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SEA WATER CREVICE CORROSION TESTS ON URANIUM-BEARING AISI TYPE 430 STAINLESS STEELS

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by

J.G.Garrison* and G.J.Biefer**

ABSTRACT

Tests were conducted to determine the effects of uranium additions in the optimum range of about 0.25-0.5% on the resistance to crevice corrosion of AISI Type 430 stainless steel when immersed in sea water.

As compared with a similar uranium-free steel, there was an improved resistance to crevice corrosion for steels containing 0.24% and 0.55% uranium. However, reproducibility of the results was poor; none of the alloys tested performed well, and it was concluded that uranium additions cannot be relied upon to suppress crevice corrosion attack in Type 430 stainless steel.

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ÉPREUVES DE CORROSION DES FISSURES DANS L'EAU DE MER SUR LES ACIERS URANIFÈRES INOXYDABLES DE TYPE 430 AISI

par

J. G. Garrison* et G. J. Biefer**

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RÉSUMÉ

Des épreuves ont été faites pour déterminer les effets des additions d'uranium, dans les proportions idéales d'environ 0.25 à 0.5 p. 100, sur la résistance à la corrosion des fissures de l'acier inoxydable de type 430 AISI lorsqu'il est immergé dans l'eau de mer.

Par comparaison avec un acier semblable sans uranium, on a noté une résistance accrue à la corrosion des fissures chez les aciers contenant 0.24 p. 100 et 0.55 p. 100 d'uranium. Cependant, la reproductibilité des résultats a été médiocre; aucun des alliages soumis à l'épreuve n'a donné un bon rendement et on en a conclu qu'il ne faut pas compter sur les additions d'uranium pour supprimer l'attaque corrosive des fissures dans l'acier inoxydable de type 430.

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INTRODUCTION

In the late nineteen-fifties there was a sudden decrease in the demand for uranium. This prompted the Canadian Government and the uranium industry to seek new non-nuclear uses for the metal, with the object of keeping the uranium mines in operation.

In 1959, as part of a large-scale effort, the Physical Metallurgy Division, Mines Branch, Department of Energy, Mines and Resources, at Ottawa, initiated research on the effects of uranium as an alloying element in metals of commercial importance. The behaviour of uranium-bearing steels was investigated intensively during the next few years, and in April 1962 an interim review of the initial results was published (1). This showed, among other results, that uranium was capable of imparting improved corrosion resistance to chromium stainless steels. The most definite favourable trends were exhibited by an AISI Type 430 (17% chromium) stainless steel containing 0.27% uranium. As compared with a similar uranium-free alloy, this steel showed improved corrosion resistance in dilute sulphuric and hydrochloric acids, and also showed improved resistance to crevice corrosion in a neutral salt solution.

Because Type 430 stainless steel is used quite widely, especially in automobile trim, the authors decided to concentrate further research on the effect of uranium on this steel, with the following main objectives:

1. To determine, by means of laboratory testing, the uranium content for optimum corrosion resistance; further, to compare the effect of uranium with that of molybdenum. Molybdenum was known to impart useful increases in corrosion resistance to Type 430 chromium stainless steel (2,3).

2. To expose uranium-bearing and uranium-free Type 430 stainless steels to appropriate field tests, in order to determine whether uranium additions imparted useful improvements in corrosion resistance.

From laboratory corrosion testing carried out by the authors subsequent to the initial work, it appeared that uranium additions could be expected to be significantly beneficial only within the comparatively narrow range 0.1-0.5%; the maximum favourable trends might be expected at the 0.25-0.5% level (4). It was then shown that Mo additions were capable of producing greater improvements in the corrosion resistance of Type 430 stainless steels than uranium additions, though greater Mo contents were needed (5). These and other findings in the laboratory corrosion testing, which has now been completed, have been summarized recently (6).

In view of the results of the laboratory testing up to the end of 1963, the authors decided to carry out field corrosion tests on Type 430 stainless steels alloyed with 0.24% and 0.55% uranium, along with similar uranium-free steels. By the beginning of 1965, the following tests were under way.

(a) Specimens had been exposed on automobiles in Ottawa, Halifax, N.S., and St.John, N.B. The specimens were attached to the front bumpers of the automobiles, in all cases, and were exposed to splashing by de-icing salts during the winter months.

