MASTER

MONEL AND NICKEL CORROSION
IN NONAQUEOUS NO₂-HF SOLUTIONS

AKIICHI KIGOSHI AND GERALD STRICKLAND

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AKIICHI KIGOSHI* AND GERALD STRICKLAND

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ABSTRACT

The corrosion rates of Monel alloy 400 and Nickel 200 were studied in several NO_2 -HF solutions that seem promising for use in reprocessing nuclear reactor fuels. Special probes fabricated of Monel or nickel wire were immersed in solutions containing up to 30 mole % NO_2 and heated in the range 25° to 150°C . The progress of surface corrosion was followed by measuring the change in electrical resistance of the wire probes. In general, nickel was superior to Monel. Increasing concentrations of NO_2 were used, and the first detectable corrosion of Monel occurred in 20 mole % NO_2 - 80 mole % HF solution at 150°C . For nickel the conditions were 25 mole % NO_2 and 125°C . In solutions containing 25 and 30 mole % NO_2 , the high initial corrosion rate of Monel gradually decreased to a very low value because of formation of a protective film. This film was strong enough to endure large changes in concentration or temperature. Moisture had a severe effect on vapor phase corrosion of both Monel and nickel. Dissolved UO_2 or the presence of H_2O increased corrosion in the liquid phase. The effect of stress on surface corrosion was insignificant in the elastic range, but in the plastic range it greatly increased both the initial corrosion rate and total corrosion during film formation. Under the conditions of these studies both Monel and nickel were satisfactory materials of construction.

MONEL AND NICKEL CORROSION IN NONAQUEOUS NO₂-HF SOLUTIONS

INTRODUCTION

During the past several years the Nitrofluor process has been investigated as a means of recovering fissionable materials from nuclear reactor fuels. In this process complete dissolution of the fuel is achieved in a nonaqueous solution of HF containing either NO₂(N₂O₄), N₂O₃, or NOF as complexing agent. After isolation of the complex metallic compounds produced during dissolution, the fissionable-material compounds are selectively volatilized and further decontaminated.¹ The system NO₂-HF is more versatile than the others since it is also capable of disintegrating graphite-containing fuels. Monel and nickel have proved to be the only common metals worthy of consideration as container materials. Although they have been used extensively in laboratory-scale studies with NO₂-HF solutions, they have shown considerable variation in behavior. Monel has suffered stress corrosion cracking at tube fitting joints and, at times, gross corrosion in the region of condensing vapor. No cracking failures definitely attributable to stress have been found in nickel, and it has generally resisted attack better than Monel.

The present study was undertaken to determine some of the more fundamental aspects of Monel and nickel corrosion in NO₂-HF solutions in pure form and in the presence of air, water, and dissolved UO₂. The effect of stress on corrosion was also determined in the pure solution. A further investigation of corrosion in process solutions and during condensation will be conducted by others.

The electrical resistance method of measuring corrosion was chosen because it is highly sensitive and is suitable for obtaining continuous data. The method is based on the fact that the conductivity of the surface corrosion product is negligible compared with that of the metal; therefore the resistance of the probe increases as the cross sectional area of the metal is reduced by corrosion.

The principles of the method are completely described in the literature.^{2,3} Basically, an increase in probe resistance causes an imbalance of a servo-operated ratio bridge, and the degree of potentiometer shaft rotation required for rebalance is re-

lated to the amount of corrosion. This movement is used to drive an indicator and provide an electrical signal for a recorder. The change in probe resistance is actually a change in the resistance ratio of two specimens connected in series and used as arms of the bridge. One specimen (measuring element) is exposed to the environment, and the other (reference element) is protected by a nonconducting protective coating. Because temperature changes affect both elements, the ratio of their resistances is unchanged under equilibrium conditions and the measurements are independent of temperature. For the probes used in the present work, the effect of stress not due to corrosion was also eliminated because both elements are on a common axis and subject to the same stress.

