Corrosion of Heat Exchanger Materials under Heat Transfer Conditions

R.L. Tapping, P.A. Lavoie, and D.J. Disney
System Chemistry and Materials Branch
Chalk River Nuclear Laboratories
Chalk River, Ontario

Abstract

Severe pitting has occurred in moderator heat exchangers tubed with Incoloy-800 in Pickering Nuclear Generating Station. The pitting originated on the cooling water side (outside) of the tubes and perforation occurred in less than two years. It was known from corrosion testing at CRNL that Incoloy-800 was not susceptible to pitting in Lake Ontario water under isothermal conditions. Corrosion testing with heat transfer across the tube wall was carried out, and it was noted that severe pitting could occur under deposits formed on the tubes in silty Lake Ontario water. Subsequent testing, carried out in co-operation with Ontario Hydro Research Division, investigated the pitting resistance of other candidate tubing alloys: Incoloy-825, 904 L stainless steel, AL-6X, Inconel-625, 70:30 Cu:Ni, titanium, Sanicro-30 and Sanicro-28.[1] Of these, only titanium and Sanicro-28 have not suffered some degree of pitting attack in silt-containing Lake Ontario water. In the absence of silt, and hence deposits, no pitting took place on any of the alloys tested.

Résumé

De fortes piqûres de corrosion se sont produites dans les échangeurs de chaleur à tubes d'Incoloy-800 du circuit de modérateur de la centrale électronucléaire de Pickering. Les piqûres ont pris naissance du côté eau de refroidissement (extérieur) des tubes et il y a eu perforation en moins de deux ans. On sait, d'après les essais de corrosion effectués aux LNCR, que l'Incoloy-800 n'est pas susceptible aux piqûres de corrosion dans de l'eau provenant du Lac Ontario dans des conditions isothermiques. On a effectué des essais de corrosion sous transfert de chaleur à travers la paroi de tubes et remarqué que de fortes piqûres de corrosion peuvent se produire sous les dépôts formés sur les tubes dans de l'eau vaseuse provenant du Lac Ontario. Lors d'essais ultérieurs, effectués en collaboration avec la division de recherche de l'Ontario Hydro, on a étudié la résistance aux piqûres de corrosion d'autres alliages pour tubes à retenir, à savoir: l'Incoloy-825, l'acier inoxydable 904 L, l'Al-6X, l'Inconel-625, le Cu:70–Ni:30, le titane, le Sanicro-30 et le Sanicro-28.[1] De tous ces alliages, il n'y a que le titane et le Sanicro-28 qui n'ont pas subi un certain degré de corrosion par piqûres dans de l'eau vaseuse provenant du Lac Ontario. En l'absence de vase et donc de dépôts, aucunes piqûres de corrosion ne se sont produites sur aucun des alliages soumis aux essais.

Introduction

Until recently it was considered that copper-based alloys, such as admiralty brass, aluminum brass, or the copper-nickel alloys, provided adequate corrosion resistance to fresh waters in heat exchanger service. Alloys such as the austenitic stainless steels or nickel-chrome-iron family were regarded as necessary only when brackish or sulphide-polluted water was used, and too expensive for most typical freshwater applications. Indeed, isothermal corrosion testing in freshwaters, in the presence of a crevice, indicated that alloys such as Incoloy-800, Inconel-600, and type 304 stainless steel were not susceptible to freshwater corrosion at temperatures up to 70°C [1].

It was somewhat surprising, therefore, to find that I-800 moderator heat exchanger tubes, installed in the Ontario Hydro Pickering Nuclear Generating Station (PNGS) (Unit 3) following fretting failure of 70:30 copper:nickel tubes, pitted to failure in approximately two years. This premature failure, the result of under-deposit crevice corrosion [2], raised concern because plans for subsequent nuclear reactors using freshwater cooling called for I-800 heat exchanger tubes.