This work, which has now been completed, showed only a slight benefit because of an addition of 0.24% uranium, and no benefit due to 0.55% uranium; a steel containing 2.03% Mo was noticeably more resistant than either of the uranium-bearing steels (7).

(b) Specimens of uranium-bearing and uranium-free Type 430 stainless steel had been exposed on the roof of the Physical Metallurgy Building, in Ottawa. On April 1, 1968 (after 3 years 9 months of exposure), corrosion attack on all alloys was observed to be negligible; this test is continuing.

(c) Specimens had been immersed in sea water, the tests having been designed so that all specimens contained a crevice and were therefore liable to crevice corrosion. It is this work that forms the subject of the present report.

EXPERIMENTAL

Material

The AISI Type 430 stainless steels were produced at the Physical Metallurgy Division as 50-lb aluminum-deoxidized induction melts. They included one heat with no alloying addition, which was used as a "control" standard, and two heats representing two levels of uranium (0.24% and 0.55%). Chemical analyses of these heats are given in Table 1.

The reference ingot (Heat No. 5555) and the uranium-bearing steel ingots (Heats Nos. 5556 and 5557) were forged and rolled at a starting temperature of 1850°F (1010°C)* to 3/16-in.-thick plates. The plates were annealed at 1450°F (790°C) for four hours, and furnace-cooled.

Corrosion specimens 2 in. square, having a $\frac{1}{4}$-in.-diameter centre hole, were obtained from these plates. To ensure uniformity of surface finish, the specimens were surface-ground on 120-grit silicon carbide. The specimens

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*I.e., below the melting temperature of the U-UFe_2 eutectic (1976°F, 1080°C), to avoid hot-shortness.

were then autoradiographed, and only specimens in which the uranium was distributed homogeneously were chosen for testing. In all, thirty-six specimens, including "control" specimens, were tested.

The dimensions of the test specimens were measured. The specimens were then cleaned in an ultrasonic cleaner and vapour degreaser, using carbon tetrachloride, and rinsed with alcohol, dried, and weighed. Following this, they were mounted in four Plexiglas racks, one of which is shown in Figure 1.

Each rack held three sets of specimens, each set consisting of one "control" specimen and one specimen containing each of the two levels of uranium.

The racks were so designed that upon their immersion in sea water, each specimen would contain a "crevice", i.e., an area of the specimen to which the bulk sea water had only a restricted access. For each specimen, the crevice was formed by metal in contact with the Plexiglas spacers and by metal in contact with the central Plexiglas rod upon which the specimens were threaded. This crevice area totalled approximately 6.0 cm^2 for each specimen.

Two of the test racks (Nos. 1 and 2) were immersed by Defence Research Establishment Atlantic, in Halifax Harbour at H.M.C. Dockyard. The remaining two racks (Nos. 3 and 4) were immersed by Defence Research Establishment Pacific, in Esquimalt, B.C.

Rack No. 1 was immersed for a twelve-month period, and rack No. 2 was immersed for eleven months. Rack No. 3 was immersed for eleven months, while rack No. 4 was immersed for seventeen months.

At the conclusion of the test periods, the racks were shipped back to the Physical Metallurgy Division, Ottawa, where they were dismantled. The marine fouling observed on the specimens (see especially Figure 3) was removed by immersion for 1 minute in a 10% (by volume) nitric acid solution at 140°F (60°C). After this, the specimens were scrubbed with a stiff-bristled brush under running tap water, rinsed with alcohol, and dried. If all the fouling material had not been removed, the procedure was repeated. After this cleaning, the specimens were re-weighed so that the weight loss during the sea water immersion could be calculated.

RESULTS

Specimens tested in Halifax Harbour and at Esquimalt were photographed in the "as-received" condition, and are shown in Figures 2 and 3 respectively. It may be seen from these photographs that most of the corrosion attack took place in the crevice areas, at the centres of the specimens; in some cases, the crevice areas were almost entirely corroded away.

The weight-loss figures obtained after removal of the sea water fouling are given in Table 2. In calculating the weight losses per unit area, the crevice area of 6.0 cm^2 was used, because most of the corrosion attack was in the crevices; only two specimens showed significant edge attack.

To facilitate interpretation of the weight-loss data of Table 2, in Table 3 the different alloys within each set of three specimens are ranked in order of resistance to corrosion: 1 signifies the least weight loss, and 3 the most, within a set.

