number of atoms present), the reactive gases should consist of approximately 80 a/o hydrogen, 5 a/o oxygen, and 15 a/o chlorine (if no PE bag is used). This would result in powder of approximately 75 w/o PuH_2 , 7 w/o PuO_2 , and 18 w/o PuCl_3 .

While no substantiating evidence is available, it is believed, by the author, that chlorine or hydrogen chloride would not be released from the PVC plastic as readily as hydrogen or oxygen. Chemical affects or solubility affects may hold these substances in the chlorinated plastic. Initial breakage of the carbon-to-chlorine bond could be followed immediately by reaction of the nascent chlorine atom with the plastic to displace a hydrogen atom, thus forming a more highly chlorinated plastic. On this basis, some hydrogen would be released in place of some chlorine in addition to the hydrogen released directly by breakage of the carbon-to-hydrogen bond. Both of these alternatives will be evaluated. Some chlorine undoubtedly reacts with the plutonium.

4. Calculations

a. Distribution Of Reactive Gases In The Container Atmosphere

Only oxygen, hydrogen, and chlorine in the gaseous atmosphere of the container should be capable of reaction with plutonium. Nitrogen and light hydrocarbons are considered inert under such conditions. If carbon dioxide is released from the plastic, as such, it should react with excess hydrogen in the highly-active environment to convert the oxygen to moisture.

The distribution of reactive substances in the plastic materials within the container is as follows:

TABLE II

<u>Substance</u>	<u>Weight g</u>	<u>Weight Percent</u>			<u>Gram Atoms</u>		
		<u>H</u>	<u>O</u>	<u>Cl</u>	<u>H</u>	<u>O</u>	<u>Cl</u>
PVC Envelope	W	5.7	5.7	37.8	0.0565W	0.00356W	0.0107W
Lacquer On Can	0.150	4	36	0	0.00595	0.00338	0
PE bag (if used)	3.29	14.4	0	0	0.470	0	0

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From the table, the total g atoms of reactive substances =
 $0.0707W + 0.00933 + 0.470$ (if PE bag used).

$$a/o \text{ oxygen} = \frac{(0.00356W + 0.00338)(100)}{0.0707W + 0.00933 + 0.470 \text{ (if PE bag used)}} \quad (1)$$

$$a/o \text{ chlorine} = \frac{(0.0107W)(100)}{0.0707W + 0.00933 + 0.470 \text{ (if PE bag used)}} \quad (2)$$

$$a/o \text{ hydrogen} = 100 - a/o \text{ oxygen} - a/o \text{ chlorine} \quad (3)$$

These equations also represent the atomic percent distribution of reactive materials in the container atmosphere, if all are released from the plastic in direct proportion to their atomic percent distribution in the plastic. If the chlorine is retained in the plastic and displaces one hydrogen atom for each carbon-to-chlorine bond broken, the distribution in the atmosphere would be:

$$a/o \text{ oxygen} = \frac{(0.00356W + 0.00338)(100)}{0.0707W + 0.00933 + 0.470 \text{ (if PE bag used)}} \quad (4)$$

$$a/o \text{ hydrogen} = 100 - a/o \text{ oxygen}$$

b. Distribution Of Oxide, Hydride, And Chloride In The Powder

The reactive gases in the atmosphere should react with the plutonium almost as rapidly as they are released from the plastic. The corresponding composition of the powder should be:

$$\text{PuO}_2, g = (0.00356W + 0.00338) \left(\frac{271}{2} \right) = 0.482W + 0.458.$$

$$\text{PuCl}_3, g = (0.0107W) \left(\frac{345.4}{3} \right) = 1.23W$$

$$\text{PuH}_{2.7}, g = [0.0565W + 0.00595 + 0.470 \text{ (if PE bag used)}] \left(\frac{241.7}{2.7} \right) \\ = 5.06W + 0.533 + 42.1 \text{ (if PE bag used)}.$$

$$\text{Total, } g = 6.77W + 0.991 + 42.1 \text{ (if PE bag used)}$$

$$w/o \text{ PuO}_2 = \frac{(0.482W + 0.458)(100)}{6.77W + 0.991 + 42.1 \text{ (if PE bag used)}} \quad (5)$$

$$w/o \text{ PuCl}_3 = \frac{(1.23W)(100)}{6.77W + 0.991 + 42.1 \text{ (if PE bag used)}} \quad (6)$$

$$w/o \text{ PuH}_{2.7} = 100 - w/o \text{ PuO}_2 - w/o \text{ PuCl}_3 \quad (7)$$

