

Acceptability of Aluminum Alloys for OTEC Heat Exchangers

The following was extracted verbatim from the Argonne National Laboratory (ANL) report "*OTEC Biofouling and Corrosion Study at the natural Energy Laboratory of Hawaii 1983-1987*" by C.B. Panchal et al, October 1990, ANL/ESD-10.

The test results were encouraging by showing that aluminum can be used in the manufacturing of Heat Exchangers (HXs) for closed cycle OTEC systems and that properly chosen alloys could achieve a life expectancy of 30-years.

Corrosion Mechanisms

A two-stage model is generally evoked to explain sea-water corrosion of aluminum. During the first stage, the uniform-corrosion rate is assumed to be a constant that is a characteristic of the metal. The second stage of corrosion is initiated when the corrosion product film starts to form. The second-stage process becomes the prevailing mode of corrosion after the seawater-saturated aluminum-oxide corrosion-product film is completely formed. During the second stage, the uniform-corrosion rate is assumed to approach an asymptote that is a characteristic of the diffusion barrier created by the corrosion-product film.

The ANL project showed that the Aluminum alloys tested exhibited two markedly different stages of corrosion in warm seawater, with the second stage prevailing after 200 days of exposure. In cold seawater, the alloys exhibited less well-defined stages of corrosion. The second-stage warm water corrosion rate is more than two orders of magnitude less than the first-stage warm water corrosion rate, whereas the second-stage cold-water corrosion rate is only one order of magnitude less than the first-stage cold-water corrosion rate. A corrosion-product film is formed on aluminum alloys in cold seawater; however, it provides less corrosion protection to the base metal than does the film on aluminum alloys exposed to warm seawater.

Acceptability of Aluminum Alloys

The principal issues in selecting materials and appropriately related designs for OTEC HXs exchangers are cost and service life. Titanium would clearly be preferred -- it does not corrode in seawater, it has high strength-to-weight ratios, and it offers unquestioned 30 year life -- were it not for its cost. Aluminum alloys offer the lowest initial cost; however, aluminum corrodes in seawater. The question then becomes one of the life expectancy of aluminum HXs in an appropriate application as that expectancy affects the overall system cost.

Satisfactory integrity of OTEC heat exchangers can be maintained only when localized corrosion produces no pits that penetrate the heat-exchanger seawater passage walls. The idea behind protecting the surface of aluminum-alloy heat-exchanger elements with zinc-rich alloys is to provide a sacrificial material that will protect the core alloy from pitting corrosion. Therefore, Zinc-protected tubes were assumed to be acceptable when the depth of localized corrosion pits did not penetrate the cladding. Given the great variability in the depth of pits observed even for a single alloy and the lack of a strong

Acceptability of Aluminum Alloys for OTEC Heat Exchangers

correlation between pit depth and time of exposure, a conservative criterion for localized corrosion was assumed to be that the acceptable depth of pits in both bare aluminum-alloy tube walls and zinc-protected tube walls be no greater than $150 \mu\text{m}^1$.

Acceptability in Warm Seawater

These data predict that brushed or unbrushed OTEC HXs, composed of any of the bare or Zinc-protected alloys that were tested, would experience acceptable amounts of uniform wall-thickness loss as well as pitting (or localized corrosion) if they were to be operated for 30 years in warm seawater.

Acceptability in Cold Seawater

All unbrushed bare alloys and Alclad tubes exposed to cold seawater had projected 30 year uniform wall-thickness losses of $200 \mu\text{m}$ or less, which is approximately one-half the maximum allowable wall-thickness loss of $380 \mu\text{m}$ and is therefore acceptable.

However, until the rate of wall-thickness loss of brushed bare alloys, or the rate of wall-thickness loss of Alclad alloys brushed after the cladding has been removed by corrosion or erosion, is established, it should be conservatively assumed that cleaning by bristle brushing will produce accelerated loss of thickness of Alclad tube walls due to corrosion and that this loss would exceed the maximum allowable wall-thickness loss of $380 \mu\text{m}$ in 30 years.

Infrequent and shallow localized corrosion or pitting was observed for the unbrushed bare alloys, and no pitting was observed in brushed samples.

A conservative posture dictates that unbrushed Alclad tubes are not acceptable for use in cold seawater.