DISCUSSION OF RESULTS

It was immediately obvious, from the results of these tests, that reproducibility had been poor and that none of the three alloys had exhibited consistently good resistance to crevice corrosion attack in sea water. Of the thirty-six tested, only four individual specimens could be said to have been "resistant" (i.e., to have shown weight losses lower than 5 mg/cm^2), namely two of each of the uranium-bearing alloys. None of the uranium-free steels was resistant, by this criterion. Loss of all the metal under the spacers -- i.e., the theoretical maximum crevice attack possible -- would have amounted to about 500 mg/cm^2 weight loss per specimen; no less than eight specimens showed very heavy attack of this order, specifically in the range 422-668* mg/cm^2. Five of these eight heavily attacked specimens were uranium-free.

A study of the distribution of the weight losses of Table 2 suggested that the crevice corrosion took place in two steps, as follows: first, an induction period, during which little or no crevice corrosion took place, and then an initiation of corrosion, which could proceed until virtually all the metal in the crevice had been consumed.

It appeared that four of the specimens -- two of each of the uranium-bearing alloys -- were still in the induction phase at the conclusion of the testing. Crevice corrosion had initiated for all the uranium-free specimens; there was, therefore, an indication that induction periods had tended to be longer for the uranium-bearing steels, though it appeared that the lengths of the induction periods must have been variable.

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* two specimens showed weight losses greater than the theoretical maximum because of edge attack.

There is an interesting difference in the trends of the results obtained at the two testing stations. From the results at Halifax, only marginal improvements are obtained by alloying with uranium; at Esquimalt, the uranium-bearing steels appear to be clearly more resistant. An examination of the weight-loss data, however, shows that this difference is attributable to the behaviour of the uranium-free alloy, which showed much greater weight losses at Esquimalt than at Halifax. Both uranium-bearing alloys showed similar behaviour at the two locations.

It is not possible to offer an explanation for the differences in behaviour noted above, but it does appear that conditions at Esquimalt must have been such that a rapid "breakaway" crevice-corrosion attack occurred for the uranium-free steel; the uranium-bearing steels were apparently more resistant during this phase of the corrosion process.

Consideration was given to various factors which might have contributed to the poor reproducibility obtained in these tests. It was suspected, at first, that the specimens might have been mixed up. However, a re-check, carried out by beta counting, indicated that the alloy identification of all specimens had been correct.

Some thought was then given to the fact that the rack design had not been optimum. Within each set of three specimens, considerable crevice corrosion of one or more specimens could have been expected to reduce the compressive stresses on the spacers, allowing the crevice widths on all three specimens to increase. It was observed that this had in fact happened; whereas the specimens had been tightly clamped in position when shipped off for testing, they were all held somewhat loosely in position upon their return after the tests.

The faulty rack design would not have exerted any interfering effect during the induction period, nor during the initial stages of crevice corrosion. In the later stages of crevice corrosion, the effect of a decrease in the compressive stresses on the spacers is difficult to assess. Obviously, this factor did not prevent a number of the specimens from corroding to the theoretical weight loss maximum of about 500 mg/cm^2. On the other hand, the crevice-widening may have been instrumental in permitting four of the specimens to have remained in the induction phase, so that they exhibited negligible crevice corrosion at the conclusion of the tests.

In summary, the faulty rack design could have had an interfering effect, but it cannot be readily assessed; in any case, this factor would not have been expected to alter the relative rankings of the different alloys with respect to their resistance to crevice corrosion.

It was also considered that the racks might have been treated differently after leaving the Physical Metallurgy Division and prior to their submersion in sea water; for example, temporary storage and rack handling might not have been optimum. However, no information was available in this regard.

Once the specimens had been immersed in live sea water, the random attachments of sea organisms might have brought about purely local differences in crevice environments from one specimen to the next. This could have contributed to the poor reproducibility in corrosion behaviour shown by different specimens of the same alloy. However, the importance of this factor could not be assessed; in any event, it was an inescapable and essential part of the field test.

It was concluded that, on the whole, the basic induction-"breakaway" pattern of the crevice-corrosion phenomenon would have been expected to favour poor reproducibility. In view of the existence of the other factors discussed above, which might have had unequal effects on different specimens, the poor reproducibility of the results was probably to be expected.

CONCLUSIONS AND FUTURE PROGRAM

Although none of the alloys tested showed good resistance to crevice corrosion in sea water, it appeared that AISI Type 430 steels containing 0.24% and 0.55% uranium were more resistant than similar uranium-free steels.

