Argonne National Laboratory

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OF FLUORINE AT ELEVATED TEMPERATURES**

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M. J. Steindler and R. C. Vogel

INTRODUCTION

A study of the corrosion of various metallic and ceramic materials by gaseous fluorine at elevated temperatures (400-750 C) has been made. This work was initiated to aid in the selection of materials of construction for the Fluoride Volatility Process applied to irradiated plutonium-uranium alloys. The data obtained in this investigation indicated that nickel and Monel were suitable materials for use in a fluorine atmosphere at temperatures up to 550 C. At higher temperatures nickel and copper exhibited the lowest corrosion rates. Ceramic materials such as calcium fluoride and alumina were resistant to attack by fluorine even at the highest temperatures, but lack mechanical strength. These data were compared with literature data from various sources.

A Fluoride Volatility Process for irradiated plutonium-uranium alloys may include the following steps:

1. Dissolution of the irradiated alloy in bromine trifluoride.
2. Separation of the volatile fluorides and unreacted bromine trifluoride from the non-volatile fission product and plutonium fluorides by distillation.
3. Fluorination of the non-volatile distillation residue at elevated temperatures using elemental fluorine.
4. Distillation of plutonium hexafluoride and subsequent purification and decontamination.
5. Removal of fission product wastes from the dissolver using a suitable high melting medium.

Although the temperature necessary for the successful operation of the fluorination step has not been finally determined, preliminary evidence has indicated that temperatures in the neighborhood of 350 C were of particular interest. Corrosion of equipment components at these temperatures has been anticipated. One object of this work was to evaluate the magnitude of this problem. The effect of the presence of plutonium on the corrosion of materials in a fluorine atmosphere was not included in this report.

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I. EXPERIMENTAL METHODS AND DATA

The apparatus used for this study is shown in Figure 1. A commercial, high purity fluorine supply (99.5% or better) was attached directly to the system. Tank-grade helium was used without purification to flush the system prior to admitting fluorine. A nickel-wool plug at one end of the $3/4$ -inch nickel furnace tube served to diffuse the gas before entering the heated zone. The nickel furnace tube of $1/16$ -inch wall thickness was flared at both ends and a small length of $1/8$ -inch tubing was soldered to the outside and served to hold the thermocouple in place. Copper gaskets were used at both ends. Three traps ($3/4$ -inch flare) were placed at the end of the train, the center trap utilizing fluorolube oil in a fluorothene test tube as a bubbler. All gases were vented to the hood exhaust system.

FIGURE 1. APPARATUS FOR THE STUDY OF CORROSION OF MATERIALS IN A STREAM OF FLUORINE.

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A typical experiment was carried out by first cleaning the coupon, obtaining an accurate weight and measuring the area to the nearest 0.1 sq mm. Samples were stamped with suitable identification marks prior to cleaning. In general, coupons of nickel or high nickel alloys were cleaned with aqua regia or suitable mixtures of nitric acid and sodium chloride until a clean surface was obtained. Copper samples were given a one-second dip in fresh concentrated nitric acid, thereby forming a clean, shiny surface. Samples were rinsed with water after cleaning. After being dried and weighed to the nearest 0.1 mg, they were introduced into the tube to a position close to the thermocouple. The system was flushed with helium during the initial heating period. Fluorine was admitted at the desired temperature and the rate of flow determined with the aid of the bubbler. At the conclusion of the experiment the fluorine flow was interrupted; helium was admitted to the system and allowed to flow until the tube had cooled to room temperature. The exposed coupon was removed, weighed and portions of it were mounted in bakelite for metallographic examination and measurements of film thickness.

A summary of the data obtained in this work is presented in Table 1.

II. DISCUSSION

A. Results of This Work

The data in Table 1 have been tabulated so that the source of the data may readily be determined. The methods used to calculate corrosion or penetration rates from weight change and film thickness measurements are given in Appendix A. Owing to the lack of statistical control and mechanical difficulty in obtaining film thickness data, the corrosion rates derived from coupon weight changes are believed to be more reliable. In contrast to other corrosion studies, film removal and subsequent determination of weight loss were in general avoided except in cases where removal of thick corrosion films left a clean metallic surface. It is believed that both physical and chemical removal of corrosion films may introduce severe errors in the extrapolated corrosion rate. A short discussion of each of the types of samples studied is presented below.

