Corrosion of Steel and Aluminum Scuba Tanks

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Contents

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List of Figures

List of Tables

Abstract

Groups of steel and aluminum scuba tanks were subjected to controlled corrosion tests for 100-day periods. A variety of interior conditions were tested, including high and low air pressure, fresh and salt water insertion, tank position, and, in the case of a group of aluminum cylinders, variations in closure-valve material and thread lubrication.

In general, the aluminum tanks showed much less corrosion damage than the steel tanks did, under all environmental conditions. Corrosion of the steel tanks, which contained sea water and were pumped to full pressure, was so rapid that the tanks were in danger of exploding after the 100-day tests.

Aluminum corrosion was much less severe but produced a destructive galling at the cylinder threads which made valve removal impossible without destroying the tank in several cases. A test of various valve configurations showed that this galling was corrosion-produced, and could be reduced and even eliminated by using a plastic or other non-brass extender on the tank valve and by minimizing the copper content in the tank water.

Project History

The Scuba Safety Project at the University of Rhode Island was first funded in 1969 by the Food and Drug Administration of the U.S. Public Health Service to investigate various aspects of scuba accidents. One study begun at that time involved the corrosion and subsequent bursting of high pressure scuba tanks. Figure 1 shows a corroded steel tank that exploded while being charged in a New Jersey dive shop in 1968. This shop had fortunately placed a cinderblock wall reinforced with steel rods between the shop area and the compressor. The 3/8-inch iron water tank holding the cylinder blew into several dozen pieces and partly pulverized the back wall of the shop.

There was a study of 40 condemned-in-service steel scuba tanks, and an experiment which proved that water could enter tanks through single-hose regulators. Then a seawater internal-corrosion test program on six new steel scuba tanks was carried out at various pressures and at an elevated temperature for 100 days. This test, planned and carried out by Lieutenant Richard Peyser of the U.S. Coast Guard, then a Master of Science candidate at URI, convincingly showed the potential explosion danger of steel tanks used in salt water. His work thus gave impetus to a request to the Department of Transportation (DOT) by Luxfer USA, a subsidiary of a European aluminum cylinder manufacturer, to be allowed an exemption to DOT regulations; in 1970 these regulations did not allow interstate shipment of aluminum high-pressure air cylinders (Peyser, 1970).

Aluminum scuba cylinders have become generally available to civilians in this country during the past five years, and in 1976 the National Sea Grant Office of the Department of Commerce provided assistance to URI, in company with Luxfer USA and U.S. Divers Co., to do a corrosion study of aluminum cylinders under conditions similar to those used in the study of steel cylinders in 1970. The results of this study, which includes tests for both general internal corrosion and galling of the valve threads in the cylinder neck, are reported in Part II of this report.

During the years 1970 to 1975, the Scuba Safety Project gathered data on fatal diving accidents in the United States as part of a general mission to improve scuba safety. Out of 720 scuba-related fatalities, four deaths and two serious injuries could be attributed to compressed-air explosions or corrosion-produced accidents. In only one of these six cases did a diving cylinder blow up, and this was a U.S. Navy surplus 90-cubic-foot aluminum cylinder whose history was obscure, since these items were never released to the civilian market. Two accidents resulted from the failure of air-pumping station components—in one case an air-storage reservoir exploded, and in the other an oil filter on the high-pressure feed line. A third explosion involved a 150-psi-rated Hooka tank that was connected to a 2400-psi source. The two other corrosion-related accidents involved old scuba tanks that were so filled with rust and water that, in one case, only 3 percent oxygen remained (Schenck and McAniff, 1975), while in the other a half-inch of wet rust product jammed the regulator. Fortunately, most dive shops have a healthy and self-interested scepticism of battered and ancient scuba cylinders. The danger comes when the outside condition and date stamp do not reflect serious internal corrosion.

Part I.
Testing of Steel Scuba Cylinders

Condemned-in-Service Steel Cylinders

About 40 old scuba tanks that had failed either visual or hydrostatic tests in dive shops were solicited from several sources in 1970, the bulk (about 30) coming from the Florida area. Eight out of these 40 were selected for study as having the most advanced and/or interesting internal-corrosion patterns. Figure 2 shows sectioned halves of five of these cylinders. The internally coated tanks showed a variety of problems including uneven coating, local lack of coating, and corrosion occurring underneath the coating. Of the eight sectioned cylinders, two had relatively drastic corrosion. Figure 3 shows various wall sections of a tank manufactured in 1961 that had been internally coated with some form of epoxy overlay. This coating had disappeared in several places, and pits with depths of one-third the wall thickness were found as shown, some of them hidden under the coating that remained.

The wall sections in Figure 4 show the worst case of pitting in the 40 cylinders. This was an unevenly coated cylinder made in 1963, with corrosion damage heavy in the lower half. The detected thinning here was almost one-half the wall thickness, but deeper pits could have been present. Out of the eight sectioned cylinders, four had "large amounts" of rust, enough to plug or stop an air regulator if the diver maneuvered so as to bring the particles down over the regulator valve inlet extender.

Figure 1. Scuba tank that exploded while being charged at the M. & E. Marine Supply Co. A roughly circular area at the tank center let go, and the crack propagated toward the base and the valve end. This can be clearly seen by the slanted tears in the metal edge. The tank shows general corrosion, with much greater thinning at the point where the crack began. A handful of rust was in the tank.

Figure 2. Sectioned halves of five condemned-in-service steel cylinders.

This cursory study of "cylinders of opportunity" suggests a similar picture to that presented by the accidents noted in the previous section. That is, some cylinders may suffer dangerous wall thinning but will tend to be spotted before they explode. The valve-blocking danger from large amounts of loose rust in the tank may well be the more serious accident possibility stemming from tank corrosion.

Water Entry into Steel Cylinders

It was perfectly evident that some salt water had entered a number of the 40 condemned-in-service cylinders. Of course, humid air may leave a small amount of fresh water in a tank after charging, but this relatively benign intrusion cannot compare in corrosive activity with ordinary sea water. Some scuba repair stations queried in 1970 claimed that water would not enter a tank through a regulator and that sea water in a tank was rare. A simple experiment proved otherwise. Two single-hose regulators from different manufacturers were attached to empty (that is, open to the atmosphere) tanks. These were taken to a 10-foot depth in a swimming pool and their purge buttons pressed 10 times for about 10 seconds each time. One regulator admitted 195 ml of water and the other 211 ml. This experiment simulates the breathing-down of a tank on the surface, a dive to 10 feet, and attempting to get air by pushing the purge button. Clearly, a channel for water exists through single-hose regulators when the tank pressure, for whatever reason, is less than the ambient pressure. As a result of these experiments, we decided to use a 500 ml water sample in the test cylinders.