The work to be described here is a program of corrosion testing, with and without heat transfer across the tube wall, carried out on various candidate heat exchanger tubing alloys used in low temperature (100°C) service. The tests with heat transfer were designed to reproduce the pitting observed in PNGS and appeared to accelerate the pitting process in I-800 by about 50%, relative to in-service failure rates. It is important to remember, in assessing the corrosion susceptibility of the austenitic alloys tested, that heat transfer criteria

Keywords: heat exchanger tube corrosion, alloy 800, alloy 825, Sanicro-28, pitting under heat transfer, fouling.

Table 1: Nominal Compositions of Alloys Tested

		Composition (wt%)					
Alloy	*UNS No.*	*Fe*	*Ni*	*Cr*	*Mo*	*Cu*	*Other*
Admiralty Brass	C44300					72	1Sn, bal. Zn
90:10 Cu:Ni	C70600	1	10			88	
70:30 Cu:Ni	C71500	0.5	30			69	0.6Mn
Monel	N04400	2.5	66			29	1.8Mn, 0.5Si
Type 304 SS	S30400	71	8	18			2Mn, 1Si
Inconel 690	N06690	9.5	60	30			
Inconel 600*	N06600	8	76	15			
Inconel 625*	N06625	2.5	61	21.5	9		
Incoloy 800*	N08800	46	33	21			
Incoloy 825*	N08825	30	42	22	3	2	1Ti
Sanicro 30*	N08830	46	33	21			0.03C
Sanicro 28*	N08028	38	31	27	3.5		
Titanium Gr 2							100Ti
AL-6X	N08366	48	24	20			2Mn
904L SS	N08904	44	25	22			2Mn

*Nuclear grade materials were used.

require the use of thin-walled tubing for efficient heat exchanger design. Thus, simple remedies, such as increasing tube wall thickness, are not really practical. Similarly, copper-containing alloys are not used for newer nuclear power stations because of the low pH which can be produced as a result of the use of gadolinium nitrate for reactivity control during outages. These considerations imply that only two alternatives exist:

1) select a copper-free alloy with sufficient resistance to under-deposit corrosion under heat transfer conditions to provide 40 years' service;
2) provide an environment which does not lead to the buildup of silt or other deposits under which corrosion may occur.

In is known [3] that austenitic alloys, such as type 304 and 316, can tolerate quite high chloride levels (up to 200 ppm) in the absence of deposits. I-800 would generally be expected to have better corrosion resistance than 316 under these conditions. The choice between (1) and (2) is thus one of cost effectiveness; the balance being between the cost of a truly corrosion-resistant alloy that is approved for use in nuclear power stations, and the cost of a high-quality water cooling system.

Experimental Details

Isothermal Tests

Samples of various heat exchanger tubing materials (see Table 1 for nominal compositions) were exposed to cooling waters taken from Lake Ontario (see Table 4) and the St Lawrence River (Gentilly Site Water, 20 ppm Cl^-, 26 ppm $SO_4^{=}$) for times up to two years. Water temperatures were maintained at room temperature (20°C average), 45°C, and 70°C. Silt and chloride ion were added to some of the waters and samples were held in a polyethylene 'tubesheet' to simulate a typical in-service crevice. The degree of corrosion was assessed by visual and metallographic examination, as necessary, following sample washing and brushing.

Heat Transfer Tests

Figure 1 shows the experimental arrangement used to conduct the tests with heat transfer. These tests were carried out primarily using Lake Ontario water. The alloys used are listed in Table 1, along with the nominal compositions. The tube inner wall temperature was controlled at 60 or 70°C. The mean moderator water temperature in the moderator heat exchanger was approximately 60°C. The silt used for the crevices was