1. Nickel

The samples of nickel used were "A" nickel. All nickel coupons were treated with mixtures of nitric acid and sodium chloride prior to exposure. This resulted in a clean, but dull, finish on the specimens. The film thickness obtained on exposure of nickel to fluorine at 550 C was too small to measure and the datum (Table 1, item 1) was obtained only from the weight gain of the coupon. Samples exposed at 650 C and 750 C showed films of measurable thickness and the corrosion rates were calculated from both of these observations. The closer agreement

Table 1

CORROSION OF MATERIALS IN GASEOUS FLUORINE AT ATMOSPHERIC PRESSURE

Material	Temp. (C)	Time (hr)	Area (sq in.)	Flow Rate (cc/min)	Wt. Change (g)	Film Thickness (mils)	Corrosion (Penetration)			
							(mils/hr)		(mils/yr)	
							Wt. Gain	Film Thickness	Wt. Gain	Film Thickness
1. Nickel	550	6.20	1.71	28	0.0005	a	0.0005	-	4.4	-
2. Nickel	650	5.28	1.71	d	0.0057	0.6	0.0067	0.036	59	314
3. Nickel	750	4.07	1.71	94	0.0265	1.2	0.040	0.093	353	816
4. Monel	650	6.00	1.61	43.5	0.0040	a	0.0046	-	41	-
5. Monel	750	6.12	1.49	77	-0.423 ^b	7.54	0.33	0.40	2900	3500
6. Inconel	550	5.00	1.54	78	0.1686	7.83	0.37	0.55	3200	4800
7. Inconel	650	5.60	1.48	78	0.3998	1.10	0.81	0.68	7100	6000
8a. Inconel	750	4.65	1.47	94	1.1184	5.09	2.74	3.82	24000	33500
8b. Inconel	750	4.65	1.47	94	-2.785 ^b	-	2.92	-	26000	-
9. Copper	550	2.42	0.52	129	0.0014	a	0.013	-	110	-
10. Copper	650	4.83	1.21	47	0.0252	1.0	0.049	0.062	430	540
11. Copper	750	5.75	1.10	110	0.0474	24	0.086	0.125	750	1100
12. Calcium Fluoride	750	4.72	0.95	99.5	0.0012	a	c	-	c	-
13. Alumina	550	5.23	0.87	110	0.0000	a	-	-	-	-
14. Alumina	750	4.50	0.79	77	0.0016	a	.012	-	110	-

^aToo thin to determine.

^bWeight loss, after film removal.

^cWeight gain probably due to reaction of fluorine with impurities.

^dNot determined.

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between the two results (weight gain and film thickness data) at the higher temperature indicates that, at least in the case of nickel, the density of the film approaches more nearly the theoretical one at the highest temperature.

Metallographic examination (See Appendix C) of the nickel specimens did not reveal any unusual features of the corrosion process. A photomicrograph of the sample exposed at 750 C (Table 1, item 3) shows a pronounced dark layer below the surface of the specimen. The lack of disturbance of the grain structure and the absence of penetration of this line by the corrosion film make a clear interpretation of the significance of the dark layer difficult. It is probable, however, that this layer has no great significance in terms of the corrosion by fluorine.

2. Monel

Monel coupons were treated with nitric acid containing a small amount of sodium chloride. The resulting surface was clean and had a dull finish. Monel exposed to fluorine at 650 C exhibited a corrosion film which was too thin to measure accurately. Monel exposed at 750 C yielded data which permitted calculation of corrosion rates from both weight changes and film thicknesses. The coupon exposed at 750 C was transferred to a screw cap bottle after cooling in a stream of helium; within five minutes after this transfer the corrosion film commenced to detach itself from the metal in a forcible manner. Eventually almost all of the film had separated from the metal and a weight loss measurement was obtained. Exposure of the corrosion film of copper and nickel fluoride to laboratory air may have resulted in reaction of the copper fluoride with subsequent changes in density or structure of the film. Such changes and the stresses set up by them could account for the separation phenomena (see discussions of copper below). The thicknesses of sample of the film were measured and an average value of 7.54 mils (11 measurements, 8.19 mils max., 6.27 mils min.) was obtained. The agreement between the rates obtained by these two measurements is considered very satisfactory. Most Monel contains small quantities of iron and manganese which have been ignored in the calculations outlined in Appendix A. Metallographic examination (see Appendix C) of Monel specimens did not reveal any unusual features of the corrosion process.

