



**STRESS CORROSION CRACKING STUDIES ON FERRITIC LOW ALLOY  
PRESSURE VESSEL STEEL – WATER CHEMISTRY AND MODELLING ASPECTS**

by

PHILIP TIPPING, ULRICH INEICHEN and ROBIN CRIPPS

Paul Scherrer Institut (PSI), Würenlingen and Villigen, CH-5232 Villigen, SWITZERLAND.

**ABSTRACT**

The susceptibility of low alloy ferritic pressure vessel (PV) steels (A533-B type) to stress corrosion cracking (SCC) degradation has been examined in refreshed loop experiments using various boiling water reactor (BWR) type coolant chemistries. Fatigue pre-cracked wedge-loaded double cantilever beam (DCB) and also constantly loaded 25 mm thick compact tension (1TCT) specimens have shown classical SCC attack in various simulated water chemistries. The importance of parameters such as dissolved oxygen content, water impurity level and conductivity, material chemical composition and stress intensity level are discussed in terms of observed occurrence of SCC in these experiments. The relevance of SCC as a life-limiting degradation mechanism for low alloy ferritic nuclear power plant (NPP) PV steel is examined. Some parameters, thought to be relevant for modelling SCC processes in low alloy steels in simulated BWR-type coolant, are discussed. General aspects of environmentally assisted cracking problems in NPP are examined in light of their impact to nuclear safety.

Keywords: Low alloy ferritic pressure vessel steels, stress corrosion cracking, boiling water reactor, loop experiments, simulated water chemistry effects, material chemistry effects, electrochemical potential, model of SCC.

## 1. GENERAL BACKGROUND AND INTRODUCTION

The possibility for environmentally assisted cracking (EAC) in NPP materials has stimulated much research into the topic because of the safety and economic issues at stake e.g. [1,2,3,4]. Whenever a susceptible material having sufficient stress intensity on a crack-like defect is subjected to a chemically active environment, then the pre-conditions for EAC are present. Additionally, the stochastic nature of EAC/SCC processes makes research into the phenomena a challenge. As NPP age, the probability for a crack-like defect to appear and then to grow under the influence of the prevailing environmental conditions, is increased. In this context, for example, the appearance of irradiation assisted stress corrosion cracking in stainless steel after having fast neutron doses (of energy  $E \geq 1$  MeV) of about  $\geq 1 \times 10^{20}/\text{cm}^2$  is a manifestation of the effect of time accumulated under operating conditions. As neutron fluence is accumulated and ageing processes are favoured, (phase stability and atomic diffusion aspects) then EAC/SCC might become a reality in material previously thought immune to the SCC degradation mechanism in the given environment.

The present work was performed (under collaboration – see Acknowledgements) to investigate the effects of various simulated BWR water compositions and conditions on the SCC behaviour of low alloy PV steel.

## 2. EXPERIMENTAL PROCEDURES

### 2.1 Material

The materials investigated are shown in Table 1.

Table 1: Chemical composition of steels (in wt.%)

Material Nr.	C	Si	Mn	S	P	Cr	Mo	Ni	Bal. Fe
20MnMoNi55	0.21	0.23	1.26	0.005*	0.004	0.14	0.53	0.81	
A533 B Cl.1	0.25	0.24	1.42	0.011	0.006	0.12	0.54	0.62	
20MnMoNi55	0.19	0.20	1.38	0.013*	0.008	0.14	0.53	0.53	

\* The two nominal categories of “low” and “high” sulphur were chosen to investigate the effect of this element in favouring SCC.

### 2.2 Specimens

Two types of specimen, namely the 10 mm thick DCB and the 25 mm (1 inch) thick CT were used. The former were wedge loaded to create various levels of stress intensity factor at the fatigue pre-crack. The 1 TCT specimens were loaded, 2 at a time, in the tensile device using a “daisy chain” set-up. Specimens were either pre-autoclaved to build a representative oxide layer or not. Degreasing was performed using pure alcohol.

