Cobalt-Based Alloy Hardfacing In Moderator System Valves

J. Higgs[1], W. Cooper[1] and S. Groom[2]
[1]Atomic Energy of Canada Limited, Saint John, NB, Canada
[2]President, J.C.S. Holdings Ltd., Saint John, NB, Canada

Abstract

For the past 30 years, materials containing cobalt have been intentionally avoided in the design and construction of moderator systems in CANDU® plants. The rationale behind this approach was based on the perceived risk of neutron activation of ^{59}Co to ^{60}Co (a hard gamma emitter), resulting in increased radiation fields and higher doses around moderator equipment. One consequence of this approach was to avoid valve hardfacings high in cobalt concentration, such as Stellite-6®, and instead relying on nickel-based valve hardfacings. Operating experience throughout the CANDU® industry has shown that the nickel-based hardfacings used in moderator valves corrode in the low pH of the moderator system. This often resulted in valves that would not provide adequate isolation for maintenance or operational requirements.

This paper will review the performance of hardfacings in CANDU® moderator systems, and compare the relative contributions of cobalt from various moderator system components.

® "CANDU" is a registered trademark of Atomic Energy of Canada Limited.
® Stellite-6 is a trade name of Deloro-Stellite.

1. Introduction

A heavy water (D_2O) moderator is used in CANDU® power reactors to moderate (slow-down) fast neutrons produced in the nuclear fuel fission process, encouraging further fissioning to maintain the nuclear chain reaction. Pumps in the moderator system draw D_2O from the calandria vessel where the heat generated from the reactor is removed via heat exchangers and cooled D_2O is returned back to the reactor. The system operates at low pressure (<2 MPa) and temperature (<70°C at outlet of calandria). A purification system (complete with ion exchange columns and filters) is connected to the main moderator system loop. A simplified flow diagram for the CANDU 6® main moderator system is shown in Figure 1.