3. Inconel

Inconel coupons were treated with aqua regia to obtain a clean, dull finish. Exposure of samples at temperatures as low as 550 C produced measurable films, and a reddish material was observed in the fluorolube bubbler. Inconel exposed at 750 C corroded severely and the growth of the corrosion layer impeded removal of the coupon from the tube.

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The film formed on Inconel exposed at 550 C was examined by using X-ray fluorescence to detect depletion of chromium in the film. According to these results, a 91 per cent (± 4 per cent) depletion of chromium in the corrosion layer was observed. X rays penetrated approximately 3 mils into the fluoride film (99 per cent I_0 loss). An examination of the physical property data for the fluorides of chromium suggests that the chromium was lost from the film by volatilization.

Metallographic examination of the Inconel samples revealed no unusual features of the corrosion process. Neither void formation nor intergranular attack was observed.

4. Copper

Copper coupons were treated with clean, concentrated nitric acid for one second to obtain a bright, shiny surface. The sample exposed at 550 C showed a film too thin to measure accurately. Samples of copper exposed at 650 and 750 showed the typical dull, brick-red corrosion layer which appeared to be fairly adherent. Agreement between the corrosion rate obtained by use of weight change data and that obtained using film thickness data is surprisingly good considering the uncertainty of the nature of the corrosion product. The X-ray density of CuF_2 has been used to calculate the conversion factor shown in Appendix A. The exact nature of the corrosion layer has not been determined. Recent data appearing in the literature would indicate that CuF is probably not formed¹ and that the corrosion film reacts rapidly with air to form a basic fluoride.

5. Alumina and Calcium Fluoride

Samples of alumina (Morganite) and calcium fluoride (crucible grade, no binder) were dried at 110 C for 8 to 16 hours prior to exposure. The calcium fluoride sample showed no external effects after exposure to fluorine; the same was true of the alumina sample treated at 550 C. The alumina sample treated at 750 C turned slightly gray on exposure to fluorine. Both of these materials showed excellent resistance to attack by fluorine at elevated temperatures.

B. General Conclusions

On the basis of the results obtained in this work several conclusions may be drawn. At low temperatures (550 C) nickel and Monel appear to exhibit good corrosion resistance to fluorine. Copper, although not as good, has acceptable resistance for many applications. As the temperature is increased Monel becomes unsatisfactory. Nickel and copper showed the lowest rates among the metals tested. The sensitivity of the copper corrosion film toward air¹ represents an important factor which

¹Crabtree, J. M. et al, J. Inorg. and Nucl. Chem., 1, 213 (1955).

has not been explored here but cannot be neglected in certain applications. Both of the non-metallic materials exhibited corrosion rates lower than any of the metals tested at the same temperatures and thus may be preferred if the important differences in physical properties inherent in ceramic materials can be tolerated.

C. Literature Data on the Corrosion of Materials by Gaseous Fluorine

There exist contradictory data in the literature on the corrosion of materials in gaseous fluorine at elevated temperatures. In order to be able to evaluate more critically the effect of fluorine under various conditions, the data of several of the literature references have been tabulated. Since the conditions of the experiments are important in the evaluation of the data, a short summary of the pertinent details is included in the discussion of each reference. The literature data are shown in Tables 2 through 7.

Table 2

CORROSION OF NICKEL IN GASEOUS FLUORINE AT ONE ATMOSPHERE

Material	Reference	Temp. (C)	Corrosion Rate (Penetration)	
			mils/hr	mils/yr
1. Foil	2	60	0.0070 ^a	61.5
2. Nickel ^b	3	400	0.0096	8.4
3. Nickel ^b	3	450	0.0026	23.
4. Sheet	2	500	0.0082	72.
5. Nickel ^b	3	500	0.0070	61.
6. "A"	ANL Results	550	0.005 ^d	4.4
7. Nickel ^b	3	600	0.040	348.
8. Electrolytic	4 ^c	600	0.0000074	0.065
9. "A"	4	600	0.0000092	0.080
10. "A"	4	600	0.000030	0.26
11. Low Carbon	4	600	0.000030	0.26
12. "D"	4	600	0.00023	2.04
13. Duranickel	4	600	0.000094	0.831
14. Nickel ^b	3	650	0.022	192.
15. "A"	ANL Results	650	0.0067 ^d	59.
16. "A"	ANL Results	650	0.0359 ^e	314.
17. Nickel ^b	2	700	0.14	1200.
18. Nickel ^b	3	700	0.046	410.
19. "A"	ANL Results	750	0.040 ^d	353.
20. "A"	ANL Results	750	0.093 ^e	816.

