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CORROSION OF VARIOUS METALS AND ALLOYS BY PHOSGENE, HYDROGEN CHLORIDE, AND CARBON TETRACHLORIDE AT 400 - 600 C

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GENERAL ELECTRIC

I. INTRODUCTION

A considerable portion of the penetrating radiation encountered in the processing of plutonium as a fluoride salt arises from an α-n reaction with fluorine in these salts. Substitution of chlorine for fluorine would reduce the neutron radiation by a factor of about 100; a much larger reduction than could be achieved with any reasonable amount of additional shielding.

In addition, the chloride salts of several of the metallic impurities present in the plutonium are more volatile than the fluoride salts. This characteristic would tend to remove or decrease the impurities in the final metal product.

A process for the preparation of plutonium metal using a chloride rather than a fluoride as an intermediate is discussed in a paper presented by M. J. Rasmussen at the New York Meeting of the American Chemical Society, in September, 1960. The process, as such, will not be discussed in this report.

From a corrosion viewpoint, the most severe step in the process is the high-temperature chlorination of plutonium oxide. Initially, hydrogen chloride, carbon tetrachloride, and phosgene were considered as potential chlorinating agents. However, further studies indicated that phosgene was the most reactive. Although a variety of metals and alloys were exposed to all three chlorinating agents, the main portion of this work was concerned with the phosgene system.

II. SUMMARY

Of the materials investigated, Hastelloy B and Hastelloy C appeared to be most suitable for service where using phosgene or carbon tetrachloride as the chlorinating agent. These alloys exhibited corrosion rates ranging from 0.2 to 11 mils penetration per month over the temperature range of 400 to 600 C. Haynes 25 and Chlorimet 2 exhibited corrosion rates nearly identical with the Hastelloys. However, the initial cost expense of Haynes 25 is about twice that of the Hastelloys. Chlorimet 2 is available only in the cast form and has undesirable mechanical properties. Commercially pure nickel also exhibited corrosion rates similar to the Hastelloys, but nickel contamination of the product is a problem.

Platinum, gold, and Baker 413 (a gold-platinum-palladium alloy) were severely attacked by the phosgene system and were considered unsuitable for the carbon tetrachloride system because of the possibility of phosgene formation. However, in the hydrogen chloride system, the precious metals and Baker 413 exhibited corrosion rates ranging from .01 to 0.4 mils penetration per month over the temperature range of 400 to 600 C.

A variety of metals and alloys were exposed to the off-gas stream from the phosgene system. Severe corrosion occurred when the sample temperatures were low enough to permit condensation.

III. EXPERIMENTAL AND DISCUSSION

A. General

The chlorination of plutonium oxide would be performed in equipment similar to that shown in Figure 1. The oxide is fed into the upper end of an inclined vibrating furnace tube. The oxide passes down the tube through a counter-current flow of the chlorinating agent, and out the lower end of the furnace tube as plutonium tri-chloride. Water vapor is present in the furnace, either as a reaction product or as a contaminant from the preceding processing steps. The environment seen by the furnace tube will depend upon the particular chlorinating agent selected. The possible environments which might occur are shown below for carbon tetrachloride, phosgene, and hydrogen chloride. The equations are not balanced.

$$
\begin{array}{lll}
 & + CCl_4 \text{ (Argon carrier)} \longrightarrow & + COCl_2 + CCl_4\text{(excess)} + H_2O^{*} \\
PuO_2\ (H_2O) & + COCl_2 \longrightarrow PuCl_3 & + Cl_2 + CO_2 + COCl_2\text{(excess)} + H_2O^{*} \\
 & + HCl + H_2 \longrightarrow & + H_2O + HCl\text{(excess)} + H_2\text{(excess)}
\end{array}
$$

* The water will react with some of the phosgene to form CO_2 and HCl.

In all three systems the chlorinator will be subjected to an atmosphere of HCl and water vapor. Depending upon the chlorinating agent selected, Cl_2, CCl_4, and $COCl_2$ may also be present in any combination. Since the chlorinator operates in the 400 - 600 C temperature range, this represents one of the most severe corrosive environments in the entire process.