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If the chlorine is retained in the plastic and displaces hydrogen, these equations become:

$$\text{PuO}_2, g = 0.482W + 0.458 \text{ (same as before).}$$

$$\begin{aligned} \text{PuH}_{2.7}, g &= [0.0565W + 0.0107W + 0.00595 + 0.470 \text{ (if PE bag used)}] \left(\frac{241.7}{2.7} \right) \\ &= 6.01W + 0.533 + 42.1 \text{ (if PE bag used)} \end{aligned}$$

$$\text{Total, } g = 6.50W + 0.991 + 42.1 \text{ (if PE bag used)}$$

$$w/o \text{ PuO}_2 = \frac{(0.482W + 0.458)(100)}{6.50W + 0.991 + 42.1 \text{ (if PE bag used)}} \quad (8)$$

$$w/o \text{ PuH}_{2.7} = 100 - w/o \text{ PuO}_2 \quad (9)$$

c. Effective SS Factor For Mixed Powder

$$\text{SS factor} = \left(\frac{239}{271} \right) \left(\frac{w/o \text{ PuO}_2}{100} \right) + \left(\frac{239}{345.4} \right) \left(\frac{w/o \text{ PuCl}_3}{100} \right) + \left(\frac{239}{241.7} \right) \left(\frac{w/o \text{ PuH}_{2.7}}{100} \right)$$

or, in simplified form

$$\text{SS factor} = 0.9887 \left[1 - 0.108 \left(\frac{w/o \text{ PuO}_2}{100} \right) - 0.300 \left(\frac{w/o \text{ PuCl}_3}{100} \right) \right] \quad (10)$$

where 0.9887 is the SS factor for 100 percent hydride.

Results calculated from this equation should be comparable to four significant figures because of the small contribution of the oxide and chloride terms.

d. Tabulation Of Results

Table III contains the results of calculations from the equations above representing the complete range of storage container variables.

E. Discussion Of Plastic Irradiation Results

The SS factor values of Table III appear to indicate that chloride is released from the plastic in approximate proportion to its atomic percentage concentration in the plastic. The SS factors calculated on this assumption agree quite well with the actual data for ingots. The assumption of chlorine retention in the plastic leads to excessively high SS factors (powder predominantly hydride).

This finding indicates that powder found in storage cans may contain from 10 to 20 percent by weight of PuCl_3 . No analyses have been obtained to date for comparison. If analysis bears out this hypothesis, the chlorine compounds must be released near the inside surface of the envelope, since no evidence of corrosion of the storage can has ever been noted. This would also indicate that most of the damage to the plastic is caused by alpha radiation.

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TABLE III

ATOMIC PERCENT DISTRIBUTION OF REACTIVE GASES
IN CONTAINER ATMOSPHERE

<u>Envelope</u> <u>Wt., g</u>	<u>PE Bag</u> <u>In</u> <u>Envelope</u>	<u>If Chlorine</u> <u>Released From Plastic</u>			<u>If Chlorine</u> <u>Retained In Plastic</u>	
		<u>Oxygen</u>	<u>Hydrogen</u>	<u>Chlorine</u>	<u>Oxygen</u>	<u>Hydrogen</u>
20 (max)	Yes	3.94	84.8	11.26	3.94	96.1
15 (avg)	Yes	3.69	85.9	10.38	3.69	96.3
10 (min)	Yes	3.29	87.7	8.99	3.29	96.7
20	No	5.24	79.8	14.98	5.24	94.8
15	No	5.31	79.7	14.95	5.31	94.7
10	No	5.44	79.7	14.88	5.44	94.6

