Influence of Alkali Metal Oxides and Alkaline Earth Metal Oxides on the Mitigation of Stress Corrosion Cracking in CANDU Fuel Sheathing

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Summary

Stress corrosion cracking (SCC)can cause failures of CANDU® Zircaloy-4 fuel sheathing. The process occurs when a corrosive element (*i.e.*,iodine) interacts with a susceptible material that is under sufficient strain at a high temperature. Currently, there is an ongoing effort to improve SCC mitigation strategies for future iterations of CANDU reactors. A potential mechanism forSCC mitigation involves utilizing alkali metal oxides and alkaline earth metal oxides that willsequester corrosive iodine while actively repairing a protective oxide layer on the sheath. SCC tests performed with sodium oxide (Na_2O) and calcium oxide (CaO) have shown to decrease significantly the sheath degradation.

1. Introduction

Stress corrosion cracking (SCC) is a phenomenon that can lead to failures inCANDU®Zircaloy-4 (Zr-4) fuel sheathing.There are three criteria required for SCC to occur: 1) a susceptible material; 2) a sufficient level of strain must be reached; and 3) the environment must allow SCC to occur [1]. It has been shown that Zr-4is critically strained while exposed to sufficiently high iodine concentrations and temperatures, SCC can occur [2].

The Zr-4 fuel sheathing is strained during normal operation through radiation and thermal induced expansion of UO_2 fuel pellets. The expansion of the pellets causes them to interact with the sheathing, which is also under the compressive force of the coolant. The release of fission products (including iodine) coincides with the thermal expansion of the pellets. These events combined with the fact that the sheathing reaches over 300 °C in temperature create an environment where SCC is possible. While present SCC mitigation strategies satisfy the current requirements (the current failure rate is ~0.01% [3]), alternative SCC mitigation strategies are being investigated that would allow CANDU reactors to reach more advanced fuel cycles (*e.g.*,higher burnups or utilize load-following regimes).

The experiments described in this paper stem from the hypothesis of Lewis*et al.* [4],which is that alkali metal oxideswithin sheath coatings comprise an alternative SCC mitigation strategy in CANDU reactors. These alkali metal oxides (e.g., Na_2O) have the potential to successfully sequester corrosive iodine while providing the added benefit of releasing oxygen to repair the protective oxide layer on the sheathing.Since alkaline earth metal oxides (e.g., CaO) may have a similar mechanism for sequestering iodine and liberating oxygen, they are also investigated in this paper. Oxides chosen for experimentation were selected for both their potential SCC mitigation properties as well as their presence in small amounts within a current SCC mitigation strategy, CANLUB [5].This would allow for easier implementation as they would not introduce any new elements into the CANDU fuel sheathing interface. Therefore calcium (Ca) and sodium (Na) were selected as they satisfied both criteria, and we have incorporated them as metal oxides (*i.e.* Na_2O and CaO) in our experiments. The experiments performed are built upon the work of Wood [6] and the results are compared to the baseline dataset collected by Metzler *et al.* [7].

2. Experimental Results and Analysis

To evaluate the response of Zr-4 sheathing under strain in a hot and corrosive environment, a series of SCC experiments were performedusing a method similar to what was originally developed by Wood.In each experiment, eight slotted ring samples cut from Zr-4 sheathing werestressed using two Zr-4 rectangular block wedges (each 6-12 mm wide). Once the rings were loaded on the wedges, they were placed into an ampoule containing iodine (1530 ± 10 mg) and metal oxide (Na_2O or CaO). Finally, the ampoulewas evacuated to a low pressure (26 ± 20μTorr) and placed in a furnace at 300 °C for five days.

After the heating period of each static ring test was complete, the samples were cleaned and subjected to elastic loads to evaluate their mechanical resistance. The corresponding ring deflections were recorded using a deflection measurement apparatus [8]. Equation 1 displays the expected deflection of a ring sample, D_y, when placed under a mass load (F_y = mg) where *R* is the radius, *l* is the width, *E* is the Young's modulus, and *t* is the ring thickness.

$$D_y = \frac{36\pi R^3 F_y}{Elt^3} \tag{1}$$

Small changes in ring thickness can be measured becausethe deflectionexperienced by a ring is proportional to the inverse cube of its thickness(Equation 1). Thus, deflection measurements can be used to quantify the severity of the corrosive attacks actively reducing the sample thickness.