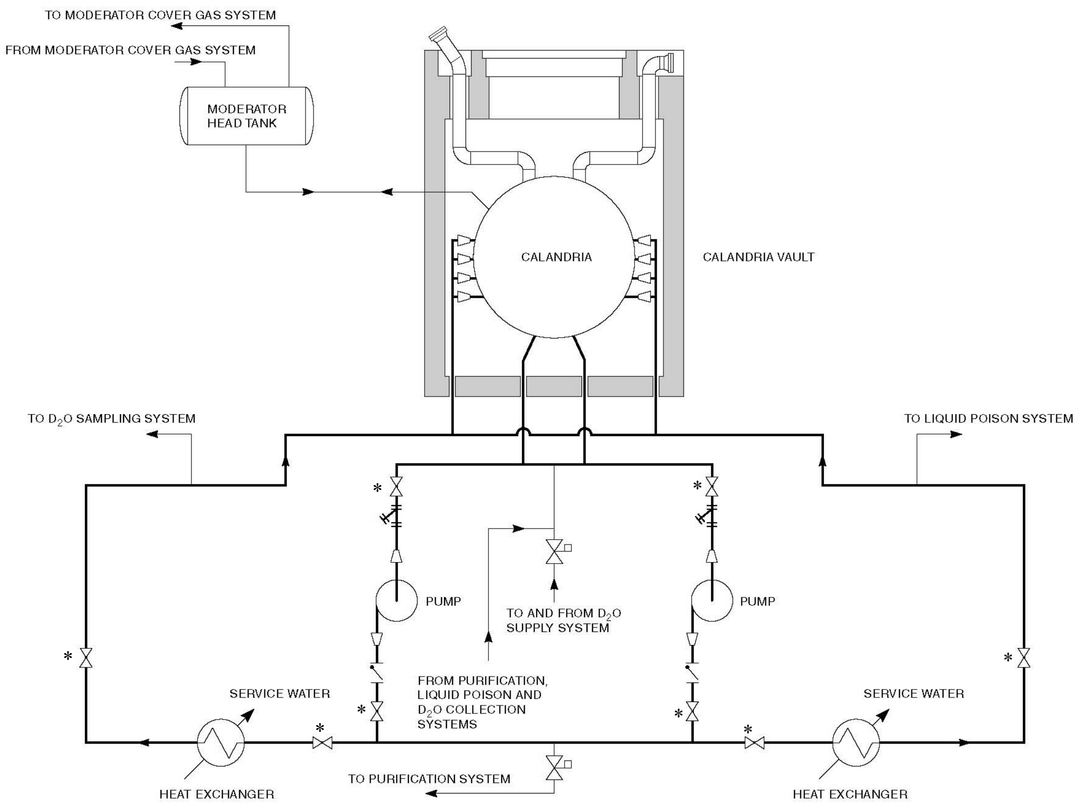

Figure 1: CANDU 6® Main Moderator Circuit Simplified Flow Diagram. Valves marked with "*" are large gate valves for equipment isolation.

As moderator water spends much of the time in the very high neutron fields of the reactor core, any impurities (e.g. corrosion products) in the water can become activated. Therefore, materials resistant to corrosion in contact with moderator water are typically chosen (e.g. stainless steel). In line with this philosophy, materials high in cobalt concentration have been avoided, as the ^{59}Co can become gamma-emitting ^{60}Co through the neutron activation reaction [$^{59}Co(n,\gamma)^{60}Co$].

With a half-life of 5.27 years, particles of ^{60}Co that collect in low flow/stagnant areas of the moderator system will become a long-term gamma radiation source, potentially increasing radiation dose to plant personnel and making maintenance on the moderator system more dose-intensive and more difficult to complete.

Soluble chemicals (often called neutron poisons) are periodically added to moderator water to control the neutron population. The addition of poisons such as $B(OD)_3/B_2O_3$, $Gd(NO_3)_3$ or $Gd_2(SO_4)_3$ during normal operation results in a slightly acidic (pH_a = 4.5 to 6.5) condition within the moderator system. During the Overpoisoned Guaranteed Shutdown State (OPGSS), moderator pH_a can be as low as 3 at some stations.

Tritium concentration in CANDU 6® moderator water can reach levels of 60-70 Ci/kg [1]. From a liquid spill of moderator water the resultant tritiated water vapour in air exposure as a result of inhalation and skin absorption can be in excess of 1000 mSv/hr.

2. Discussion

2.1 Valve Hard-Facing Materials

Hardfacings are alloys added (usually by welding) to component wear surfaces to improve their abrasion-resistance. For example, in gate valves, the seat rings and gate sealing surfaces would normally be hardfaced to minimize erosion and thus ensure a positive seal (see Figure 2).

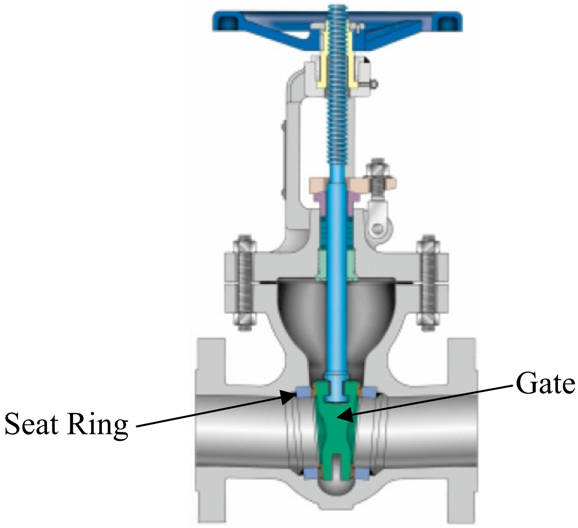

Figure 2: Cross-section of typical manual gate valve

For many process applications, Co-based valve hardfacings such as Stellite-6® are used due to excellent wear and corrosion resistance. However, since these hardfacings contain high concentrations of cobalt (Stellite-6® contains approx. 58% Co by weight), they were not used in the design and construction of recent CANDU® moderator systems. The concern was that the cobalt hardfacing could be released from the valve(s) and carried into the reactor with the moderator water, thus becoming activated to ^{60}Co and becoming a radiation hazard for plant personnel.