WEIGHT PERCENT DISTRIBUTION OF COMPOUNDS IN POWDER

<u>Envelope</u> <u>Wt, g</u>	<u>PE Bag</u> <u>In</u> <u>Envelope</u>	<u>If Chlorine</u> <u>Released From Plastic</u>			<u>If Chloride</u> <u>Retained In Plastic</u>	
		<u>PuO₂</u>	<u>PuH_{2.7}</u>	<u>PuCl₃</u>	<u>PuO₂</u>	<u>PuH_{2.7}</u>
20 (max)	Yes	5.66	80.6	13.8	5.84	94.2
15 (avg)	Yes	5.32	81.9	12.7	5.48	94.5
10 (min)	Yes	4.77	84.2	11.1	4.89	95.1
20	No	7.41	74.6	18.0	7.72	92.3
15	No	7.51	74.5	18.0	7.82	92.2
10	No	7.69	74.6	17.7	8.01	92.0

EFFECTIVE SS FACTOR FOR POWDER

<u>Envelope</u> <u>Wt, g</u>	<u>PE Bag</u> <u>In</u> <u>Envelope</u>	<u>If Chlorine</u> <u>Released</u> <u>From Plastic</u>	<u>If Chlorine</u> <u>Retained</u> <u>In Plastic</u>	<u>SS Factor Values</u> <u>From Ingot Data</u> <u>For Comparison</u>	
20 (max)	Yes	0.9419	0.9825	FAD-22-5-47	0.9737
15 (avg)	Yes	0.9453	0.9829	FAD-22-5-113	0.9236
10 (min)	Yes	<u>0.9501</u>	<u>0.9835</u>	FAD-22-5-214	0.9461
				FAD-22-5-187	<u>1.08*</u>
		Avg. 0.9457	0.9830	Avg. (excl. 187) <u>0.9478</u>	
20	No	0.9274	0.9804		
15	No	0.9275	0.9804		
10	No	<u>0.9280</u>	<u>0.9811</u>		
		Avg. <u>0.9276</u>	<u>0.9803</u>		

(*) Inaccurate because of short storage and small amount of powder.

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While the presence of PuO_2 , $\text{PuH}_{2.7}$, and PuCl_3 has been hypothesized, these compounds are only representative of many possible combinations of the reactants. The actual chlorine compounds formed may be oxychlorides of indefinite composition. The general conclusions are valid regardless of compositions assumed.

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APPENDIX B

VII. EVALUATION OF DATA FOR METAL LOSS AND POWDER FORMATION

A. Introduction

Four low-density ingots were obtained in 1962 for investigation of a liquid-metal purification process. The metal had lost density due to impurity pickup during extensive recycling through casting, machining, and briquet recovery operations. As such, the metal was quite uniform in age, density, and impurity content.

The ingots had been stored for three weeks to three months in normal HAPO storage containers. The extreme volume of powder found with some ingots was entirely unexpected (90 to 150 g). For this reason and for accountability reasons, the powder weight was determined quite accurately.

Similar data had been recorded on other occasions for powder found with stored buttons. The amount of such powder was usually negligible (2 to 4 g). Data for two buttons recently shipped to the Rocky Flats Plant after 500 days in storage, provided a striking contrast (15 to 70 g).

The availability of the fairly-accurate data for ingots has enabled an evaluation of the storage container problem of far more significance than could have been obtained from storage data for buttons. Data for the latter are much less accurate and extremely random.

The data of Table VI for ingots and Table VII for buttons is evaluated, compared, and discussed in the following topics.

B. Evaluation Of Ingot Data

1. Description Of Ingots

The first three ingots of Table VI (page 27) were cast in a tantalum mold with internally-welded dividers as shown in the adjacent sketch. The metal usually pours in such a manner as to provide one quadrant of full divider height, two quadrants of $1/2$ to $3/4$ of divider height, and the fourth of $1/4$ to $1/2$ of divider height.

The four pieces of each ingot were placed together in a polyethylene freezer bag, which was sealed in PVC plastic and then sealed in a can for storage. These ingots were found to be extensively "oxidized" after storage. In one case (FAD-22-5-47), the ingot pieces were poorly con-

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solidated; attack had been sufficiently extensive to cause separation along a cold shut.

The fourth ingot of Table VI was cast in a mold without dividers as a single, cylindrical piece. This metal was somewhat different from the other ingots. It was poured from briquet metal scalped from the tops of about 50 production ingots, hence may have had a different distribution of impurities. This ingot was in storage a much shorter time than the other three, hence had formed very little powder.

