

# INFLUENCES OF H<sub>2</sub>SO<sub>4</sub> AND NaCl CONCENTRATIONS ON STRESS CORROSION CRACKING OF AISI 304 STAINLESS STEEL

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**Abstract.** This paper presents the influence of H<sub>2</sub>SO<sub>4</sub> and NaCl concentrations on the corrosion mode of AISI 304 stainless steel in H<sub>2</sub>SO<sub>4</sub>-NaCl aqueous solutions. Immersion test was conducted at room temperature using U-bend specimens. The specimens in annealed and sensitized conditions were immersed in aqueous solutions containing H<sub>2</sub>SO<sub>4</sub> concentration in the range of 0 to 3.0 kmol/m<sup>3</sup> with 1.5 kmol/m<sup>3</sup> interval, and NaCl concentration in the range of 0.5 to 2.0 kmol/m<sup>3</sup> with 0.5 kmol/m<sup>3</sup> interval. Results showed that, specimens in sensitized condition have a higher mass loss and higher corrosion rate. In addition, the experimental result also indicates that the two solutes have synergistic effect on corrosion mode of the material that is stress corrosion cracking (SCC) and general corrosion, which occur within a specific range of concentration. SCC region became smaller as the H<sub>2</sub>SO<sub>4</sub> and NaCl concentration increased. However, the occurrence of SCC was high when sensitization treatment was subjected to the specimens. The appearance of surface damage and crack morphology were revealed by using scanning electron microscopy (SEM).

## Introduction

Austenitic stainless steels are known to be a major contributor in a variety of industries ranging from the pulp and paper industry to chemical, petrochemical and nuclear industries. Their wide-ranging applications are facilitated by virtue of their good fabricability, weldability, high toughness and excellent corrosion resistance in various service environments. According to Khatak and Baldev Raj [1], the general corrosion resistance of austenitic stainless steels is attributed to the formation of a thin, adherent and self-healing 'passive film' developed on the surface in most environments. However, when the 'passive film' is broken, austenitic stainless steels could fail with different types of corrosion modes when exposed to severe service environments. Stress corrosion cracking (SCC) is one of the most important causes of corrosion failures that affects the performance of austenitic stainless steels especially AISI 304 stainless steel. This type of corrosion is usually difficult to be detected since it occurs at condition when the structure undergoes sensitization treatment and stress simultaneously. The source of these stresses may be due to the applied stress, residual stress, and thermal or from the welding. Austenitic stainless steels will not fail mechanically unless the stress applied is adequate to facilitate the cracking process [2].

Many researchers have dealt with SCC in austenitic stainless steels in various conditions such as using different source of stress and corrosive medium. However, the first study of SCC in a U-bend AISI 304 stainless steel specimen in aqueous solutions of H<sub>2</sub>SO<sub>4</sub> - NaCl at 303K was reported by Acello and Green [3]. After this report, many researchers [4-7] dealt with SCC in these solutions, and they [6-7] reported that SCC occurs in a particular concentration range of NaCl and in the other range general corrosion occurs or cracking is suppressed.

Corrosion mechanism of SCC is still not well understood due to complexity of the process. Thus, more experimental works should be conducted to create better understanding of SCC corrosion mechanism and to find unsolved phenomena. This research intends to investigate the influence of

H<sub>2</sub>SO<sub>4</sub> and NaCl concentrations and sensitization treatment on SCC of AISI 304 stainless steel in H<sub>2</sub>SO<sub>4</sub>-NaCl aqueous solutions.

### Experimental Procedure

**Test material.** Material used in this study was a commercial grade AISI 304 stainless steel with 120 mm in length, 20 mm wide and 1 mm thickness. The chemical composition obtained by emission spectroscopy is shown in Table 1. 12 specimens of AISI 304 stainless steel were set to be in annealed condition whereas another 12 were subjected to heat treatment. The heat treatment was done to make sure that the specimens were in sensitized condition. The specimens were subjected to heat treatment at 800 °C for 120 mins followed by air cooling in order to remove the internal stresses induced by heat treating, forming or machining.

