CONSIDERATIONS IN SELECTING TUBING MATERIALS FOR CANDU STEAM GENERATORS

Corrosion resistance is the major consideration in selecting tubing material for CANDU (Canada Deuterium Uranium) steam generators. The consequences of failure of steam generator tubing are: loss of expensive heavy water coolant, and discharge of primary circuit radionuclides to the environment. Even if the tubing does not fail, high corrosion rates can lead to high radiation fields around the primary circuit caused by activated corrosion products.

Thus, corrosion, and additional considerations, lead to the following steam generator tubing material recommendations: for CANDU-BPHWR's (boiling pressurized heavy water reactors) low-cobalt Incoloy-800; for CANDU-PHWR's (pressurized, non-boiling, heavy water reactors), low-cobalt Monel-400.

NOMENCLATURE

In this paper, abbreviated forms of the common alloy names are used:

M-400 denotes the nickel-copper alloy specified in ASIM-SP-163, commonly known as Monel-400.*

I-600 denotes the nickel-chromium-iron alloy commonly known as Inconel-600*, but with a more restrictive composition.

I-800 denotes the nickel-iron-chromium alloy commonly known as Incoloy-800*, but with a more restrictive composition.

HISTORY

Steam generator tubing selection has previously been discussed by Atomic Energy of Canada Limited[1,2].

I-600 tubing was used for the horizontal steam generator at the NPD (Nuclear Power Demonstration) 25 MW(e)** demonstration plant and has given excellent service. This is attributed in part to the horizontal configuration and in part to the lower operating temperature as compared to pressurized water reactors (PWR's). M-400 alloy was used for Douglas Point, Rajasthan Atomic Power Project (RAPP), Karachi Nuclear Power Project (KANUPP) and Pickering and was selected for these plants because at that time there had been good experience with fossil-fired plant feedwater heaters and I-600 was considered too expensive. M-400 is being used again for the four new reactors at Pickering (Pickering B), with low cobalt content specified.

The Bruce A station steam generators have I-600 tubing that was chosen at that time (1969) because it was being extensively used in the nuclear industry with apparent success. M-400 was thought to be incompatible with the more oxidizing conditions of the Bruce coolant.

PRIMARY SIDE CONSIDERATIONS

Corrosion Effects

The chances of steam generator tubing failing are minimized by choosing a tubing material with

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**Electrical.

good corrosion resistance. However, the corrosion resistance of a material depends on the environment to which it is exposed. In our CANDU reactors (pressurized heavy water *(PHW)* types), the primary circuit is constructed mostly of carbon steel, and the coolant is dosed with lithium to give a high apparent pH of 10.3*. Oxygen production by radiolysis is suppressed by providing an excess of dissolved D_2 gas (about 10 cm^3/kg). This primary circuit chemistry gives acceptably low corrosion rates for the carbon steel in the circuit, and also for the high-nickel alloys that are used for steam generator tubing.

Steam generator tubing, relatively large in surface area, and also thin-walled when compared to the carbon steel main circuit piping, is selected from the following: M-400, I-600, and I-800. (A typical 600 MW(e) reactor has about 20,000 m^2 of boiler tubing, and about 2,000 m^2 of carbon steel, mainly in feeder piping.) The compositions of these materials are shown in Table 1. Austenitic stainless steel, although reportedly used successfully in the USSR, has not proven successful in large-scale plants elsewhere (probably because of its sensitivity to chloride stress cracking), and is not now considered a viable tubing material.

In our CANDU reactors these materials have good corrosion resistance, and acceptable corrosion product release rate at the apparent pH discussed above. However, our newest versions of CANDU's are not true PHW's, in that some boiling is allowed in the core, and some net quality (~4%) actually enters the steam generators. In this case, where there is boiling in the core, the production of the steam interferes with oxygen suppression, and results in a slightly oxygenated coolant entering the steam generators. These reactors are indicated as *(BPHW)*, for boiling, pressurized heavy water. This oxygenated coolant seriously increases the corrosion product release rate of M-400, but does not significantly affect that of I-600 or I-800.

*The apparent pH is the reading obtained from a D_2O solution, using ordinary (H_2O) electrodes. Empirically it is $_pD_{25°C} + 0.4$.