To avoid the perceived radiation risk associated with cobalt-based materials in moderator valves, nickel-based hardfacings, such as Deloro® or Colmonoy®, were specified. Ni-based hardfacings were chosen for the moderator system in part based on successful performance of these hardfacings in laboratory tests under simulated Primary Heat Transport System (PHTS) conditions.

® Deloro is a trade name of Deloro-Stellite.

® Colmonoy is a trade name of Wall Colmonoy Corporation.

2.2 Failure of Ni-based Valve Hardfacings in Moderator Service

Over time, excessive corrosion of the Ni-based hardfacings often resulted in moderator system valves unable to perform their intended isolation function. For example, the main moderator equipment isolation valves (manual gate valves- see Figure 1) would pass, preventing their use as isolation points for worker protection during pump or heat exchanger maintenance if the moderator was to remain filled during this maintenance.

The acidic conditions within the moderator system, especially during OPGSS, are the likely cause of excessive corrosion of the Ni-based valve hardfacings. Research has also shown that Deloro-50® experiences excessive sliding wear loss rates at temperatures below 100°C [2]. It is interesting to note that the same research showed acceptable sliding wear behaviour for Deloro-50® at temperatures above 200°C.

Besides impacting worker protection, moderator valves that fail to be leak-tight can also contribute to operational issues. For example, moderator purification isolation valves assumed to be leak-tight may in fact be passing and thus unintentionally removing neutron poisons from moderator water. This situation is especially important to avoid during the OPGSS where typically many moderator valves are locked closed and relied upon to be leak tight.

Poor valve performance often results in maintenance work-arounds, such as ice plugs, which add considerable complications and manpower, as well as significant extension to the time required to perform the maintenance. In addition to creating difficulties for maintenance, passing moderator valves can also lead to an increased risk of worker exposure to highly-tritiated moderator water.

2.3 Sources of Cobalt in the Moderator System

The surface area of the hardfacing alloy represents a small portion of the total of all moderator system surfaces that are wetted by the process heavy water, as shown in Table 1.

Table 1: Typical Moderator System Major Components

Equipment	Material	Nominal Composition	Surface Area in Contact with D_2O (m^2)*
Calandria Vessel	304L SS	18%Cr, 8%Ni, Fe Bal. (500 ppm Co)	142
Piping	304L SS	18%Cr, 8%Ni, Fe Bal. (100 ppm Co)	50
Heat Exchanger Tubes	SA-669/3RE-60®	18.5%Cr, 4.5%Ni, 2.6%Mo, 1.6% Si, 1.5% Mn, Fe Bal. (150 ppm Co)	1262
	Alloy 800	41%Fe, 22%Cr, 33.8%Ni, 0.1%Mn, 0.03%C (150 ppm Co)	
Calandria Tubes/Guide Tubes/LISS** Nozzles	Zircaloy-2	0.1%Cr, 0.05% Ni, 0.1% Fe, Zr Bal. (20 ppm Co)	1200
Hardfacing Alloys – small valves	Comonoy-4/5®	14%Cr, 15%Fe, Ni Bal. (1600 ppm Co)	0.26
Hardfacing Alloys – large valves	Deloro-50®	13.7%Cr, 16%Fe, Ni Bal. (1600 ppm Co)	1.64

* Typical for CANDU 6.
**Liquid Injection Shutdown System.

® 3RE-60 is a trade name of Sandvik AB.