Table 1 Chemical Composition of AISI 304 Stainless Steel (wt%)

Material	C	Si	Mn	P	S	Ni	Fe	Cr	Cu
AISI 304 Stainless Steel	0.063	0.49	1.53	0.030	0.005	8.75	71.2	17.2	0.303

**SCC Test.** The SCC tests were carried out in 12 different concentration mixtures of H<sub>2</sub>SO<sub>4</sub> and NaCl solution for each set. The H<sub>2</sub>SO<sub>4</sub> concentration ranged from 0 to 3.0 kmol/m<sup>3</sup> whilst NaCl concentration was set to range from 0.5 to 2.0 kmol/m<sup>3</sup>. Table 2 shows various corrosion test solutions for this study. The experiment was divided into two sets of SCC test which were in annealed and sensitized conditions, respectively. The surface specimens were wet-polished with a series of silicon carbide abrasive papers, rinsed in alcohol thoroughly, followed by rinsing in acetone and then dried. The specimens were formed in the shape of U-bend (constant strained samples) as per ASTM G30 [8]. The standard ASTM G30 procedure for preparing U-bend sample gives the average strain in the sample based on the following equation:

$$\varepsilon = \frac{T}{2R} \quad (1)$$

where T is the thickness and R is the radius of curvature of the U-bend, and the average strain is assumed to be constant throughout the sample. The average strain was found to be 0.0156 based on the previous equation. The stress applied to the specimen was obtained by using the corresponding value of strain of the stress-strain curve for austenitic stainless steel. By using this method the stress in the specimen was found to be 310 MPa. The immersion tests were carried out for 168 hours (7 days) at room temperature. The mass of the test specimens were measured before and after the immersion test by using a digital weighing balance in order to determine mass loss of each specimen. The specimens were cut in parallel to the direction of stress and normal to the surface after the immersion test. Then, the specimens were polished and cleaned like the previous methods before they were subjected to etching process to reveal the microstructures. The cross section of the samples was observed by scanning electron microscope (SEM) and the type of corrosion was obtained.

Table 2 Various Corrosion Test Solutions

Specimen Number	1	2	3	4	5	6	7	8	9	10	11	12
NaCl Concentration	0.5	0.5	0.5	1.0	1.0	1.0	1.5	1.5	1.5	2.0	2.0	2.0
+ H <sub>2</sub> SO <sub>4</sub> Concentration (kmol/m <sup>3</sup> )	+	+	+	+	+	+	+	+	+	+	+	+
	0.0	1.5	3.0	0.0	1.5	3.0	0.0	1.5	3.0	0.0	1.5	3.0

## Result and Discussion

**Effects of H<sub>2</sub>SO<sub>4</sub> and NaCl Concentration on Mass Loss.** Table 3 shows the data for U-bend specimens of AISI 304 stainless steel in annealed and sensitized condition.

Table 3 Data for U-bend Specimens of AISI 304 Stainless Steel in Annealed and Sensitized Condition

Concentration of NaCl (kmol.m <sup>-3</sup> )	Concentration of H <sub>2</sub> SO <sub>4</sub> (kmol.m <sup>-3</sup> )	Annealed		Sensitized	
		Mass Loss (g)	Corrosion Rate (mmpy)	Mass Loss (g)	Corrosion Rate (mmpy)
0.5	0.0	0.239	0.319	0.928	1.236
0.5	1.5	4.242	5.628	5.137	6.952
0.5	3.0	1.630	2.149	5.222	6.957
1.0	0.0	0.168	0.222	0.995	1.321
1.0	1.5	1.554	2.095	2.089	2.736
1.0	3.0	1.260	1.665	2.195	2.901
1.5	0.0	0.582	0.769	0.863	1.148
1.5	1.5	1.507	1.974	2.528	3.408
1.5	3.0	1.576	2.080	1.821	2.435
2.0	0.0	0.505	0.669	0.887	1.182
2.0	1.5	2.659	3.551	1.926	2.545
2.0	3.0	1.788	2.386	2.622	3.471

Based on the previous table, it is shown that specimens with addition of H<sub>2</sub>SO<sub>4</sub> have higher mass loss as compared to specimens that were immersed only in NaCl solution. This condition happened due to the rate of intergranular corrosion of AISI 304 stainless steel increases with increasing sulfur concentration at grain boundaries in highly oxidizing solutions [9]. Furthermore, the maximum SCC tendency was associated with elemental sulfur formation around the cracks [10]. From the experiment, it showed that sulfide ions were highly aggressive SCC agents for sensitized specimens at room temperature. In addition, it is also noticed that sensitized specimens have higher mass loss than annealed specimens. It is caused by the precipitation of the chromium rich carbide such as Cr<sub>23</sub>C<sub>6</sub> along the grain boundaries and lead to chromium depleted zones at the grain boundaries.