Corrosion tests were made on a number of metals and alloys as listed in Table 1. No attempt was made to evaluate the effect of abrasion by the moving powder in the laboratory tests.

[redacted]

TABLE 1

Nominal Alloy Compositions - Weight Percent

Alloy	Ni	Cr	Fe	Mo	Mn	Si	Cu	W	Co	Others
Hastelloy B	61	1	6	28	1	1	--	--	--	
Hastelloy C	55	15	6	16	1	1	--	4	--	
Hastelloy F	46	22	19	6	1	1	--	1	2	2 Cb-Ta
Haynes 25	10	20	2	--	1	1	--	15	50	
Ni-o-nel	42	22	28	3	1	1	2	--	--	1 Ti
Inco 804	40	30	balance unknown							
Monel	70	--	2	--	2	0.5	25	--	--	
Chlorimet 2	62	--	3	32	--	1	--	--	--	
304-L Stainless Steel	10	19	69	--	1	1	--	--	--	
312 Stainless Steel	10	28	61	--	1	1	--	--	--	
316-L Stainless Steel	12	17	69	--	1	1	--	--	--	
Duriron	--	--	84	--	1	14	--	--	--	1 C
Baker 413	--	--	--	--	--	--	--	--	--	60-Au 25-Pd 15-Pt

The testing equipment, shown in Figure 2, consisted of two gas bubblers in parallel on a line leading into a 2.5 inch diameter Vicor furnace tube. The outlet of the gas line was at the extreme end of the tube to provide for preheating of the gas before it came in contact with the samples. Gases leaving the furnace passed through an air-cooled flask and then to a caustic scrubber. In the latter part of the investigation, the cooling flask was equipped with a Glascol heating mantle so that the temperature in the flask could be controlled in order to study the corrosivity of off-gases from the furnace tube. The samples in the furnace tube were held on a Vicor rack, which prevented contact between them and eliminated any galvanic effects. Samples exposed in the off-gas studies were simply placed on a bed of glass beads in the bottom of the flask in a manner which avoided contact between them.

Most of the runs made in this investigation were about 70 hours long. Gas flow through the furnace tube was on the order of 500 to 1000 cc's per hour. All corrosion rates are expressed as mils penetration per month, and were calculated from the weight losses of the samples - assuming a uniform attack. On those samples which exhibited pitting attack, the pitting rate is also expressed as mils penetration per month.

At the time this investigation was performed only small quantities of some of the alloys were available. Consequently, metallographic examinations were not performed. All comments regarding the mode of attack are based on visual observations only, at magnifications up to 250 diameters.

The data collected on the three different systems - HCl, CCl_4, and $COCl_2$ - will be discussed separately, in their respective order. The data collected in the investigation of off-gas corrosion in the phosgene system will also be discussed.

B. Hydrogen Chloride

Samples of gold, platinum, Baker 413, Hastelloy B, Hastelloy C, and Haynes 25 were exposed to water-saturated HCl gas at temperatures of 400, 500, and 600 C for 72-hour periods. Hydrogen gas was not mixed with the HCl gas in this investigation since the contribution of hydrogen to the corrosion rate was considered to be negligible. Gas flow through the system was on the order of 500 cc/hr. The corrosion rates observed are shown in Table 2.

TABLE 2

Corrosion of Metals and Alloys by $HCl-H_2O$ at 400, 500, 600 C

Rates are Expressed in Mils/month

Material		400°	500°	600°	Remarks
Gold	Less than	.01	.04	0.4	
Platinum	" "	.01	.01	0.2	
Baker 413	" "	.01	0.2	0.4	
Hastelloy B		.04	0.8	11	Pitting at 500° - 30 mpm
Hastelloy C		.09	0.8	9	" " " - 15 mpm
Haynes 25		0.15	1.4	7	" " " - 60 mpm

The precious metals and Baker 413 exhibited a slightly etched appearance at the higher temperatures. At 400 C, the gold sample appeared as if some other silvery metal had been deposited at a few spots on the surface of the sample. This deposit was very adherent.