^a0.03 atm fluorine pressure.

^bNature of coupon not specified.

^cCyclic exposure of coupons to fluorine and air.
See discussion of Reference 4.

^dFrom weight gain.

^eFrom film thickness.

Table 3
CORROSION OF MONEL IN GASEOUS
FLUORINE AT ONE ATMOSPHERE

Material	Reference	Temp. (C)	Corrosion Rate (Penetration)	
			mils/hr	mils/yr
1. Tubing	2	120	nil ^a	nil ^a
2. Monel ^b	3	400	0.0007	6
3. Monel ^b	3	450	0.0025	18
4. Sheet	2	500	0.0027	24
5. Monel ^b	3	500	0.0027	24
6. Monel ^b	3	600	0.082	720
7. "K"	4	600	0.000013	0.12
8. Monel ^b	4	600	0.000014	0.12
9. Monel	ANL Results	650	0.0046 ^c	41
10. Monel ^b	3	650	0.110	960
11. Sheet	2	700	0.027	240
12. Monel ^b	3	700	0.21	1800
13. Monel	ANL Results	750	0.33 ^c	2900
14. Monel	ANL Results	750	0.40 ^d	3500

^a5 psig F₂.

^cFrom weight gain.

^bNature of coupons not specified.

^dFrom film thickness.

Table 4
CORROSION OF INCONEL IN GASEOUS FLUORINE
AT ATMOSPHERIC PRESSURE

Material ^a	Reference	Temp. (C)	Corrosion Rate (Penetration)	
			mils/hr	mils/yr
1. Inconel	3	400	0.052	456
2. Inconel	3	450	0.13	1152
3. Inconel	3	500	0.085	744
4. Inconel	ANL Results	550	0.37 ^b	3200
5. Inconel	ANL Results	550	0.55 ^c	4800
6. Inconel	3	600	0.23	2000
7. Inconel	4	600	0.00068	5.9
8. Inconel	3	650	0.18	1560
9. Inconel	ANL Results	650	0.81 ^b	7100
10. Inconel	ANL Results	650	0.68 ^c	6000
11. Inconel	3	700	0.70	6120
12. Inconel	ANL Results	750	2.74 ^b	24000
13. Inconel	ANL Results	750	2.92 ^d	25600
14. Inconel	ANL Results	750	3.82 ^c	33500

^aNature of coupons not specified.

^cFrom film thickness.

^bFrom weight gain.

^dFrom weight loss.

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Table 5

CORROSION OF COPPER IN GASEOUS FLUORINE
AT ATMOSPHERIC PRESSURE

Material	Reference	Temp. (C)	Corrosion Rate (Penetration)	
			mils/hr	mils/yr
1. Copper ^a	3	400	0.22	1,920
2. Sheet	2	500	0.27	2,400
3. Copper ^a	3	500	0.16	1,440
4. Copper ^a	ANL Results	550	0.013	111
5. Copper ^a	3	600	1.35	11,900
6. Copper ^a	ANL Results	650	0.049 ^b	430
7. Copper ^a	ANL Results	650	0.062 ^c	540
8. Sheet	2	700	4.11	36,000
9. Copper ^a	3	700	3.97	34,800
10. Copper ^a	ANL Results	750	0.086 ^b	750
11. Copper ^a	ANL Results	750	0.125 ^c	1,100

^aNature of coupons not specified.^bFrom weight change.^cFrom film thickness.

Table 6

CORROSION OF MATERIALS IN GASEOUS FLUORINE

Material	Reference	Temp. (C)	Corrosion Rate (Penetration)	
			mils/yr	mils/yr
1. Aluminum Sheet	2	500	0.055	480
2. Aluminum Sheet	2	600	0.082	720
3. CaF ₂ (cemented with Na ₂ SiO ₃)	2	~200	nil	nil
4. Low silicon iron (0.004% Si)	2	200	0.00039 ^a	3.43 ^a

^a0.5 atmospheres fluorine.