**Effects of H<sub>2</sub>SO<sub>4</sub> and NaCl Concentration on Corrosion Mode.** Figure 1 and 2 show the mapping of corrosion type for AISI 304 stainless steel in annealed and sensitized condition, respectively. The region for SCC is shown by the broken line drawn surrounding it. From those figures, it can be seen that the occurrence of SCC happens only within a specific concentration range of H<sub>2</sub>SO<sub>4</sub> and NaCl while general corrosion dominates for the other range of concentrations. It is also noticed that SCC region becomes smaller as the H<sub>2</sub>SO<sub>4</sub> concentration increased and NaCl concentration increased. The same result was also reported by Satoshi Sunada [7] where SCC happened only in certain range of concentrations whereby general corrosion took place at the other range of concentrations. In addition, it is clearly seen that SCC occurs more in specimens that undergo sensitization treatment. It is again due to the grain boundaries attack and chromium precipitation in specimens that undergo sensitization. Specimens with sensitization treatment are associated with the precipitation of the chromium rich carbide such as Cr<sub>23</sub>C<sub>6</sub> along the grain boundaries. During the carbide precipitation, interstitial carbon diffuses rapidly to the grain boundaries. Slower diffusion rate of the chromium results in the chromium depleted zones at the grain boundaries. In this state, specimens that undergo sensitization treatment are susceptible to intergranular stress corrosion cracking. This eventually leads to higher occurrence of SCC in sensitized specimens.

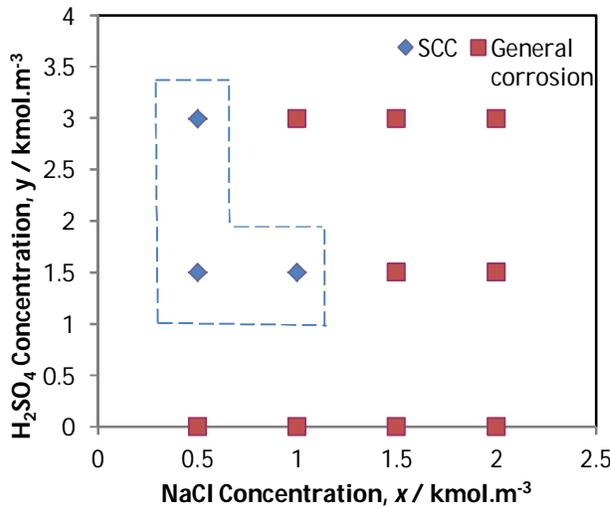


Fig. 1 Corrosion type map of AISI 304 stainless steel in annealed condition after the SCC test in various concentrations of H<sub>2</sub>SO<sub>4</sub>-NaCl aqueous solutions.

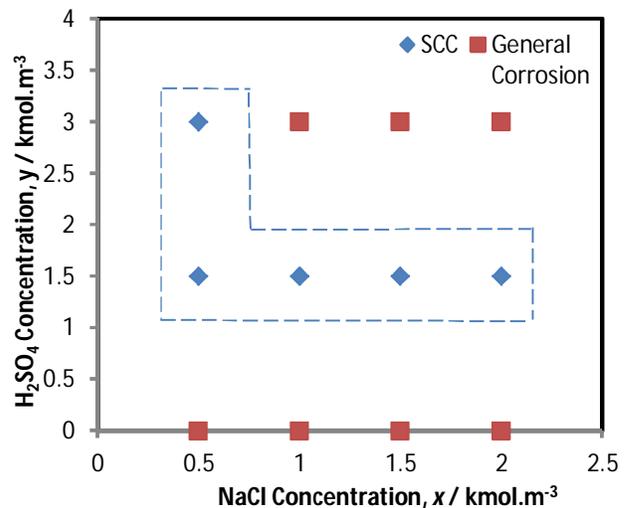


Fig. 2 Corrosion type map of AISI 304 stainless steel in sensitized condition after the SCC test in various concentrations of H<sub>2</sub>SO<sub>4</sub>-NaCl aqueous solutions.

Figure 3 shows SEM micrograph of the cross sections of the specimens in annealed condition when subjected to immersion test in 0.5 kmol/m<sup>3</sup> NaCl with 0, 1.5 and 3.0 kmol/m<sup>3</sup> H<sub>2</sub>SO<sub>4</sub>. General corrosion with no grain boundary corrosion or cracking can be seen for the solution without H<sub>2</sub>SO<sub>4</sub>. However, SCC is dominant in specimens having H<sub>2</sub>SO<sub>4</sub> concentrations of 1.5 and 3.0 kmol/m<sup>3</sup>. It can be concluded that SCC at this region is active compared with other regions.