All specimens were insulated electrically from another using ceramic spacers and were mounted onto a stainless steel frame; a total of 16 specimens could be tested at a time. Platinum leads

were used to connect the silver/silver chloride reference electrode, the working electrodes were specimens and the counter electrode a platinum sheet. Further experimental details can be found in [2].

### 2.3 Constant load experiment

Constant loading was applied to 1TCT specimens in the second loop. The tensile test device, integral with the autoclave was a spindle machine, driven by a high torque electric motor under computer control. Two 1TCT fatigue pre-cracked specimens in a “daisy chain” were tested per experiment. The applied load was used to induce nominal stress intensity factors of between 30 to 80  $\text{MPa}\sqrt{m}$  depending on the original length of the fatigue crack. It should be noted that only 3 experiments have been performed to date (6 specimens) and therefore the results from these are to be regarded as preliminary.

### 2.4 Water chemistry and its control

The types of water chemistry selected for the loop are shown in Table 2

Table 2: Experimental conditions – Autoclave water chemistry (Averages)

Expt. No.	$\text{O}_2/(\text{ppm})$		$\chi/(\mu\text{S}/\text{cm})$		pH	$q/(\text{l}/\text{h})$	$t/(\text{h})$
	In	Out	In	Out			
1	1.15	0.8	1.0	1.1	6.3–6.6	10	400
2	0.6	0.4	1.0	1.1	6.4–6.9	10	450
3	0.38	0.2	1.0	1.1	6.2–6.8	10	580
4	0.40	0.2	1.0	1.1	6.5–6.9	10	540
5	0.34	0.2	1.0	1.1	6.3–7.2	10	920
6	0.6	0.4	0.5	0.6	5.6–6.1	10	580
7	0.6	0.4	0.5	0.6	6.0–6.2	10	620

All parameters were kept sensibly within the chosen ranges by continual adjustments. The dissolved oxygen content was measured by “Orbisphere” instruments; the conductivity ( $\chi$ ) for these particular experiments was reached by restricting the flow of water through the ion exchange resins. (Later experiments, not reported here, have used controlled dosing of known impurities e.g. sodium sulphate, to reach desired conductivity values more rapidly). The flowrate ( $q$ ) was quasi stagnant. Table 3 shows typical results of the water chemistry analysis, (in ppb = parts per  $10^9$ ), experiment 6.

Table 3: Cations and Anions: Experiment 6

Ion	Feedwater-In			Returned water-Out		
	$\bar{x}$ ppb	min. ppb	max. ppb	$\bar{x}$ ppb	min. ppb	max. ppb
Si	23.8	23	25	21	15	24
Mg	1.79	1.31	2	1.89	1.12	3.01
Ca	3.75	1.62	11.5	2.63	1.3	6.15
Zn	0.33	3*nn	0.4	0.73	4*nn	1.7
Mn	0.24	1*nn	0.3	1.53	1*nn	4.9
Fe	0.76	3*nn	1.2	0.78	2*nn	1.3
Cr	3.5	3	5	3.64	nn	5
Cu	1.2	3*nn	1.4	3.2	5*nn	4.1
Al	1.42	nn	2.4	2.73	2*nn	6.5
Ba	0.1	nn	0.14	0.18	nn	0.31
K	10	4	14	9.5	4	24
Cl	15.08	10	17.9	17.25	13.9	21
NO <sub>3</sub>	nn	-	-	nn	-	-
SO <sub>4</sub>	10.34	nn	12.8	10.7	nn	18.1

\*\*nn – not detectable.

In all water samples, the following ions were below the 5 ppb limit (Values in ppb): 5 P, 2 S, 3 As, 2 Sn, 1 Mo, 0.5 Co, 2 Pb, 0.2 Cd, 0.5 Ni, 1 V, 0.1 Be, 0.5 Ag, 0.3 Ti, 0.5 Zr, 0.05 Sr, 2 Na, 0.05 Li.