Moderator process conditions and normal chemistry control conditions generally provide a benign corrosion environment for materials typically used in the system. Therefore, the overall releases of corrosion and wear products into the moderator are not expected to be large, except for the Ni-based hardfacings. Using published corrosion rates for the materials of construction, an estimate of the Co-release rates for the various moderator system components can be constructed, as shown in Table 2.

Table 2: Estimated Corrosion and Cobalt Release Rates into the Moderator System – Current Situation

Equipment	Surface Area in Contact with D_2O (m^2)	Estimated Corrosion Rate (mg/dm^2-yr)	Corrosion Release Rate (g/yr)	Co Conc. (ppm)	Co Release Rate (mg Co/yr)	% of Total Co Release
Calandria Vessel 304L SS	142	5	71	500	35.5	22
Piping 304L SS	50 (est.)	5	25	100	2.5	1.6
Heat Exchanger Tubes 3RE-60®/Alloy 800	1262	5*	631	150	94.7	58
Calandria Tubes/Guide Tubes/LISS Nozzles Zr-2	1200 (est.)	1	120	20	2.4	1.5
Hardfacing Alloys – small valves Colmonoy 4/5®	0.26	30**	0.8	1600***	1.3	0.8
Hardfacing Alloys – large valves Deloro 50®	1.64	100**	16.4	1600***	26.2	16.1
TOTAL			864		162.6	100

* Assumed the same as 304LSS.
** From corrosion tests in moderator system conditions.
*** As measured by spectrographic techniques.

From Table 2 it can be seen that the heat exchanger tubes and calandria vessel contribute 80% of the cobalt released into the moderator system, while the valve hardfacings contribute approximately 17%.

It should be pointed out that the significance of the calandria vessel as a source of cobalt is not fully appreciated from this type of analysis. This is due to the fact that the vessel is continuously exposed to high neutron flux, thus converting some cobalt in the stainless steel of the vessel from ^{59}Co to ^{60}Co, whereas the heat exchanger tubes are located out-of-core, and thus cobalt released from the tubes will be mostly ^{59}Co (photo-neutron activation of out-of-core components is expected to be very low). Therefore, the calandria vessel would contribute more than 22% of the ^{60}Co to the moderator. A subsequent result is that the ^{60}Co attributable to the valve hardfacing would be even less than 17%. Decontamination experiments have confirmed that high activities of ^{60}Co in stainless steel samples were the result of activation of elemental ^{59}Co in the base metal and not due to deposition of ^{60}Co onto the surface from solution.

Stellite-6® has a much lower release rate in moderator conditions as compared with Ni-based hardfacings. Therefore, even with the much higher cobalt concentration in Stellite®, the overall contribution of Co to the moderator system is not expected to increase with the introduction of Stellite® hardfacings in moderator valves, as shown in Table 3.

Table 3: Estimated Corrosion and Cobalt Release Rates into the Moderator System – Alternate Situation with Co-Based Hardfacing

Equipment	Surface Area in Contact with D_2O (m^2)	Estimated Corrosion Rate (mg/dm^2-yr)	Corrosion Release Rate (g/yr)	Co Conc. (ppm)	Co Release Rate (mg Co/yr)	% of Total Co Release
Calandria Vessel 304L SS	142	5	71	500	35.5	24
Piping 304L SS	50 (est.)	5	25	100	2.5	1.7
Heat Exchanger Tubes 3RE-60®/Alloy 800	1262	5	631	150	94.7	64
Calandria Tubes/Guide Tubes/LISS Nozzles Zr-2	1200 (est.)	1	120	20	2.4	1.6
Hardfacing Alloys – small valves Stellite-6®	0.26	0.1	0.006	580 000	3.5	2.4
Hardfacing Alloys – large valves Stellite-6®	1.64	0.1	0.016	580 000	9.3	6.3
TOTAL			847		147.9	100

In comparing the cobalt release rates from Ni-based hardfacings (Table 2) and Co-based hardfacings (Table 3), it is interesting to note that the Co-based hardfacings are actually a smaller source of cobalt (approx. 13 mg Co/year) than Ni-based hardfacings (approx. 27 mg Co/year). This is due to the very high corrosion rate of Ni-based hardfacings in moderator conditions, as compared to excellent corrosion and wear resistance of Co-based hardfacings.