Steel Cylinder Corrosion Tests

The question of corrosion rate under controlled conditions is obviously central to any study of this problem. Six new uncoated cylinders were obtained from the same manufacturer and a small underground World War II ammunition bunker on the Narragansett Bay Campus was refurbished to hold the test cylinders in safety. In addition to the 500 ml of water in the test cylinder, a test temperature of 105°F was chosen as the highest sustainable temperature in the test room using electric heating on thermostatic control. Actual temperature in the space during all the tests to be described did not vary more than three or four degrees on either side of the set temperature. One hundred days was arbitrarily chosen for the exposure.

The six tanks were constructed of 4130 steel, as specified by DOT regulations for 3AA high-pressure cylinders. All tanks were equipped with chromed-brass K-valves and were purchased pumped to full pressure. When bled and examined internally with a borescope, it was evident that small patches of superficial corrosion already existed inside the tanks. While

Figure 3. Various wall sections from a tank manufactured in 1961. Some of these pits extend one-third of the way into the wall.

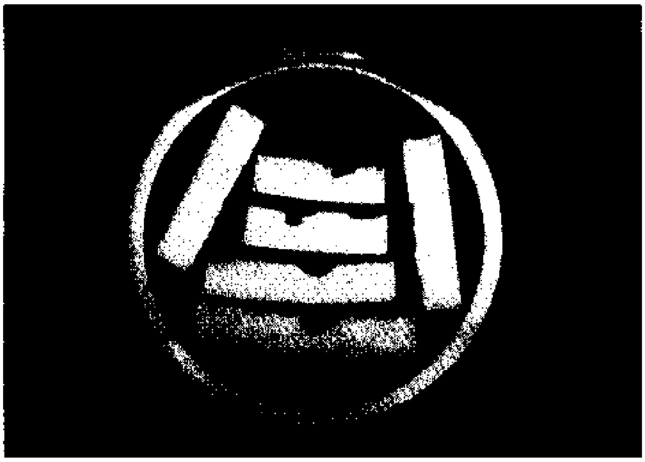

Figure 4. Various wall sections from a tank manufactured in 1963 that was unevenly coated. These were the deepest and most serious pits found in the condemned-in-service cylinders.

this was in no way a safety problem, it may have accounted for the corrosion differences noted between tanks receiving apparently identical treatments. Table 1 gives the test treatments for each cylinder. The manufacturer's numbers suggest that the first four tanks may have been made together, or from similar material, while the last two cylinders appear to be from a later lot.

The salt water was an artificial mixture, purchased to insure that future tests would be conducted with the same corroding agent. The fresh water was Narragansett tap water, a material that proved more complex than expected during the later aluminum tests. Mounting choice in Table 1 was really based on the typical storage attitudes that might be expected with scuba cylinders in stores and homes. Each cylinder had thermocouples attached, and the mean temperatures resulted from weekly readings.

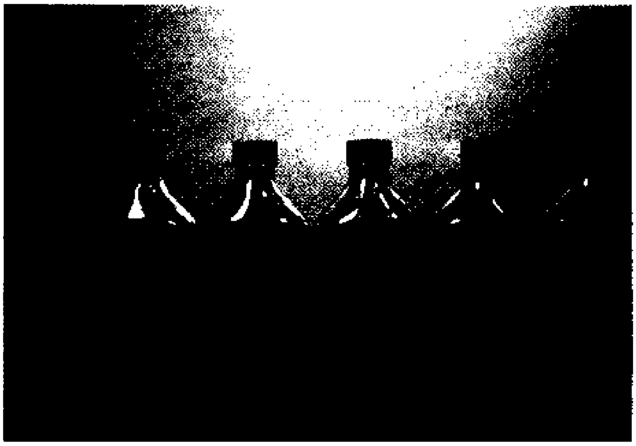

Figure 5. Water and filtered products from, left to right, Tanks 16026, 9535, 8422, 8464, 8390, and 8019. Almost no free water remained in 16026.

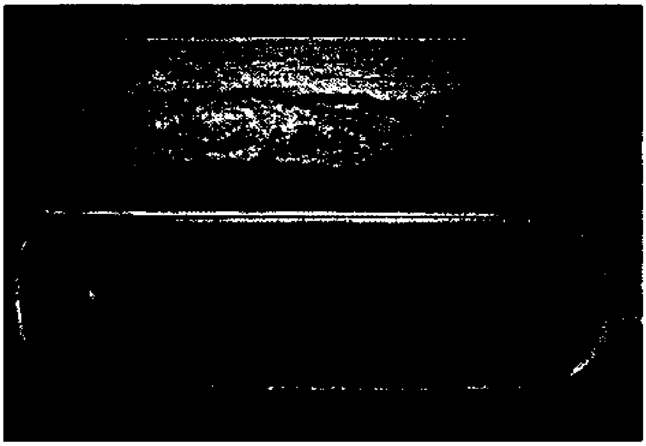

Figure 6. View of Tank 16026. Drastic corrosion damage occurred under seawater layer (upper half).

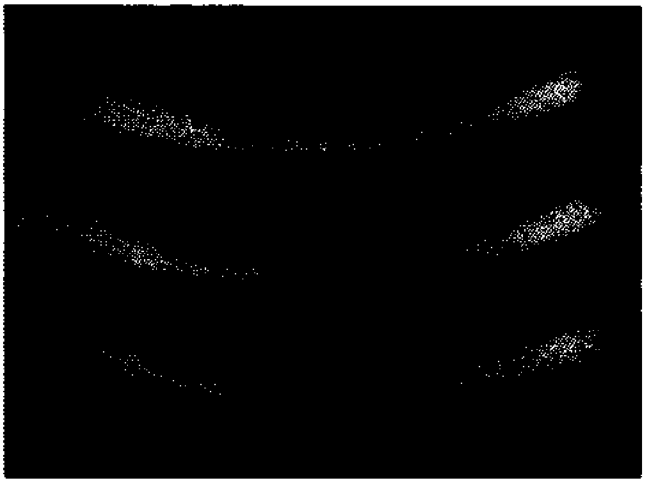

Figure 7. Wall sections from Tank 16026. The heavy product shown in Figure 6 was cleaned away, and this drastic wall thinning was discovered underneath it; up to two-thirds of the wall is gone. These deep craters are over one inch across and run the entire length of the cylinder.