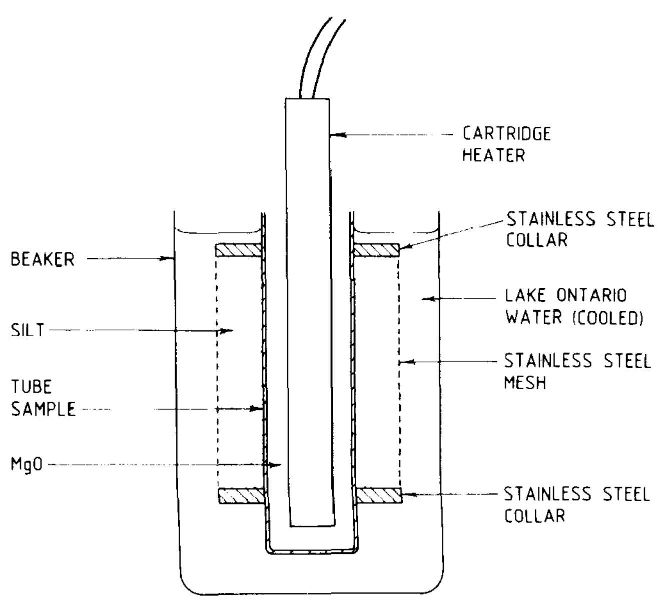

Figure 1: Schematic of test apparatus used for corrosion tests with heat transfer and silt crevices. The stainless steel used for collars and mesh was type 304.

Table 2: Summary of Long-Term Isothermal Corrosion Test Results*

Alloy	*St Lawrence River, 20°C Silt + 1000 mg / kg NaCl*	*St Lawrence River, 45°C*	*St Lawrence River, 70°C*	*Lake Ontario, 45°C*
Incoloy 800	crevice attack 0.1 mm / a	NA	NA	NA
Inconel 600	crevice attack 0.04 mm / a	NA	NA	NA
Inconel 690	crevice attack 0.09 mm / a	NA	NA	NA
Type 304 SS	NA	NA	NA	NA
Monel 400	crevice attack 0.05 mm / a	NA	NA	NA
90:10 Cu:Ni	patchy attack 0.01 mm / a	etch 0.01 mm / a	NA	NA
70:30 Cu:Ni	patchy attack 0.06 mm / a	etch 0.01 mm / a	NA	NA
Admiralty brass	–	crevice attack 0.07 mm / a	crevice attack 0.2 mm / a	crevice attack 0.03 mm / a
	pH 7.7	pH 7.8	pH 9.1	

*Corrosion rates are average of 3 deepest portions of pit or crevice.
'–' = no data.
NA = not attacked.

obtained from the PNGS forebay, and used as received. Lake Ontario water, again obtained from PNGS, was cooled with a simple cooling coil using tap water, which maintained the Lake Ontario water at 16–22°C, depending on the season.

Testing times varied from four weeks to six months, and after exposure samples were washed and brushed. Pitting was generally only observed under very adherent deposits, and these were removed either chemically (Clarke's solution) or mechanically in order to locate the pitted areas. Pit depths were measured using metallography. Chemical analyses were carried out using X-ray diffraction (XRD) on a Scanning Electron Microscope (SEM) equipped with energy-dispersive analysis of X-rays (EDX). Surface analyses were carried out using Scanning Auger Microscopy.

Results and Discussion

Isothermal Tests

Selected results are shown in Table 2. None of the alloys tested at room temperature in natural freshwaters showed any evidence of attack after two years' exposure. Those alloys which suffered some degree of corrosion at 45 and 70°C are shown in Table 2. This was invariably crevice attack. The copper-based alloys, specifically admiralty brass, 70:30 and 90:10 copper: nickel, were slightly attacked in St Lawrence River water, the severity increasing with temperature.

In the presence of silt and chloride contamination (1,000 mg / kg Cl^- in H_2O; during spring run-off the near-shore concentrations of Cl^- in Lake Ontario water in the vicinity of PNGS frequently reach 200 mg / kg or more), both the nickel-based and copper-based alloys suffered some attack at room temperature. The degree of attack appeared to increase with temperature, but this observation is based on visual examination only.

