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# Effects of chloride transients on stress corrosion crack in pressure vessel low alloy steels in high temperature water

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### ABSTRACT

This paper evaluated the effects of chloride transients that may occur in boiling water reactor on stress corrosion cracking of pressure vessel low alloy steels. Crack growth rate and the delayed cracking response were enhanced by chloride transient in normal water chemistry while no chloride effect was observed in hydrogen water chemistry. The effects of chloride concentration, stress intensity factor, corrosion potential, and steel heat on the crack growth were discussed. The results from this work provide direct inputs to crack growth disposition models for low alloy steels, water chemistry guidelines and the plant operation practice during chloride transient.

### 1. Introduction

### 1.1. Research background

The importance of water quality control in boiling water reactors (BWRs) is well documented in the Electric Power Research Institute (EPRI) BWR water chemistry guidelines [1]. Over the past 40 years, extensive lab and field experience has demonstrated that good water chemistry can significantly reduce stress corrosion cracking (SCC) of structural materials in the reactor [2–4]. Three chemistry action levels are established by the guideline based on the effects of the chemistry variables on the SCC behaviour of reactor materials, fuel performance and radiation field build-up. Table 1 shows the 2014 BWR Vessel and Internal Project (BWRVIP) guideline for chloride and sulphate transients in primary cooling water [1]. The lowest action level for chloride is 5 parts-per-billion (ppb) by mass for both low corrosion potential  $(E_{corr})$  hydrogen water chemistry (HWC) and high corrosion potential normal water chemistry (NWC). However, recent work by General Electric (GE) and Paul Scherrer Institute (PSI) confirmed that chloride levels down to 3 ppb can accelerate SCC growth in pressure vessel low alloy steel (LAS) [5-10]. Based on these results, BWRVIP issued an interim guidance in 2016 that revised the chloride action limit to 3ppb.

Further study showed that the stress corrosion crack in low alloy steel can exhibit a delayed response after a chloride transient at all action levels [5]. There is an incubation time before the crack growth rate starts to increase after chloride is added. Similarly, there is a delayed time or "memory" effect after chloride is removed before the

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crack growth rate starts to decrease. The delayed response is attributed to the concentration and dilution processes of chloride anion inside the crack.

The new observations of SCC susceptibility of pressure vessel steel at < 5 ppb chloride raised a concern for SCC in boiling water reactors. Chloride can be introduced into the reactor cooling system during periods of significant condenser in-leakage or other incidents. To determine the impact of chloride transients on possible flaws in pressure vessel steels, it is critical to obtain the crack growth rate data of the steel in chloride containing environments and understand how long the fast growth rate can be sustained after clean-up. The current BWRVIP-60-A SCC disposition lines need to be re-evaluated for chloride transients.

## 1.2. Current stress corrosion crack growth rate/stress intensity disposition relationships of low alloy steel in BWR water

Over the past 30 years, lab data and field experience show that SCC of LAS does not occur under steady state and transient free BWR operating conditions at low to moderate *K* values. Various crack propagation theories have been developed. The Ford & Andresen model, validated using high fidelity lab data, is considered the best model for the high and low sulphur bounding lines for low alloy steels in BWR water [3,4,11,12]. Based on the best lab data, EPRI proposed an interim disposition rationale which was accepted by the US Nuclear Regulatory Commission (NRC) [13]. Fig. 1 shows various disposition lines for BWR water. In BWRVIP-60-A, the bottom two curves (GE low sulphur line

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#### Table 1

2014 EPRI boiling water reactor water chemistry control guideline for normal water chemistry, hydrogen water chemistry, hydrogen water chemistry + noble metal chemical application, and on-line noble metal chemistry (data from [1]). The concentration parts-per-billion is defined by mass.

	Action Level 1	Action Level 2	Action Level 3
Chloride	≥5 ppb	> 20 ppb	> 100 ppb
Sulphate	>5 ppb	> 20 ppb	> 100 ppb

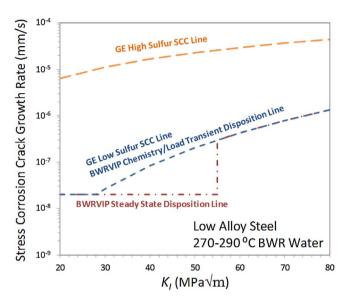


Fig. 1. EPRI BWRVIP stress corrosion crack growth rate/stress intensity disposition lines.

and BWRVIP steady state/constant load disposition line) were proposed for BWR environments. The BWRVIP steady state line is recommended when no water chemistry or load transients exist, which covers most of the lifetime of the reactor. Low alloy steel shows no or minimum SCC susceptibility in these conditions under low and intermediate *K*. The maximum stress intensity value is restricted to be < 55MPa $\sqrt{m}$ , after which the disposition line transitions to the GE low sulphur line. The equations for the BWRVIP steady state lines are:

$$V = 2 \times 10^{-8} \text{ mm/s (steady state line, for } K < 55 \text{ MPa/m})$$
(1)

$$V = 3.29 \times 10^{-14} \, \text{K}^4 \, \text{mm/s} \text{ (steady state line, for } K > 55 \, \text{MPa} \sqrt{\text{m}})$$
(2)

where V represents crack growth rate.