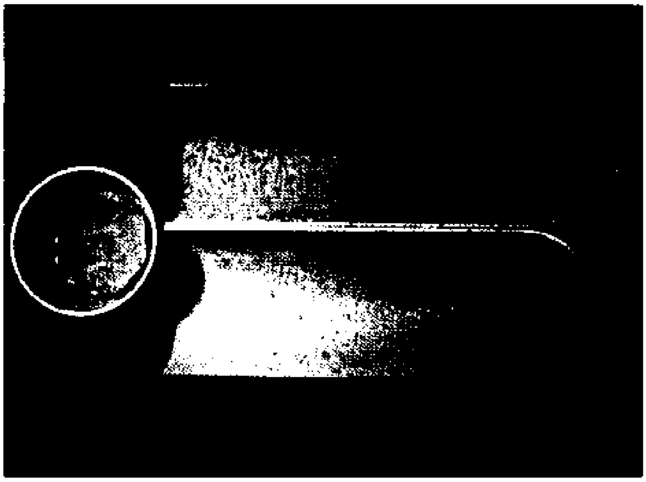

Figure 8. General view of Tank 8422. Corrosion is light except in bottom, where an extensive corrosion ring appeared.

At the end of the 100-day test, the cylinders were bled remotely, from outside the bunker, and the tanks carefully emptied. Figure 5 shows the result of pouring out what fluid remained in each tank and filtering this residue. Tank 16026 was so heavily corroded, Figure 6, that no free water remained, the water being entirely retained in the spongy corrosion product. Tank 9535, though given the identical treatment, showed both less corrosion and less water retention in the product.

Because the two freshwater tanks (8390 and 8464) had such minor corrosion, these were subjected to, and passed, a hydrostatic test, each giving less than the 10 percent remaining permanent expansion which, when exceeded, fails the cylinder (Compressed Gas Association, 1970).

Table 1. Exposure Test I — Initial Conditions of Steel Tanks (April 4, 1970–July 13, 1970)

Cylinder No.	*Water*	*Position*	*Pressure*	*Avg. Temperature*
8019	500 ml salt water*	vertical upright	100 psi	103° F
8390	500 ml fresh water	vertical upright	2200 psi	102° F
8464	500 ml fresh water	horizontal	2200 psi	104° F
8422	500 ml salt water*	vertical upright	2200 psi	103° F
9535	500 ml salt water*	horizontal	2200 psi	105° F
16026	500 ml salt water*	horizontal	2200 psi	104° F

**Artificial sea water: ASTM D, 1141, 52.*

Note: All tanks rated to contain 72 cu. ft. of air at 2475 psi.

As Table 2 shows, the horizontal cylinders with full pressure and salt water had by far the most dangerous corrosion. Figure 7, which shows wall thinning of two-thirds of the wall thickness, suggests that Tank 16026 could not have lasted much longer without an explosion. Yet Tank 9535, a replicate of 16026 as far as treatment is concerned, showed only about half the thinning and, as Figure 5 shows, less water absorption. The only explanation for these differences appears to lie either in the mild initial corrosion seen inside the tanks before the test or in the two tanks being somehow different as to steel lot, manufacturing methods, or something we did not detect.

Because water surface area obviously has a large effect in the rate at which this attack proceeds, Tank 8422, Figure 8, showed less wall thinning, although a complete and complex corrosion ring formed at the water surface to steel interface. The section, Figure 9, shows how the ring grows by depleting the parent metal beneath.

Tables 1 and 2 reveal the following: (a) corrosion is accelerated greatly under increased oxygen partial pressure; (b) corrosion is accelerated even more by the presence of sea, as opposed to fresh, water; and (c) any tank position that spreads the interior water into a large area will show much greater corrosion.

We can say, then, that steel scuba tanks should be: (a) stored with only enough excess interior pressure to keep out water and contaminants (say, 50 psi); (b) when opened for inspection, they should be washed internally with fresh water and dried; and (c) stored, if there is a choice, in a vertical, upright position. Removal of fresh water contamination by compressor filtering is far less important than keeping salt water out, or removing it after it gets in.

Table 2. Exposure Test I — Results

Cylinder No.	*Corrosion Damage*	*Hydro Test/Permanent Expansion*		*Sectioned*	*Avg. Wall Thickness Measured*	*Min. Wall After Test (in.)*	*Min. % of Avg. Wall Thickness*
8019	substantial	no	-	yes	.217″	.202″	93.1%
8390	minor	yes	5.36%	yes	(not recorded)		
8464	minor	yes	0.39%	yes	(not recorded)		
8422	severe	no	–	yes	.217″	.181″	88%
9535	very severe	no	-	yes	.179″	.096″	53.6%
16026	very severe	no	-	yes	.179″	.055″	28.7%

Part II.
First Test of Aluminum Scuba Cylinders

Selection of Test Treatments

In 1969 it was noted by U.S. Navy personnel at Indian Head, Maryland, that aluminum scuba cylinders, used because of their desirable magnetic properties, contained quantities of gelatinous corrosion products. An ensuing study by Battelle Memorial Institute and the Navy (Henderson et al., 1970) revealed the following:

a) By March 1970, 1623 aluminum cylinders had been inspected at naval diving facilities. Of these, 20.2 percent were considered to be moderately corroded and 4.4 percent severely corroded.

b) Analysis of the corrosion products showed an abnormally high level of fluorine, about .3 percent in some cases, which was sufficient to account for the observed corrosion.

c) Battelle estimated that the rupture strength had been reduced by 4 percent in the corroded cylinders and that they did not constitute an immediate personnel hazard.

These Navy tanks were made of a slightly different alloy (6061 T6) than those now used in civilian scuba tanks (6351 T6). The composition and properties of these alloys are shown in Table 3.

The Battelle findings, which appeared to place the blame for aluminum cylinder corrosion on the hydrofluoric acid that is sometimes used to clean aluminum, did not seem to pose safety problems for the sport-diving industry. By 1975, however, a problem involving neck galling—that is, the lock-up and destruction of aluminum neck threads when valve removal was attempted—had appeared. Thus, a study of aluminum corrosion similar to that undertaken with steel seemed advisable to establish just what kinds and rates of corrosion were possible.

Because of the new problem with neck corrosion and the known problems when aluminum and brass are immersed in an electrolyte, it was evident that some inverted tests would be necessary to place the water, brass valve extender, and aluminum neck in proximity. When the tank was inverted, however, it was noted that 500 cc of water covered the inside valve extender completely. To test for any area or surface effects, one tank was tested inverted and with 250 cc of water. The other inverted tanks had plastic extender tubes added which covered the upper one-quarter inch of brass, air-inlet, extender tubing, and prevented water loss when the tank valves were remotely opened to check tank pressure. Other conditions are shown in Table 4.