TABLE 1

COMPOSITIONS OF M-400, I-600, AND I-800 CANDU STEAM GENERATOR TUBING MATERIALS

	Composition, wt%		
	M-400	**I-600**	**I-800**
Nickel	63.0 – 70.0	72.0 min.	32.5 – 35.0
Chromium	– – – –	14.0 – 17.0	21.0 – 23.0
Iron	2.5 max.	6.0 – 10.0	Remainder
Carbon	0.3 max.	0.03 max.	0.03
Manganese	2.00 max.	1.00 max.	1.00 max.
Sulphur	0.024 max.	0.015 max.	0.015 max.
Phosphorus	– – – –	0.015 max.	0.015 max.
Nitrogen	– – – –	0.05 max.	0.03 max.
Copper	Remainder	0.50 max.	0.75 max.
Silicon	0.50 max.	0.50 max.	0.75 max.
Aluminium	– – – –	– – – –	0.15 – 0.45
Cobalt	0.015 max.	0.015 max.	0.015 max.
Titanium	– – – –	– – – –	0.35 min.
Ti/C	– – – –	– – – –	12 min.
Ti/C + N)	– – – –	5 min.	8 min.

The resulting corrosion product release rates are shown in Table 2 [2]. Carbon steel is shown for comparison.

Thus, it is clear that M-400 is an acceptable material for steam generators in true PHW reactors, but should be avoided in the BPHW tvpes.

The phenomenon known as Coriou attack. or intergranular attack of high nickel alloys, has to be considered when choosing steam generator tubing. It has been reported [3] that this attack is:

- dependent on nickel concentration (alloys having less than 65% Ni seem to be immune),
- dependent on temperature (stressed samples, exposed to 350°C water, failed within 6 months; whereas at lower temperatures, <315°C, the time to failure increases greatly),
- dependent on stress,
- independent of carbon concentration in the alloy.

It should be noted that CANDU reactors normally operate at 290 – 310°C outlet temperature (the newest versions at about 305°C and the Bruce reactors at 300°C). It is felt that I-600, operating at these lower temperatures, and partially stress-relieved in the manufacturing process, is adequately protected from this attack. I-800, with its lower nickel, is an even safer choice.

Radiation Field Effects

AECL has placed considerable importance on the reduction of radiation exposure of CANDU operators. Over the past several years, a group involving many AECL sites (the research and development sites of Chalk River Nuclear Laboratories and Whiteshell Nuclear Research Establishment, and the design office of Power Projects) Ontario Hydro and Hydro-Quebec has looked at some of the problems of radiation exposure reduction. It concentrated on one of the more important sources of exposure: radiation fields from activated corrosion products. This group, the Activity Transport Working Party (ATWP), very quickly saw that cobalt-60 was the most troublesome isotope, and encouraged the design office to limit the amount of source material of cobalt-60 (i.e. non-radioactive cobalt-59, the naturally occuring isotope commonly found as an impurity in nickel, chromium and iron alloys).

Naturally, the steam generator tubing was one of the first targets of cobalt control, and all the post-Pickering A reactors have strict limits (<0.015%) on the maximum allowable cobalt concentration in the steam generator tubing alloy.

However, cobalt-60 is not the only problem. As is always the case, once you have solved (or controlled) one problem, there is another one facing you. In this case, it appears that once cobalt-60 is under control, other isotopes (such as cobalt-58, iron-59 and manganese-54) assume importance as sources of activity. The sources of these isotopes are not impurities in the base alloys, but the constituents of the alloys themselves.

Of these other isotopes, the largest contributor to fields is cobalt-58 the source of which is nickel. It becomes obvious, then, that for BPHW reactors, the lower nickel I-800 has an advantage over I-600. The fractional contribution to radiation fields is shown in Table 3, and has indicated that I-800 will give 26% lower radiation fields than will I-600, after 30 years operation, both assumed to have the same low cobalt-59 impurity level.

The importance of this effect was not realized at the time of selecting I-600 as the boiler tubing for Bruce-GS "A". At the decision time for Bruce (about 1969), I-600 was thought to be the best steam generator tubing available.

TABLE 2

APPROXIMATE CORROSION PRODUCT RELEASE RATES IN CANDU PRIMARY CIRCUITS

Material	Release Rate of Metal $mg \cdot dm^{-2} \cdot d^{-1}$	
	PHW	BPHW
M-400	0.02	0.15 – 0.5
I-600, I-800	0.02	0.02
Carbon Steel	0.3	0.3

TABLE 3

FRACTIONAL CONTRIBUTIONS TO RADIATION FIELDS AT VARIOUS TIMES FOR BPHW STEAM GENERATORS OF I-600 AND I-800

		Fractional Contribution Years of Operation			
Material	Nuclide	1	5	15	30
I-600	Fe-59	0.06	0.05	0.04	0.04
	Mn-54	0.03	0.03	0.03	0.03
	Co-58	0.82	0.65	0.54	0.51
	Co-60	0.09	0.27	0.39	0.42
I-800	Fe-59	0.17	0.11	0.09	0.08
	Mn-54	0.06	0.08	0.06	0.05
	Co-58	0.61	0.41	0.32	0.30
	Co-60	0.16	0.40	0.53	0.57

