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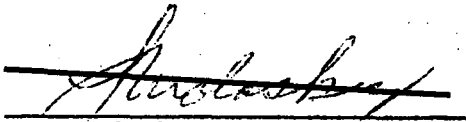
OPTICAL TECHNOLOGY DIVISION
OPTO-MECHANICAL DESIGN ENGINEERING

Memorandum ME 50

TO: Project File - Recovery of RV #3 ✓ DATE: August 5, 1971
FROM: L.B. Molaskey
SUBJECT: Effect of Salt Water on Beryllium

At the meeting of 30 July 1971 held at MWC concerning the recovery of RV #3, a question of the survivability of the beryllium when immersed in salt water was brought up. Investigation into the matter has produced evidence that although there is certain to be corrosion on the beryllium, it is very doubtful that serious damage to the structural integrity of the core and/or shaft components will occur as a result of corrosion. The attached data indicates that even when cycled through salt water immersion and elevated temperatures in air, the effects of corrosion are insignificant compared to the structural function of the take-up core and shaft.

It is therefore concluded that corrosion of the beryllium components will be negligible compared to the other effects of water impact and subsequent immersion in sea water.


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It is pointed out, however, that corrosion rates in such service are higher than can be tolerated, so that additional protection is required for satisfactory service life.

Salt Fog

Bare beryllium specimens (nominal 2 percent BeO content) were exposed to a 5 percent salt-fog spray at 100 F for 30 days at the Astropower Laboratory. (7) Localized pitting occurred on the bare pieces after only 1 day of exposure. The attack increased with exposure time. The specimens were rinsed in distilled water after 30 days and then were weighed. The weight loss at several time intervals is given in Table 4. The values in the last column (actual) were obtained by dissolving the corrosion product in 49 percent HNO₃ and 1 percent HF and adjusting for the bare metal dissolved. The corrosion rate corresponding to weight losses in the range shown is 2.2 mpy. Pit depths of 15 to 25 mils were measured on the coupons.

TABLE 4. WEIGHT LOSSES OF FORGED 1x2-IN. IN 5 PERCENT SALT-FOG SPRAY AT 100 F (Reference 7)

Specimen	Day	Weight Loss at Indicated Exposure Times, mg								30 Days (Actual) ^(a)
		1 Day	2 Days	4 Days	7 Days	14 Days	21 Days	30 Days	30 Days	
3-4		0.33	0.50	0.90	1.6	3.8	5.6	7.3	23.1	
5-4		0.42	0.7	0.89	1.2	2.3	2.7	3.1	27.2	
5-5		0.40	0.7	0.91	1.1	2.0	2.4	2.9	17.6	
1-1	--	0.5	0.71	0.9	1.9	2.6	3.5	22.5		

(a) (Actual) values indicate weight losses of specimens after corrosion products were stripped from coupons, and are equivalent to about 2.2 mpy.

In another study at the same laboratory, coupons were alternately exposed to a 5 percent salt fog at 100 F for 16 hours, and then immediately placed in an oven for 8 hours at 200, 400, 600, or 800 F.

The following observations were reported for polished beryllium when exposed to alternate cycles of salt-fog spray and elevated temperatures.

- (1) Chemical attack was observed on polished bare beryllium following the initial cycle at all of the above temperatures.
- (2) At 200 F the pitting observed after the first initial cycle increased with each subsequent cycle as evidenced by the increase in the number and size of the pits. The behavior at this condition is very similar to the results obtained for the 30-day, 5 percent salt-fog spray.
- (3) At 400, 600, and 800 F, the cyclic effect of temperature and salt contamination was found to proceed by two independent mechanisms.

Initially, weight loss was observed, due to chemical attack by the salt environment. After the first few cycles, a thin oxide coating was formed, due to oxidation in air at the elevated temperature.