All of these test cylinders were sealed with standard chrome-plated brass K-valves, to which the manufacturer had applied a light coating of Molycote 557, a silicone lubricant. The brass extender tubes, which reached inches into the bottle, were not chromed but had a natural brass finish. The salt water was the same artificial mixture noted in Table 1 and the fresh water, again, was Narragansett tap water. All of the aluminum cylinders were rated to contain 72 cubic feet of air at 3000 psi.

One steel scuba cylinder of current manufacture was added to the test group for two reasons: we had not tried an inverted steel cylinder in the Table 1 treatment group, and it seemed reasonable to have a steel cylinder as a control so as to permit direct and unequivocal comparison between steel and aluminum tanks of current manufacture. Figure 10 shows some

Table 3. Chemical Composition Limits for 6061 and 6351 Aluminum Alloys

									*Other Elements***		
*Alloy**	*Si*	*Fe*	*Cu*	*Mn*	*Mg*	*Cr*	*Zn*	*Ti*	*Each*	*Total*	*Al*
6061	0.40–0.80	0.70	0.15–0.40	0.15	0.80–1.20	0.04–0.35	0.25	0.15	0.05	0.15	remainder
6351	0.70–1.30	0.50	0.10	0.40–0.80	0.40–0.80	—	0.20	0.15	0.05	0.15	remainder

**These designations were established in accordance with ANSI H 35.1.*

***Analyses shall regularly be made for the elements specified in this table. If, however, the presence of other elements is suspected or indicated in amounts greater than the specified limits, further analyses shall be made to determine that these elements are not present in amounts in excess of the specified limits.*

Note: Limits are in percent maximum unless shown as a range.

Source: American Society for Testing Materials. B 221-73. *Standard Specification for Aluminum Alloy Extruded Bars, Rods, Shapes, and Tubes. 1973 Annual Book of A.S.T.M. Standards.* Part 6: Die-Cast Metals; Light Metals and Alloys (Including Electrical Conductors). Easton: A.S.T.M., 1973. p. 180.

of the tanks mounted in the old ammunition bunker with remote-valving wires and gas tubing leading to pressure gauges outside the space.

Results of the First Aluminum Tests

Pressure was monitored during the 100-day test using remote wires to open and close the K-valves and remote gauges at the end of high-pressure tubing. During the 1970 steel tests, pressures measured at the end of the test had remained unchanged except for Tank 16026 (Tables 1 and 2), which lost only 90 psi of pressure, in spite of its huge amount of corrosion end product. We suspected, however, especially after the accident involving 3 percent oxygen mentioned in the introductory section, that the 1970 readings may have been the result of small and insensitive gauges. Unfortunately, we did not have access to air-analysis testing in 1970, so the true amount of oxygen left in the Table 1 tanks remains speculation.

At the end of the 1976 tests, the only tank that showed a significant pressure loss was 46343, of steel (see Table 4), which was down about 80 psi, after corrections were made for bleed-off losses due to periodic pressure-monitoring checks. When the air in Tanks 31622, 31700, and 46343 were tested by the Rhode Island Department of Health, the air in Tanks 31622 and 31700 (aluminum) showed 20.9 percent oxygen, 3.0 and 3.5 ppm carbon monoxide, and .03 percent carbon dioxide, but the steel tank 46343 showed 15.0 percent

Table 4. Exposure Test II — Initial Conditions (July 28, 1975-November 5, 1975)

Cylinder No.	*Water*	*Position*	*Pressure*	*Avg. Temperature*
30943 aluminum	500 ml salt water	vertical inverted	100 psi	105° F
31173 aluminum	500 ml salt water	vertical inverted	2200 psi	104° F
31365 aluminum	250 ml salt water	vertical inverted	2200 psi	104° F
31374 aluminum	500 ml salt water	vertical upright	2200 psi	105° F
31622 aluminum	500 ml fresh water	vertical inverted	2200 psi	105° F
31698 aluminum	500 ml salt water	horizontal	2200 psi	104° F
31700 aluminum	500 ml salt water	horizontal	2200 psi	103° F
46343 steel	500 ml salt water	vertical inverted	2200 psi	105° F

Note: All test cylinders were sealed with standard chrome-plated brass K-valves, to which the manufacturer had applied a slight coating of Molycote 557, a silicone lubricant. The aluminum test cylinders are rated at 72 cu. ft. of air at 3000 psi, and the steel test cylinder is rated at 72 cu. ft. of air at 2475 psi.

Figure 9. Close-up (1½ inches wide) of cross-section of corrosion ring in Tank 8422. Note that the ring grows by depleting the parent wall metal beneath it.

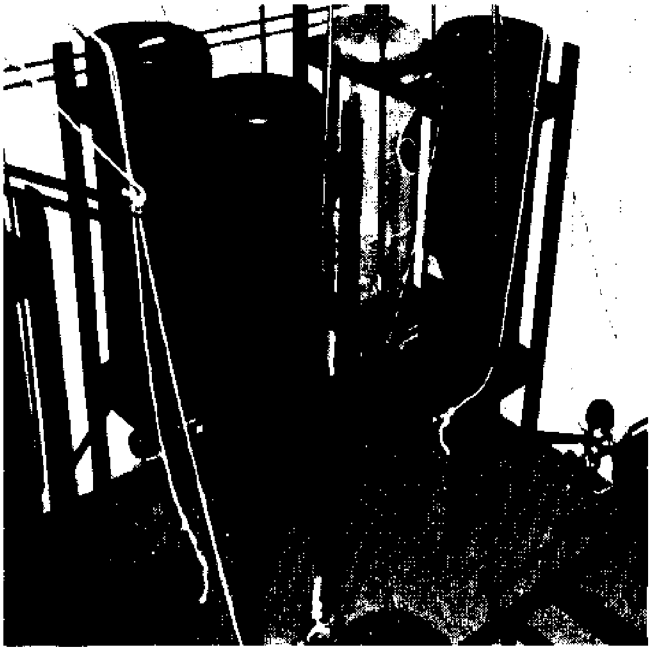

Figure 10. Setup of vertical test cylinders 30943, 31173, 31365, and 46343 in ammunition bunker.

oxygen, 10 ppm carbon monoxide, and .01 percent carbon dioxide. On the basis of this reduction of 20.9 percent to 15.0 percent oxygen due to corrosion, 46343 should have lost about 150 psi in tank pressure instead of the noted 80 psi, suggesting, again, that these gauges are not accurate at such high pressures and that the Table 1 tanks probably also suffered at least this percentage oxygen reduction. As a safety matter, the reduction to 15 percent oxygen is not as serious to the immediate health of the diver as the mass of heavy corrosion product that could have readily clogged his air inlet.