EXPERIMENTAL PROCEDURE

The progress of corrosion was measured with the Corrosometer,* a commercial instrument that utilizes the increase in electrical resistance of a special probe to indicate the extent of corrosion. The Corrosometer was connected to a strip chart recorder to obtain a continuous record of the data.

The probes were constructed from annealed wire of either 0.030-in.-diam Monel alloy 400 or 0.033-in.-diam Nickel 200. The electrical lead wires were attached by resistance welding, and the entire assembly was coated with Teflon. Prior to use, a 2-in. length of the measuring element was stripped of its coating and then rubbed with fine emery paper, washed, and degreased. The lead wires were fitted in drilled holes of a Teflon ferrule, which served as a pressure seal. The completed probe (see Figure 1) was inserted through a tube fitting on the corrosion vessel head. When the fitting nut was tightened, the wires were effectively sealed and the system was leak-tight as measured by a halogen leak detector.

In the vapor phase experiments the corrosion vessel was connected to a similar Kel-F vessel which was automatically cycled from about 60°C to 26°C over a 10-min period. The temperature change

*Magna Corporation, 1001 South East St., Anaheim, Calif.

Figure 1. Probe for measuring corrosion. The 2-in.-long section of the measuring element stripped of its Teflon coating is near the lower end.

Figure 2. Experimental apparatus for stress corrosion experiments.

provided enough movement of the vapor to avoid segregation of its components. A protective film was formed on the metal surfaces of the system at the start of each experiment. The amount of vapor used in the 260-ml system was more than enough for determination of the probe corrosion rate. The chemical components were added to the corrosion vessel, which had been evacuated. When water (1 ml) was used, it was frozen prior to evacuation, and when air was used it was rapidly admitted after the vapor was frozen and until atmospheric pressure was reached.

For the tensile stress experiments the probe was contained within a tube-type holder which was coupled to the corrosion vessel by a swaged tube fitting. This assembly and the means of applying axial stress to the probe are shown in Figure 2. The holding device was provided with a pair of elongated windows to allow solution to circulate around the probe, and the lower end of the probe was secured at the base of the holder. The upper end of the probe was hooked to a section of heavier wire which passed through the lead-wire ferrule to the loading lever arm. A free-hanging weight was used to obtain the desired stress. The wire was free to move in the ferrule without leakage (halogen test); however, this seal introduced a frictional force of up to 4 lb. The corresponding reduction in stress actually applied to the probes was a maximum of 5500 psi. All values reported are uncorrected.

The corrosion vessel (9 in. long) was constructed of Monel or nickel and was designed to withstand

vapor pressures as high as 330 psig at 150°C. Solutions were prepared by condensing the required amounts of HF and NO₂ in the vessel. The HF was purified by sorption and desorption with use of NaF after preliminary treatment with CoF₃. The NO₂ was vaporized from a cylinder of liquid and was determined to be free of impurities by infrared spectroscopy. Heating of the vessel was performed in a Kel-F oil bath which also served to stabilize the temperature. The solution temperature was controlled to $\pm 0.1^\circ\text{C}$, and its rate of change was $< 0.03^\circ\text{C}/\text{min}$. When a probe was inserted, the solution was cooled to lower its vapor pressure, and the vessel was continuously purged with helium to prevent the entry of air through the tube fitting.

Monel and Nickel Corrosion Without Applied Stress

The corrosion of Monel vs time was measured in HF solutions containing 0.2, 1.0, 2.0, 4.0, 6.0, 10, 15, 20, 25, and 30 mole % NO₂ at 25°C intervals in the range 25° to 150°C. The data are plotted in Figure 3. The sloping lines at the top and right side of this and the following corrosion graphs represent rates in mils per year (MPY). The first detectable corrosion occurred in 20 mole % NO₂ at 150°C; none ($< 10^{-4}$ mil) was found in lower concentrations at any temperature during exposures of > 18 hr. The corrosion in 20 mole % NO₂ seemed to be linear with time. In the 25 mole % solution, corrosion occurred only at 125° and 150°C and stopped after ≈ 30 hr. The protective films formed were grayish green. In the 30 mole % NO₂ solution, increasing temperatures showed an interesting and helpful effect on the reaction rate in that they accelerated the rate of formation of a protective film. At 100°, 125°, and 150°C the high initial rates decreased to very low values as the films increased in effective thickness. The surface product formed on Monel at 75°C was only partially protective and was soft, black, and porous. The films formed at 100° and 125°C were hard and black, and that at 150°C was hard and dark gray.