The Hastelloy B and C, and the Haynes 25 samples appeared as if they had been heavily etched, after cleaning. All three alloys exhibited loose, porous films which could be easily removed by rubbing with ones fingers.

C. Carbon Tetrachloride

Samples of gold, platinum, Baker 413, Hastelloy B, Hastelloy C, Haynes 25, and 304-L stainless steel were exposed for 70 hour periods to CCl_4 carried in an air stream of about 500 cc/hr, at temperatures of 500 and 600 C. Several attempts were made to perform exposures at 400 C, but the off-gas line was blocked by some unknown compound each time. The corrosion rates observed are shown in Table 3.

TABLE 3

Corrosion of Metals and Alloys by CCl_4-Air at 500 and 600 C

Rates are Expressed as Mils/month

Material	500	600	Remarks
Gold	0.7	0.5	Outlet line blocked after 50 hours at 500 C. The samples were re-run successfully.
re-run	0.3		
Platinum	0.9	0.1	
re-run	0.4		
Baker 413	4.1	7	
re-run	0.2		
Hastelloy B	0.8	4.8	
re-run	0.5		
Hastelloy C	1.2	6.7	
re-run	0.8		
Haynes 25	2	16	
re-run	2		
304-L Stainless Steel	29	105	
re-run	10		

No pitting was observed on any of the samples in the CCl_4 system. The precious metals and Baker 413 were attacked uniformly, and appeared to have been etched. The Hastelloys, Haynes 25, and 304-L samples were covered with a porous, loosely adherent film which could be removed by rubbing with ones fingers.

D. Phosgene

As stated earlier, phosgene appeared to be the most suitable chlorinating agent because of its higher reactivity. This would permit the processing of more plutonium at a given temperature, or processing the same amount of plutonium at a lower temperature, as compared to either HCl or CCl_4.

Initially, samples of gold, platinum, Baker 413, Hastelloy B, Hastelloy C, and Haynes 25 were exposed for 70-hour periods to 500 cc/hr phosgene at 400 and 600 C. The gas flow was doubled for the run at 500 C in order to determine if this had any effect on the corrosion rates. The data collected are shown in Table 4.

TABLE 4

Corrosion of Metals and Alloys By $COCl_2$ at 400, 500, and 600 C

Rates are Expressed as Mils/month

Material	400	500	600	Remarks
Gold	1.6	100*	15	*Sample completely destroyed. The rate shown is a minimum.
Platinum	11	50*	16	
Baker 413	0.2	14	40	
Hastelloy B	.02	0.6	8	
Hastelloy C	.02	0.8	7	
Haynes 25	less than .01	2	40	

It would appear that gold and platinum are quite sensitive to flow rate in the phosgene system, and that Baker 413 is severely attacked. All samples exhibited relatively uniform attack, with loosely adherent film formation.

Since the phosgene system will contain some water vapor, another series of exposures was made for survey purposes. Single samples of a variety of materials were exposed at 600 C to a mixture of equal volumes of phosgene and water-saturated air, flowing at a combined rate of about 1000 cc/hr. The data collected are shown in Table 5, expressed as mils penetration per month.

TABLE 5

Corrosion of Materials By $COCl_2$ and Water-Saturated Air At 600 C

Rates are expressed as mils/month

Material	Rate	Material	Rate
'A' Nickel	7	Hastelloy F	14
Monel	16	Duriron	700*
Chlorimet 2	8	312 Stainless Steel	20
Ni-o-nel	2	316-L Stainless Steel	15
A-55 Titanium	160	Inco 804	10
Tantalum	60*		

*Sample completely destroyed - rate shown is a minimum

From the survey runs, and the runs made without water present, the following materials were selected for further testing: Hastelloy B, Hastelloy C, 'A' nickel, Chlorimet 2, Inco 804, and Ni-o-nel. Two experimental alloys were also included, a 40 Ni - 60 W alloy, and a Ni - Cr - W alloy of unknown proportions. Samples of these alloys were exposed at 400, 500, and 600 C to a mixture of equal volumes of phosgene and water-saturated air flowing at a rate of about 1000 cc/hr. In some instances, duplicate runs were made because the 400 C rate was higher than the 500 C rate in the first set of samples. No reason for this behavior is known, but it might be due to a malfunction of the temperature controller during this particular run. The data collected are shown in Table 6.

