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CORROSIVE EFFECTS OF METHYL PHOSPHONIC ACID (MPA) AND HF SOLUTIONS ON THIN-SHEET 1010 STEEL, 321 STAINLESS STEEL AND 200 NICKEL

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Thin-sheet 1010 steel, 321 stainless steel, and 200 nickel, (6 to 10 mils), which have been considered as candidate diaphram materials for a binary chemical shell, were assessed for corrosion damage in a methylphosphonic acid solution, and in hydrofluoric acid solutions, at room temperature.

After 96 days in the methylphosphonic acid solution (15 percent MPA - 1/1.8 ethanol/water) penetration of the different metals was: (Cont'd)

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steel, 12 percent; stainless steel, none; nickel, 32 percent. After the same period in 1 percent HF solution, penetration was: steel, 14 percent, with pitting; stainless steel, 16.8 percent, no pitting; nickel, 22 percent, with appreciable pitting. Stainless steel specimens in different concentrations of HF solution (1 to 48 percent) exhibited straight-line, progressive penetration with increasing HF concentration.

The 321 stainless steel is indicated suitable for the intended use; whereas the 1010 steel and 200 nickel are contraindicated. Attention is directed to the importance of exposed, metal-surface area vs volume of solution, or vs concentration of the electrolyte; and to air-oxidative conditions which can influence corrosion. Further, it is mentioned that circumferential welding of the diaphram may lead to susceptibility to its corrosion at or in the heat affected area.

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INTRODUCTION

Assessment of the corrosive effects of methylphosphonic (MPA) and hydrofluoric acid (HF) solutions on thin-sheet 1010 steel, 321 stainless steel and 200 nickel were made. The intent was to establish the adviseability of the use of the alloys as diaphram materials for an internal container of the binary shell being developed at Edgewood Arsenal. Specifically, the diaphram is being considered for use in the difluoro-constituent container of the shell system.

In the design of the binary chemical shell, two containers are involved, each holding one reactant of the ultimate chemical constituent. One end of the container for the difluoro ingredient, requires a thin metal diaphram closure which will resist the effects of the difluoro compound or its hydrolysis products, such as, hydrofluoric acid and methylphosphonic acid. Resistance of the diaphram to corrosion and penetration is required for an extended period, i.e., for at least ten years, since the shells may be stored for such length of time.

Previous discussions with Edgewood personnel revealed that specific candidate thin-sheet metals were being considered. These preselected materials were required to be evaluated, so as to provide a basis for the adviseability of their use for the intended purpose.

MATERIALS

The thin-metal sheets supplied for assessment were: 1010 steel, 321 stainless steel, and 200 nickel. Specimen particulars are given in Table I.

ENVIRONMENTS

Solutions in which the specimens were immersed were:

MPA - Methylphosphonic acid, 15 percent in ethyl alcohol/water (1/1.18)

HF - One (1) percent F^- in water

HF(v) - Various concentrations of HF, namely, 1, 2, 4, 6, 12.5, 25, 35, 48 percent in water

TABLE I.

Specimen and Environment Particulars

Metal	MPA Solution / HF ($1ZF^-$) Solution		HF(v) Solutions
	Flat	U-Bend	Curved Slightly
1010 Steel	1 x 2 x 0.010 in. (c.2.5 x 5 x 0.025 cm)	from: 1 x 4 x 0.010 in. (c.2.5 x 10 x 0.025 cm)	----------
321 Stainless Steel	1 x 2 x 0.006 in. (c.2.5 x 5.0 x 0.025 cm)	from: 1 x 4 x 0.006 in. (c.2.5 x 10 x 0.015 cm)	1 x ½ x 0.006 in. (c.2.5 x 1.25 x 0.015 cm)
200 Nickel	1 x 2 x 0.010 in. (c.2.5 x 5.0 x 0.025 cm)	from: 1 x 4 x 0.010 in. (c.2.5 x 5.0 x 0.025 cm)	----------

The MPA and 1 percent HF solutions were chosen to separate and accentuate the individual chemical actions that might ensue in the event the difluoro compound undergoes hydrolysis. The selection of the HF sclution (1 percent F^-) is based on previously reported analysis of GB agent representing samplings of GB agent from numerous ammunition items taken from storage.[1,2] A typical analysis is presented in Table II.

