

# Corrosion Activity of Carbon Steel in Oxalic Acid Solution

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## Introduction

Carbon steel (CS) is most commonly used materials in the primary circuit of the Pressurized Heavy Water Reactor (PHWR). Primary circuit includes reactor cooling pipe, primary loop, reactor pressure vessel (RPV), residual heat removal system (RHR), reactor water cleanup system (RWCU), feeder, condenser, cooler and steam generator. These components, especially feeder, undergo corrosion because of high temperature coolant with structural material during the operation

The metallic oxide layer formed during reactor operation over the base material (such as carbon steel) traps radioactive corrosion products and radionuclides of transition metals (Co<sup>60</sup>, Mn<sup>54</sup>, Cr<sup>51</sup>, etc.). The radionuclides must be removed to minimize the radiation exposure dose and removal of this radioactivity can be achieved by chemical decontamination; removing the magnetite or other oxide layer in PHWR by dissolving it with a reductive chemical reagent without causing excessive corrosion of the base metal. Different types of commercialized reductive reagents are used such as CORD (Chemical Oxidation Reduction Decontamination), CITROX (Citric Oxalic Acid), LOMI (Low Oxidative Metal Ion), and CANDECON (CANadian Decontamination and REMdiation). But the CORD families are being extensively used in both operating power plants and prior to dismantling [1]. The chemical reagents used for decontamination may have a corrosion affect as well after the oxide dissolution. Among all organic acids, oxalic acid has been using for leaching purpose because it has good complexing ability and high acid strength. Oxalic acid can be removed completely after decontamination by the process calcination.

The goal of this work is to examine the corrosion behavior of Carbon Steel Grad. B (mild steel) in various concentrations of oxalic acid (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>). Carbon steel (CS) specimens were exposed in the acidic media for 18 hours at 95°C and corrosion rates were evaluated, using the weight loss method. The dissolved Fe concentration was analyzed by the Atomic Absorption Spectrometry. The corrosion products were characterized by EPMA including

surface and element analysis. Fe dissolution and corrosion rate were found to be increased with the increasing concentration of the oxalic acid. The Intergranular corrosion (IGC) seems to be happened earlier than the formation of corrosion products and oxalate passivation. These corrosion behaviors may provide pathways for contaminants to diffuse into the bulk substrate.

## Methods and Results

### 2.1 Specimen and materials

The chemical composition of CS was analyzed by XRF (X-250, SciAps) and was given in Table 1. CS coupon of size for 10mM OA was 15.08mm in length, 11.99mm in width, and 3.00mm in height. And, one of 20 mM OA was 15.03mm in length, 12.14mm in width, and 2.99mm in height. As shown in Fig. 1, each of them has different dimension

### 2.2 Preparation of Oxalic Acid Solution and Dissolution Studies

Two solutions of each 10 mM and 20 mM oxalic acid (Lot no.050922, from Dc Chemical Co.Ltd.) of 150 mL is prepared in distilled water. Before reaction, the pH of all solutions was recorded. Dissolution tests of CS coupon were performed separately in batch reactors with volume of 150mL oxalic solution at 95°C for 18 hours. The coupons were taken out from the glass jacketed reactor after 18 hours and then dried in a desiccator. The yellow texture of complex over the surface has been removed by ultrasonication. And measured the weight and dimension. The pH was measured after one day. These solutions were filtered using syringe filter of 0.45µm then diluted 100 times and performed atomic absorption spectrometry (AAS) for iron analysis.

### 2.3 Weight Loss Measurement

The 10 mM and 20 mM oxalic acid have Fe dissolution of 276 and 401 ppm, respectively. The atomic absorption spectrometry data shows higher concentration of the Fe in both solutions. The dissolution activity of CS coupon in oxalic acid solutions are seen in the weight and dimension loss data.

Table 1. Chemical Composition of reference CS grade. b and coupon used in this work by XRF

Elements wt%	C	S	Pb	Mn	Nb	Ni	Mo	Cr	Cu	P	Si	Fe
Reference	0.115	0.020	-	0.33	-	0.021	0.005	0.043	0.04	0.018	0.020	Bal.
Coupon	0.30	-	0.055	0.926	0.009	-	0.005	0.038	-	-	0.383	Bal.

The weight loss of CS coupons before and after the reaction were given in Fig. 2. The coupons have percent weight loss of 1.02% and 1.51% in 10 mM and 20 mM oxalic acid solution, respectively. While the dimensions indicate the wall-thinning has been taken place in both solutions.



Fig. 1. Carbon Steel (CS) coupon (a) before, and (b) after dissolution reaction, left 10 mM, right 20 mM.