As indicated in Table 2, I-800 was susceptible to crevice attack in room-temperature chloride-contaminated St Lawrence River water, the rate being 0.1 mm / a. No direct comparison of the pitting rate can be made with either the in-service data for I-800, 0.5 mm / a, or the heat transfer test results, because the isothermal tests at 70°C for contaminated Lake Ontario water were not carried out. However, it is clear that chloride contamination appears to be necessary in these isothermal tests to induce pitting attack of I-800 and the nickel-based alloys.

The comparisons of the admiralty brass results with in-service data are quite good. In-service admiralty brass condenser tube pitting rates of 0.13 mm / a over a ten-year period appear to be typical, and this value is in good agreement with the isothermal laboratory test results ranging from 0.03 to 0.2 mm / a, depending on temperature and water chemistry. Similarly, 70:30 copper:nickel in service in PNGS has shown onlt slight corrosion, usually an insignificant surface etching and dealloying, which is consistent with the results reported here. In both cases, 70:30 copper:nickel and admiralty brass, it is likely that heat transfer conditions would increase the corrosion rate.

Heat Transfer Tests

The results presented here are limited to alloys suitable for moderator heat exchanger service, and thus include only those alloys listed in Table 3. Where no silt crevices were used, no pitting was observed on any of

Table 3: Under-Deposit Pitting Depths for Various Alloys in Heat Transfer Tests*

	Exposure time (weeks)				
Alloy	*6*	*8*	*12*	*24*	*26*
Incoloy 800		0.45 mm			0.75 mm
Sanicro 30					0.4 mm
Incoloy 825	no pits	0.15 mm	no pits	0.2 mm†	0.7 mm (few pits)
Sanicro 28	no pits		no pits	no pits	
904L SS	no pits	0.3 mm	no pits	no pits	0.3 mm
Al-6X	no pits		no pits	no pits	0.9 mm (few pits)
Titanium Gr 2	no pits		no pits		no pits
Inconel 625	no pits		no pits	no pits	no pits
70:30 Cu:Ni	no pits		slight etch		slight etch

*Tube inner wall temperature 60°C.
†One measurement was at 70°C inner wall temperature; pitting depth there was 0.3 mm.
200 ppm Cl in water.

these materials. The results in Table 3 represent an average, at each temperature, of several tests. In the case of I-800, I-825, and Sanicro-28, four or five tests were carried out, particularly at the longer exposure times. The statistical distribution of the pitting was such that results ranged from no pitting to severe pitting on materials such as I-825, and I-800 always suffered some pitting; Sanicro-28 never did show any evidence of pitting attack. Figure 2 presents the pitting data in terms of pit depth as a function of time.

The results for the other alloys tested, AL-6X, type 904L stainless steel, titanium grade 2, Inconel-625, and 70:30 Cu:Ni are an average of only two tests at each temperature. In these cases, the results were very reproducible within the duplicates, but insufficient sampling was carried out to provide statistically-significant predictability. The results in these cases do provide, however, a clear guide as to the type of alloy that would be suitable for corrosion-free service as tubing in moderator heat exchangers.

As shown in Table 3, I-800 is quite susceptible to pitting, I-825 somewhat less so but still susceptible, and AL-6X and type 904L stainless steel subject to occasional deep pitting. Figures 3 to 6 show some maximum depth pits for I-800, I-825, AL-6X, and type 904L stainless steel. The pit shapes are characteristic of under-deposit chloride attack. Sanicro-30 was less sus-