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Table 7

CORROSION OF MATERIALS IN GASEOUS FLUORINE
AT ATMOSPHERIC PRESSURE^a

Material	Temp. (C)	Corrosion Rate (Penetration)	
		mils/hr	mils/yr
1. 2 S Aluminum	400	nil	-
2. 2 S Aluminum	450	nil	-
3. 2 S Aluminum	500	0.018	160
4. 2 S Aluminum	600	0.025	220
5. 347 Stainless	200	nil	-
6. 347 Stainless	250	0.198	1700
7. 347 Stainless	300	0.292	2560
8. 347 Stainless	350	0.710	6200
9. 347 Stainless	400	1.09	9500
10. Sheet Steel (0.007% Si)	400	0.016	144
11. Sheet Steel (0.007% Si)	450	0.41	3600
12. Sheet Steel (0.007% Si)	500	10.0	88000
13. Armco iron	200	nil	-
14. Armco iron	250	0.0027	24
15. Armco iron	300	0.012	110
16. Armco iron	350	0.011	100
17. Armco iron	400	0.033	290
18. Armco iron	450	0.041	360
19. Armco iron	500	15.9	139200

^aMyers, W. R. and W. B. DeLong, Chem. Eng. Prog.,
(May 1948).

1. Landau and Rosen² presented data for the rates of attack by fluorine. No indication was given as to the source of data or how it was obtained. These authors noted that the value for nickel foil (Table 2, item 1) was probably high and that the values for aluminum (Table 6, items 1 and 2) represented the maxima of several values.

2. Myers and DeLong³ used a flow system for studying the effect of fluorine. Fluorine was placed from a small electrolytic cell through both a sodium fluoride scrubber and a cold trap and then through a heated Monel tube containing the specimens. These authors removed the corrosion film by mechanical polishing or electrolytic methods and obtained data by both the weight gain and the weight loss methods. The average exposure time in this work was about four hours. The authors mention, however, that the fluorine used probably contained fairly large

²a. Landau, R. and R. Rosen, Ind. Eng. Chem., 39, 281 (1947).

b. Landau, R. Corrosion, 8, 283 (1952).

³Myers, W. R. and W. B. DeLong, Chem. Eng. Progress, (May 1948).

quantities of oxygen. The data obtained on copper (Table 4, items 1, 3, 5, and 9) indicated this most clearly, for the film observed was flaky and black. Consequently, much of these data, including those on steels, is subject to considerable question. In addition, no indication as to the pretreatment of the specimens is given.

3. Miles et al⁴ made little mention of the experimental details, the purity of the fluorine employed or the pretreatment of the samples. The data were reported in terms of weight gain (mg/sq cm) as a function of exposure time. Samples were exposed to fluorine for a given period of time, removed, weighed and then re-exposed for an additional period. The temperature was fixed at 600 C. The extremely low values obtained by these workers may be due to the cyclic exposure of the samples to fluorine and the laboratory atmosphere.⁵ The original weight gain data was converted to penetration per unit time for tabular presentation, using factors listed in Appendix A. The original data are shown in Appendix B. The values given in Tables 2-4 utilize the average weight gain/sq cm/hr obtained by simple averaging of the available data.

Myers and DeLong³ indicated that in their experience no decrease in corrosion rate was observed on longer exposure of the samples and that the films formed were not protective. Landau,^{2b} on the other hand, indicated that the protective film on nickel and aluminum accounted for the resistance of these metals to attack by fluorine, and this view was reinforced by the International Nickel Co.⁶ All authors agree that pure nickel exhibits the lowest corrosion rate in fluorine at comparable temperatures. In no reference may be found a discussion of intergranular corrosion or comments on the micro-structure of exposed specimens. Table 8 presents the available data in summary form, correlating the resistance of the materials as a function of temperature. It can be seen that extreme variations are present which probably indicate that resistance of the materials is a sensitive function of the conditions under which they were tested. Nickel appears to have the most consistent record of the best resistance to attack by fluorine on metal. The values for copper obtained elsewhere seem to indicate that this metal is not very suitable for use at temperatures above 500 or 600 C. The data obtained in this work differ from this, possibly

⁴a. Miles, F. T., et al., Progress Report of the Reactor Science and Engineering Dept., Jan. 1 - March 31, 1952; BNL-176, p. 17-18.

b. Ibid; April 1 - June 30, 1952; BNL-190, p. 17.

