



Aluminum corrosion product release kinetics



Matt Edwards*, Jaleh Semmler, Dave Guzonas, Hui Qun Chen, Arshad Toor, Seanna Hoendermis

Canadian Nuclear Laboratories, Chalk River Laboratories, Chalk River, Ontario, Canada K0J 1J0

HIGHLIGHTS

- Release of Al corrosion product was measured in simulated post-LOCA sump solutions.
- Increased boron was found to enhance Al release kinetics at similar pH.
- Models of Al release as functions of time, temperature, and pH were developed.

ARTICLE INFO

Article history:

Received 28 February 2014
Received in revised form 23 February 2015
Accepted 5 March 2015

Keywords:

Aluminum release
Emergency core cooling system
Sump buffering agents

ABSTRACT

The kinetics of aluminum corrosion product release was examined in solutions representative of post-LOCA sump water for both pressurized water and pressurized heavy-water reactors. Coupons of AA 6061 T6 were exposed to solutions in the pH 7–11 range at 40, 60, 90 and 130 °C. Solution samples were analyzed by inductively coupled plasma atomic emission spectroscopy, and coupon samples were analyzed by secondary ion mass spectrometry. The results show a distinct “boron effect” on the release kinetics, expected to be caused by an increase in the solubility of the aluminum corrosion products. New models were developed to describe both sets of data as functions of temperature, time, and pH (where applicable).

Crown Copyright © 2015 Published by Elsevier B.V. All rights reserved.

1. Introduction

The function of an ECCS strainer is to filter solids from water, much like a household strainer. But, unlike a household strainer, its design conditions are not immediately obvious. The strainer usually sits at the bottom of the containment sump, and it has only a very remote chance of ever being put to use. The design conditions must be surmised from simulated LOCA scenarios, and includes such solid obstructions as metal signs, insulation fibers, and concrete dust. Although tiny, large quantities of insulation fibers and dust can combine on a strainer to form a flow-restricting bed.

In recent years, the design conditions of the ECCS strainer have been extended to include the chemistry of the sump water. Hidden

from the eye, the sump water is really a solution of many chemical species, some of which can form precipitates under the right conditions. Like dust, when these precipitates meet with fibers on a strainer, the result is unwanted flow restriction. The design conditions must therefore include an accurate, or at least conservative, specification of the sump water chemistry.

The term “chemical effects” is used broadly to describe the effects of chemicals in the ECCS sump water after a postulated LOCA on the performance of the ECCS or on core cooling in general. The tendency of some chemical species to form precipitates that adversely affect the performance of the strainer (chemical effects) has gained significant attention since the ICET (Dallman et al., 2006) results were first published in 2004. Those and subsequent tests (Lane et al., 2008) have shown the importance of aluminum as a chemical effects source term; aluminum components are often found in containment and have a propensity to release corrosion products, which under relevant conditions form strainer-clogging precipitates.

Sump water chemistry has a significant bearing on the solubility of aluminum corrosion products, and hence the driving force for corrosion product release. The sump water can be borated or non-borated depending on reactor type; it may contain LiOH and NaOH, and it may be pH-controlled through the use of a dry

Abbreviations: ECCS, emergency core cooling system; ICET, integrated chemical effects tests; ICP-AES, inductively coupled plasma atomic emission spectroscopy; LOCA, loss of coolant accident; NaTB, sodium tetraborate; NMR, nuclear magnetic resonance; PHWR, pressurized heavy water reactor; PID, proportional-integral-derivative; PWR, pressurized water reactor; PWRONG, PWR Owners Group; SIMS, secondary ion mass spectrometry; TSP, trisodium phosphate.

* Corresponding author at: 286 Plant Road, Stn. 61, Chalk River, ON, Canada K0J 1J0. Tel.: +1 613 584 3311x46188.

E-mail address: Matthew.Edwards@cnl.ca (M. Edwards).

<http://dx.doi.org/10.1016/j.nucengdes.2015.03.006>

0029-5493/Crown Copyright © 2015 Published by Elsevier B.V. All rights reserved.

buffer placed in the sump or actively controlled through NaOH injectors. Both $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ (trisodium phosphate or TSP) and $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$ (sodium tetraborate or NaTB) are suitable buffers for placement in containment.

Currently, many PWRs and PHWRs use TSP in their containment sump as a buffering agent. The TSP is stored in baskets that become submerged within the containment sump pool as the post-LOCA water level rises. In the event of a LOCA, the TSP dissolves to increase the pH of the sump water to greater than 7. However, under post-LOCA conditions, calcium released from containment materials (such as calcium silicate insulation, glass fiber insulations, and concrete) can react with TSP to form insoluble calcium phosphate precipitates, which can also adversely affect strainer performance. To minimize the potential for precipitate formation, some US PWRs have evaluated the impact of changing from TSP to NaTB. Studies sponsored by the PWROG concluded that NaTB was a suitable replacement for TSP (Reid et al., 2006).

The specified sump water chemistry is replicated or imitated in chemical effects tests, which are just one kind of strainer qualification test. Chemical effects tests can be integrated or single effects. In the former, scaled surface areas of aluminum, concrete and other representative source term materials are placed in the test rig and, with time, they corrode and dissolve, and release chemicals in the imitated sump water. In the latter, the release of chemicals from source term materials is modeled, and the chemicals are scaled and added to the test rig either in a batch addition or stepwise over time to mimic time-dependent release. The models used require reliable data on corrosion product release over the expected range of sump parameters (pH, temperature, etc.). The kinetics of corrosion product release from aluminum was studied by Lane et al. (2008) for application to PWR chemical effects analyses and testing. In their tests, AA 1100¹ sheet was exposed to solutions of pH 12 NaOH, pH 8 NaOH and pH 4.1 $\text{B}(\text{OH})_3$ at 88 and 130 °C for 90 min, and the solution was sampled at prescribed times. They developed an empirical model, Eq. (1) (Lane et al., 2008), to describe their results as a function of temperature, T (K), and pH (at 25 °C). Since the Al release rate is often found to decrease with time, such short-term tests can give an overly conservative value for the release rate.