The temperature stability of the films was checked by cooling the solutions to 0° and -196°C and reheating them to their original temperatures over a 15-min period. Breakdown and re-formation of the films was apparent in the 25 mole % solution, the extent of breakdown being considerably less at 150°C than at 125°C. The films formed in 30

mole % NO₂ were much more resistant to thermal cycling. The film formed at 100°C was the most stable, and those formed at 100° and 125°C were superior to that formed at 150°C. The black surface film formed on Monel in 30 mole % solution at 125°C remained protective in solutions containing 10, 15, 20, and 25 mole % NO₂.

The data for 30 mole % solution at 100° and 125°C are in good agreement with a mechanism allowing growth of a superficial protective film from the grain boundary and maintenance of a constant thickness. The rate of corrosion can be represented by

$$dS/dt = C(1 - c_2t), \quad (1)$$

where S is the amount of corrosion for the time of growth t , and C and c_2 are constants pertaining to the type of metal and the fluid temperature. Integration of Eq. (1) gives

$$S = -(C/2c_2)(1 - c_2t)^2 + c_1, \quad (2)$$

where c_1 is the constant of integration. Since $S = 0$ when $t = 0$, $c_1 = C/2c_2$. Therefore the following equation is obtained.

$$S = c_1[1 - (1 - c_2t)^2] \quad \text{for } c_2t \leq 1. \quad (3)$$

A comparison of the results obtained with Monel at 100°C in 30 mole % NO₂ solution with S calculated by means of Eq. (3) is given in Table 1.

Figure 3. Monel corrosion in NO₂-HF solutions. ↑, Cooled to 0°C and reheated to original temperature. ↑, Cooled to liquid nitrogen temperature and reheated to original temperature. Numbers indicate mils per year.

Table 1

Comparison of the Calculated and Observed Corrosion of Monel in 30 Mole % NO_2 - 70 Mole % HF at 100°C

$$S = 0.03854[1 - (1 - 0.01803t)^2]$$

Time, hr	Total corrosion, mil	
	Calculated	Observed
0	0.0000	0.0000
5	0.0072	0.0069
10	0.0126	0.0129
15	0.0180	0.0190
20	0.0229	0.0236
25	0.0270	0.0278
30	0.0305	0.0319
35	0.0333	0.0347
40	0.0356	0.0362
45	0.0372	0.0375
50	0.0382	0.0380
55	0.0385	0.0383

The experimental results are in good agreement with those calculated. The initial effective rate of film growth vs temperature is shown in Figure 4, the relationship being

$$\log C = 3.11 - (2.18 \times 10^3/T), \quad (4)$$

where C is the rate constant from Eq. (1) and T is the temperature in degrees Kelvin. The energy of activation was calculated to be 9970 cal/mole.

When the surface film did not become completely protective, as in 30 mole % NO_2 solution at 75°C, corrosion during the first 35 hr proceeded in accordance with Eq. (1) and after 40 hr the rate became inversely proportional to the surface film thickness. The following equations apply for this case. For 0 to 35 hr,

$$S = 0.03634[1 - (1 - 0.00857t)^2]. \quad (5)$$

After 40 hr,

$$S = 0.00615 \sqrt{t} = 0.0182. \quad (6)$$

A nickel probe exposed to 10, 15, and 20 mole % NO_2 solutions was not significantly corroded ($< 10^{-3}$ mil) in experiments of 20- to 70-hr duration at 100°, 125°, and 150°C. In 25 mole % solution, corrosion was detected only at 125°C. As shown in Figure 5, the rate was initially relatively high, but decreased to a very low value after about 10 hr. Corrosion may occur at this temperature if the rate of protective film formation is lower than

Figure 4. Temperature dependence of the initial effective rate of film growth on Monel in 30 mole % NO_2 - 70 mole % HF solution.