2. Weighing Of Ingots

Since all of the ingots were feed materials for a purification process evaluation, densities were determined as accurately as possible by multiple weighing. Each individual piece was checked for density, except the first ingot which was handled as a cluster. Hence, the final ingot weights were quite precise. Initial ingot weights were those recorded by the Foundry, when cast, and should be accurate to a whole gram. Hence, these weights must be considered to have a random error of ± 0.5 g.

All weights have been carried through calculations with the number of significant figures shown in Table VI. This procedure appears warranted because all correlations were made by the method of least squares, $(\frac{s}{s})(\frac{s}{s})$ which treats errors as being purely random. Rounding the metal-loss and powder weights to whole grams would introduce the possibility of doubling the uncertainty of calculations.

3. Surface Area Calculation For Ingots

The surface area of a single ingot quadrant was calculated as metal at its freezing point at a density of 16.50 g/cc, when in contact with the quadrant ingot mold. The surface area was calculated as a function of depth of metal in the mold. Figure 1 is a plot of this calculated surface area in a more convenient form as a function of ingot quadrant weight. The correction for density, based on linear coefficient of expansion, permits use of a single line for metal of any final density.

The initial surface area of individual ingot pieces was obtained from this plot, after correction for metal lost during storage (calculated on the basis of uniform loss distribution from the entire ingot surface area).

C. Correlation Of Ingot Data

The only valid correlation that could be found for metal loss from ingots, and powder formation, during storage is presented in Figure 3, p. 30. The best correlation by the method of least squares was obtained by treating

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the quadrant ingots separately from the single-piece ingot.

The rate of formation of powder from the quadrant ingots is represented by the equation

$$\frac{\text{Powder Formed, g}}{\text{Initial Surface Area, cm}^2} = 0.001842 (\text{days in storage})^{1.888}$$

The average deviation of data from this correlation is only 1.33 percent. The maximum deviation is only 1.98 percent.

The rate of metal loss from quadrant ingots is represented by the equation

$$\frac{\text{Metal Lost, g}}{\text{Initial Surface Area, cm}^2} = 0.001555 (\text{days in storage})^{1.314}$$

The average deviation is 3.23 percent; the maximum deviation is 4.77 percent.

These correlations provide a far better fit to the data than was originally thought possible.

For the single-piece ingot, only the metal loss data are valid. Storage time was short; very little powder was formed, hence the powder weighing error was very large.

The metal loss for the single-piece ingot fits the correlation for the quadrant ingots within 22 percent deviation, which is reasonable. A correlation to fit all four ingots results in a 10.2 percent average deviation, with the maximum deviation of 19.4 percent for the single-piece ingot. This is a much poorer correlation, overall, than a fit to quadrant ingots only, and provides very little improvement for the single-piece ingot. From these results, it is evident that the single-piece ingot differs significantly from the quadrant ingots, whether by geometry alone, or due to differences of impurities in the metal.

It is reasonable to expect the time effect (slope) for the single-piece ingot to be quite similar to the time effect for the quadrant ingots. The SS factor for the single-piece ingot depends only on the plastic envelope composition (Appendix, p. 16), as is true for the quadrant ingots. A set of lines has been approximated on Figure 3 (p. 30) for the single-piece ingot, based on its correlation having the same slopes and SS factors as the correlation for the quadrant ingots.

The correlation obtained by this procedure is represented by the equations

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$$\frac{\text{Powder Formed, g}}{\text{Initial Surface Area, cm}^2} = 0.0015 (\text{days in storage})^{1.29}$$

$$\frac{\text{Metal Lost, g}}{\text{Initial Surface Area, cm}^2} = 0.0012 (\text{days in storage})^{1.31}$$

These lines projected to 100 days in storage, indicate a rate of powder formation approximately half of that for the quadrant ingots, which would be expected for an ingot having only half the surface area of the quadrant ingots. Hence, this approximation appears justified. This correlation for the single-piece ingot will permit a comparison with buttons, because of similarity of geometry.