Calibration standard for anions (ppb): 20 Cl, 10 NO<sub>3</sub>, 10 SO<sub>4</sub>.

### 3. RESULTS

The number of specimens having SCC are shown below in Table 4.

Table 4: Observed stress corrosion cracking in DCB specimens – Summary of results

Expt. No. Nr.	Autoclave		Probes		Time/h		Number Cracked Probes	Flowthrough l/h		** Stress- intensity MPa√m
	1	2	1	2	* Run-in	Expt.		1	2	
1	Yes	Yes	15	15	136	376	8	10	10	15–79
2	Yes	Yes	15	15	9	453	4	10	10	15–84
3	Yes	Yes	13	13	24	578	0	10	10	18–65
4	Yes	Yes	15	15	24	538	0	10	10	19–68
5	Yes	Yes	15	15	17	918	0	10	10	26–76
6	Yes	Yes	15	15	51	581	0	10	10	21–47
7	Yes	Yes	15	15	53	620	1	10	10	33–63

\* Run-in time to allow the conductivity ( $\chi/(\mu\text{S/cm})$ ) to reach selected value for the particular experiment.

\*\* Range investigated within the experiment.

The types of steel showing SCC were:

**Expt.No. 1** – 20MnMoNi55 with 0.05 wt.% S (5 Probes), 20MnMoNi55 with 0.010 wt.% S (2 Probes) and A533 B Cl.1 with 0.011 wt.% S (1 Probe). Total = 8 Probes.

**Expt. No. 2** – 20 MnMoNi55 with 0.005 wt.% S (3 Probes) and 20MnMoNi55 with 0.010 wt.% S (1 Probe). Total = 4 Probes.

**Expt. No. 7.** – A 533 B with 0.011 wt.% S (1 Probe).

A specimen with SCC (Expt.No.1, stress intensity factor =  $76.1 \text{ MPa}\sqrt{\text{m}}$  is shown in Figure 1.)

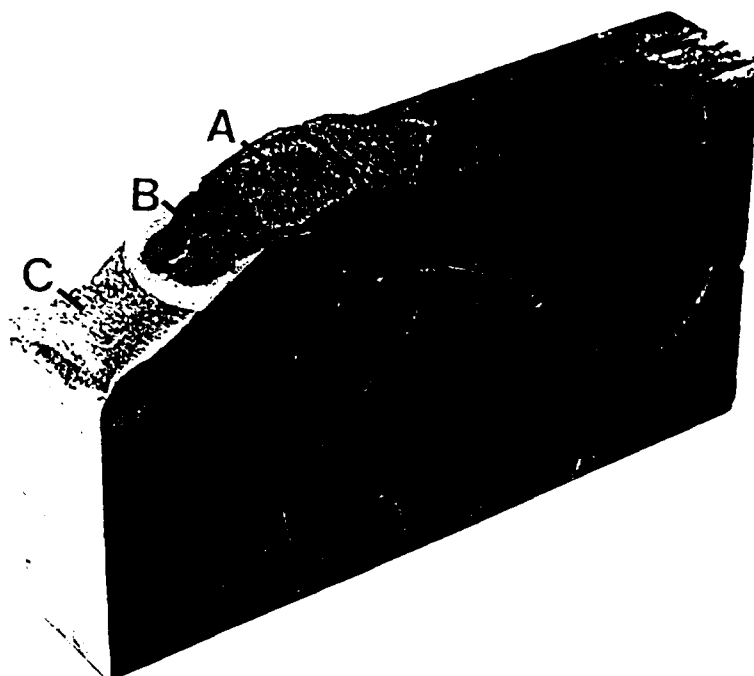


Figure 1: DCB probe (half).  
Expt. Nr.1, 20MnMoNi55, 0.005 wt.% S,  $K_I = 76.1 \text{ MPa}\sqrt{\text{m}}$   
A: Pre-crack (fatigue), B: Stress corrosion cracking region, C: Mechanical break