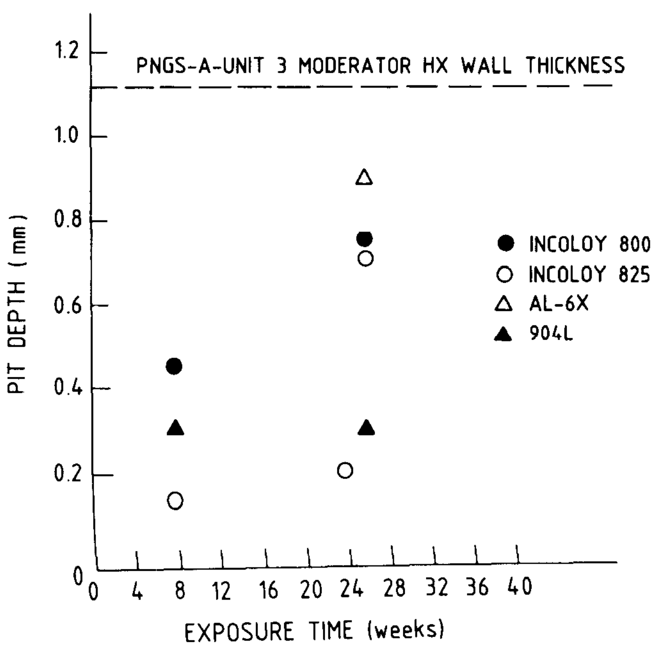

Figure 2: Average maximum pit depths for moderator heat exchanger tube materials subjected to laboratory testing in Lake Ontario water.

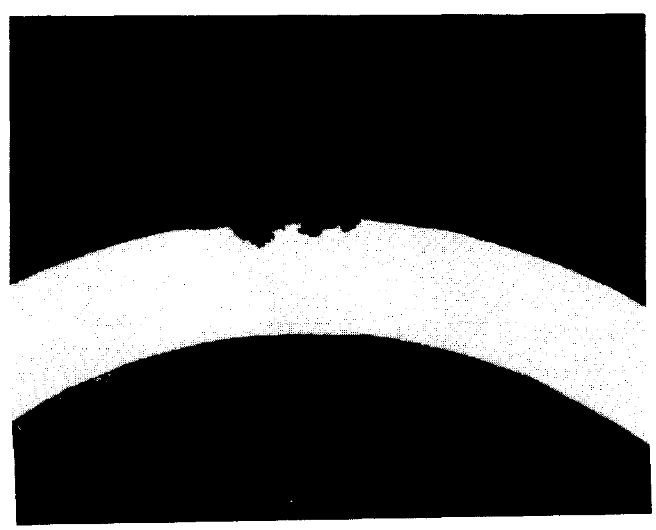

Figure 3: Typical deep pit in Incoloy 800 after two months' exposure to Lake Ontario water (with a crevice).

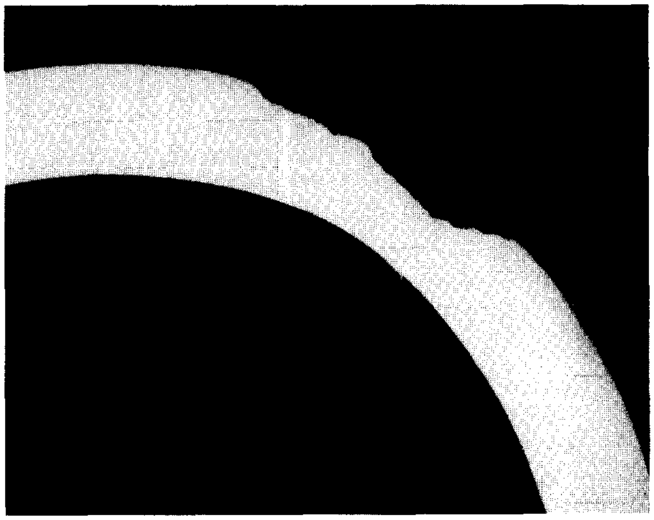

Figure 4: Typical deep pit in Incoloy 825 after 26 weeks' exposure to Lake Ontario water (with a crevice).