The improvements in corrosion behaviour attributable to uranium were not considered to be sufficient to warrant further research, and work in this area has been terminated.

ACKNOWLEDGEMENTS

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JGG:GJB:(PES):T

TABLE 1

Chemical Analyses of Uranium-Bearing AISI Type 430 Stainless Steels

Heat No.	Composition, %						
	C	Mn	Si	S	P	Cr	U
5555	0.13	1.14	0.96	0.019	0.020	17.29	--
5556	0.14	1.10	0.93	0.017	0.018	17.29	0.24
5557	0.12	1.10	0.91	0.021	0.021	16.95	0.55

TABLE 2

Weight Losses of the Specimens (in mg/cm^2)*

Rack No.	Test Location	Immersion Period	Set No.	Alloy 5555 (U-free)	Alloy 5556 (0.24% U)	Alloy 5557 (0.55% U)
1	Halifax, N.S.	12 mos.	1	325	224	62.8
			2	306	22.8	47.2
			3	112	328	19.2
2	" "	11 mos.	4	472	245	121
			5	25.1	0.4	476
			6	233	422	269
	Averages, Halifax			246	207	166
3	Esquimalt, B.C.	11 mos.	7	461	104	257
			8	489	67.6	1.2
			9	196	114	152
4	"	17 mos.	10	668**	338	15.3
			11	628**	317	485
			12	272	2.9	4.6
	Averages, Esquimalt			452	182	159

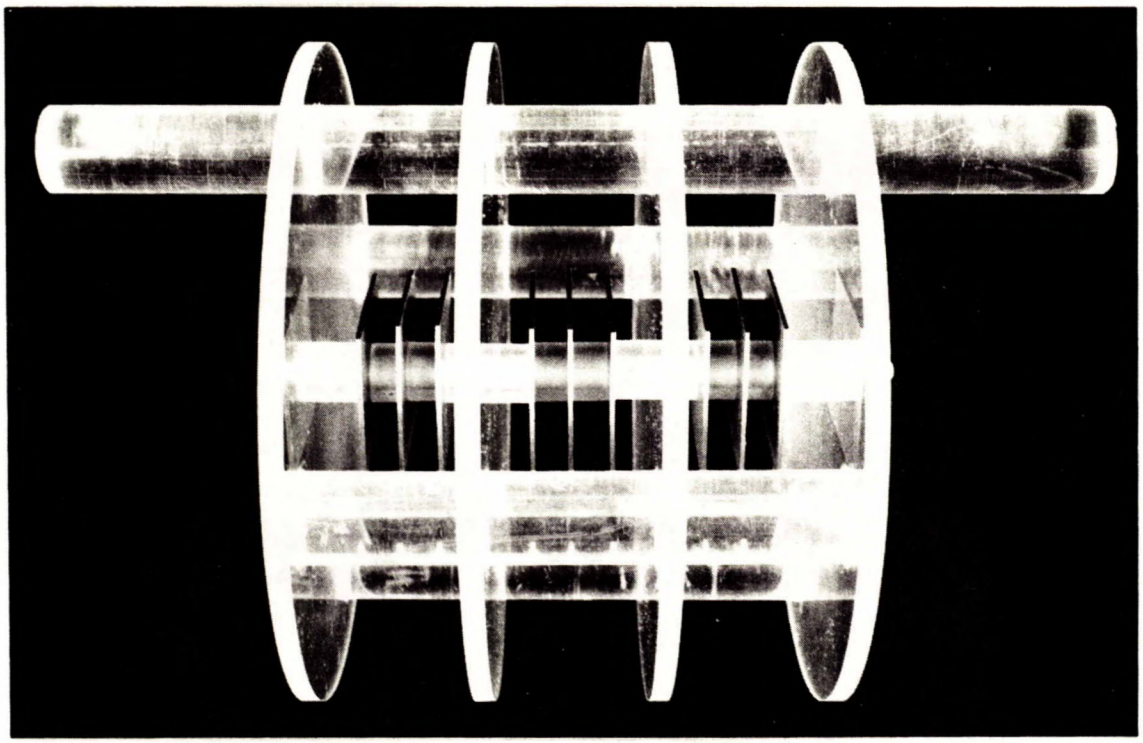
*Based on crevice area of 6.0 cm^2.
**Specimens showed significant edge attack.