The state of steel cylinder 46343 readily confirmed the work of Lieutenant Peyser in 1970. Its minimum remaining wall percentage of 46.4 percent (see Table 5) was between the values for cylinders 9535 and 16026 in Table 2. A corrosion ring had completely covered the neck region, Figure 11, leaving only a hole through which the valve extender protruded. The entire interior was heavily attacked with large sheets of corrosion scale hanging on the walls. Based on the loss of oxygen, a production of about 1.5 pounds of rust was predicted—a quite reasonable estimate of the amount actually seen. Since this cylinder underwent much heavier attack than the vertical cylinder 8422 in Tables 1 and 2 (compare Figures 8 and 11), it is reasonable to suppose that the brass valve extender may have aided corrosive attack in the water-covered neck region (although these are not comparable cylinders as to either manufacturer or time of manufacture). The valve and its parts underwent no major attack, however, and the brass extender mainly showed discoloration.

194 ml of water was recovered from Tank 46343, which compares with 30 ml for Tank 16026, 110 ml for Tank 9535, and 280 ml for Tank 8422 in Tables 1 and 2.

Seawater corrosion studies never lack for surprises, but the results of the seven aluminum tank treatments shown in Table 5 seemed especially baffling. Three aspects stand out:

(1) Two tanks, 31173 and 31374, had their valve threads lock tight, with valve removal only possible by stripping the threads completely out with a pipe wrench. Yet these two tanks underwent negligible corrosive and pitting attack compared with Tanks 31365 and 31622. Furthermore, Tanks 31698 and 31700, which should certainly have showed effects similar to the upright tank, 31374, did not suffer the problem. A study of the valve threads on the several aluminum tanks revealed that 30943, 31698, and 31700 showed small amounts of corrosion products in the threads. Cylinders 31173, 31365, 31374, and 31622 all showed considerable white corrosion products either covering the threads or partly covering the lower threads. Although the fact that Tanks 31365 and 31622 did not jam their valves seems anomalous, this aluminum-tank-galling result clearly identified an important consumer problem, since we had succeeded

Please substitute this corrected table for table on page 12.

Table 5. Exposure Test II — Results

Cylinder No.	*Corrosion Damage*	*Hydro Test/ Permanent Expansion*		*Sectioned*	*Max Wall Penetration (%)*	*Pit Depth (in.)*	*Min. Wall Thickness (in.)*	*Min. Wall Remaining (%)*
30943	negligible	yes	1.54%	no	no pits		.467	100
31173	negligible*	no		yes	no pits		.467	100
31365	substantial	no		yes	14.58	.084	.467	100
31374	negligible*	no		yes	no pits		.467	100
31622	substantial	no		yes	7.12	.047	.467	100
31698	negligible	yes	1.48%	no	no pits		.467	100
31700	negligible	yes	0.32%	no	2.0 (max.)	.020 (max.)	.467	100
46343 steel	very severe	no		yes	58.6	.099	.151	46.4

Note. Despite the negligible corrosive attack, these cylinders had their valves locked in place due to a formation of corrosion products between the mating threads. This problem, defined as a form of galling, led to the third exposure test.

Also, in all test cylinders the average wall thickness is substantially greater than the minimum allowable wall thickness. Therefore, it is possible for a pit to penetrate a percentage of the wall thickness and leave 100% of the minimum wall remaining.

in jamming a quarter of our sample by a single, saltwater exposure. Further, there can be little doubt that the locking or galling was corrosion-related and not, as some had suggested, the result of thread distortion or temperature effects. This result led to a third test, which is discussed in Part III.

(2) The worst attack was suffered by 31365, the tank with the least water (250 ml). At first glance unusual, this result is readily explained. This tank had the brass valve stem, water surface, and high-pressure oxygen in direct contact. In the case of Tanks 30943, 31173, and 31622, oxygen would have to diffuse through about 1.25 inches of water to reach the brass extender, whereas the attack on 31365 was immediate and continuous. The literature on galvanic couples (Evans, 1960, and Uhlig, 1963) notes that when connecting a cathodic metal to a corroding metal, the corrosion rate will not increase as long as the cathode is completely submerged, since the corrosion rate is now controlled by the diffusion rate of oxygen from the surface.

Figure 11. Close-up of the neck section of test cylinder 46343. Note the large corrosion ring. The hole in its center was caused by the plastic valve extender which protruded through the water-gas interface.

Another accelerating effect in 31365 was the direct corrosion of the brass extender and the resulting continual introduction of copper ions into solution. The combination of anionic species contained within the salt water, such as chloride and bicarbonate ions (present as NaCl and $NaHCO_3$), dissolved oxygen, and copper ions, will have a synergistic effect, thus increasing the overall rate of attack (Becerra and Darby, 1974; Porter and Hadden, 1954; and Davies, 1959). Corrosion of the actual brass was verified by running X-ray fluorescent patterns on the corrosion products removed from the brass extender (see Figure 12). The results showed these products contained substantial quantities of both copper and zinc. In addition, copper depositions were found throughout the entire wetted surface area of 31365 as brown or reddish-brown stains, indicating areas where the copper had actually plated out on the aluminum (Figure 13).

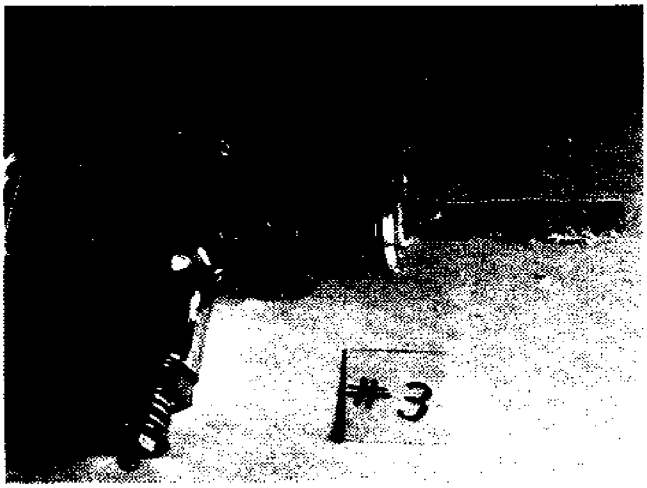

Figure 12. Valve of test cylinder 31365. Note the accumulation of corrosion products on the brass extender and within the threads.