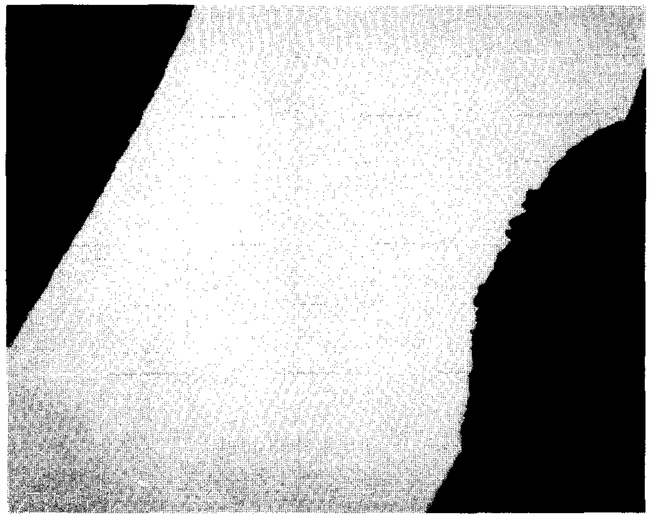

Figure 6: Pit noted on 904L sample after 26 weeks' exposure to Lake Ontario water (with a crevice).

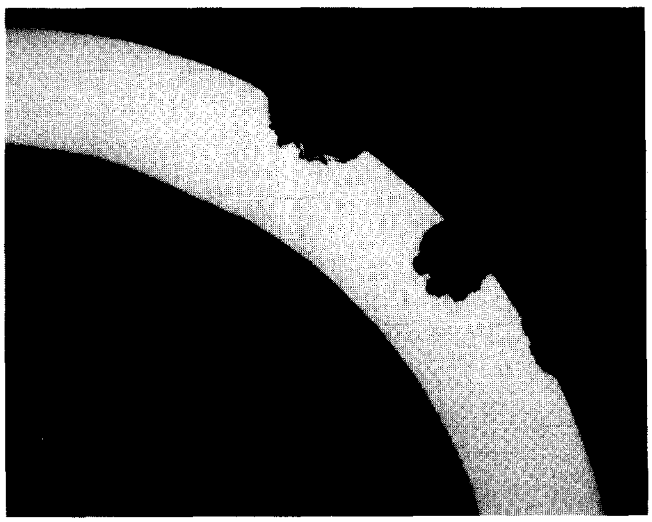

Figure 5: Typical deep pits found on AL-6X sample after 26 weeks' exposure to Lake Ontario water (with a crevice).

ceptible to pitting than I-800, but insufficient testing was carried out to confirm this conclusion. Sanicro-28 was completely resistant to pitting over the range of tests carried out here. This was also true of grade 2 titanium and Inconel-625.

PNGS has operated sucessfully with 70:30 Cu:Ni tubes for some years, and the results of the experiments reported here are in agreement with this observation. The only sign of corrosion on the material was under very adherent deposits, where redeposition of leached copper was noted. The corrosion in this area was limited to slight etching which had penetrated less than 1 μm in six months.

In most instances, the observed corrosion on alloys suffering attack was associated with dark green or black deposits, which had formed at the tube-silt deposit interface. Analyses of these dark areas showed them to be rich in Ca, S, and Cl, as well as containing significant amounts of chromium. The outer portion of the overall silt deposit (i.e. at the water interface) was found to contain Ni, Fe, Si, Ca, and Cl. Before the test the silt was found to be composed mostly of Ca and Si, with small amounts of S (probably as sulphate) and Cl (present as 30 mg / kg Cl^-). Table 4 shows the typical Lake Ontario water chemistry. Because EDX can detect elements such as Cl and S only at concentrations greater than 0.1 atomic %, it is apparent that considerable concentration of these elements has occurred in the dark deposits found on the tube surface. The concentration mechanism is diffusion of chloride ion to the acidic environment that is found in crevices formed

Table 4: Typical Lake Ontario Water Chemistry

pH	8.7
Conductivity	365
Cl^- (mg / kg H_2O)	30
$SO_4^=$ (mg / kg H_2O)	75
Ca^{2+} (mg / kg H_2O)	38–41
Mg^{2+} (mg / kg H_2O)	7.5–8
Na^+ (mg / kg H_2O)	10–14
Alkalinity (mg / kg H_2O)	115
Hardness (mg / kg H_2O)	126
Silt* (turbidity units) (surface)	350–400
Suspended solids (mg / kg) (5 foot length)	50
Total dissolved solids (mg / kg)	309

*Samples taken 1973.04.06 at various depths of intake channel.

in aerated water. Under these deposits, Fe and Ni appear to have been selectively leached from the alloy, and redeposited on the outer silt surface, leaving a Cr-rich region in the vicinity of the pit.