D. Discussion Of Ingot Data Correlation

The ingot correlations demonstrate the importance of surface area in the corrosion phenomenon, but not for the same reason area is important in normal corrosion problems. In this case surface area governs the amount of radiation that is available to degrade the plastic envelope in which the metal is sealed.

Because the plastic is in intimate contact with the plutonium, degradation of the plastic is caused almost entirely by alpha radiation. The radiation dose rate is governed by the geometry of the plutonium. For these reasons, the ideal correlation would substitute an integrated dose rate in place of surface area, if such a dose rate could be calculated. Correlation with respect to area is adequate for this report.

The increase of corrosion rate with time (slope of correlation equation greater than unity) shows that the plutonium is forming powder, which provides a more diffuse media for radiation release, hence the radiation dose-rate increases. The powder is in more intimate contact with the plastic, intensifying degradation.

Because degradation is caused almost entirely by alpha radiation, the substances released from the plastic will be released at the interior plastic surface, hence all reactive substances released will be available to attack the plutonium. This condition also implies that, if the plutonium is in contact with PVC plastic, the powder should contain hydrogen, oxygen, and chlorine in approximate proportion to their atomic percentages in the plastic. If the plutonium is in contact with polyethylene, the powder should contain a larger proportion of hydride.

Some degradation will be caused to other organic materials in the container by neutron and gamma radiation. Reactive materials so released can also reach the plutonium (Appendix, p. 13), but the amount of corrosion from this source should be small.

E. Significance Of SS Factor, Powder Composition

The correlations for the quadrant ingot data permit a correlation for

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SS factor of the form

$$SS \text{ Factor} = \frac{W_M/A}{W_P/A} = \frac{a_M}{a_P} D^{(b_M - b_P)} = 0.8444D^{0.02624*}$$

This correlation effectively averages the SS factors for the range of the data, as shown in Table IV.

TABLE IV

Ingot FAD--22-5-	Days Stored	SS Factor			Comparison Of Data With Correlation	
		Correlation	Data	Theor. ⁽⁴⁾	Deviation	% Deviation
47	99	0.9527	0.9737		+ 0.0210	2.21
113	91	0.9506	0.9236		- 0.0270	2.84
214	59	0.9398	0.9461		+ 0.0063	0.66
187	22	0.9158 ⁽¹⁾	1.08 ⁽²⁾			
	Average ⁽³⁾	0.9477	0.9478	0.9458		1.90

- (1) Reasonable value, since initial powder should be almost entirely oxide from original air and moisture.
 (2) Meaningless because of small powder weight (less than metal loss weight).
 (3) Excluding last item.
 (4) Table III, p. 17. Ingots in PE bag, then sealed in PVC.

Because of this close agreement, the powder may be expected to have a composition approximately as follows, after prolonged storage (from Table III, p. 17).

TABLE V

Probable Composition Of Powder, Weight Percent						
	PuO ₂	Oxygen	PuH _{2.7}	Hydrogen	PuCl ₃	Chlorine
Plutonium in polyethylene bag	5.3	0.62	82	0.93	13	3.9
Plutonium sealed in PVC only	7.5	0.89	75	0.84	18	5.5

If the plutonium has been stored for a limited time (less than one month), it should have a composition near that of pure oxide (SS factor about 0.90).

- (*) Precision used in least squares calculations of correlations permit use of these significant figures here to enable the comparisons of Table IV. The closeness of Table IV results appear to justify the liberties taken with significant figures.

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F. Evaluation Of Button Data

All buttons are believed to have been packaged directly in PVC. In general, little powder was formed. The surface of the metal was smooth in most cases, though some surface pitting was observed, indicating possible hydriding.

A plot was prepared for button geometry as a function of button weight, based on reduction vessel liner specifications. The plot (Figure 2, p. 29) should be reasonably representative of buttons produced in actual liners. The surface area of the button was obtained from this plot at the particular button weight, then corrected to ambient density.

All data for the correlations are contained in Table VII, page 28.

G. Correlation Of Button Data

Powder formation rate for buttons was correlated by the same means found so effective for ingots. The correlation (Figure 4, page 31) is represented by the following equation, determined by the method of least squares:

$$\frac{\text{Powder Formed, g}}{\text{Initial Surface Area, cm}^2} = 0.000053 (\text{days in storage})^{1.41}$$

This correlation, with average deviation of 41 percent and maximum deviation of 65 percent, shows powder formation from button metal to be immensely variable, and provides some useful comparisons with the corresponding ingot data.