TABLE II.

Typical Analysis of Stabilized GB Agent

NOTE: Sampled from containers stored at 70°C, ca. 3 years in steel.[1,2]

Acidity; mg H^+/100g GB	70.
Ionic fluorine, %	1.2
Purity, %	83.0

METHOD

Quadruplicate flat specimens and duplicate U-bend specimens, degreased in naphtha then rinsed with acetone, were immersed in 300 ml. of each solution. The ratio of metal surface area to volume of solution was 206 cm^2/300 ml., 1/1.46, (cf. ratio 1/1.11 = 0.9 for M-121 projectile). High-density polyethylene containers with press-fit covers of the same material were used to hold the specimens and test

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[1] L. C. Buckles, W. C. Crawford, Jr. and A. S. Hutchcraft, Jr., Report CRLR 578, Chemical and Radiological Laboratories, Army Chemical Center, Maryland, 28 May 1956, p. 13.

[2] Communications, re: Rocket M55 with Mr. S. R. Eckhaus, Weapons Development Engineering Laboratory, Edgewood, Maryland, May 1966.

liquid. No effort was made to exclude air above the solution.

Precracked thin-sheet specimens, held in special stressing fixtures, also were immersed in the MPA and HF (1 percent) solutions, so that the apex of the fatigue crack was about 6 mm. (¼ in.) below the liquid surface. The specimens and special fixtures were designed, fatigue cracked, and assembled by personnel performing the fracture mechanics studies. Examinations of the specimens after exposure in the test solutions also were performed by the same persons. Results for the precracked specimens are not presented in this report.

Flat specimens were weighed prior to immersing them, and after each exposure interval were cleaned by light brushing in water and rinsed with dry acetone.

U-bend specimens were not weighed initially, nor on removal from the solutions. These were cleaned and examined for pitting or cracking, particularly in the region of the bend.

For the purpose of observing the action of HF solutions of different concentrations on the dissolution of the stainless steel thin-sheet, one specimen was immersed in each of the HF(v) solutions. In this case, the volume of solution used was 50 ml., and the surface/solution volume ratio was 1/15.7. The specimens were bent into shallow curves so that they could be set on a long edge on the bottom of the container, for maximum surface exposure. Each specimen was weighed prior to placing it in the test solution, and again on removal after washing with water and drying with acetone.

RESULTS

Percentage weight loss and resultant thickness for the 1 x 2 in. (ca. 2.5 x 5.0 cm.) flat specimens are given in Table III. Figures 1, 2, and 3 are plots of these.

Visual observations of the U-bend specimens are presented in Table IV. Figure 4 is a photograph of the specimens after the exposures.

Results of exposures of the stainless steel specimens to HF(v) solutions are presented in Figure 5.

TABLE III.

Percent Weight Loss, Percent Reduction Thickness, and Surface Condition-
Flat Specimens after Exposure in MPA and HF Solutions

		MPA Solution			HF Solution		
Metal	Days Exposed	Percent Wt. Loss	Percent Reduction Thickness[a]	Surface Condition	Percent Wt. Loss	Percent Reduction Thickness[a]	Surface Condition
1010 Steel (10 mil)	10	11.1	8	Dark; rust spots	22.5	10	Dark, rust film, pits, some loss of metal.
	24	13.2	8	Dark; rust film	36.5	10	Pits & perforations[b]
	60	18.0	11	Same	30.0	11	Same[b]
	96	19.4	12	Same	36.0	14	Same[b]
321 Stainless Steel (6 mil)	10	0	0	Bright, no pits	8.1	8.4	Slightly dull, no pits.
	24	0	0	Same	17.0	8.4	Same
	60	0	0	Same	19.9	16.8	Same
	96	0	0	Same	20.0	16.8	Same
200 Nickel (10 mil)	10	1.6	0	Slightly dull, no pits	6.4	15	Slightly dull, small pits
	24	3.3	2	Same	15.0	20	Pits & perforations 1/3 Area[b]
	60	13.4	12	Same	23.0	22	Same-2/3 Area[b]
	96	32.9	32	Grey, no pits.	31.4	22	Same-3/4 Area[b]

[a] For two surfaces exposed; one-half of reduction shown applicable for one surface with same total area exposed.