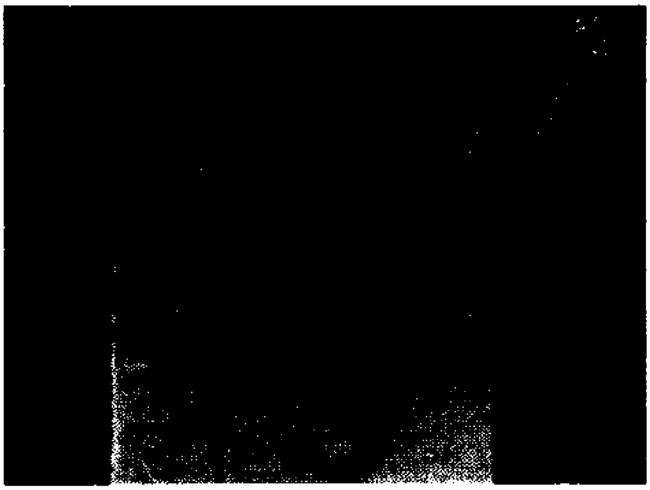

Figure 13. Immediate neck section of test cylinder 31365. The deepest pit within this cylinder is shown in the center of the photograph with many "satellite pits" surrounding it. Copper depositions, the reddish-brown stains, can readily be seen on the aluminum surface, especially near the pit formations.

(3) Cylinder 31622, which contained fresh water, was the only other aluminum cylinder to show significant pitting. This surprising result was soon explained when it was noted that reddish-brown stains appeared in the neck area similar to those found in 31365. A new sample of Narragansett tap water was analyzed by the Rhode Island Nuclear Science Center located at the URI Narragansett Bay Campus by atomic absorption spectrophotometric analysis. The results showed the water contained the very high value of 180 ppb (.18 ppm) of copper. Further, water-quality data on this local water gave maximum concentrations for the

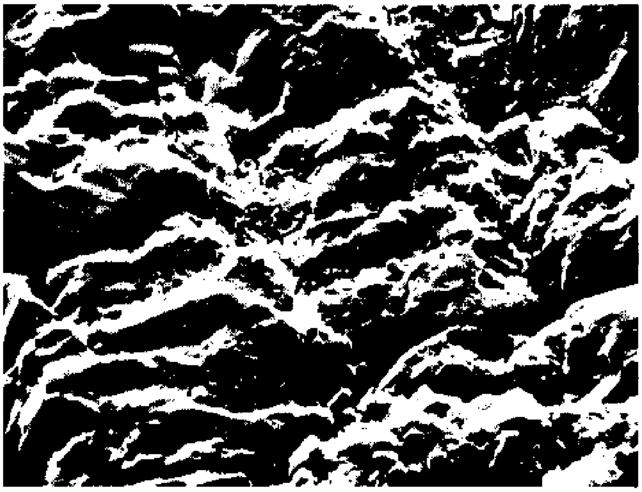

Figure 14. A sample of the flaws in the anodized oxide film, taken with a scanning electron microscope at 500X. Similar flaws were observed in all samples, generally taken from the immediate neck sections.

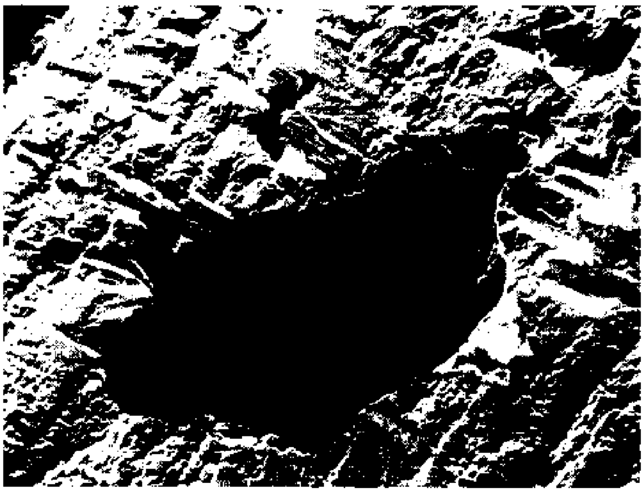

Figure 15. Overall view of pit in Tank 31365, using a scanning electron microscope at 50X. Note the initiation of pits at major flaws in the oxide film.

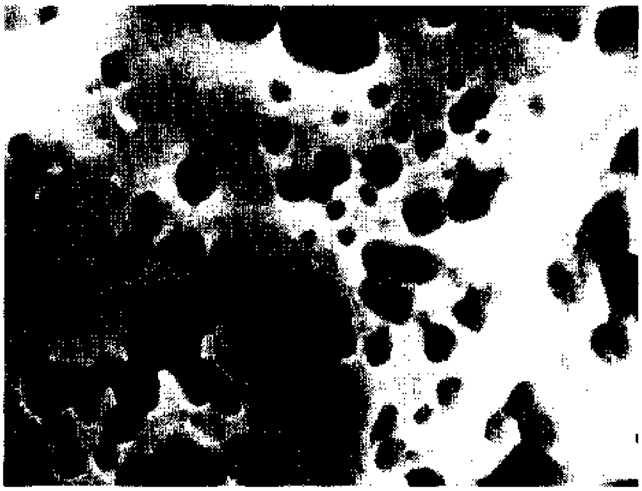

Figure 16. Characteristic bottom structure of the aluminum pits, taken with a scanning electron microscope at 5000X. The many small pits present at the very bottom of the pit appear to initiate and guide further growth. This pattern of attack was observed in all aluminum pits studied with the SEM, regardless of their location.

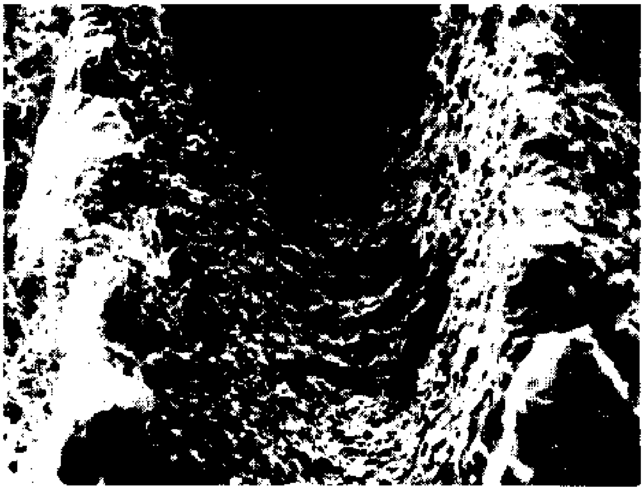

Figure 17. Exposed threads in Tank 31365 (scanning electron microscope at 50X). Since the exposed threads were virtually adjacent to the brass valve, which had an easily accessible supply of oxygen, the extensive corrosive damage can be attributed to galvanic corrosion.

chloride ion of 1 ppm; the calcium ion, 40 ppm; the bicarbonate ion, 40 ppm; and a pH of about 6.5. These species, combined with the copper, provided a very aggressive environment for Tank 31622. Unlike 31365, Tank 31622 did not have an easily accessible supply of oxygen, and thus the supply of copper ions introduced with the water probably were depleted, while the copper depositions became covered with corrosion products and lost their cathodic efficiency. Thus, Tank 31365 was probably maintaining or accelerating its rate of corrosion, whereas the damage in 31622 may have been done early in the 100-day test, yet both effects were related to the presence of copper ions.