#### **4. CONSIDERATIONS ON MODELLING SCC PROCESSES AT THE TIP OF A SHARP CRACK IN LOW ALLOY FERRITIC PRESSURE VESSEL STEEL IN SIMULATED BWR WATER.**

According to [5], if the electrochemistry is “favourable”, then SCC is almost inevitable. The processes of SCC have been the subject of various modelling attempts over the years, see [6,7]. The basic idea that is often found concerning SCC, at least in low alloy pressure vessel steels, is one which involves the rupture of a protective magnetite ( $\text{Fe}_3\text{O}_4$ ) film by the emergence of dislocations which then permit freshly exposed metal (“active”) to come into contact with a chemically effective environment (when upset water chemistry is present locally). The motion of the dislocations is provided by the applied tensile loading or even the material’s own internal stress.

The usual approach for modelling is to identify the possible contributing mechanisms in the given situation. The following first examines the environmental (water chemistry) aspects and then the material aspects.

##### **4.1 Water Chemistry**

###### **4.1.1 Dissolved oxygen**

The importance of dissolved impurity oxygen in the coolant of BWR has long been recognized. The need to suppress this impurity has led to the use of the so-called “hydrogen water chemistry (HWC) approach. The dissolved oxygen in the feedwater can be controlled (stripping) and there are guidelines available [8]. The actual amount of dissolved oxygen in BWR reactor core water is very difficult to assess due to radiolysis; the HWC approach is to inject hydrogen into the reactor water so that it will combine with oxygen to form water, thus suppressing the amount of dissolved oxygen. The importance of dissolved oxygen in the water lies in its effect on raising the electrochemical potential of the low alloy steel, thus setting up a potential drop down a possible crack-like defect; a high water conductivity favours the concentration of damaging ionic species in the crack tip electrolyte under the action of the potential gradient down the crack. Dissolved oxygen in feedwater, above 0.2 ppm, should be avoided accordingly. Dissolved oxygen content is therefore an important parameter for a model of SCC.

###### **4.1.2 Conductivity and impurities**

The conductivity of the water is important since it will influence the rate at which electrochemical reactions (redox) can occur. The types and concentrations of impurity ions will vary depending on factors such as materials used in the BWR construction, local water flow (deadlegs), water chemistry transients or upsets due to start-up or shut-down or ion exchange resin incursions (e.g. sulphate) etc. Variations in feedwater chemistry will also influence the reactor water, irrespective of radiolysis effects occurring in the core region. The concentration of such anions as sulphate ( $\text{SO}_4^{--}$ ) or chloride ( $\text{Cl}^-$ ) is important since they may be further locally increased in a crack tip due to the differential oxygen effect causing a potential drop down the crack (see above section concerned with oxygen). This anion concentration “pump” may cause sufficient enrichment of impurities which, together with hydrolysis (lowered pH), can accelerate local corrosion and SCC processes. The presence of manganese sulphide (MnS) in the steel can also aid the water acidification at the crack tip by hydrolysis (see also below under material aspects). The types and amounts of impurities are important in SCC models.

##### **4.2 Material Aspects**

The material aspects can be sub-divided into two parts namely 1) chemical composition and 2) stress state.

#### 4.2.1 Chemical composition

The importance of sulphur (in the form of manganese sulphide, MnS) lies in its ability, in unfavourable water conditions, to dissolve and yield particularly aggressive sulphide ions which can acidify the crack tip water and therefore favour corrosion. Not only the amount of MnS is important but also its morphology. Low sulphur PV steels are to be favoured not only to ensure good mechanical properties (e.g. high Charpy upper shelf energy) but they also offer less chance (statistically) for a local attack at a crack tip if a crack forms and propagates; if it does not meet a MnS particle then the rate of crack propagation is likely to be less. Large plate-like inclusions or stringers of MnS lying in the crack plane are likely to give rise to high crack growth rates whilst discrete globules of MnS are less likely to cause rapid rates since relatively large distances of "immune" material will lie between the MnS globules. Product form (forged, cast, rolled, welded) will influence the microstructure and morphology of phases and is therefore an important aspect in trying to quantify observed SCC occurrence.