[b] Perforations first occurred at edges and on surfaces closer to the liquid-air interface.

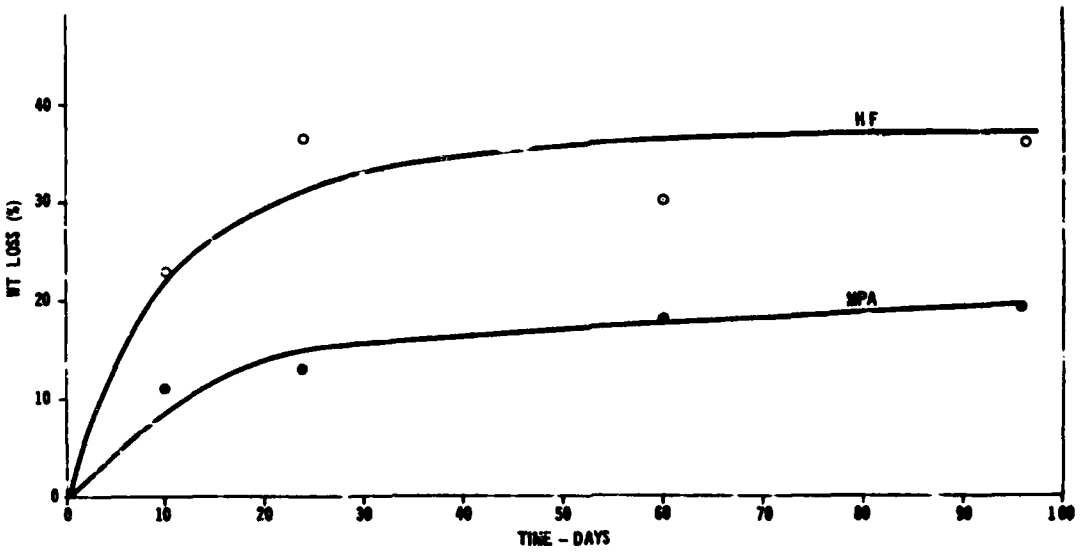

Figure 1. Percent Weight Loss - 1010 Steel Specimens (2.5 x 5.0 cm - Two Surfaces) in MPA and in HF (1% F^-) Solutions