When water chemistry or load transients exist, the GE low sulphur line is recommended to assess crack advance:

$$V = 3.29 \times 10^{-14} K^4 \text{ mm/s (low sulphur line, for all K values)}$$
(3)

When there is an aggressive chemistry or load transient involved, GE high sulphur line serves as an upper bound for stress corrosion crack growth rate in BWR water. The aggressive conditions include high sulphur steel, high corrosion potential, stagnant or low flow rate water, highly impure water conditions (above Action Level 1 in BWR water chemistry guideline). The high sulphur disposition line was not proposed in BWRVIP-60-A because such aggressive environmental conditions are not expected during normal BWR operating conditions. The

equation for high sulphur line is:

 $V = 9.6 \times 10^{-8} K^{1.4} \text{ mm/s (high sulphur line, for all K values)}$ (4)

BWRVIP-60-A does not specify the range of water chemistries or load transients for the three disposition lines in Fig. 1. The original approach for distinguishing low vs. high sulphur response was based on the sulphur activity at the crack tip ( $S^{2-}$  concentration at the crack tip), which requires engineering judgement.

The disposition curves were developed based on the widely-recognized sulphur effects in low alloy steel, where the dissolution of MnS inclusions, intersected and exposed by a growing crack defines the crack chemistry and influences the corrosion fatigue and SCC of carbon steel and low alloy steel. Chloride has a much stronger effect, and is the primary interest of this research. Chloride anions diffuse and concentrate in the crack and influence the dissolution of MnS at the crack tip although it is still unclear what roles chloride may have in the SCC of low alloy steel. Thus, the validity of the existing disposition lines needs to be re-evaluated for chloride environments. The response of the crack to transients – the memory effect – can be significant for chloride.

The main purpose of this research was to evaluate the effects of chloride on the stress corrosion cracking growth rate, assess the memory effect of high sulphur low alloy pressure vessel steels and provide data and a technical basis for changes to the low alloy steel stress corrosion crack growth rate disposition curves and plant operation practice during chloride transient at all three action levels. Quantitative analysis of the memory effect is conducted to determine its consequence during chloride transient. Two different heats of pressure vessel steel from actual reactor pressure vessels (RPV) were evaluated under both cyclic loading condition and constant load/K condition. A wide range of chloride levels (below 5 ppb, 20 ppb, 100 ppb, 500 ppb for NWC, and 5 ppb, 50 ppb, 200 ppb, 500 ppb for HWC) were evaluated to provide adequate data to all three action levels, including chloride levels above the Action Level 3. Effects of corrosion potential, stress intensity factor (K), and heat-to-heat difference were also studied.

### 2. Experimental

#### 2.1. Material procurement and microstructure

Two different heats of high sulphur pressure vessel low alloy steels were studied in this program. They were chosen because they were from the actual reactor hardware and representative of the high sulphur steels used in the plant. The materials were from two different plants and used in the previous EPRI-GE program that evaluated the impact of < 5 ppb chloride on SCC of LAS in high temperature water [5]. The first steel heat was received from South West Research Institute (SWRI, San Antonio, TX, USA) and originally cut from the central portion of the reactor vessel upper head in a cancelled plant. This heat has been extensively studied and documented in EPRI's RPV boric acid corrosion testing program [14]. In this paper, this heat is designated as "SWRI" heat. The second steel heat was received as residual materials from the plant hardware manufacturer and studied in previous EPRI BWRVIP-60-A testing program [13]. To be consistent with its designated name in previous EPRI and industry reports, this second heat is named as "1bG" heat in this paper. The measured chemical compositions of the steels are listed in Table 2. Both steels were SA533 Grade B Class 1 pressure vessel steel with similar composition required by ASTM standard [15].

Table 2

Chemical compositions of the steels tested (wt%) in this program. The samples analysed were taken from the tested specimens.

Heat	Туре	S	С	Al	Со	Cr	Cu	Mn	Мо	Ni	Si	Р	v
SWRI	SA533B	0.015	0.2	0.021	0.018	0.066	0.07	1.25	0.55	0.58	0.23	0.01	0.0015
1bG	SA533B	0.013	0.19	0.028	0.017	0.078	0.099	1.25	0.53	0.62	0.25	0.01	0.003

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