TABLE 6

Corrosion of Materials by $COCl_2$ and Water-Saturated Air at 400-600 C

Rates are Expressed as mils/month

Material	400	500	600	Remarks
Hastelloy B	0.2	0.8	4	
	0.2	0.9	7	All samples exhibited loosely adherent films which could be removed by rubbing with the fingers.
Hastelloy C	0.2	0.2	4	
	0.1	0.6	6	
'A' Nickel	0.4	0.1	2	All samples, with the exception of Inco 804, exhibited essentially uniform attack.
	0.2	0.6	4	
Chlorimet 2	0.2	0.7	3	
	0.2	0.8	3	
Ni-o-nel	0.5	0.1	6	
	0.6	0.9	12	
Inco 804	0.8	0.5	6	Pitting attack
60 Ni - 40 W	0.4	0.7	6	
Ni - Cr - W	0.6	0.8	6	

Examination of the data above indicates that the test is reasonably reproducible. The weight losses used to calculate the corrosion rates at the lower temperatures were only on the order of 5 to 20 miligrams, and small absolute differences can result in very large differences in the calculated corrosion rate.

It would appear that any of the alloys listed above with the exception of Inco 804 would be satisfactory for service in high temperature phosgene and water, strictly from a corrosion viewpoint. However, only Hastelloy B and Hastelloy C appeared suitable, from an overall viewpoint.

Commerically pure nickel was considered undesirable because nickel contamination of the final plutonium metal product is a serious problem. Chlorimet 2 is available only in the cast form, and has undesirable mechanical properties. At the time of the investigation, Ni-o-nel was not commercially available in the tubing size required. The 60 Ni - 40 W and Ni - Cr - W alloys were not commercially available.

As stated earlier, no attempt was made to duplicate the abrasive effect of the moving powder in the corrosion tests. The nature of the corrosion product film which formed on the test samples indicated that it would offer little or no protection. In order to obtain some idea of the corrosion rate which would be encountered in actual service, a Hastelloy B sample was exposed during one run in the prototype plutonium chlorinator.

The sample consisted of a 36 inch long Hastelloy B welding rod, .093 inches in diameter. The sample was weighed to the nearest tenth of a gram and placed in the calciner tube. The calciner operated for a total of 83 hours, at an average temperature of 460 C. The sample was removed, cleaned, and re-weighed. The weight loss was between 0.2 and 0.3 grams, giving a corrosion rate of between one and two mils penetration per month. A more accurate determination of the rate was not possible because of an analytic balance of succificient size to contain the sample was not available. The agreement between this rate and a rate predictable from laboratory tests is reasonably good.

E. Off-Gas Corrosion Tests

As a part of the investigation of the phosgene system, some corrosion tests were performed in the off-gas stream from the furnace tube to determine the corrosion rates of metallic materials of construction for handling these gases. The first two runs were made without the use of the supplementary heater, and the temperatures are only approximations. The third and fourth runs were made with the supplementary heater, and the temperatures are probably correct to plus or minus two degrees centigrade. The data collected are shown in Table 7.

TABLE 7

Corrosion In $COCl_2$ - Air - H_2O Off-Gases

Rate expressed as mils/month

Material	Rate	Sample Temp.	Furnace Temp.	Remarks
Hastelloy B	5	apprx. 100 C	500 C	
Hastelloy C	9	" "	"	
304-L Stainless	67	" "	"	Serious end grain attack
	70	" "	"	
Hastelloy B	0.9	apprx. 200 C	"	
	2.3	" "	"	
Hastelloy C	1	" "	"	
	3	" "	"	
Hastelloy B	2	97 C	400 C	
	7	"	600	
Hastelloy C	2	"	400	
	9	"	600	
'A' Nickel	52	"	400	
	11	"	600	
Chlorimet 2	1	"	400	
	11	"	600	
Ni-o-nel	8	"	400	
	19	"	600	
60 Ni - 40 W	2	"	400	
	12	"	600	
Ni - Cr - W	2	"	400	
	15	"	600	

Two things are apparent from the data shown: the corrosivity of the off-gases is inversely proportional to the sample temperature, and the corrosivity of the off-gases at a sample temperature of 97 C is proportional to the furnace temperature. In all instances, the corrosion rates of the samples exposed in the off-gases are equal to, or greater than, the rates observed in the furnace tube itself, at much higher temperatures.