The results being presented in this paper are part of a larger dataset of static SCC experiments and corresponding deflection results. The results presented by Metzler *et al.* analyzed the baseline dataset in an attempt to determine the effect of iodine concentration, temperature, and wedge size on ring deflection. Those measurements form the baseline to compare the oxide experiments discussed by this paper.

The dataset used for this investigation is comprised of144 slotted rings that were placed on static wedges of various sizes in a hot (300 °C) and corrosive (1530 mg of I_2) environment for five days. From the 144 rings, 24 were placed in ampoules without any oxide additives (baseline measurements), 24 were placed in ampoules containing various amounts of Na_2O, and the remaining 96rings were in ampoules containing various amounts of CaO.

To develop a quantifiable understanding onwhetherthe presence of metal oxides (Na_2O or CaO)actively limited iodine-induced corrosive attack, a multivariable linear regression was performed using Microsoft Excel^{TM}. The regression was performed to model the deflections experienced by each ring when loaded with 95 g. The parameters included are: mass of Na_2O powder, mass of CaO powder, and wedge size. Temperature and iodine concentration were not included as their values were constant in all experiments. The statistics for each parameter from the preliminary regression results are shown inTable 1. The regression model also produced a y-intercept value of 1.06 with a standard error of 0.04 and a *p*-value of 1.4 x 10^{-14}.

Table 1: Initial regression results

Parameter	Coefficients (mm g^{-1})	Standard Error	*p*-value
Na_2O (g)	-0.22	0.03	2 x 10^{-12}
CaO (g)	-0.82	0.06	7 x 10^{-26}
Wedge Size (mm)	1 x 10^{-3}	3 x 10^{-3}	0.69

Negative coefficients and low *p*-values (<0.05) in Table 1 indicate that increasing the Na_2O or CaOmass will *significantly decrease* the slotted ring deflection induced by a 95-g mass load. Conversely, the large *p*-value (> 0.05) for wedge size indicates that the value of wedge size (and therefore induced stress) does not display a correlation with 95-g induced ring deflection. However, as these oxides have different molar masses (Na_2O = 62 g/mol and CaO = 56 g/mol) it is difficult to compare the relative impact of these oxides on ring deflection purely based on mass (where the coefficient unit is mm g^{-1}). Therefore, the regression was modified to determine the deflection decreases resulting from one mole of each oxide. The mass valuesare converted into moles using Equations 2 and 3:

$$n_{Na_2O} = \frac{m_{Na_2O}}{M_{Na_2O}} \tag{2}$$

$$n_{CaO} = \frac{m_{CaO}}{M_{CaO}} \tag{3}$$

Where *n* is moles, *m* is mass, and *M* is molar mass. This conversion is important because it allows for one to compare the magnitude of the decrease in deflection caused by both of the oxides across the neutral plane of moles. The results from an updated regression using mole values (with a y-intercept value of 1.06 with a standard error of 0.02 and a *p*-value of 4.14 x 10^{-81}) are shown below in Table 2.

Table 2: Regression results using moles of alkaline oxide as input

Parameter	Coefficients (mm $mole^{-1}$)	Standard Error	*p*-value
Na_2O	-14	2	2 x 10^{-12}
CaO	-46	4	4 x 10^{-26}

It can be seen that both of the *p*-values are quite low, suggesting that the effect of both oxides have remained statistically significant. In addition, with the units of the input converted to moles, it is possible to compare the effect of the oxides on a more neutral basis. From this analysis it can be stated that the negative slope in deflection results from inlcuding small amounts of CaO is approximately three times more negative than the slope seen from including small amounts of Na_2O. It should be noted that the regression analysis used to perform this investigation presupposes that the factors being analyzed follow a linear trend. Figures 1 and 2 display the results from the experiments in an attempt to determine whether the assumption of linearity holds true for the dataset.