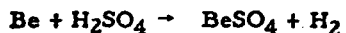
- (4) At 800 F, very small white oxide patches started to appear at about about the tenth cycle. At this stage the coupons started to show small weight increases. The appearance of the white oxide is indicative of the onset of the catastrophic oxidation, which is discussed later in this report.

Acids

Beryllium reacts with the halogen acids in all concentrations at room temperature. It reacts with dilute sulfuric acid readily and with concentrated sulfuric acid slowly. It is attacked by dilute nitric and acetic acids, but not glacial acetic acid or concentrated nitric acid at room temperature. With concentrated nitric acid, reaction occurs and becomes violent as the temperature is increased above room temperature.

Straumanis and Mathis report studies with premium-grade vacuum-cast metal (assaying 99.0 percent Be) in HF, HCl, and H₂SO₄. (12) The metal is removed uniformly in HF and H₂SO₄. The reaction with HCl is more localized, and a black deposit forms which has been identified as fine needles of metallic beryllium. The black deposit was not found when concentrations greater than 0.5N HCl were used.

The reaction mechanisms were checked by measuring the volume of hydrogen evolved from weight samples. It was concluded that the reactions with acids are:



Rapid attack and the formation of a black deposit were observed in HClO₄ and HBr.

It is interesting that a similar black deposit, consisting mainly of fine beryllium needles, is formed on beryllium anodes when the metal is electrolytically dissolved in a 0.5N HCl solution. (13)

Alkalies

Beryllium is vigorously attacked by aqueous alkaline solutions. Molten alkalies may react explosively with the metal.

TABLE 2. CORROSION OF BERYLLIUM IN SALT SOLUTIONS AT 60 F (Reference 9)

Environment	Overall Corrosion Rate ^(a) , mpy	Max Pit Depth, mils
Distilled water	0.8	0.8 ^(b)
Synthetic seawater	13.7	4.6
Natural seawater	18.4	4.6
3% NaCl solution	21.5	--
3.5 NaCl solution	33.4	6.8 ^(c)

(a) 30 days.

(b) 18 days.

(c) 8 days.

TABLE 3. CORROSION IN NATURAL SEAWATER AT ABOUT 60 F

Continuous total immersion. (Reference 9)

Time, days	Corrosion rate, mpy	Max Pit Depth, mils	Percent of Surface Pitted
2	--	1.5	Negligible
5	--	1.6	1
20	13.0	3.0	5
30	10.5	3.0	12
40	9.0	2.5	15
60	6.5	3.0	20
182 ^(a)	2.4	--	--

(a) Extrapolated value.

It should be pointed out that the maximum pit depth also increased in a similar manner from about 1.6 to 3.2 mils as the exposure time increased from 5 to 150 days. A summary of the results concerning pitting is given in Figure 4. It can be noted that the percentage of the surfaces pitted increased linearly from about 2 to 45 percent as the exposure period increased from 5 to 150 days.

In work at Battelle, a very low general rate of attack was found for beryllium in seawater, but evidence of possible pitting was also observed. The beryllium was exposed in aerated seawater (except for a period of about 6 hours a day, for 5 days a week, when it was suspended above the water). After 2 weeks' exposure, the corrosion rate was equivalent to 3.6 mpy. The surface appeared to be coated with a white powder, probably BeO, and had small-size clear hygroscopic bubbles on its surface. Underneath these bubbles some pitting was found.

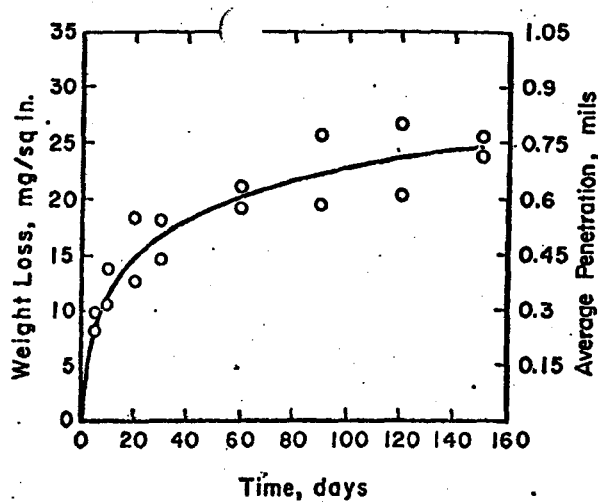


FIGURE 3. CORROSION OF UNSTRESSED, PICKLED BERYLLIUM SHEET MATERIAL EXPOSED TO SYNTHETIC SEAWATER AT 77 F (Continuous total immersion testing. Reference 11).