#### 2.4 Corrosion Rate Analysis

Fig. 3 shows the corrosion rate obtained through mass loss tests of the samples. Weight of the carbon steel coupon were lost in both of the solutions after the 18 hours of reaction in the oxalic acid solution indicating the possible corrosion of the coupon surface. In case of 20 mM, even though the wall thinning effect is seen in length, but the width and breadth were found to be thicker, which may indicate the metal dissolution was occurred in length orientation. Because the carbon steel has been found to undergo by corrosion by the anodic dissolution of the metal due the presence of oxalic acid. This corrosion rate of carbon steel was shown by Fig. 3 is because of hydrogen evolution by the oxalic acid as there was no degassing to remove the evolved hydrogen during the reaction. Higher corrosion rate in oxalic acid is also because of the fact that we haven't degassed the oxygen and dissolved oxygen before the dissolution reaction. Because  $Fe^0$  can activate  $O_2$  to generate reactive oxygen species, such as,  $\cdot OH$ ,  $H_2O_2$ , and  $O_2^-$ . The dissolved oxygen is utilized by oxalic acid is faster than phosphate containing chelates [2]. The corrosion rate was calculated by the equation (1) [3,4]:

$$\text{corrosion rate} \left( \frac{mm}{y} \right) = \frac{87600 \cdot \Delta m}{\rho \cdot A \cdot t} \quad (\text{Eq. 1})$$

Where,  $\Delta m$  is the weight loss of carbon steel,  $\rho$  is the carbon steel density ( $7.83 \text{ g/cm}^3$ ),  $A$  is the

surface area of coupons after reaction, and  $t$  is the exposure time (18 h).

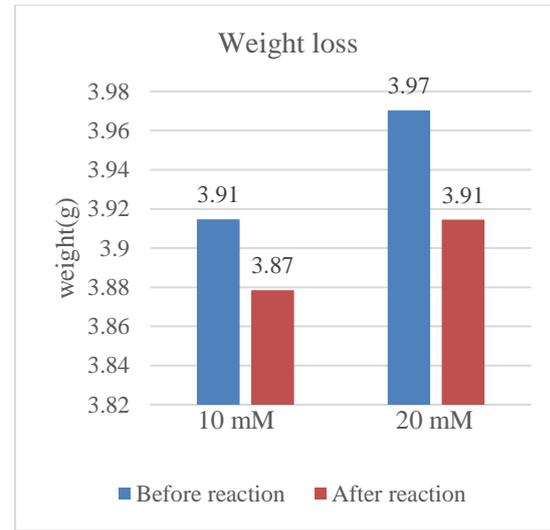


Fig. 2. The weight of CS coupon before and after dissolution reaction.

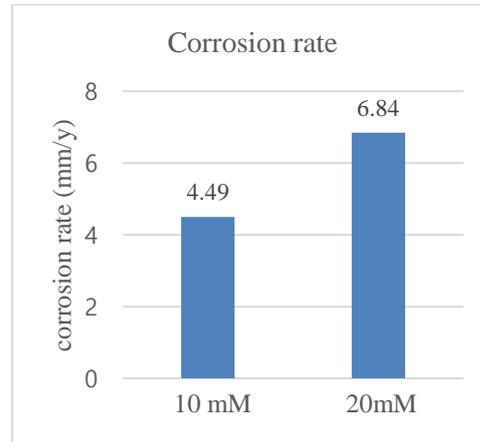


Fig. 3. Corrosion rate of CS coupon in 10 mM and 20 mM oxalic solution.

#### 2.5 EPMA for Surface Analysis

After the weight loss measurement, the surface morphology, roughness, and elemental composition of CS coupons before and after the corrosion test was characterized by EPMA (JEOL, JXA-IHP200F) with 20 kV of accelerating voltage. Fig.4. shows the SEI of coupon in 10 mM and 20 mM oxalic acid just

to see the effect of reaction. Interestingly the colour of coupon was changed as shown in Fig.1(b). Both CS coupons have cracks over the surface which shows the corrosive nature of the oxalic acid shown in Fig. 4. In 20 mM oxalic acid solution, the oxalate formation is higher. Intergranular attack can be seen over the surface easily because of low Cr and higher Si content. The environment is susceptible for IGA first then the corrosion products formation. The surface was seen covered by particles. But the X-ray spectrum in Table 2 shows no magnetite formation. Secondly, the morphology of these particles is different from the magnetite particles. Therefore, prolonged exposure to the oxalic acid solutions at elevated temperature may lead to microstructural changes on the surface of carbon steel, potentially affecting its corrosion resistance. The corrosion products are specified as iron oxy hydroxide and iron hydroxide. The higher atomic weight% of oxygen by x-ray result may represent iron oxalate, hydroxide or oxyhydroxide species.