#### 4.2.2 Material stress state

The process of SCC depends also on whether enough tensile stress is acting on the crack tip; the linear elastic stress intensity factor  $K_I$  must exceed a lower critical value, known as  $K_{ISCC}$ , before measurable crack growth rates are seen. The level of  $K_{ISCC}$  varies from material to material and also the environment. For the presently investigated low alloy PV steels, a value of  $K_{ISCC}$  can be 20–30  $\text{MPa}\sqrt{\text{m}}$  in loop experiments and upset water conditions (0.4 ppm dissolved oxygen and 0.5  $\mu\text{S}/\text{cm}$  conductivity). As the value of  $K_I$  is increased above  $K_{ISCC}$  then the rate of crack growth also increases, usually reaching a plateau behaviour when multi-fissuration causes the rate to appear independent of the stress intensity value. Eventually, a point is reached when the critical fracture mechanical value  $K_{IC}$  is approached and rupture occurs rapidly, without any aid from the environment. The level of stress intensity on a crack in a susceptible material in a chemically active environment is an additional modelling consideration.

### 5. DISCUSSION AND CONCLUSIONS

Results of autoclave (loop) experiments with wedge-loaded double cantilever beam (DCB) and 1TCT specimens of pressure vessel (PV) steel in simulated quasi-stagnant off-specification BWR water have been presented. Two basic types of ferritic reactor PV steel, having sulphur contents between 0.005 to 0.013 weight % S have now been shown to exhibit environmentally assisted cracking (EAC) in these type of experiment. Cracking occurs in times as short as 400h in these experiments. Dissolved oxygen contents in the water at levels of 1.5 ppm and less, and conductivities at 1  $\mu\text{S}/\text{cm}$  (at a room temperature pH of 6.3 to 6.9) can cause SCC when the  $K_I$  value exceeds 27  $\text{MPa}\sqrt{\text{m}}$ .

The results indicate that the conductivity of the water is important; when the dissolved oxygen content is 0.4 ppm (conductivity of 1  $\mu\text{S}/\text{cm}$ ), cracking has still occurred in 400h at relatively medium-range values of stress intensity values for these type of steel. In these experiments, the impurities causing the conductivity were not all known. The water analysis indicated low levels of impurity generally but all together they contributed to the conductivity observed. The possibility of synergistic effects should not be forgotten; some combination of ions may be worse than others for a given level of conductivity.

The stress corrosion cracking observed in these steels in refreshed loop experiments must be addressed in terms of ageing effects (phase stability), the dominantly prevailing water chemistry history and the actual stress intensity at the tip of the crack in order to assess the overall transferability of such loop experiment data to NPP's. The problem of crack nucleus initiation under SCC conditions is complex in PV steels. It may take years before a viable nucleus can form;



the stochastic nature of SCC makes interpretation and transferability of relatively short-term laboratory results to real situations quite problematic. The verification of existing water chemistry operating limits (e.g. dissolved oxygen and conductivity ranges) of BWR appears to be worthwhile under consideration of impurity concentration in a possible crack-like defect which is growing under load control conditions.

The type of specimen loading appears to be important. The wedge loaded DCB specimens showed cracking but it could not be stated at which point in time the cracks started. With the wedge loaded DCB specimen, the stress intensity factor will decrease as the crack progresses and therefore it will eventually fall below  $K_{ISCC}$ ; crack growth will stop. The 1TCT specimens, loaded in a constant manner, have a  $K_I$  value which will increase as crack growth takes place; the crack growth rate will increase and lead, eventually, to failure as  $K_{IC}$  is reached. For the few data available, the constant load test appears more severe than the wedge-loaded test for a given equivalent water chemistry and stress intensity.