Photographic Studies of Pitting and Dezincification

All seven aluminum cylinders in the Table 4 test had an interior anodized coating produced by the cylinder manufacturer using a proprietary method. Figure 14 shows the character of this coating at 500X magnification. It averaged about one-thousandth of an inch in thickness, but cracks, some of which pierce the film, can be seen. Figure 15, showing one of the larger pits in Tank 31365, at 50X, suggests that damage starts where major flaws in the film, shown at the top and right of the photo, may initiate pitting. When the bottom of the Figure 15 pit was examined under the high magnification of 5000X, tiny new pits, already joining to form crevices, could be seen (Figure 16), and this condition was found in all the pits so studied in cylinders 31365 and 31622.

The two lowest of the exposed aluminum threads in cylinder 31365 are shown in Figure 17, and here the surface is a continuous formation of pits. Clearly, no amount of future oxidation would be likely to passivate this surface.

When the brass valves of Tanks 31173 and 31374 were sectioned and etched, obvious dezincification could be seen in their threads. Tank 31173's valve showed this in its most pronounced form (Figure 18, dark area), where the top of the lowest engaged thread is sectioned. The distortion of this thread by removal attempts is also apparent, as well as its broken chrome plating.

The brass valve of an aluminum scuba cylinder that had been sent to the Scuba Safety Project by an Ohio diver because it had galled and then stripped out the lower three aluminum threads on valve removal was sectioned and etched. As Figure 19 shows, a similar pattern of dezincification was found in this "failed-in-service" cylinder. From these studies it appeared that both the valve and the aluminum tank neck undergo attack and that, as already suggested, the valve galling is corrosion-related.

Figure 18. Dezincification of valve in Tank 31173 (light microscope at 100X). Shown is the top of the last thread which has been etched in order to show the characteristic microstructure associated with two-phase brass (40% Zn, 60% Cu). The reddish-brown areas mark the locations where dezincification took place. The silver-colored outline is the chrome coating. Also note the small pieces of chrome, brass, and aluminum which apparently broke off under the applied torque.

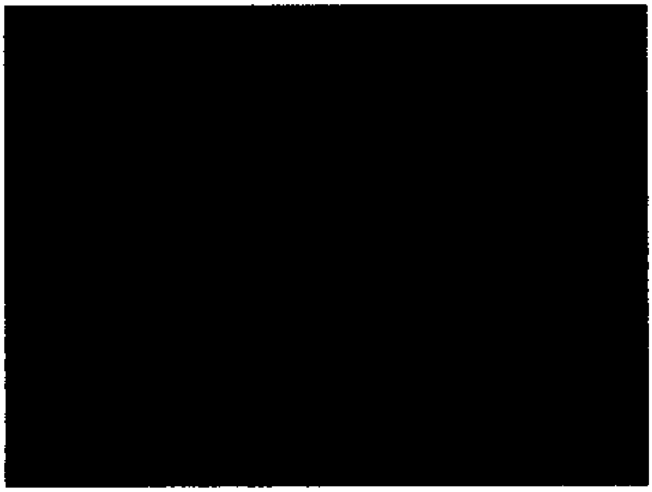

Figure 19. Dezincification of valve in Tank 31173 (light microscope at 100X). This is the bottom of the second thread, which has been etched to show microstructure. A fair amount of dezincification has taken place. In the center of the picture can be seen aluminum that was literally "deposited." Also note the deformation of the thread and the cracks in the chrome coating caused by the applied torque.

None of this evidence points to a safety problem with aluminum, however, since the worst pitting under the most unrealistic and corrosive treatment of Tank 31365 is still modest and would almost certainly not have affected Tank 31365 as regards its ability to pass a hydro test. The dramatic differences between the results of Lieutenant Peyser in 1970, in Table 2, plus the single steel tank, 46343 in Table 5, and the results of the worst aluminum cases, 31365 and 31622, suggest that if explosion or valve-clogging by-product is ever to occur with aluminum scuba tanks, it will result from interior conditions or treatments that we have not yet imagined. On the other hand, the sensitivity of aluminum corrosion to trace elements, such as copper, in a corrosive and saline atmosphere does suggest consumer caution when cleaning out aluminum tanks. Steam cleaning and hot-air drying is probably the most benign treatment, and the user should rigorously avoid fluorine compounds, which caused the Navy aluminum tanks to corrode, or any other chemical on which high-pressure-oxygen tests in a saline atmosphere have not been carried out.

Part III.

Second Test of Aluminum Scuba Cylinders — Galling Experiment Study of the Corrosion Product

The destruction of neck threads during valve removal does not, at first glance, seem to offer any safety problem. In fact, if civilian purchasers cannot be convinced that aluminum cylinders will withstand valve removal, they will continue to use the less safe steel tanks, and these, of course, get older and thinner as the years pass. Thus, a study of the aluminum corrosion product and a second exposure test were undertaken to find ways of reducing any aluminum oxide and to protect the neck threads from this galling material.

The predominantly white product was scraped off the threads of Tanks 31173 and 31374, the two galled tanks in the first aluminum test. X-ray diffraction showed the product to be entirely amorphous in nature. X-ray fluorescence showed an abnormally high level of zinc, thus exactly confirming the visual evidence of dezincification shown in Figures 18 and 19. The Nuclear Science Center subjected the product to neutron activation analysis, which showed a substantial quantity of aluminum, with minor traces of sodium, chlorine, manganese, and magnesium. Referring to Pourbaix diagrams (Pourbaix, 1966) for aluminum and zinc with a pH of around 8.2 (natural sea water), the predicted corrosion products are $Al(OH)_3$ and $Zn(OH)_2$, both of which are white in color and can be amorphous in nature. Such products can generate up to 10,000 psi in constricted regions (Fontana, 1967) and are able to stop all motion in these tanks until the aluminum threads strip out. The evident problem is that very little corrosion need occur, in an absolute sense, to ruin the tank.