Figure 5. Nickel corrosion in NO_2 -HF solutions. Numbers indicate mils per year.

that of metal dissolution, or if the film is simply less protective. Although both rates may increase as the temperature is raised, it is possible that the metal dissolution rate is low at 100°C and the rate of protective film formation is very high at 150°C. These differences might also be the cause of higher Monel corrosion in 30 mole % NO_2 at 125°C.

The behavior of nickel in 30 mole % NO_2 at 125° and 150°C was remarkably different from that of Monel, which had a higher initial corrosion rate and corroded more before the surface film became protective. The rate for nickel was also highest initially, but it decreased during a lengthy induction period before attaining a linear rate of about 3 MPY. This seems to be a case of protective film formation followed by film breakdown. The effect of briefly cooling the corrosion vessel from

150° to 0°C and reheating it to 150°C was unexpected. No further corrosion was detected in the 30 mole % solution during the next 45 hr, and repeating the cycle resulted in no further corrosion after an additional 65 hr. Almost the same behavior was found in the experiment at 125°C. Evidently the surface film became completely protective during the cooling and heating cycle.

Vapor Phase Corrosion of Monel and Nickel

Monel equipment has at times shown serious corrosion in areas subject to condensing vapor from NO_2 -HF solutions; the attack on nickel has not been as great. Heating of the equipment to prevent inadvertent condensation has prevented corrosion; however, the problem of controlling corrosion in a condenser remains. Such corrosion may be due to the fact that the rate of protective film formation is lower than the rate of attack at the particular local temperature. It may also be caused by the formation of HNO_3 upon heating the solution above 75°C. Anhydrous mixtures of HF and HNO_3 have proved to be very corrosive to Monel. Alternatively, this corrosion may have been caused by air entering the equipment.

The following experiments were performed with vapor isolated from its liquid phase, a condition that might occur in process lines. The corrosive effect of vapor alone and in combination with water and air was determined at 26° and 100°C by using

vapor that had been in equilibrium with 30 mole % NO_2 - 70 mole % HF solution at 26° (139 ml) and 100°C (1640 ml). These conditions approximate those in a line containing a leak to the atmosphere. The condensation was undoubtedly low and intermittent under such conditions. The corrosion in a condenser might be considerably different, since vapor of changing composition is continuously being condensed.

As shown in Figures 6 and 7, corrosion in the vapor alone was very low for both metals at room temperature, and the addition of dry air caused only a slight change in corrosion. Vapor mixed with moist air caused a further increase in Monel corrosion and probably would have had a similar effect on nickel; the corrosion rates decreased to essentially zero in a few hours. Much more corrosion occurred in the presence of water, especially without air. Here the initial corrosion rate of Monel was 300 MPY in the presence of vapor and water, and the presence of air substantially reduced both the rate and amount of attack. In the absence of air a protective film formed after 5 hr, the total corrosion being 0.059 mil. Nickel withstood the attack of vapor and water somewhat better than Monel; its initial rate was about 100 MPY and it showed evidence of a semiprotective film. Its behavior with air also present was similar to that of Monel, although the initial rate was slightly lower.

Figure 6. Monel corrosion in vapor from 30 mole % NO_2 - 70 mole % HF solution at room temperature. Numbers indicate mils per year.

Figure 7. Nickel corrosion in vapor from 30 mole % NO_2 - 70 mole % HF solution at room temperature. Numbers indicate mils per year.