SECONDARY SIDE CONSIDERATIONS

To date, steam generator tubing failures have proven to be very costly to the nuclear industry although not in Canada. No steam generator tubing failures attributable to corrosion have occurred in CANDU reactors. Most of the failures of PWR steam generator tubing have been caused by secondary side attack, and it has been I-600 that has suffered; no failures of I-800 have been reported. The secondary side boiler water chemistry must be carefully tailored to minimize the build-up of undesirable impurities. For both I-600 and I-800, AECL makes the following recommendations for boiler water treatment:

with no known condenser leaks:

pH – as high as compatible with turbine/condensate/feedwater system, controlled by volatile amine addition.

O_2 – less than 5 ppb, controlled by deaeration and by (volatile) hydrazine addition.

blowdown – continuous at 0.1% of full power steaming rate.

with condenser leaks:

phosphate – up to 10 ppm during period of leakage. Na/PO_4 ratio 2.2 to 2.6.

blowdown – increased to 0.3% of steaming rate for duration of high impurity levels.

It is our opinion that the main cause of boiler tube failure is leakage of various scaling and corrosive impurities into the boiler water via condenser tubes. The most harmful condenser leaks are not the catastrophic ones resulting from rupture of condenser tube by flying turbine blade pieces, but the long-term, low-level leakage (or weeping) through the condenser tube-to-tubesheet joints, or pin-hole penetration by corrosion of the tubing itself (i.e. wrong material selection). The solution is to prevent the disease, not to try to cure it (with condensate polishing). That is, condenser tubes should be made of high quality materials, and should be welded to the tubesheet wherever possible. Indeed, because of the deleterious effects of copper on the system (as a "*hardness*" scale on boiler tubes, and as a restriction on amounts of amine, hence pH), AECL recommends the use of stainless steel condenser tubes on fresh-water sites, and titanium on salt water – the feed-water system should also be ferrous, with stainless steel the best choice.

Some mention should be made of the effects of blowdown. It is known that steam generator tubing failures have occurred in the layer of heavy insoluble corrosion products (and other impurities) that accumulate on the tubesheet. Blowdown, as currently practised in CANDU steam generators, can have no significant effect on this sludge blanket because the tubeface velocities are not high enough at 0.1 – 0.3% (of steaming rate) blowdown to penetrate more than 1 or 2 tube lanes around the blowdown locations in the tube-free lane or periphery. Very much higher blowdown rates are not practicable. Some means of improving blowdown as a means of sludge control should be investigated.

Crevice corrosion has not been shown to be a cause of failure of steam generators; however, this does not mean that this type of corrosion can be ignored. Current Canadian practice is to roll the tube at the back side of the tubesheet to close up the crevice to minimize the problem.

Stress corrosion (either by caustic or chloride) so far has not been a problem in CANDU steam generators. However, this problem is likely the reason for the poor record of austenitic stainless steels as steam generator tubing. M-400 is relatively immune to this attack, while both I-600 and I-800 seem to be somewhat susceptible. Concentrations of caustic should not be permitted to build up in the steam generator.

COST CONSIDERATIONS

Cost must also be considered in the selection of tubing material. Currently I-800 has a lower cost per unit length than I-600 although the cost differential depends on the tubing supplier and the world market conditions for the supply of raw materials.

The net cost difference between a steam generator tubed with I-600 and I-800 depends not only on tubing cost but also on the cost of contained heavy water. These costs are determined in part by thermal conductivity, of which the values for I-800 are slightly lower than for I-600.

However, irrespective of the initial capital cost, the cost of lost power due to a forced shutdown (to repair failed tubes) makes it imperative that the selected tubing be extremely reliable.

CONCLUSIONS

Considerations as discussed above lead to certain recommendations for steam generator tubing. Currently, we recommend low-cobalt I-800 for all boiling pressurized heavy water (BPHW) reactors (e.g., Gentilly-2). This alloy is considered to be as good as or better than I-600 with respect to corrosion resistance and neutron activated corrosion products. The relative advantage with respect to activation products is substantiated by a recent comparison of Obrigheim (I-600 tubes) and Stade (I-800 tubes) [4].

For CANDU non-boiling PHW reactors, we recommend low-cobalt M-400 alloy, which has excellent corrosion resistance under de-oxygenated conditions and has the lowest net cost when heavy water holdup is considered.

R.L. Hemmings

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