Treatment Choices in the Second Aluminum Test

Table 6 shows the treatments chosen for the next six aluminum cylinders, the intent being to attempt overall reduction in corrosion activity and to make a preliminary assessment of three valve thread lubricants, as shown. Treatment for Tank 27247 was an exact replicate of Tank 31365 in the first test, and all tanks now contained 250 ml of water. Cylinders 27853 and 27264 had two improvements: their valve extenders were plastic and their threads were teflon-coated. Cylinders 26862 and 27237 had both K-valves and extenders made of 6061 T6 aluminum alloy, completely anodized except for the valve extender. Cylinder 155A had a standard brass valve and extender modified with two O-rings to attempt to prevent water from reaching the threads, a device provided for the test by one of our sponsors, U.S. Divers Co. The three thread lubricants were distributed as shown in Table 6. Cylinders 27247 through 27237 were 50-cubic-foot cylinders rated at 3000 psi, and Cylinder 155A was an 80-cubic-foot 3000-psi cylinder.

Results of the Second Aluminum Test

Cylinder 27247, the replicate of 31365 in the first test, showed a substantial pitting attack similar to that seen in the first aluminum test, with a maximum pit about 20 percent greater than that found in 31365, as can be seen in Table 7. Cylinder 155A, which had the same brass extender as 27247, showed similar attack. When compared with the other four tanks, 27853 through 27237, it is clear that this small brass extender is a primary source of corrosion activity in aluminum scuba tanks.

Since all the tanks could be opened, it was not pos-

Table 6. Exposure Test III — Initial Conditions (August 5, 1976–November 13, 1976)

Cylinder No.	*Avg. Temperature*	*Lubricant*	*Valve Description*
27247 aluminum	102°F	High Purity Goop	standard chrome-plated brass K-valve
27853 aluminum	104°F	Molycote 557	standard brass K-valve • chrome-plated except threads • threads coated with teflon • valve extender was plastic
27264 aluminum	103°F	High Purity Goop	same as valve of 27853
26862 aluminum	105°F	High Purity Goop	standard aluminum K-valve • 6061 T6 aluminum alloy • completely anodized, including the valve extender • G 05704 (serial number)
27237 aluminum	103°F	Dow Corning III	same as valve of 26862 • G 05691 (serial number)
155A aluminum	104°F	High Purity Goop	same as valve of 27247 • 4-inch-long brass valve extender. This valve seated into the female end of a male-female adapter. The male end, which was seated into the tank, had a double O-ring seal designed to prevent any electrolyte from reaching the brass aluminum joint.

Note: All test cylinders contained 250 ml of salt water, were tested in the vertical, inverted position, and pressurized at 2200 psi. Test cylinders 27247 through 27237 contained 50 cu. ft. of air at 3000 psi and test cylinder 155A contained 80 cu. ft. of air at 3000 psi.

Table 7. Exposure Test III — Results

Cylinder No.	*Corrosion Damage*	*Hydro Test/ Permanent Expansion*		*Sectioned*	*Max. Wall Penetration (%)*	*Pit Depth (in.)*	*Min. Wall Thickness (in.)*	*Min. Wall Remaining (%)*
27247	substantial	yes	4.52%	yes	15.59	.118	.467	100
27853	negligible	yes	3.72%	no	no pits		.467	100
27264	negligible	yes	3.46%	no	3.5 (max.)	.020 (max.)	.467	100
26862	negligible	yes	1.39%	no	1.75 (max.)	.010 (max.)	.467	100
27237	negligible	yes	3.42%	no	3.5 (max.)	.020 (max.)	.467	100
155A	substantial	yes	1.30%	yes	12.64	.078	.488	100

sible to make an assessment of possible differences among the lubricants. However, since much more attention was paid to thread lubrication in this second aluminum test, the results suggest it is this fact, rather than any specific lubricant characteristic, which contributed to the relatively easy removals.

Tanks 27853 and 27264 had the most difficulty in valve removal, since the teflon-thread protection came off and jammed in the threads. As suggested, it is probable that the plastic extender, rather than the teflon, reduced the corrosion activity in these two cylinders. Tanks 26862 and 27237 show a similar low activity.

It is our belief that present brass scuba K-valves could be made much more inert by simply covering the brass extender with some tight-fitting and inert plastic tube. This reduction in brass area should make pit initiation a far longer process than found in these tests. However, the dezincification and in-threads aluminum corrosion would not be affected too greatly, so heavy amounts of thread lubricant are also probably required.

Lubricants might present a possible health problem because their behavior under long-term high oxygen partial pressure is not understood. One of the common complaints of divers involving aluminum tanks is the "smell" and "taste" of the air, especially after long storage periods. This appears to be the result of volatile agents in the lubricant mixing in the breathing air. This problem can be eliminated by allowing two to three hours between application of the lubricant to the valve and insertion of the valve into the cylinder. This effect is not, in our opinion, of the same urgency and damage potential as the accumulation of old rusting steel tanks. The aluminum tank, especially if it is given proper care, should certainly outlast the steel tank by several lifetimes.

Conclusions

These three tests give ample evidence that the present aluminum scuba tanks offer unparalleled safety in the containment of high-pressure air under the stringent environmental requirements of scuba diving. If the aluminum tank is carefully cleaned, the brass K-valve extender covered as noted earlier, and the neck threads liberally and carefully covered with a proper lubricant, there is no reason why the tank should not last through several generations of a diving family. The use of aluminum valves in aluminum tanks would appear to almost eliminate corrosion problems except under the most exceptional conditions of saltwater exposure.

Aluminum tanks, on the basis of these tests, should be stored on their sides (first preference) or upright (second preference), but never inverted. Since any corrosion attack is less in reduced oxygen partial pressures, the reduction of tank pressure in aluminum tanks is desirable but by no means as important as in long-term storage of steel scuba tanks. When practical, valves of stored aluminum tanks should be left partly unscrewed. Nothing that could get into a stored tank with an open end could possibly damage it as much as having a tight valve gall in place.

Steel tanks should be stored at minimum (50 psi) pressure, upright if possible, and the interior should be checked at least annually, and perhaps as often as every three months if service involves tropical conditions and/or very frequent use. Any time a diver breathes down his tank in the water to local pressure, there is a good chance that water may have entered. Whether of steel or aluminum, the tank should be opened and washed out with fresh water, then thoroughly dried.

The fact that very few injuries and deaths are caused by scuba tank corrosion is quite remarkable, considering the highly corrosive nature of salt water and oxygen at such high pressures. However, no steel tank is getting any younger; replacing them with aluminum tanks would appear, on the basis of these several tests, to offer even surer defense against a compressed-air explosion in a crowded dive shop or university gymnasium.

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Corrosion of Steel and Aluminum Scuba Tanks