TABLE 3

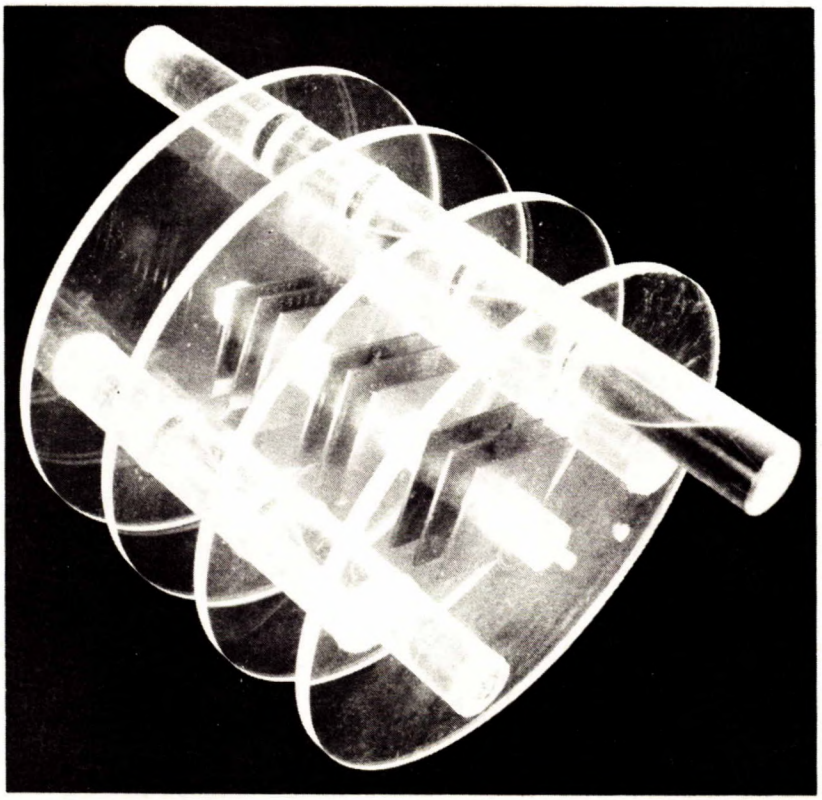
Rankings of the Specimens According to Weight Losses*

Rack No.	Test Location	Immersion Period	Set No.	Alloy 5555 (U-free)	Alloy 5556 (0.24% U)	Alloy 5557 (0.55% U)
1	Halifax, N.S.	12 mos.	1	3	2	1
			2	3	1	2
			3	2	3	1
2	" "	11 mos.	4	3	2	1
			5	2	1	3
			6	1	3	2
	Averages, Halifax			2.33	2.0	1.66
3	Esquimalt, B.C.	11 mos.	7	3	1	2
			8	3	2	1
			9	3	1	2
4	"	17 mos.	10	3	2	1
			11	3	1	2
			12	3	1	2
	Averages, Esquimalt			3.0	1.33	1.66

*"1" signifies the highest and "3" the lowest weight losses, in each set.