H. General Correlation

In Figure 5 (page 32), the powder formation rates for buttons and ingots are plotted in terms of length of storage. In each case the correlation equation was converted to a weight basis by means of the average surface area per gram of metal for the data specimens used in the correlation. Each equation was then adjusted to a 2000 g plutonium weight to permit comparison.

I. Discussion Of Correlations

The buttons for which data were available for the correlations were quite similar to the single-piece ingot in weight, surface area, and density, hence should provide a valid comparison of corrosion rates.

The corrosion rate or powder-formation rate for buttons is 15-fold less, as an average, than that for the single-piece ingot, based on the correlation equation without allowance for deviation. With allowance for the extreme variability observed, this difference of corrosion rates for individual buttons could be as little as eight-fold to as great as 45-fold.

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Powder formation from the single-piece ingot was smaller by a factor of two than for the quadrant ingots. Hence, powder formation for the quadrant ingots was greater than for buttons by a factor of 18- to 90-fold.

J. Significance Of Corrosion-Rate Differences

While the single-piece ingot was the only one of its kind for which powder formation details were available, and even these details were not complete, the correlation for the single-piece ingot is believed to represent a valid order-of-magnitude difference. The correlations have allowed for surface-area differences, hence the reasons for corrosion-rate differences must lie elsewhere.

No packaging details were recorded for the single-piece ingot; the quadrant ingots are known to have been placed in PE bags before sealing in PVC. At the time these data were obtained, most buttons and ingots were sealed directly in PVC. It is possible that packaging may account for the differences of corrosion rate of the ingots--packaging in PE may lead to more severe corrosion of plutonium than packaging in PVC, because of the greater percentage of hydrogen available in the PE. In addition, PE may be more seriously degraded than PVC when subjected to the same radiation dosage.

It is also possible that the single-piece ingot was different in metal characteristics from the quadrant ingots. The former was a briquet ingot melted down from scalplings (top machinings) from about 50 briquet ingots processed to float out impurities. The latter ingots were of recycled metal that had been processed through one or more casting operations. Impurities in unalloyed metal have been found to inhibit corrosion.⁽⁴⁾ The single-piece ingot definitely contained the greater amount of impurities, hence, may have been more effectively passivated.

K. Button Corrosion Apparently Inhibited

The limited corrosion of buttons and its extreme variability appear to indicate an inhibition mechanism. Inhibition could arise because of total impurity content as noted previously. It appears more likely that the inhibition is associated with specific impurities.

Buttons X-22-8-57 and -59 should have been as identical as any two buttons could be prepared. They were prepared the same shift of the same day in the same furnace, and presumably by the same operator. The feed should have been essentially the same. The buttons were virtually identical in size, weight, density, and recorded impurities. Yet these buttons represented the extremes of corrosion rate data available.

The most logical explanation for this extreme difference between these two buttons, and for the extreme difference between buttons (in general) and ingots, appears to be a difference of calcium content of the metal (or possibly calcium and magnesium). This appears to be the only difference of significance possible between the two buttons cited. Ingot metal should

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have far less of these volatiles than buttons and should be most free of such impurities after repeated ingotting.

Hence, it appears reasonable that ingot metal corrodes more severely than button metal because of lower impurity content, especially calcium. The same mechanism appears to account for the extreme variability of button corrosion during storage.

L. Significance Of General Correlation

Figure 5 appears to indicate that the slope of the correlation equations will be essentially the same regardless of the source or type of metal. This may indicate a similar degree of plastic degradation, due to quite similar plutonium metal weight and alpha irradiation dosage to which the plastic is subjected. The slope of these correlation equations, then, would represent an amount of reactive gases available to cause corrosion-hence, represent a potential or driving force available for corrosion.

The spread between the corrosion-rate equations (intercepts) may represent a resistance to corrosion, or degree of inhibition of the metal.