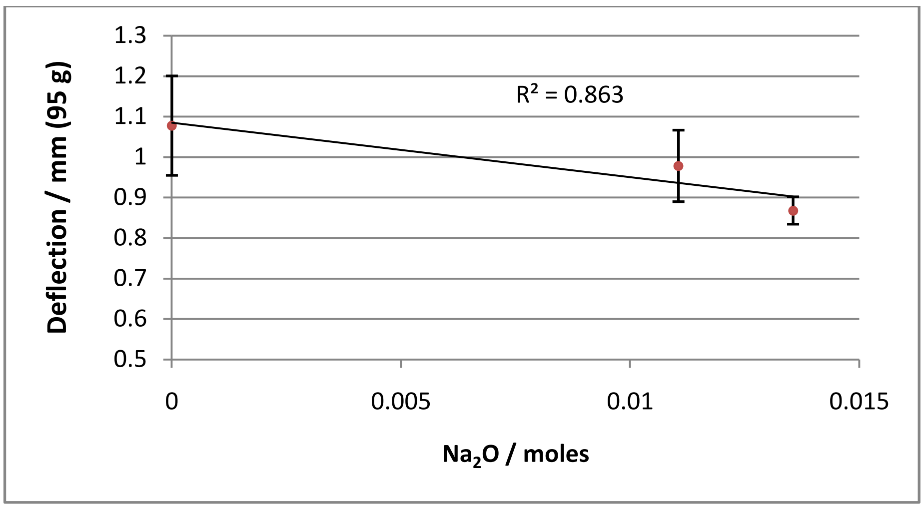

Figure 1: Average Na_2O deflection results (error bars = 1 σ).

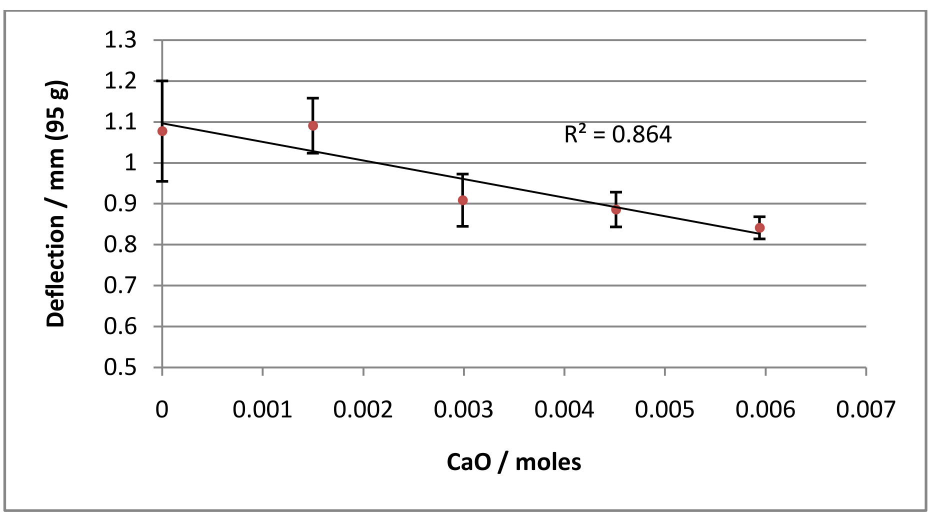

Figure 2: Average CaO deflection results (error bars = 1 σ).

Although Figure 1 indicates a trend whereby the ring deflection decreases with increasing moles of oxide, it is difficult to conclusively state that this indicates alinear trend because there are only three oxide amounts tested for each compound. For this reason a larger range of CaO values were tested, as seen in Figure 2. The R^2 values displayed on Figure 1-2 represent how close the data fit the trend line displayed (an R^2 of 1 represents a perfect fit). The R^2 values are promising, especially for the CaO results that test across a larger range of test conditions. Although the current results are preliminary, the decreasing trend in ring deflection suggests that adding small amounts of these oxides may assist in SCC mitigation.

3. Conclusion

In conclusion, a series of tests were performed to investigate the ability of alkali metal oxides and alkaline earth metal oxides to prevent iodine-induced stress corrosion cracking in CANDU Zr-4 fuel sheathing. Results were analysed using deflection measurements, which can reflect small changes in ring thickness from corrosion. A regression analysis of results determined that both CaO and Na_2Ocreated statistically significant decreases in deflection results (*i.e.*, improved performance). The regression analysis was then repeated using molar values as opposed to mass values and it was determined that one mole of CaO decreases deflection approximately three times more than one mole ofNa_2O. For the molar quantities tested, the relationship betweenCaO amount and deflection has been characterized as a negative, linear trend.Future experiments including other compounds, such as magnesium oxide, are planned.

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