The CS surface was badly corroded and covered by lots of corrosion products. Because the permeation of aggressive ions into the oxalate coating is reduced. Some fraction of the coupon surface is empty may be because of the oxalate formation in early stage before any corrosion product formation, then these oxalate covers is removed by ultrasonication. As the oxalate complex, has poor adhesion ability compared to phosphate, can be removed by rolling and surface conditioning method. The addition of oxalic acid in the oxidized carbon steel coupon may yields a series of anionic iron oxalate complexes including Fe(III) forms:  $[\text{Fe}^{\text{III}}\text{HC}_2\text{O}_4]^{2+}$  (stable  $\text{pH} < 1$ ),  $[\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_2]^-$  (stable  $\text{pH} 1-2$ ),  $[\text{Fe}^{\text{III}}\text{C}_2\text{O}_4]^+$  (stable  $\text{pH} 1-2$ ),  $[\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_2]^+$ ,  $[\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3]^{3-}$  (stable  $\text{pH} > 3$ ). Fe(II) form:  $[\text{Fe}^{\text{II}}(\text{C}_2\text{O}_4)_2]^{2-}$  (stable  $\text{pH} > 3$ ),  $[\text{Fe}^{\text{II}}(\text{C}_2\text{O}_4)_2\text{CO}_2]^-$ , Fe(I) form:  $[\text{Fe}^{\text{I}}(\text{C}_2\text{O}_4)]^-$  [1]. Based on these pH conditions, most feasible oxalate form in our system are  $[\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_2]^-$  and  $[\text{Fe}^{\text{III}}\text{C}_2\text{O}_4]^+$ .

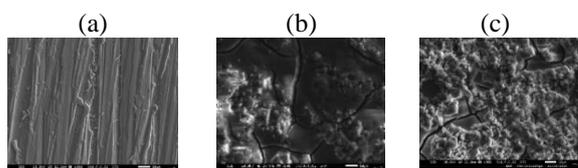


Fig. 4. SEM image and X-ray spectra of (a) undissolved carbon steel, carbon steel coupon dissolved in (b) 10 mM (c) 20 mM oxalic acid solution.

Table 2. EPMA Elemental Analysis

Sample	%	Fe	O	C
Base	mass (%)	95.97	0.51	2.72
	atom (%)	86.28	<b>1.60</b>	11.39
	K (%)	97.18	0.29	0.76
10 mM	mass (%)	66.81	29.10	4.08
	atom (%)	35.64	<b>54.20</b>	10.14
	K (%)	67.31	18.18	1.22
20 mM	mass (%)	80.79	16.98	1.95
	atom (%)	54.06	<b>39.67</b>	6.06
	K (%)	62.36	8.11	0.42

### 3. Conclusions

Corrosion behavior was studied by dissolving carbon steel Grad.B in two different concentration of oxalic acid. The corrosion rate of carbon steel was 35 % higher in 20 mM than 10 mM oxalic acid solution.

Intergranular corrosion (IGC) was observed over the surface of CS. Which can lead to material catastrophic structural damage and reduces the corrosion resistance. At the same time the oxalate species play a role of passivating agent to stop further formation of species over the surface and inhibits promoted the iron ion to release from the solid.

### REFERENCES

- [1] T. Christian, Full System Decontamination (FSD) with the CORD Family prior to Decommissioning - Experiences at the German NPP Obrigheim 2007 Switzerland, 2003.
- [2] Y. Pan, M. Zhou, Q. Wang, J. Cai, Y. Tian, and Y. Zhang, EDTA, oxalate, and phosphate ions enhanced reactive oxygen species generation and sulfamethazine removal by zero-valent iron, Journal of hazardous materials, Vol.391, p.122210, 2020.
- [3] K. Zheng, H. Hu, Z. Wang, Y. Zheng, X. Shang, W. Zhang, and L. Zhao, Influence of chromium of low content on the corrosion behavior of SA106B carbon steels in high-temperature pressurized LiOH medium, Nuclear Engineering and Design, Vol.414, p.112635, 2023.
- [4] R. Haldhar, D. Prasad, I. Bahadur, O. Dagdag, and A. Berisha, Evaluation of Gloriosa superba seeds extract as corrosion inhibition for low carbon steel in sulfuric acidic medium: A combined experimental and computational studies, Journal of Molecular Liquids, Vol.323, p.114958, 2021.