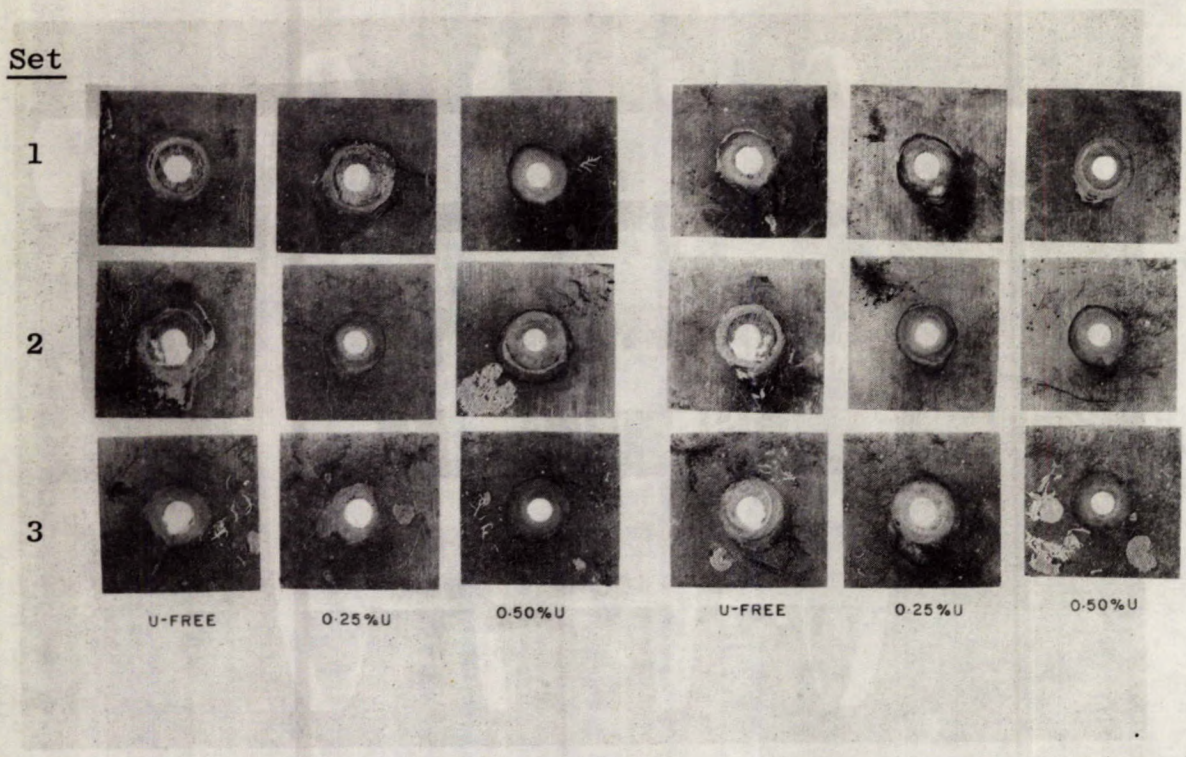
(a)



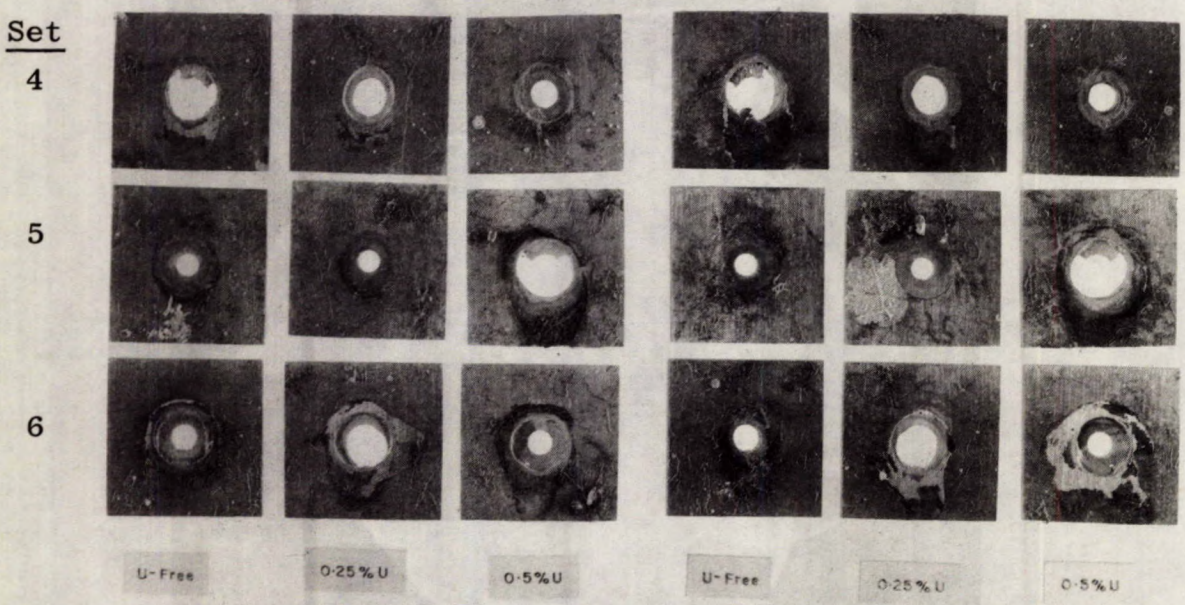
(b)

Figure 1. Two views of one of the Plexiglas test racks used for the sea water tests, showing three sets of three specimens mounted.