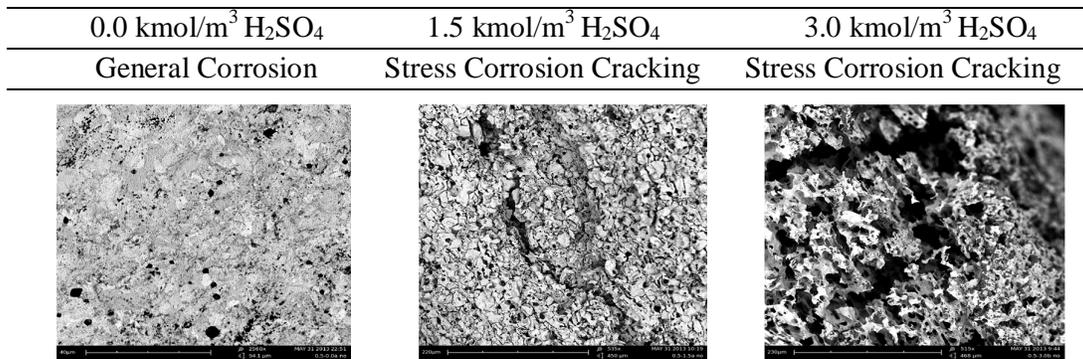


Fig. 3 SEM micrograph of the cross section of the specimens in annealed condition after SCC test in 0.5 kmol/m<sup>3</sup> NaCl with 0, 1.5 and 3.0 kmol/m<sup>3</sup> H<sub>2</sub>SO<sub>4</sub>.

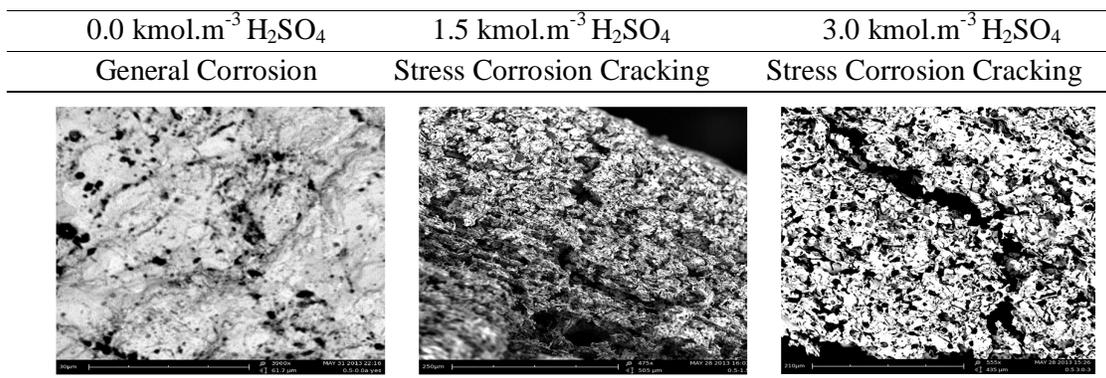


Fig. 4 SEM micrograph of the cross section of the specimens in sensitized condition after SCC test in 0.5 kmol/m<sup>3</sup> NaCl with 0, 1.5 and 3.0 kmol/m<sup>3</sup> H<sub>2</sub>SO<sub>4</sub>.

Figure 4 illustrates the corrosion mode of sensitized AISI 304 stainless steel in aqueous solution containing  $0.5 \text{ kmol/m}^3$  NaCl with 0, 1.5 and  $3.0 \text{ kmol/m}^3$   $\text{H}_2\text{SO}_4$ . Specimen without  $\text{H}_2\text{SO}_4$  shows no sign of SCC and general corrosion takes place. However, specimens subjected to immersion test in 1.5 and  $3.0 \text{ kmol/m}^3$   $\text{H}_2\text{SO}_4$  show sign of SCC since there are cracks when observed under SEM.

## Conclusion

As a conclusion, mass loss was influenced by the sensitization treatment of the AISI 304 stainless steel and the concentration mixtures of NaCl and  $\text{H}_2\text{SO}_4$ . Mass loss increased as the specimens undergo sensitization treatment due to the effect of grain boundaries attack and chromium precipitation in the test specimens. This will eventually increase the corrosion rate of the SCC test specimens. In addition, SCC occurred at certain concentration mixtures of NaCl and  $\text{H}_2\text{SO}_4$  whilst general corrosion took place in other ranges of concentration. SCC region becomes smaller as the  $\text{H}_2\text{SO}_4$  concentration increased and NaCl concentration increased. However, the occurrence of SCC is high when sensitization treatment is done to the specimens.

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