Conclusions

All the tested materials, with and without brushing, would be acceptable for use in warm seawater. In cold seawater, the bare alloys would be acceptable, but neither the unbrushed nor the brushed Alclad alloys would be satisfactory materials. (See Figure reproduced in p.5 and Table given in p. 6)

Additional conclusions derived from the Argonne National Laboratory test conducted in 1983-1987 at NELHA were as follows:

¹ μm (micrometer): 10^{-6} meters

Acceptability of Aluminum Alloys for OTEC Heat Exchangers

Biofouling

- On a long-term basis, there was no significant difference in the rate of biofouling on aluminum alloys and on corrosion-resistant materials (e.g., stainless steel and titanium) in the tropical seawater used in the tests.
- Biofouling deposition on aluminum alloys in cold seawater was negligibly small, as shown by the biofilm analysis.
- For aluminum alloys, chlorination at 70 to 100 ppb applied for one hour per day was adequate to maintain the biofouling resistance to an acceptable level in warm seawater (OTEC Evaporator). No chlorination required in cold seawater (OTEC Condenser).
- The level of chlorination required for aluminum alloys was about 30% greater than that required for corrosion resistant materials (stainless steel and titanium) to maintain the biofouling resistance within a comparable value.

Corrosion

- For all the alloys tested in warm seawater, the corrosion behavior could be characterized as uniform wall loss, with minimal localized attack (i.e., pitting). In addition, flow interruptions had minimal effects on the rate of corrosion.
- After initial high values, the corrosion rate reached an asymptotic value after about 200 days in warm seawater and after about 100 days in cold seawater.
- The asymptotic corrosion rates in warm seawater for bare and clad alloys were comparable, in the range of 1.7 to 2.5 $\mu\text{m}/\text{yr}$. However, the total wall-thickness loss during the initial stage of fast corrosion varied with particular alloys.
- The asymptotic corrosion rates in cold seawater for bare and clad alloys were comparable, in the range of 3.5 to 6.5 $\mu\text{m}/\text{yr}$. However, as in the warm-seawater experiments, the total wall-thickness loss during the initial stage of fast corrosion (although relatively small) varied with particular alloys.
- For aluminum alloys tested, the expected wall thickness losses in 30 years due to uniform corrosion in warm and cold seawater were in the ranges of 56 to 84 μm and 108 to 198 μm , respectively.
- Periodic (on average, monthly) brushing accelerated the rate of corrosion in both warm and cold seawater.

Acceptability of Aluminum Alloys for OTEC Heat Exchangers

- No severe localized pitting corrosion was observed for aluminum alloys tested in warm seawater.
- Cold-seawater experiments produced mixed results with regard to localized corrosion; Al-5052 showed good resistance, while Alclad materials showed severe pitting. In most cases the pitting corrosion for Alclad samples was confined to the cladding thickness; however, selected samples showed penetration beyond the cladding. Loss of cladding in masses was also observed, which casts doubt upon the reliability of cladding in cold-seawater applications.
- Bare and diffused-zinc Al-3003 showed adequate resistance to localized corrosion in cold seawater. However, initiation of pits indicated the relatively small margin of safety for the long-term service of these alloys. No apparent trend in pit growth (depth and diameter) could be established based on the present set of data.
- Brazed joints fabricated using commercial fluxes have a good chance of success in warm seawater. However, they cannot survive in cold seawater. The analysis showed that the aluminum-phase from the joint was corroded away in cold seawater, leaving behind silicon-rich dendrites. This made the joint weak and porous to the penetration of corrosion deep into the brazed joint. It should be noted that the long-term effects of ammonia on the brazing alloy were not evaluated in the program; appropriate tests should be carried out before brazing joints are qualified for OTEC applications.

RECOMMENDATIONS

The ANL report provided suggestions regarding future research directions for further reducing the technical uncertainty in using aluminum alloys for OTEC heat exchangers.

The following recommendations were offered:

- Use of aluminum alloys with seamless flow channels in warm seawater has low risk and can be recommended, based on the present data base.
- Use of aluminum alloys in cold seawater does entail some risk; however, with proper design and good operating practice, these alloys can be considered as heat-exchanger materials with a potential life expectancy of 30 years.
- Alclad tubes should not be considered as a first choice of material. However, low-cost diffused-zinc coatings can be evaluated for protecting aluminum alloys in cold seawater.