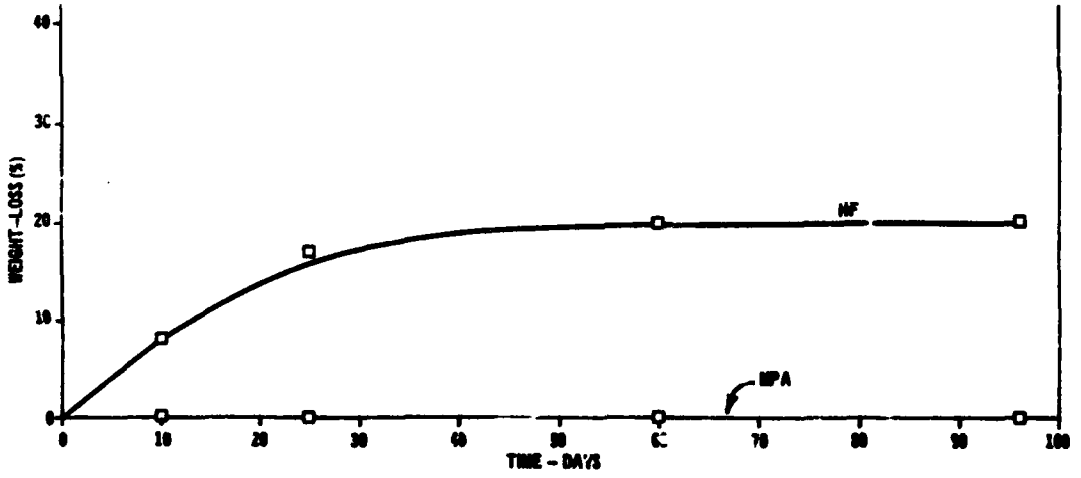

Figure 2. Percent Weight Loss - 321 Stainless Steel Specimens (2.5 x 5.0 cm - Two Surfaces) in MPA and HF (1% F^-) Solutions

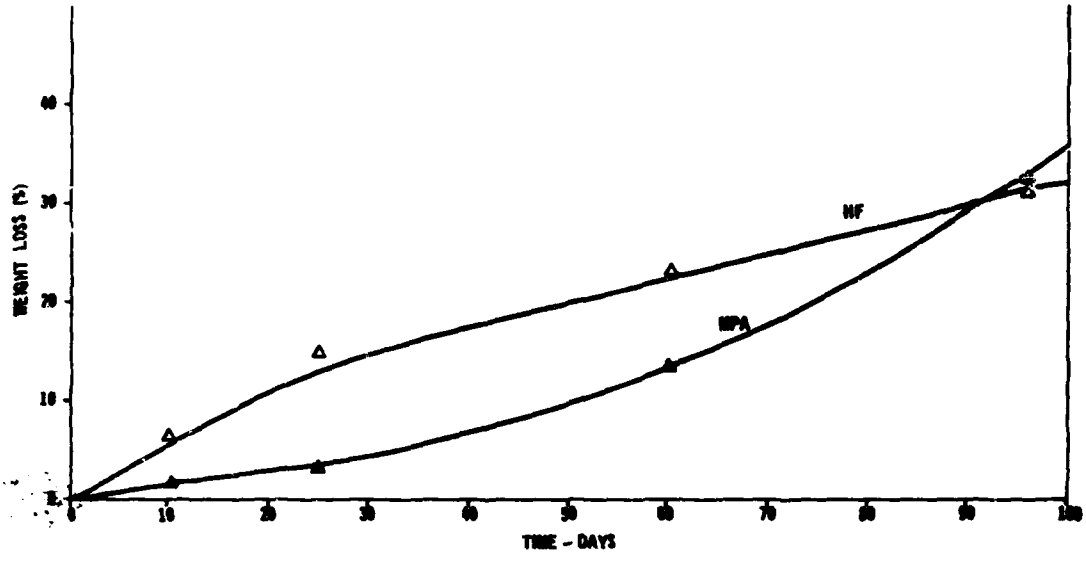

Figure 3. Percent Weight Loss - 200 Nickel Specimens (2.5 x 5.0 cm - Two Surfaces) in MPA and in HF (1% F^-) Solutions

TABLE IV.

Condition of U-Bend Specimens After 96 Days in MPA and HF (1% F^-) Solutions

Material	MPA Solution	HF Solution
1010 Steel	Dark, oxide film. Small pits and perforations along edges and in bent portion, few sparsely distributed in surfaces. Not strictly related to nearness to liquid-air interface. No cracking.	Dark, oxide film. Small pits and perforations. Sparsely distributed along edges and in bent position. Condition less pronounced than that of MPA. No cracking.
321 Stainless Steel	Bright. No pitting. No perforations. No cracking.	Some loss of brightness. No pitting. No perforations. No cracking.
200 Nickel	Dull. No pits. No perforations. No cracking.	Dark, dull. Pits along edges. No pits in bent area. No cracking.