As the cobalt-based hardfacings contribute only ~10% of all cobalt sources, it would appear that a more effective means to control cobalt in the moderator system would be to tighten the limits of cobalt content in the high surface area components, such as the heat exchanger tubes and the calandria vessel, if economically feasible. It should be noted that current cobalt concentrations of 700-1000 ppm in the calandria shell and system piping are possible. If these higher values were used in the analysis above, the relative contribution of valve hardfacings to cobalt release would be even less than that estimated.

A further consequence of high corrosion rates of the Ni-based hardfacing is the activation of ^{58}Ni [$^{58}Ni(n,p)^{58}Co$] released from the hardfacings to produce radioactive ^{58}Co (half life of 71 days).

2.4 Recent Industry Experience

The decades-old decision to avoid materials rich in cobalt for the moderator system has recently been reconsidered in the CANDU® industry. Some stations are considering, or have begun to, replace Ni-based hardfacings in moderator valves with Stellite®. The rationale is partly based on the fact that Stellite® has an excellent performance track record as a valve hardfacing. Perhaps a bigger reason, however, is that the perceived radiation risks with Co-bearing hardfacings is insignificant when compared to the radiation risks, maintenance issues and operational concerns associated with Ni-hardfaced moderator valves that will not provide isolation. Similar conclusions have been reached in the PWR industry [3]. AECL has also adopted this philosophy, as the current CANDU 6® reference design calls for Stellite-6® hardfacing on moderator valves.

The analysis shown above demonstrates that the in-service contribution of cobalt from moderator valve hardfacings is small in comparison to the heat exchanger tubes and the calandria vessel. It should be noted, however, that excellent maintenance practices must be followed when installing, refurbishing or repairing Co-hardfaced valves to ensure loose Co-bearing particles are not introduced into the system. One example of Foreign Material Exclusion (FME) practices than can be applied to cobalt-hardfaced valve maintenance is the use of X-ray fluorescence (XRF) to detect Stellite® particulate debris following in-situ valve repair activities.

Research work is in progress to find suitable non-cobalt alternatives to Stellite-6® as moderator valve hardfacings. Should a suitable replacement be found for this application (moderator chemistry), valve replacement or refurbishment with the alternative hardfacings should be considered, since with cobalt in the valves the risk remains that some cobalt could be introduced into the system.

3. Conclusions

CANDU® moderator system conditions pose unique challenges to safe and efficient plant operation. There are nuclear safety issues associated with passing valves, tritium exposure concerns when dealing with highly-tritiated heavy water and gamma source terms introduced with material released into the flowing moderator water, all within an aggressive (acidic) environment. Such unique challenges require unique solutions.

Cobalt-based hardfacings for moderator system valves should not be avoided simply based on the risk of Co-activation. Cobalt from valves is not necessarily the largest contributor of cobalt in the moderator system and the current Ni-based hardfacing may in fact be releasing more cobalt into the moderator than if the hardfacing was Co-based, due to excessive corrosion in moderator conditions. For this application (low pH, very highly tritiated water) where positive isolation is critical for work protection, effective equipment maintenance and operational reliability, at this time Co-based hardfacings are considered a suitable alternative to Ni-based hardfacings.

Research should continue to find suitable non-Co alternatives for this application. Regardless of the material chosen for use in the moderator system, diligent monitoring and control of moderator system chemistry (through an efficiently-operated purification system, comprehensive chemical sampling practice and throughout foreign material exclusion policies) is required to minimize the effect of contaminants. For future CANDU® projects, reducing cobalt content in calandria vessel steel and moderator heat exchanger tubes should be considered if not financially prohibitive.

4. Acknowledgements

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5. References

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