A very important aspect concerned with the growth of cracks in pressure boundary components under service conditions is whether such defects will eventually cause leak before break (LBB) or not. More research is required to assess parameters likely to influence LBB.

It is important to note that the types of water chemistry used in these experiments were nominally "upset" with regard to "normal" operating conditions. In particular, the dissolved oxygen and conductivity values were somewhat higher than what is thought to be present in operating BWR. However, the possibility of local water chemistry variations, with increases of impurities, must be addressed. Furthermore, there was no radiolysis in these experiments and so the undesirable production of oxidising species, e.g. peroxides, was not possible; this latter effect is present in operating water cooled reactors. The presence of dissolved oxidizing radicals will raise the electrochemical potential of the material. The rate of occurrence of SCC which has been observed in these laboratory loop experiments has shown the importance of studying and monitoring this (potentially) dangerous and costly NPP degradation mechanism.

## 6. FUTURE WORK

The SCC investigations will continue to explore the combinations of material, water chemistry and stress state which will lead to SCC. Backfitting of the loops will be undertaken to implement "on-line" monitoring of crack initiation and propagation. Water chemistry monitoring will be improved using high temperature pH, conductivity and electrochemical potential measurements.

The effects of cyclic loading and slow strain rate testing will be also looked into. The autoclaves will be modified to allow jets of coolant to impinge onto erosion/corrosion specimens; in this way two sorts of experiment will be performed simultaneously.

## 7. ACKNOWLEDGEMENTS

Our sincere thanks go to Prof. Dr. Markus O. Speidel, Dr. Ruth Magdowski and Dr. Andi Kraus of the Swiss Federal Institute of Technology in Zürich for the good collaboration and help in all aspects of this project. The financial support of the Swiss Federal Nuclear Safety Inspectorate for one author (U.Ineichen) and Swiss utilities is also gratefully acknowledged.

## 8. REFERENCES

[1] Speidel, M.O and Magdowski, Ruth.: Stress corrosion cracking of nuclear reactor pressure vessel and piping steels. International Journal of Pressure Vessels and Piping, Vol. 34, 1988.

- [2] **Kraus, A.:** Stress corrosion cracking of pressure vessel steels in high temperature water. Dissertation Swiss Federal Institute of Technology in Zürich. Dissertation Nr. ETH 10644, 1994.
- [3] **Magdowski, R., Kraus, A. and Speidel, M.O.:** Stress corrosion cracking of reactor pressure vessel steel in 288°C water: The effect of oxygen, electrochemical potential and steel composition. Corrosion '94, Paper No. 133, NACE. April 1994.
- [4] **Scott, P.M.:** A review of environmental effects on pressure vessel integrity. Proceeds of the third International Symposium on Environmental Degradation of materials in nuclear power systems—water reactors. Traverse City, Michigan, USA, 1987.
- [5] **West, J.M.:** in “Basic Corrosion and Oxidation” , ISBN 0-85312-196-6 Chapter 12, p 145-162, Pub. Ellis Horwood, 1980.
- [6] **Andresen, P.L. and Ford, F.P.:** Use of fundamental modeling of environmental cracking for improved design and lifetime evaluation. Journal of Pressure Vessel Technology, Vol.115, p 353-358, Nov. 1993.
- [7] **Andresen, P.L. and Ford, F.P.:** Life prediction by mechanistic modelling and system monitoring of environmental cracking of Fe and Ni alloys in aqueous systems. Materials Science and Engineering, A 103, p 167-183, 1988.
- [8] Electrical Power research Institute (EPRI), Palo Alto, California, USA guidelines for BWR Normal Water Chemistry.