The corrosion of Monel and nickel in vapor taken from 30 mole % NO_2 solution at 100°C and mixed with dry air at room temperature was similar to that reported above. Any HNO_3 that might have formed upon heating to 100°C had little apparent effect.

Monel and nickel probes were also exposed at 100°C by using vapor taken from 30 mole % NO_2 solution at room temperature, but no corrosion was detected. Corrosion rates at 100°C were also determined for the vapor- H_2O mixture, which was very corrosive at room temperature. The rates for nickel at intervals of 3, 5, and 12 hr were 8.3, 5.3, and 0.0 MPY, respectively, and the total corrosion was only 0.006 mil. No Monel corrosion was detected. Some of these experiments were repeated with a tube of the 30 mole % NO_2 solution connected to the reaction vessel, and almost the same results were obtained.

These experiments have shown that room-temperature condensation of vapor caused negligible corrosion of Monel or nickel, even in the presence of dry air. Thus a leak-tight line under these conditions would not present a corrosion problem. With the addition of a small amount of water in the air, a condition that exists at the start of a leak, corrosion substantially increased, probably be-

cause of HNO_3 formation. The more serious corrosion found in the case of vapor and water approximates that found after a leak has existed for some time, since the solution is hygroscopic. The superiority of nickel in this case has also been verified in practice. The absence of probe corrosion in noncondensing vapor at 100°C also indicates that line corrosion can be avoided by preventing condensation.

It was expected that corrosion would be enhanced in the presence of water and O_2 from air, since such is the case in aqueous HF .⁴ The fact that it was not might be attributed either to air preventing the diffusion of vapor to the metal surface or to the formation of a more protective film in the presence of air. The absence of significant corrosion at 100°C in the case of vapor and water is most likely due to the absence of condensation.

Monel and Nickel Corrosion Due to UO_2 Fuel Dissolution

The mechanism by which UO_2 dissolves in NO_2 - HF solutions is not known, but if the oxide-acid reaction occurs, the water formed could increase corrosion. The behavior of Monel and nickel probes was determined in 25 mole % NO_2 - 75 mole % HF (96 ml) containing dissolved UO_2 (5 and 10 g) at 25°C intervals over the range 50° to 150°C . The UO_2 was dissolved at 100°C and the solution was cooled to room temperature before the probe was inserted.

In the case of nickel, corrosion was detected only at 125°C with 5 g dissolved UO_2 . The average cor-

Figure 8. Monel corrosion due to UO_2 dissolution in 96 ml of 25 mole % NO_2 - 75 mole % HF solution. Numbers indicate mils per year.

Figure 9. Monel corrosion due to addition of H_2O to 25 mole % NO_2 - 75 mole % HF solution. Numbers indicate mils per year.

rosion rate of 5.6 MPY for the first 8 hr was somewhat higher than that in the solvent alone (3 MPY). The total corrosion was also higher, but the film that formed protected the surface for the remaining 32 hr of exposure. Although the corrosion prior to film formation was still very low, it could become significant if the film were subsequently destroyed.

The behavior of Monel in the two solutions containing dissolved UO_2 was more nearly like that in the 30 mole % solution. No corrosion was detectable at 50°C, and, as shown in Figure 8, corrosion with 5 g dissolved UO_2 proceeded linearly at 75°C. The amount of corrosion prior to formation of a protective film decreased progressively at the higher temperatures. Although the total corrosion was higher than in the absence of UO_2 , the amount was lower for 10 g than it was for 5. Another major difference was that the protective films formed much sooner than they did in pure 25 mole % solution. The hard, black surface film was similar to that formed in 30 mole % solution and was evidently promoted by the products of the dissolution reaction. Both surface products formed at 75°C were black and soft. For 10 g dissolved UO_2 there was no detectable corrosion at 125° and 150°C.