Acceptability of Aluminum Alloys for OTEC Heat Exchangers

- Infrequent brushing (e.g., once every one to two years) or high water flow is recommended to remove debris from the surface and reduce the risk of localized corrosion (i.e., pitting).
- Future research on seawater corrosion of aluminum alloys for heat-exchanger applications should include the following:
 - Experimental data for optimized flow channels for compact heat exchangers, including brazed joints;
 - Flux development for brazed joints in seawater;
 - Characterization of other bonding techniques (e.g., pressure bonding and epoxy-bonded aluminum alloys);
 - Fundamental investigations to understand the differences in corrosion behavior of aluminum alloys in warm and cold seawater; and,
 - Validation of the single-channel data with experimental results for a modular test-unit that incorporates design features of prototypical heat exchangers, including the water box.

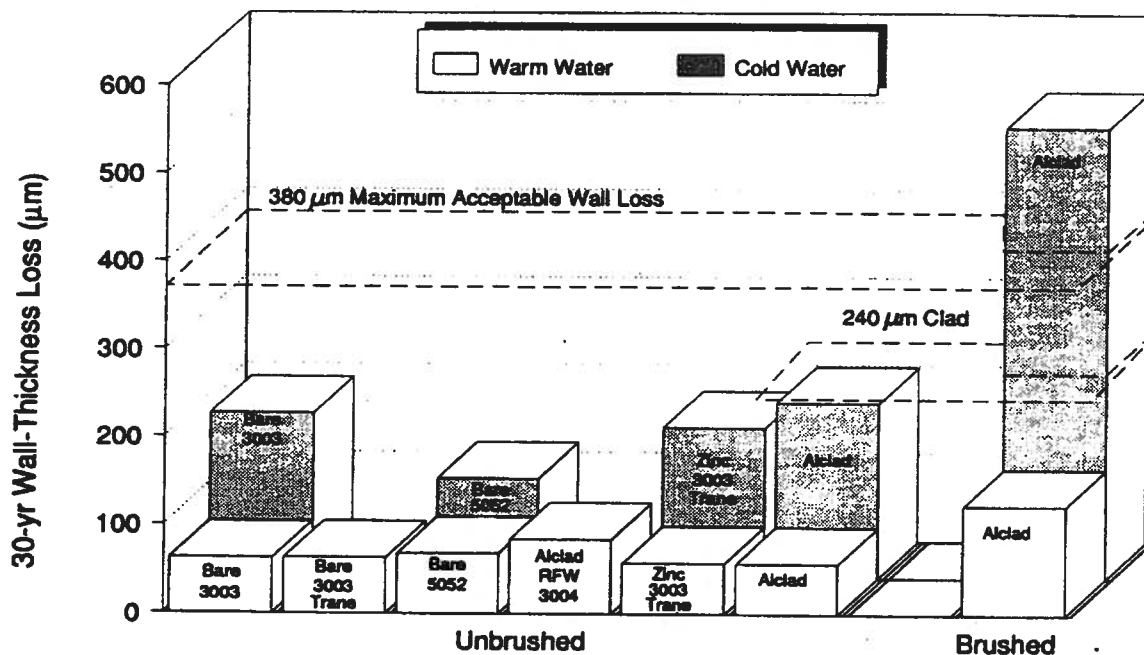


FIGURE S-1 Wall-Thickness Loss for Candidate Aluminum Alloys

Acceptability of Aluminum Alloys for OTEC Heat Exchangers

Environment	Material	Comments	Conclusions
Warm Seawater	Bare Al-3003 Drawn or Brazed Elements	No pitting of drawn tubes; some pitting at joints of brazed elements.	Acceptable
	Bare Al-3003 Trane Extrusions	No pitting.	Acceptable
	Bare Al-5052 Drawn Tubes	No pitting.	Acceptable
	Alclad 3004 RFW Tubes	Small percent of sampling showed pitting, which was confined to cladding.	Acceptable
	Diffused-Zn Al-3003 Trane Extrusion	Shallow pitting, evidence of cathodic protection.	Acceptable
	Alclad Drawn Tubes	Infrequent, shallow pitting.	Acceptable
	Alclad Brushed Drawn Tubes	No pitting.	Acceptable
Cold Seawater	Bare Al-3003 Drawn Tubes	Some samples showed initiation of pitting.	Acceptable with caution
	Bare Al-5052 Drawn Tubes	No pitting.	Acceptable
	Diffused-Zn Al-3003 Trane Extrusion	Some samples showed pitting.	Acceptable with caution
	Alclad 3004 RFW Tubes	Pitting penetrated cladding; cathodic protection occurred.	Welding process adversely affects cladding.
	Alclad Drawn Tubes	Severe pitting. Cathodic protection occurred. Lost cladding.	Unacceptable
	Alclad Brushed Drawn Tubes	No severe pitting.	Acceptable