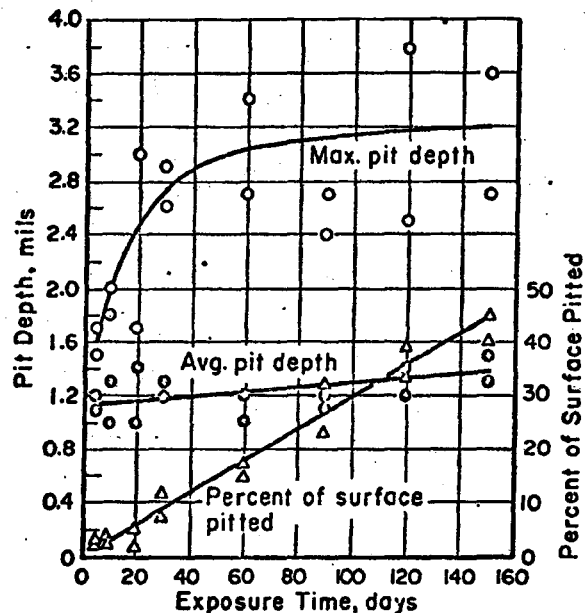


FIGURE 4. PITTING ATTACK OF UNSTRESSED, PICKLED BERYLLIUM SHEET MATERIAL EXPOSED TO SYNTHETIC SEAWATER AT 77 F (Continuous total immersion testing. Reference 11).

Workers at Astropower exposed bare beryllium (nominal 2 percent BeO content) specimens alternately to a 5 percent salt solution at 100 F for 16 hours, followed by air exposure at elevated temperatures up to 800 F for 8 hours. (7) Tests were continued for a total of 14 cycles. The specimens were first attacked at localized areas (pitting). The maximum corrosion resistance was found at 600 F and was attributed to the formation of a protective oxide film.