X $\frac{1}{4}$

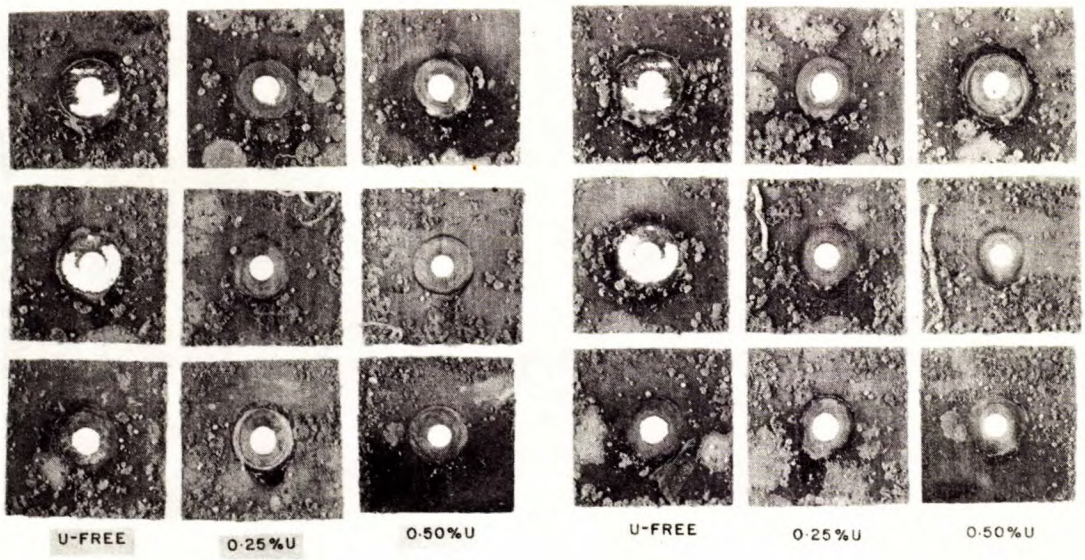


Rack No.1 X $\frac{1}{2}$

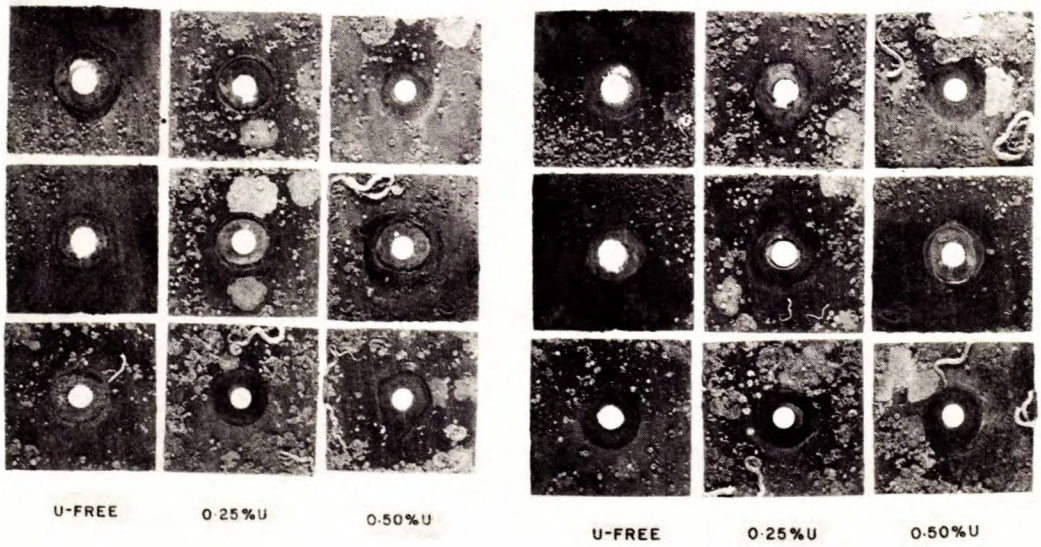


Rack No.2 X $\frac{1}{2}$

Figure 2. Photographs of both sides of specimens tested at Halifax, N.S. (As received. Sea water fouling had not been removed.)



Rack No.3 X $\frac{1}{2}$



Rack No.4 X $\frac{1}{2}$

Figure 3. Photographs of both sides of specimens tested at Esquimalt, B.C. (As received. Sea water fouling had not been removed).