⁵The effect of cycling of fluorinated nickel has been described in the literature. A rather remarkable degree of protection was obtained for nickel tubes by allowing them to stand for some time at room temperature open to the atmosphere after an initial prefluorination. See R. N. Doescher, J. Chem. Phys. 20, 330 (1952).

⁶International Nickel Co. Private communication.

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Table 8

THE CORROSION OF MATERIALS IN FLUORINE
AT VARIOUS TEMPERATURES

(Summary of Data from all Investigators)

Temp. (C)	Material	Corrosion Rates Observed (mils/yr)
400	2 S Aluminum	nil
	Monel	6
	Nickel	8.4
	Sheet Steel (Low Si)	144.
	Armco Iron	290.
	Inconel	460.
	Copper	1900.
	347 Stainless Steel	9500.
500	Monel	24,
	Nickel	61, 72
	2 S Aluminum	160
	Aluminum	480
	Inconel	740
	Copper	1400, 2400
	Sheet Steel (Low Si)	88000,
	Armco Iron	139000
550	Alumina (Crucible Grade)	nil
	Nickel	4.4
	Copper	110
	Inconel	3200, 4800
600	2 S Aluminum	220, 720
	Nickel	350, 0.065, 0.080, 0.26, 0.26
		0.83, 2.01
	Monel	720, 0.12, .0125
	Inconel	2040, 5.9
	Copper	11900
650	Nickel	314, 192, 59
	Monel	41, 960
	Copper	430, 540
	Inconel	1560, 6000, 7100
700	Nickel	410, 1200
	Monel	240, 1800
	Inconel	6100
	Copper	36000, 35000
750	Calcium Fluoride (Crucible grade)	nil
	Alumina (Crucible grade)	110
	Nickel	353, 816
	Copper	750, 1100
	Monel	2900, 3500
	Inconel	24000, 25600, 33500

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due to the use of very pure fluorine. The use of Monel at temperatures up to 600 C seems to be warranted on the basis of the data indicated. Ceramic materials such as calcium fluoride and alumina are most resistant to fluorine. Unfortunately, their mechanical strength is severely limiting.

Finally, it must be remembered that the application of these data to systems involving a transport medium such as a solvent may be very misleading. All of the metals tested rely on the formation of protective films to effect the corrosion resistance. The rate of removal of this film in a solvent will be a determining factor in the rate of corrosion of these metals in a solvent medium.

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The authors are indebted to R. Schablaske who carried out the X-ray fluorescent examination of the Inconel and to W. Seefeldt who took the photomicrographs and who offered valuable advice.

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APPENDIX A

In the cases of metals whose composition represent alloys, it is necessary to convert certain data obtained in the laboratory to penetration per unit time, using a suitable factor. These factors are derived below.

I. From weight gain data:

(a) Nickel (assume 100% Ni)

$$\begin{aligned} \text{in. Ni/hr} &= (\text{g/sq in./hr}) \left[\frac{\text{MW}_{\text{Ni}}}{\text{MW}_{\text{F}_2}} \frac{0.06102}{\rho_{\text{Ni}}} \right] \\ &= (\text{g/sq in./hr}) (0.010589) \end{aligned}$$

(b) Monel (assume 70 w/o Ni, 30 w/o Cu)

$$\begin{aligned} \text{in. Monel/hr} &= (\text{g/sq in./hr}) \left[\frac{\text{MW}_{\text{Monel}}}{\text{MW}_{\text{F}_2}} \frac{0.06102}{\rho_{\text{Monel}}} \right] \\ &= (\text{g/sq in./hr}) (0.011183) \end{aligned}$$

"Molecular weight"
of Monel = 60.1

Density of Monel = 8.63 g/cc

(c) Copper (assume 100% Cu)

$$\begin{aligned} \text{in. Cu/hr} &= (\text{g/sq in./hr}) \left[\frac{\text{MW}_{\text{Cu}}}{\text{MW}_{\text{F}_2}} \frac{0.06102}{\rho_{\text{Cu}}} \right] \\ &= (\text{g/sq in./hr}) (0.011438) \end{aligned}$$

(d) Inconel (assume 77 w/o Ni, 15 w/o Cr, 7 w/o Fe)

$$\text{in. Inconel/hr} = (\text{g/sq in./hr}) (0.01676)$$

This factor was calculated on the assumption that all of the chromium has been volatilized (as CrF_4 , CrF_5 , or possible CrF_6). This assumption is valid for thin corrosion films, i.e., relatively low temperatures (see discussion on Inconel corrosion).