Al Release Rate ($\text{mg m}^{-2} \text{min}^{-1}$)

$$= 10^{14.69039 - 4.64537 \cdot (1000/T) + 0.044554 \cdot (\text{pH}_{25})^2 - 1.20131 \cdot (\text{pH}_{25}) \cdot (t/1000)} \quad (1)$$

In an effort to expand the set of available data on aluminum corrosion product release, we have conducted 34 long-term tests, each lasting between 6 and 21 days. The length of each test was chosen to ensure that release kinetics could be well characterised. The test conditions were chosen to cover a range of temperature seen in many LOCA simulations, from 130 °C down to 40 °C; a range of chemistries were chosen, from borated to non-borated, from pH 7 to pH 11; and a range of buffers were used, including TSP, NaTB, boric acid, NaOH or LiOH. The tests were conducted on alloy AA 6061, which is a common alloy found in the containments of Canadian nuclear reactors. The influence of aluminum alloy type on corrosion rates has been described as “not significant” by Delegard et al. (2009).

The tests were divided into two series. The objective of the first series was to quantify aluminum release in non-borated solutions of NaOH, LiOH, TSP or NaTB. The objective of the second series was to quantify aluminum release in borated solutions of boric acid and

Table 1
Test matrix for first series.

Test ID	pH	Temperature (°C)	Coupons	Solution
TSP-40	10.5	40	10	54 mg L ⁻¹ TSP (4 L)
TSP-60	10.5	60	10	54 mg L ⁻¹ TSP (4 L)
TSP-90	10.5	90	10	54 mg L ⁻¹ TSP (4 L)
Na-40	9.5	40	10	NaOH (4 L)
Na-60	9.5	60	10	NaOH (4 L)
Na-90	9.5	90	10	NaOH (4 L)
Li-90	9.5	90	10	LiOH (4 L)
B-40	9.5	40	10	1.25 g/L anhydrous NaTB (4 L)
B-60	9.5	60	10	1.25 g/L anhydrous NaTB (4 L)
B-90	9.5	90	10	1.25 g/L anhydrous NaTB (4 L)
Na-130-pH“X”	X=7–10	130	4	NaOH (1.4 L)

NaOH. The solubilities of aluminum species under these different chemistries were not assessed.

The first series of tests were conducted at nominal pH values of 10.5 for TSP-buffered solutions at 4.4 mg L⁻¹ P, 9.5 for NaTB-buffered solutions at 0.25 g/L B, and 9.5 for NaOH and LiOH solutions. Although it is to be expected that tests conducted at pH 10.5 would produce results with higher aluminum corrosion rates than tests conducted at pH 9.5, the nominal pH values were chosen to represent the expected equilibrium values of these buffered solutions in containment. Thus, the test results provide a fair comparison of the corrosion rates of aluminum in these different buffered solutions. The second series of tests were conducted at nominal pH values of 7, 8, 9, 10 and 11 in boric acid buffered solutions at 2.8 g/L B.

Both series of tests used an approximate surface area to solution volume ratio of 0.34 m²/m³. This surface area to volume ratio was chosen as representative of some reactor containments. By comparison, Lane et al. (2008) used 17.8 m²/m³ in their tests, which they claimed was the maximum ratio among plants surveyed, while Dallman et al. (2006) used a submerged surface area to volume ratio of 0.59 m²/m³ in the ICET tests, which they claimed was representative of U.S. nuclear power plants. Too high of a ratio may cause early saturation of the test solution and hinder the release rate, much like trying to dissolve salt in a heavy brine. Conversely, too low of a ratio may eliminate the possibility of reaching saturation, and would not be representative. As most of the aluminum in containment is above the sump water level, the lower ratios used here and in the ICET tests are arguably more representative.

2. Experimental

Tests conducted at 40, 60 and 90 °C were performed in 5L three-necked round-bottom flasks (Fig. 1). The flasks were partially filled with the solutions described in Tables 1 and 2. The flasks were fitted with a condenser and a soda lime CO₂ trap. The flasks were heated to the temperatures indicated using heating mantles, type K thermocouples and PID controllers prior to

Table 2
Test matrix for second series.

Test ID	pH	Temperature (°C)	Coupons	Solution
Na-B-40-pH“X”	X=7–11	40	10	2.8 g/L B using $\text{B}(\text{OH})_3$ and NaOH (4 L)
Na-B-60-pH“X”	X=7–11	60	10	2.8 g/L B using $\text{B}(\text{OH})_3$ and NaOH (4 L)
Na-B-90-pH“X”	X=7–11	90	10	2.8 g/L B using $\text{B}(\text{OH})_3$ and NaOH (4 L)
Na-B-130-pH“X”	X=7–10	130	4	2.8 g/L B using $\text{B}(\text{OH})_3$ and NaOH (1.4 L)

¹ “AA” is a designation used to indicate that the alloy meets the standards set forth by the Aluminum Association.

Download English Version:

<https://daneshyari.com/en/article/6761108>

Download Persian Version:

<https://daneshyari.com/article/6761108>

[Daneshyari.com](https://daneshyari.com)