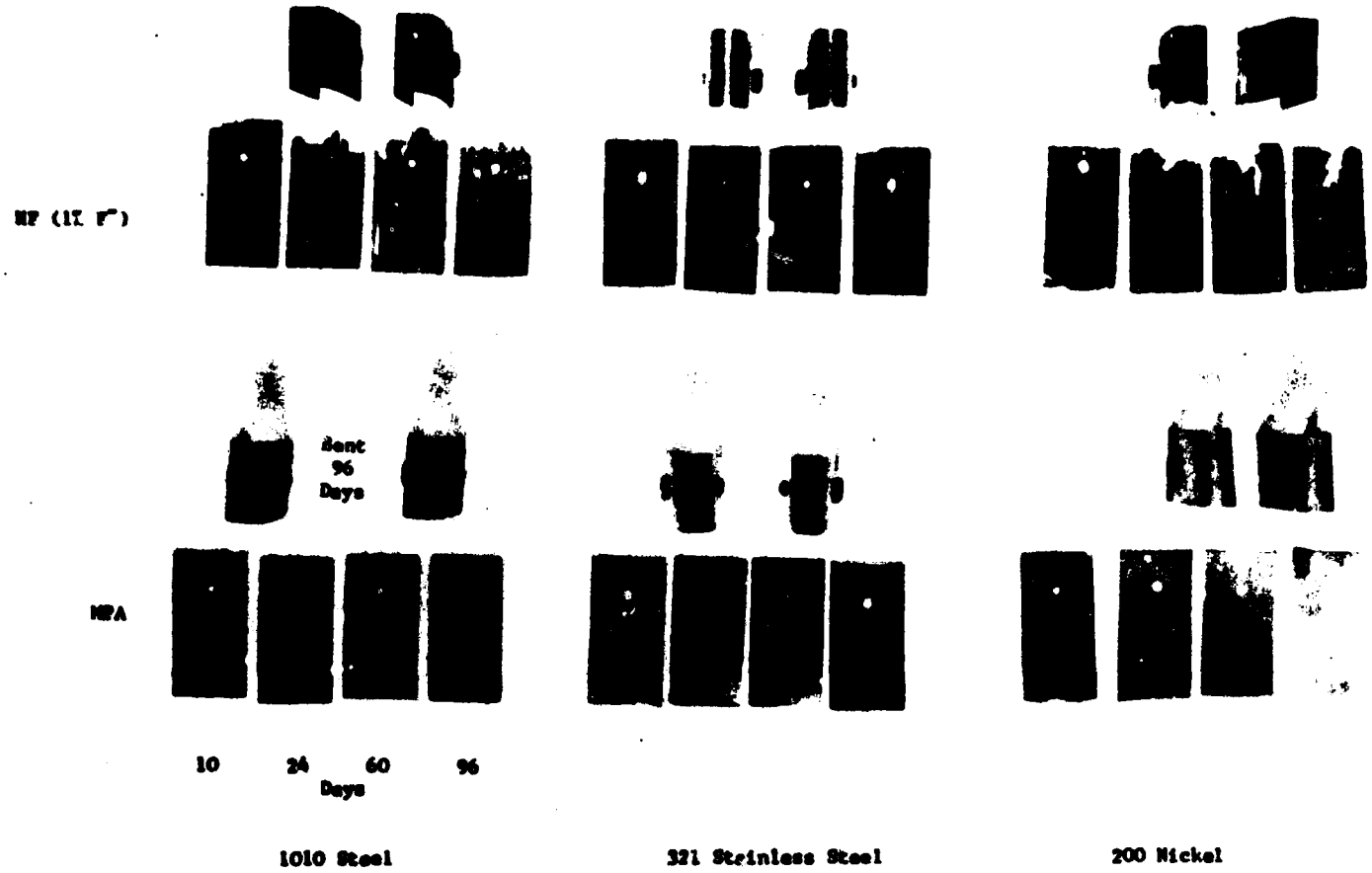

Figure 4. Condition of Specimens after Exposure to Test Solutions

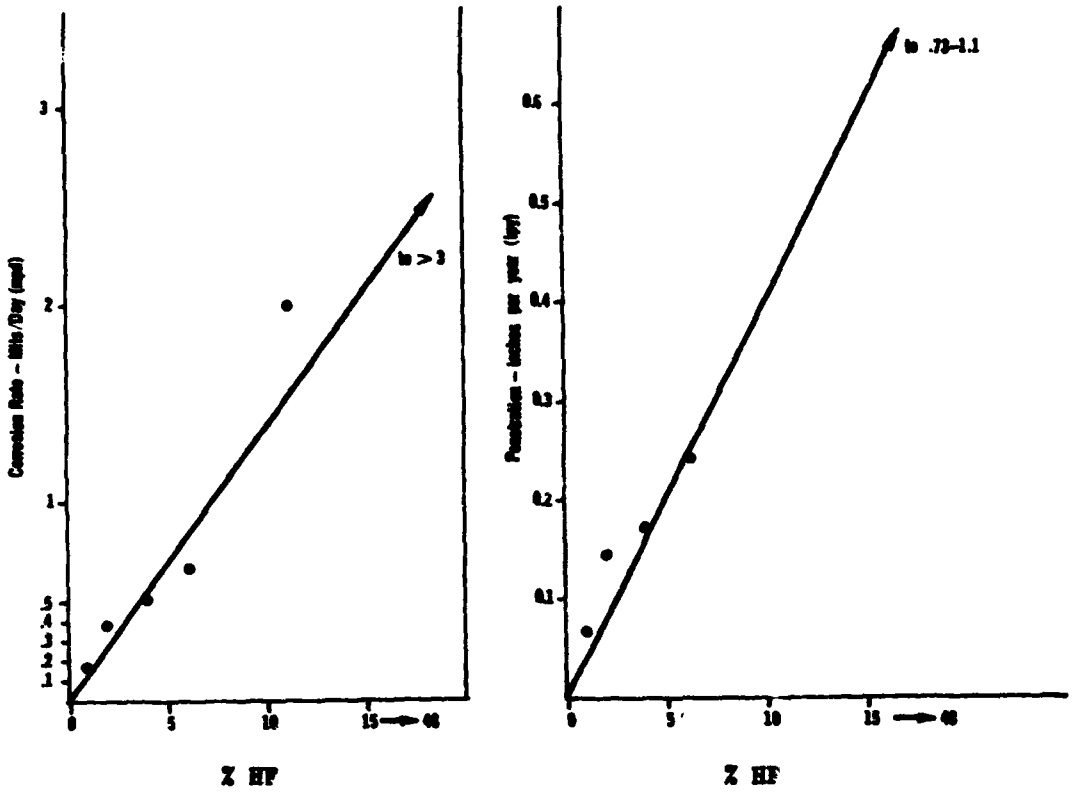

Figure 5. 321 Stainless Steel Specimens (2.5 x 1.25 cm - Two Surfaces) Corrosion Rate vs Concentration of HF

MPA Solution

In the MPA solution, steel is attached at about half the rate it is in the HF(1XF⁻) solution. This action subsides and approaches an asymptotic condition at about 50 days, or about half the exposure duration, and the ultimate weight loss is more than 19 percent. The thickness reduction of the thin-sheet ultimately is approximately 12 percent (two surfaces exposed). This apparent discrepancy is dispelled when perforations and the loss of metal is considered (Figure 1 and Table III).

Stainless steel is unaffected by this solution; no weight nor thickness reduction occurred (Figure 2 and Table III). Nickel, on the other hand, undergoes a regular increase in corrosion, slow initially, then steadily increasing on longer contact with the solution. At the end of 96 days' exposure, the percent weight loss of the nickel exceeds that obtained with the HF solution. Percent weight loss and percent thickness reduction (two surfaces exposed) after 60 and 96 days, respectively, are in close agreement (Figure 3 and Table III).