If these interpretations are correct, they imply that the powder formed from ingot metal may be less completely reacted with the corrosive gases than that from button metal. The ingot metal may spall more readily because of hydriding action; the interior of the powder particles may be unreacted metal. In this case, the SS factors would be too large and might imply the presence of more hydride than is actually present. In this case, the fire hazard for ingots should be more severe than for buttons.

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TABLE VI
INGOT DATA

Ingot Identity (1)	Days Stored (2)	Weight, g		Metal Loss (5)	Powder Formed (6)	Metal Density Final g/cc	SS Factor (7)	Metal Surface Original ⁽⁸⁾ cm ² Notes	
		Metal Start (3)	Metal Final (4)						
FAD-22-5-									
47	99	1799	1651.94	147.05	151.03	18.96	0.9737	217.5	(9)
113	91	2155	2028.90	126.10	136.53	18.93	0.9236	227.0	(10)
214	59	2358	2272.40	85.60	90.48	19.02	0.9461	256.4	(11)
187	22	1881	1872.17	8.83	8.21	19.21	1.08	124.7	(12)

FOOTNOTES

- (1) Low-density ingots processed during zone-cooling investigations.
- (2) Date of ingotting to date can opened and powder weighed. Reliable within 1 day.
- (3) Weight at time of canning for storage. Accurate to whole-gram value.
- (4) Brushed ingot weight at time can opened. Accurate within 0.05 g.
- (5) By difference between (3) and (4). Accurate to ± 0.5 g (indicated to two decimals to avoid introduction of further rounding error).
- (6) Weight at time can was opened. Believed accurate within 0.2 g, except last item.
- (7) Ratio of metal loss to powder formed. Last item inaccurate because of short storage time and small amount of powder formed.
- (8) Calculated original surface area based on final weights, corrected for metal loss, and on geometry of tantalum molds used. See Figure 3, pp. 30 and discussion, p. 20.
- (9) Poorly consolidated quadrant ingot, severely "oxidized".
- (10) Well consolidated quadrant ingot, four pieces, no fines.
- (11) Well consolidated quadrant ingot, few fines.
- (12) Well consolidated single-piece ingot, prepared from scalpings of Process Test 62-7.

TABLE VII

BUTTON DATA

Button Identity	Days Stored	Weight, g		Metal Powder Formed	Metal Density g/cc	Metal Surface Original cm ²	Reliability
		Metal Start	Metal Final				
<u>Unalloyed</u>	(1)	(2)	(3)	(4)	(5)	(6)	
NX-21-5-55	92	1951	1947.10	4.75	19.43	127.3	(7)
NX-22-4-23	38	1511	1509.56	1.62	19.25	113.9	(8)
X-22-8-57	500	1788	---	15	19.02	123.9	(9)
X-22-8-59	500	1756	---	70	19.07	122.7	(9)
X-23-3-33	95	1851	1846.40	3.90	19.38	124.3	(8)
<u>Alloyed</u>							
X-23-2-39	58	1918	1915.51	1.48	15.8*	145.0	(10)

FOOTNOTES

- (1) Date produced to date can opened and powder weighed. Reliable within 1 day.
- (2) Weight at time of canning for storage. Accurate to whole-gram value.
- (3) Brushed button weight at time can was opened. Accurate within 0.1 gram.
- (4) Weight at time can was opened. Believed accurate to 0.2 g, except Items 3 and 4.
- (5) Value reported at time of production. *Alloy density not determined; estimated.
- (6) Surface exposed to reaction. Calculated from reduction vessel liner geometry. See Figure 2, p. 29.
- (7) Most reliable of values available. Best powder-weighing techniques.
- (8) Reasonably reliable by reason of weighing techniques and powder quantity.
- (9) Powder weights obtained from RFP. Accuracy of weighing not known, but should be reasonably reliable by reason of large powder quantity.
- (10) Reliability questionable. Powder quantity small. Not all details recorded.

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FIGURE 1

SURFACE AREA OF ONE INGOT QUADRANT

FIGURE 2

SURFACE AREA OF QUADRANT

FIGURE 3.

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FIGURE 4

CORRELATION OF CORROSION
OF BOTTOMS DURING CLOSED STORAGE

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FIGURE 5

GENERAL CORRELATION OF CORROSION
OF THEORETICAL LAL DURING CAPED STORAGE

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