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Note: 1 mole Fe reacted = 783.51 g Inconel reacted
 = 335.24 g weight gain (NiF_2 , FeF_3)

"Molecular weight" of Inconel 56.90

Density of Inconel 8.51 g/cc

II. From film thickness data:

$$\begin{aligned} \text{(a) Nickel} \quad \text{in. Ni/hr} &= \text{thickness (in./hr)} \left[\frac{\text{MW}_{\text{Ni}}}{\text{MW}_{\text{NiF}_2}} \frac{\rho_{\text{NiF}_2}}{\rho_{\text{Ni}}} \right] \\ &= \text{thickness (in./hr)} (0.31577) \end{aligned}$$

This assumes the density of the nickel fluoride film to be the theoretical (X-ray) density of 4.63 g/cc.

$$\text{(b) Copper} \quad \text{in. Cu/hr} = \text{thickness (in./hr)} (0.29780)$$

This assumes the film to be unhydrated CuF_2 with a density equal to the X-ray value of 4.245.

$$\begin{aligned} \text{(c) Monel} \quad \text{in. Monel/hr} &= \text{thickness (in./hr)} \\ &\left[\frac{\text{MW}_{\text{Monel}}}{\text{MW}_{\text{Monel Fluoride}}} \frac{\rho_{\text{Monel Fluoride}}}{\rho_{\text{Monel}}} \right] \\ &= \text{thickness (in./hr)} (0.32054) \end{aligned}$$

This assumes a density of the film ("Monel fluoride") given by $(0.7)(4.63) + (0.3)(4.245) = 4.514$ g/cc and a "molecular weight" of "Monel fluoride" (NiF_2 , CuF_2) of 98.07. The density of Monel is 8.63 g/cc and its "molecular weight" (mol % Ni x at. wt. Ni + mol % Cu x at. wt. Cu) is 60.1.

$$\begin{aligned} \text{(d) Inconel} \\ \text{in. Inconel/hr} &= \text{thickness (in./hr)} \left[\frac{\text{MW}_{\text{Inconel}}}{\text{MW}_{\text{Inconel Fluoride}}} \times \right. \\ &\quad \left. \frac{\rho_{\text{Inconel Fluoride}}}{\rho_{\text{Inconel}}} (1.201) \right] \\ &= \text{thickness (in./hr)} (0.34847) \end{aligned}$$

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This assumes loss of all chromium by volatilization and a composition of the fluoride layer of 91.28 mol % NiF_2 and 8.72 mol % FeF_3 , having a composite density of 4.509 g/cc and a molecular weight of 98.10. Inconel has a density of 8.51 g/cc and a molecular weight of 53.72.

$$\begin{aligned} \text{Note: Moles Inconel/mole of fluoride} &= (\text{moles Inconel/mole Fe}) \times \text{mol \% Fe.} \\ &= (0.0872)(13.77) = 1.201 \end{aligned}$$

III. From weight loss data:

- (a) Nickel $\text{in/hr} = (\text{g/hr/sq in.}) (0.006856)$
- (b) Copper $\text{in/hr} = (\text{g/hr/sq in.}) (0.006841)$
- (c) Monel $\text{in/hr} = (\text{g/hr/sq in.}) (0.007071)$
- (d) Inconel $\text{in/hr} = (\text{g/hr/sq in.}) (0.007170)$

These factors represent $\frac{0.06102}{\rho}$ where 0.06102 converts cc to cu in.

It is clear from these discussions that the most reliable method of obtaining corrosion in terms of penetration is given by III. Weight loss data are obtained by assuming selective removal of only the corrosion film and complete retention of all unattacked metal. The difficulty in achieving this is clearly a function of the nature of the system and the means employed to remove the adhering corrosion film. Next in reliability is procedure I. Only the density and molecular weight of the metal need be considered. In the case of alloys containing a volatilized constituent, estimation of the degree of removal of this constituent introduces an uncertainty. Method II involves the estimation of the density of the corrosion layer, which may be in error by a large factor. Consequently, the latter method is the least reliable.

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APPENDIX B

Data from BNL-176(4) are reproduced below. These data have been converted to mg/sq cm/hr by suitable division of the published data by the numbers of hours listed at the head of the table.