Surface analysis was carried out on samples of I-825 and Sanicro-28, using Scanning Auger Microscopy, to determine if any obvious correlation existed between pitting resistance and surface composition. It was found that the as-received I-825 surfaces were severely contaminated with carbonaceous material, whereas Sanicro-28 was very clean. Composition-versus-depth profiles were carried out in order to estimate the oxide thickness on the tubes. Beneath the silt deposits the oxide on Sanicro-28 was thicker (2.5 nm versus 1.0 nm) than that on I-825. Comparison with degreased as-received samples showed that the Fe-rich oxide on Sanicro-28 appeared to be unaffected by the presence of silt deposits, whereas that on I-825, which was Ni-rich, was considerably thinned. Sulphur contamination was found in the sub-silt I-825 oxide, whereas none was noted on the Sanicro-28 surface. These results suggest that the initial surface condition of the tubing material is of some importance. This is clearly related to the composition of the passive film, but more work needs to be carried out to substantiate this. The role of biological agents also needs to be clarified, and work of this nature is underway at Ontario Hydro Research Division.

Summary and Conclusions

Laboratory studies have shown that the under-deposit pitting attack observed on I-800 tubes in PNGS moderator heat exchangers may be simulated with a simple corrosion test incorporating heat transfer across the tube wall. The laboratory test may be somewhat more aggressive than in-service conditions, and the data summary presented in Figure 2 indicates that the time to failure for I-800 in laboratory tests would be approximately one year, and actual in-service failures were occurring in approximately one to two years. [2]. This small discrepancy may be at least partially the result of temperature differences. Indications from this work are that an increase in inside-wall temperature from 60 to 70°C results in a 50% increase in pitting rate. These data have not been published here (there is one point in Table 2) because variations in pitting susceptibility are too high to demonstrate effectively the temperature effect. Almost all these laboratory studies were carried out using Lake Ontario water taken from one sampling (approx. 30 mg / kg chloride), whereas in-service impurity concentrations fluctuate from less than those shown in Table 4 to considerably more. Biological activity is also seasonal and may prove to have a significant effect on variations in pitting rate.

On the basis of results given here, isothermal corrosion testing is inadequate to reproduce and / or predict in-service failure of heat exchangers, where heat transfer and deposit formation is occurring. The heat transfer tests show that most of the alloys tested are susceptible to pitting under deposits forming in silty water. Only Sanicro-28, titanium, and Inconel-625 were resistant to pitting under these conditions.

In order to maintain the integrity of low-temperature heat exchanger tubes, two approaches seem viable. The easiest, from a design point of view, is to use once-through coolant, such as Lake Ontario water, and a tube material that is completely resistant to under-deposit corrosion in that water. This choice requires the use of alloys such as titanium for the tube material, or, based on the tests carried out here, highly alloyed materials, such as Sanicro-28 and Inconel-625. The use of such materials will involve regulatory code approvals and, often, special fabrication techniques, in addition to high raw materials costs. Titanium is being used, however, in increasing amounts where seawater cooling is used, and other materials are simply not adequate to guarantee long-term service.

Another approach, that was used by several CANDU 600 stations, is to use a recirculating cooling system (which itself uses a titanium-tubed heat exchanger) to provide clean, chemically controlled coolant. Under these circumstances, the use of materials such as Incoloy-800, and even type 304 SS, should be quite adequate to provide a long service life.

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Notes

1. Incoloy and Inconel are trade names of the International Nickel Company of Canada, AL-6X is a trade name of Allegheny-Ludlum, and Sanicro is a trade name of Sandvik Steel.

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