The higher rates observed in the off-gases is probably a condensation effect. Water and HCl are present in the gas stream, and at temperatures below the boiling point, they would condense out as hydrochloric acid. This would also account for the difference in the corrosion rates of samples at 100 and 200 C. At the higher temperature, there is less water present on the sample, and consequently, a lower corrosion rate.

The effect of furnace temperature on the corrosivity of the off-gases is probably a reaction acceleration effect. Phosgene reacts with water to produce HCl and CO_2, and the reaction rate increases with temperature. At higher temperatures, more HCl is formed in a given time in a given volume of gas. This results in a higher concentration of hydrochloric acid in the condensate, and consequently, a higher corrosion rate on a sample exposed to the condensate.

A relatively simple solution to the problem of off-gas corrosion is to heat the off-gas lines to 300 - 400 C to a point where a transition to a ceramic-lined pipe can be made, or until the gases can be passed through a caustic scrubber.

IV. CONCLUSION

Hastelloy B and C appear to be the most suitable of the materials tested in this investigation for service in high temperature phosgene and carbon tetrachloride systems. Gold, platinum, and Baker 413 appear suitable for service in high temperature hydrogen chloride systems. A plutonium chlorinator fabricated from welded Hastelloy B has been used intermittently with a phosgene atmosphere at HAPO for two years, to date, without a corrosion failure.

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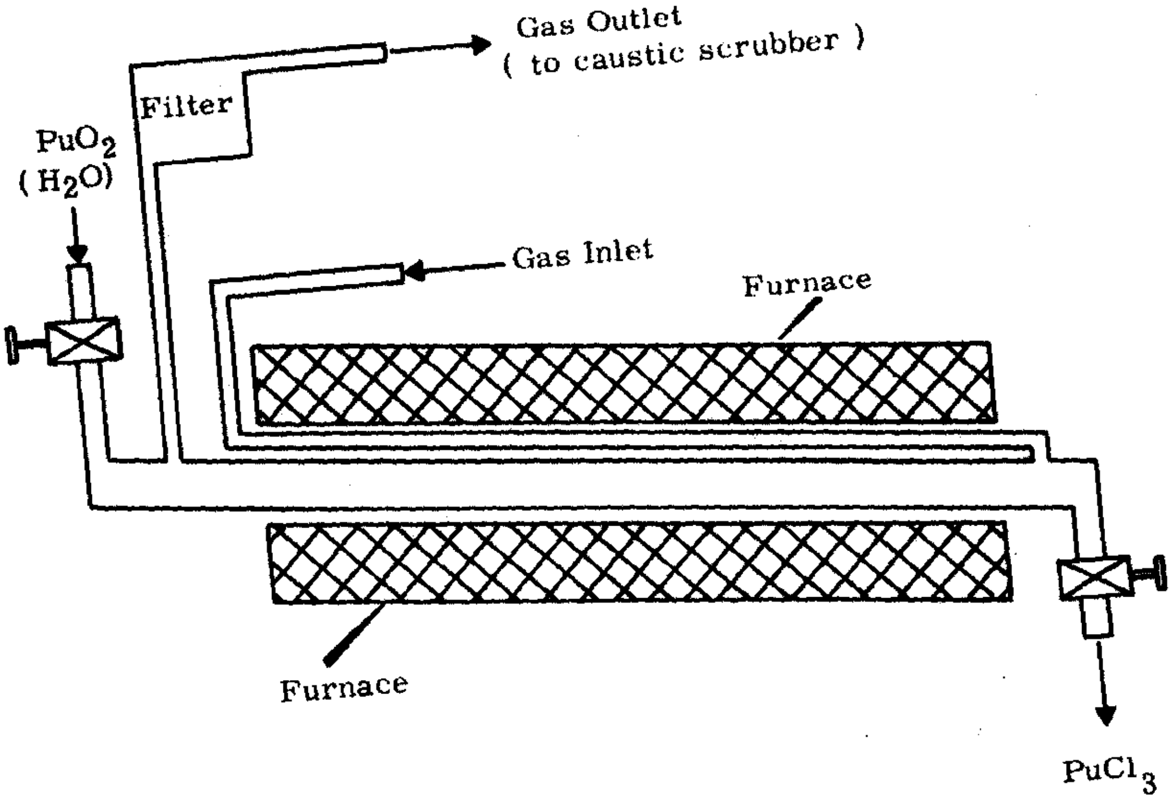