HF (1%F⁻) Solution

In the HF solution the corrosion of 1010 steel and 321 stainless steel proceed actively at first. In an overall consideration, the steel corrodes at about twice the rate of the stainless steel. The corrosion rate of each sheet material steadily diminishes and becomes asymptotic at about 50 days, about half the full exposure time. Pitting and loss of metal resulting from complete penetration and holes in the steel sheet occurs; consequently weight loss and thickness reduction (two surfaces exposed) differ; the steel showing a greater change. The nickel sheet exhibited a slower initial rise in corrosion rate than did the other metals, but rose steadily over the entire exposure period. Thickness reduction is not in agreement with weight percent losses.

From the data it would appear that the discrepancy persists but with smallest differences in the intermediate periods. At the final point (96 days) the percentage weight loss is greater than that which might be accounted for from thickness reduction. Again, this is attributed to holes and small perforations (in some nickel specimens solid particles were able to be picked out leaving through holes) which result from the action of the liquid on the metal sheet (Figure 3 and Table III).

Metal-surface area to volume of solution relationship is a factor which is of importance. Contrast the corrosion of 321 stainless steel in HF (1%F⁻), at 1/1.46 ratio, to that in the same solution at 1/15.7. In the former the penetration (considering one surface exposed, but same total area) the average of the total is ca. 0.006 mil/day (0.015 cm.) (Figure 2) and in the latter ca. 0.1 mil/day (ca. 0.25 cm.) (Figure 5) or nearly 17 times greater. These rates are more representative of the earlier exposure times. Further, as the concentration of HF increases the corrosion of 321 stainless steel increases at appreciable rate (Figure 5).

DISCUSSION

In limited access of difluoro liquid to available surface area of the metal such as described above, and in the virtual absence of oxygen (air), two favorable conditions would be expected to be realized. This applies to 1010 steel and 321 stainless steel, but is not indicated for the 200 nickel.

First, the initial rate of uniform surface corrosion would diminish for the steels and would eventually cease, considering a ratio of metal surface and of liquid of 1/1.46 (.69) or greater. Second, the absence of oxygen would be expected to preclude progressive pitting and perforation of the thin-sheet material. In the case of 200 nickel, even if pitting and penetration of the thin-sheet would not occur because oxygen is precluded, uniform dissolution and appreciable and progressive thickness reduction is indicated. In any event, any minute leakage at the weld seam of the diaphram and container base, could provide conditions for breaching the diaphram by corrosion. This would also apply to 1010 steel.

As a result of welding diaphrams in the container end, a circumferential heat affected region in the diaphram would be expected to result. Some probable consequences of this, e.g., accentuated corrosive damage in the heat affected region, and enhanced susceptibility to stress corrosion cracking failure, cannot be ignored.

CONCLUSIONS

Thin-sheet 321 stainless steel is indicated as a suitably serviceable diaphram material for use in the difluoro compound container.

Thin-sheet 1010 steel and 200 nickel are considered unsuitable for that purpose because of their propensity to pitting and perforation when subjected to aerated HF (1%F^-) solution, and to excessive reduction of thickness when in contact with the HF and MPA solutions, representative of certain conditions of the difluoro compound.

The relationship of metal surface area to volume of the HF solution will markedly affect the corrosive action of the stainless steel and the other metals; the larger is the volume of corrosive liquid relative to the metal surface, the more pronounced will be the corrosive action. Also, higher concentrations of corrosive electrolyte in solution, accelerate metal dissolution, and air-oxidative conditions in the solution will accentuate pitting and perforation of two of the three materials.

A highly likely result of welding a diaphram to the container, is that a circumferential heat affected region will result in the diaphram metal. This would promote the susceptibility of the diaphram to localized corrosion, including stress corrosion and cracking failure.

REFERENCES

1. L. C. Buckles, W. C. Crawford, Jr. and A. S. Hutchcraft, Jr., Report CRLR 578, Chemical and Radiological Laboratories, Army Chemical Center, Maryland, 28 May 1956, p. 13.

2. Communications, re: Rocket M55 with Mr. S. R. Eckhaus, Weapons Development Engineering Laboratory, Edgewood, Maryland, May 1966.