Monel and Nickel Corrosion Due to Water Addition

Since the dissolution of UO_2 could result in water formation, Monel and nickel corrosion were

determined in a 25 mole % NO_2 - 75 mole % HF solution to which the water (0.66 g, equivalent in oxygen content to 5 g UO_2) was added. A nickel wire probe was exposed to this solution at 75°C for 65 hr, but no corrosion was detectable. The behavior of Monel, as shown in Figure 9, was similar to that found in the solution containing 5 g dissolved UO_2 , especially at 75°C. At 100°, 125°, and 150°C the initial corrosion rates were slightly lower in the case of substituted water, but the total corrosion was greater at 125° and 150°C. These differences show that reaction products other than water probably affect corrosion.

Monel and Nickel Corrosion Due to Stress

Wire probes made of Monel and nickel were subjected to several tensile stresses in 25 mole % NO_2 - 75 mole % HF solution to determine what change in corrosion would occur. The intent in the case of Monel was to determine what value of stress would cause stress corrosion cracking, which has been encountered in Monel tubing (Monel alloy 400) and Monel tube fittings (Monel alloy R-405, the free-machining type). The apparatus shown in Figure 2 was used for this work. The average yield points (0.2% offset) of the Monel and nickel probe wires were 37,800 and 31,500 psi, respectively.

The results obtained from Monel at 35,500 psi (uncorrected for seal friction) and 100°, 125°, and

Table 2

Corrosion of Monel in 25 Mole % NO_2 - 75 Mole % HF Under a Tensile Stress of 35,500 psi*

T , °C	Time, hr	Total corrosion, mil	Average rate,** mils/year	Conditions
100	0-116	<0.0001	—	
125	0- 40	0.0036	0.79	
125	40- 45	0.0036	—	Continued exposure
125	45- 50	0.0044	1.3	After cooling to 0°C
125	50- 64	0.0060	0.98	After cooling to 0°C
125	64- 92	0.0082	0.19	Continued exposure
125	92-110	0.0082	—	Continued exposure
125	110-128	0.0085	0.15	After cooling to 0°C
125	128-135	0.0085	—	Continued exposure
150	0- 25	0.0031	1.1	
150	25- 46	0.0033	0.13	Continued exposure
150	46- 53	0.0048	1.9	After cooling to 0°C
150	53- 68	0.0065	0.9	Continued exposure

*Actual stress is reduced by a maximum of 5500 psi because of friction in the seal.

**Average rate for the time interval.

150° C are shown in Table 2. They are similar to those shown in Figure 3 for unstressed Monel in that the total corrosion was low and brief cooling to 0° C and reheating to the original temperature caused breakdown and re-formation of the protective film. The additional corrosion that occurred increased the degree of protection afforded by the surface film.

Monel corrosion in the plastic range at uncorrected stresses of 42,800 and 50,000 psi is shown in Figure 10. At these stress levels the behavior of Monel was remarkably different. There was corrosion at 75° C, and at the three higher temperatures the protective film formed much more rapidly, the initial rate at 150° C being 500 MPY. The

Figure 10. Monel corrosion due to stress in 25 mole % NO_2 - 75 mole % HF solution. —, 50,000 psi; ---, 42,800 psi; O, cooled to 0° C and reheated to original temperature; X, removed load and reloaded. Numbers indicate mils per year.

Figure 11. Nickel corrosion due to stress in 25 mole % NO_2 - 75 mole % HF solution. —, 42,400 psi; ---, 36,400 psi; O, cooled to 0° C and reheated to original temperature; X, removed load and reloaded. Numbers indicate mils per year.

total corrosion was greater by about an order of magnitude than that found at a stress of 35,500 psi, and it became higher as the temperature increased. Except at 125° C, the higher stress caused the greater amount of corrosion. Cooling and reheating of the solution caused breakdown and re-formation of the surface film at 100° C and 50,000 psi, and removal of the stress for 2 to 5 min produced no change in corrosion.