Table 9

WEIGHT GAIN IN MG/SQ CM/HR OF SAMPLES
EXPOSED TO FLUORINE AT 600 C

Material	Hours							
	13	28	77	93	124	132	195	243
Electrolytic Nickel	Neg	-	0.00285	-	0.00516	-	0.00589	-
	Neg	-	0.00246	-	0.00524	-	0.00543	-
"A" Nickel	0.01	-	0.00545	-	0.00491	-	0.00517	-
	Neg	-	0.00324	-	0.00562	-	0.00471	-
	-	0.0386	-	0.0211	-	0.0180	-	-
	-	0.0218	-	0.0117	-	0.0104	-	0.00625
Low Carbon Nickel	-	0.0246	-	0.0171	-	0.0158	-	-
	-	0.0164	-	0.0175	-	0.0176	-	-
"D" Nickel	-	0.171	-	0.110	-	0.148	-	-
	-	0.192	-	0.016	-	0.127	-	-
Duranickel	-	0.109	-	0.0711	-	0.0276	-	0.0535
	-	0.0854	-	0.0441	-	0.0383	-	0.0311
Monel	0.0131	-	0.00766	-	0.00741	-	0.00717	-
	0.00784	-	0.00766	-	0.00774	-	0.00748	-
"K" Monel	-	0.105	-	0.0638	-	0.0549	-	0.0867
	-	0.0936	-	0.0586	-	0.0546	-	0.0938
Inconel	0.444	-	0.0902	-	-	-	-	-
	0.442	-	0.0652	-	-	-	-	-
Hastelloy "B"	0.633	-	0.196	-	-	-	-	-
	0.678	-	0.366	-	-	-	-	-

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Table 10

CORROSION OF METALS BY GASEOUS FLUORINE AT 600 C⁽⁴⁾

	Average Rate ^a mg/sq cm/hr	mg/sq in./hr ^b	Factor X ^c	in./hr x 10 ³	in./yr x 10 ³
Electrolytic Nickel	0.00451	0.000699	0.010589	7.4 x 10 ⁻⁶	6.49 x 10 ⁻²
	0.00559	0.000866	0.010589	9.17 x 10 ⁻⁶	8.04 x 10 ⁻²
"A" Nickel	0.0183	0.00284	0.010589	3.01 x 10 ⁻⁵	0.264
Low Carbon Nickel	0.0182	0.00282	0.010589	3.00 x 10 ⁻⁵	0.263
"D" Nickel	0.142	0.0220	0.010589	2.33 x 10 ⁻⁴	2.04
Duranickel	0.0575	0.00891	0.010589	9.43 x 10 ⁻⁵	0.827
Monel	0.00823	0.00128	0.01183	1.43 x 10 ⁻⁵	0.125
"K" Monel	0.0764	0.00118	0.01183	1.32 x 10 ⁻⁵	0.116
Inconel	0.260	0.0403	0.01676	6.76 x 10 ⁻⁴	5.93
Hastelloy "B"	0.468	0.0725	-	-	-

^aObtained by simple averaging of data shown in Table 9 for the appropriate metal.

^bThe factor here is 0.155 cm/sq in.

^cFor derivation of these factors see Appendix A. The same factor was used for all types of nickel even though slight difference in composition make these factors slightly erroneous. The same is true of the factor for Monel. It was not felt necessary to derive a factor for Hastelloy "B."

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APPENDIX C

Photomicrographs of selected specimens.

All photomicrographs were taken with the cooperation of W. Seefeldt. In no case was it felt necessary to obtain the best possible polish on the specimens since only qualitative observations were desired. All pictures represent a magnification of X100.

a. Nickel, Control. KCN-K₂S₂O₈ etch.

b. Nickel treated at 750 C with fluorine.
KCN-K₂S₂O₈ etch. Corrosion layer
not visible.

FIGURE 2. EFFECT OF FLUORINE ON NICKEL

a. Monel, Control. Carapella etch, 15 sec

b. Monel treated with fluorine at 650 C. Carapella etch, 15 sec

c. Monel treated with fluorine at 750 C. Carapella etch, 15 sec

FIGURE 3. EFFECT OF FLUORINE ON MONEL

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a. Inconel Control. Oxalic Acid electroetch

Corrosion film →

b. Inconel treated with fluorine at 550 C. Oxalic Acid electroetch

← Corrosion film

c. Inconel treated with fluorine at 650 C. Oxalic Acid electroetch

FIGURE 4. EFFECT OF FLUORINE ON INCONEL