FIGURE 1

Sketch of Equipment for Chlorinating Plutonium Oxide. The entire assembly is vibrated in order to move the oxide through the unit.

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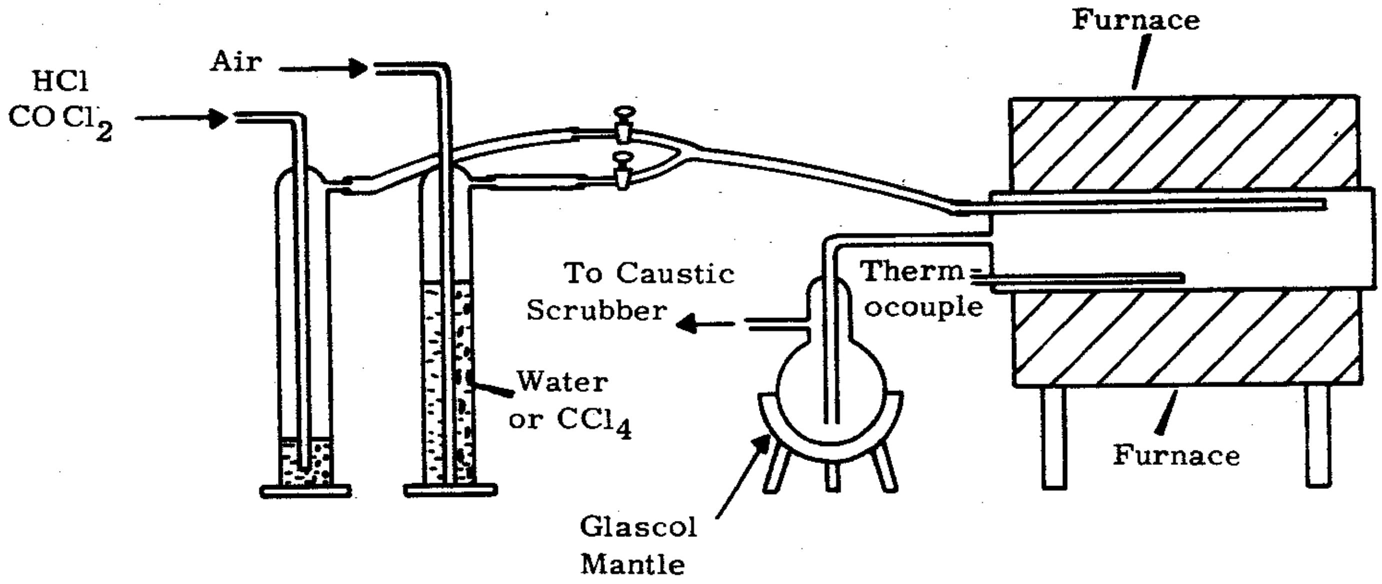

FIGURE 2

Sketch of High-Temperature Corrosion Testing Equipment. The phosgene and hydrogen chloride bubbler was filled with mineral oil, and the air bubbler was filled with water during runs on these two systems. During the carbon tetrachloride run, the air bubbler was filled with carbon tetrachloride.