Nickel probes were tested at uncorrected stresses of 24,300, 30,400, 36,400, and 42,400 psi. Here too, stressing in the elastic range caused no significant increase in corrosion, but the protective film formed in 1 hr rather than 10. The effect of stressing above the yield point is shown in Figure 11. At both stresses there was corrosion at 75°, 100°, and 150° C, whereas none was detected in the absence of stress. As in the case of Monel, the total corrosion of nickel was greatly increased in the plastic range and the rates prior to formation of a protective film were substantially higher, the highest being about 200 MPY at 150° C. Neither temporary cooling nor removal of the load caused film breakdown whenever such changes were made.

The remarkable increase in the initial corrosion rates of Monel and nickel stressed above their yield points in 25 mole % NO_2 - 75 mole % HF solution is attributed to the formation of sites of chemical activity during plastic deformation. The data indicate that these sites increase in number and depth with an increase in stress in the plastic range. No evidence of stress corrosion cracking of the Monel or nickel probes was found, even though the metals were stressed to 71 and 73%, respectively, of their tensile strengths.

CONCLUSIONS

The use of electrical resistance probes proved very satisfactory in studying the behavior of Monel and nickel as materials of construction for the Nitrofluor process. The conditions under which these metals form protective films in various NO_2 -HF solutions and their rates of formation have been determined.

In HF solutions containing ≤ 30 mole % NO_2 , unstressed Monel and nickel were significantly attacked only at concentrations of 25 and 30 mole % NO_2 , the rate and amount of attack being greater at 30 mole %. Brief cooling of these solutions to 0° C resulted in breakdown of the protective film on Monel under certain conditions, but it always

re-formed on reheating to the initial temperature. For nickel this thermal cycle caused the formation of a protective film that subsequently remained stable.

Experiments simulating the leakage of room air into a line containing vapor at room temperature showed that both the rate and amount of attack greatly increased in the presence of water; however, this attack was very nearly eliminated when the system temperature was maintained at 100°C.

In the presence of dissolved UO_2 in 25 mole % NO_2 solution, the total corrosion of Monel decreased with increasing temperature and amount of dissolved UO_2 . The substitution of water, which might be produced during dissolution of the UO_2 , produced a similar temperature effect on Monel. Nickel was measurably attacked only at 125°C with the smaller amount of UO_2 used.

The experiments conducted with Monel and nickel under stress did not result in failures such as the stress corrosion cracking experienced with Monel tubing and fittings. The behavior of Monel did not significantly change below its yield point, but the stressing of nickel below its yield point greatly reduced the time necessary for protective film formation.

At stresses in the plastic range, protective films formed on both metals in 25 mole % solution at

75°, 100°, 125°, and 150°C. The total corrosion increased greatly; protective films formed much sooner and were more thermally stable.

This research has shown that both Monel and nickel are satisfactory for the conditions tested. However, nickel was superior in general because of its lower corrosion rate and lower total corrosion prior to protective film formation. Although this work has provided much basic information pertinent to the corrosion of Monel and nickel in NO_2 -HF solutions, further investigation is necessary to determine the conditions under which more severe corrosion of process equipment occurs.

REFERENCES

1. G. STRICKLAND, F.L. HORN, AND R. JOHNSON, The Nitrofluor process for reactor fuel, *Chem. Eng. Progr. Symp. Ser.* 60, No. 47, 62-8 (1964).
2. G.H. ROHRBACK, Determination of corrosion rates in a variety of different processes by means of the Corrosometer, Paper presented at 6th Western Regional Div. Conf. Natl. Assoc. Corrosion Engrs., Long Beach, Calif., Nov. 1956 (reprint available from Magna Corporation, Anaheim, Calif.).
3. E.C. WINEGARTNER, Recording electrical resistance corrosion meters, *Corrosion* 16, No. 6, 265-70t (1960).
4. W. J. BRAUN, F.W. FINK, AND G. LEE ERICSON, *The Corrosion of Monel and Cupronickel in Hydrofluoric Acid*, Battelle Memorial Inst. Rept. BMI-1237, Dec. 3, 1957.