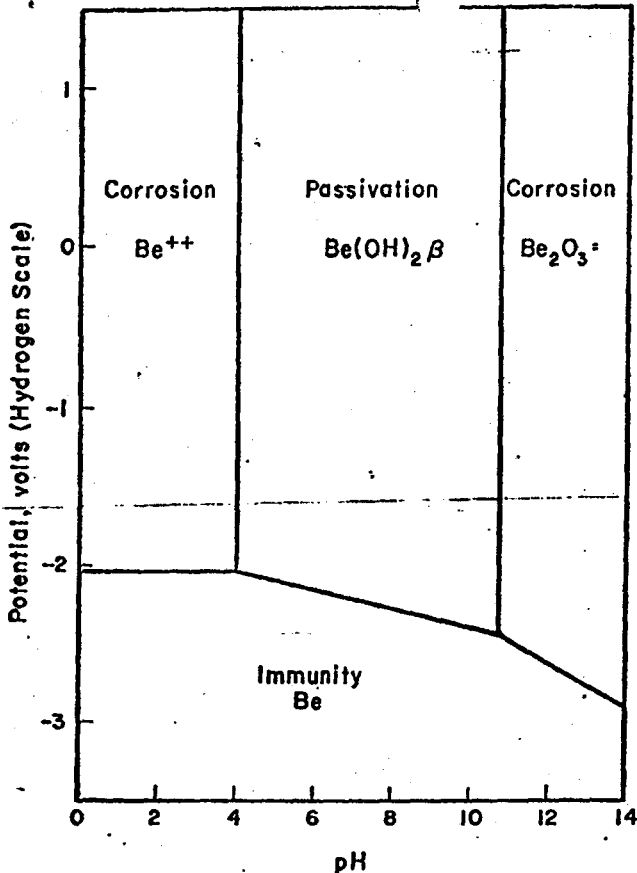


FIGURE 1. EQUILIBRIUM POTENTIAL - pH FOR THE SYSTEM BERYLLIUM - WATER AT 77 F⁽⁶⁾

Alloy additions of nickel or combinations of nickel and iron (4000 ppm Ni, 2000 ppm Ni-2000 ppm Fe, or 5000 ppm Ni-5000 ppm Fe) greatly improved the corrosion resistance of high-purity beryllium. For example, specimens made from alloyed Pechiney CR-grade powder showed no signs of attack for times up to 43 days in water at 650 F. The beneficial effect from nickel was not confirmed by Stonehouse and associates. (2)

Additional research will be required to clarify the cause of the unpredictable behavior of beryllium. There is some indication that it is related to the presence of small amounts of copper contamination in the water. General results can be summarized as follows:

- (1) Specimens with acid etched surfaces were less corrosion resistant than those not etched.
- (2) Mechanical removal of more than 12-14 mils of the outer surface also rendered the specimens less corrosion resistant.
- (3) Localized boiling on specimen surfaces increased the corrosion rate.

Beryllium specimens exposed to steam at 752 F at 1500 psi were attacked in much the same manner as those in water at 650 F. The localized attack in steam was somewhat more severe.

Salt Solutions

As was mentioned in an earlier section, beryllium is subject to pitting attack in aqueous environments containing chloride ion. Intermittent immersion tests conducted by Prochko and associates^(9,10) at ambient temperatures (about 60 F) and 30 days of exposure indicated overall corrosion rates and penetrations listed in Table 2. Corrosion-test specimens were prepared from cross-rolled, surface-ground, flash-pickled (HF-HNO₃) sheet. The 60-mil beryllium sheet of commercial purity assayed 98.3 percent Be, 1.63 percent BeO, and 0.113 percent carbon.

Figure 2 shows the weight losses and penetrations for the specimens in the five test solutions after intermittent exposures.

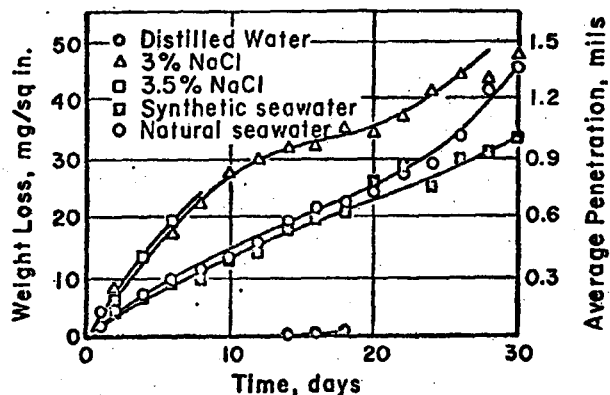


FIGURE 2. CORROSION OF PICKLED BERYLLIUM SHEET IN FIVE ENVIRONMENTS (Intermittent total immersion testing was conducted using these selected chloride solutions at 60 F. (Reference 9))

Exposures at 60 F and 95 F showed that the corrosion rate increased as the temperature was raised. For example, after 14 days of intermittent total immersion in natural seawater the rates for the above temperatures were 17.1 and 25.9 mpy, respectively. By comparison, the corrosion rate for anodized beryllium was only 0.3 mpy after 60 days in seawater.

The corrosion rates decreased with time of exposure for samples exposed continuously at 60 F in natural seawater. Results are summarized in Table 3.

A later report from the same laboratory indicates that the corrosion rate of beryllium in synthetic seawater decreases from about 21.2 mpy at 5 days' exposure to about 3.0 mpy at 150 days. (11) Figure 3 illustrates these results.