



Letter to the Editors

**Optimum EDTA solvent chemistry for
iron oxide removal at 150 °C**Do Haeng Hur ^{a,*}, Myung Sik Choi ^a, Han Sub Chung ^b, Uh Chul Kim ^a^a Korea Atomic Energy Research Institute, 150 Deokjin-dong, Yuseong-gu, Daejeon 305-353, Republic of Korea^b Korea Electric Power Research Institute, 103-16 Munji-dong, Yuseong-gu, Daejeon 305-380, Republic of Korea

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Abstract

The influence of hydrazine, pH and inhibitor concentration were evaluated with respect to the dissolution effectiveness and material corrosion when using the iron oxide removal solvent composed of ethylenediaminetetraacetic acid (EDTA), N₂H₄, NH₄OH and the corrosion inhibitor CCI-801 at 150 °C. The optimum EDTA solvent chemistry at 150 °C was found to be 1% N₂H₄, pH 7 and 1% corrosion inhibitor. This formula is quite similar to the conventional 200 °F (93 °C) process.

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1. Introduction

Corrosion products formed in the steam, feed water and condensate systems on the secondary side in pressurized water reactors are deposited on the tube sheet, tube surfaces and tube support structures in the steam generators. These deposits can act as hideout sites for impurities contained in the secondary water and thus induce corrosion degradation of steam generator tubes. Furthermore, sludge can hinder heat transfer from the primary to secondary side and also distorts eddy current signals from the tubes during in-service inspection. Chemical cleaning is an effective method to remove the corrosion deposits and thus to mitigate the secondary side degradation of the tubes.

Two typical solvent formulae have been developed for iron oxide removal. One is as follows [1]: 10–20% EDTA (ethylenediaminetetraacetic acid), 1% N₂H₄, pH 7 (adjusted with NH₄OH), 0.5–1% CCI-801 ¹ corrosion

inhibitor. The solvent is maintained at 93 °C (200 °F) and is recirculated by external recirculation systems during the chemical cleaning process [1,3]. In this case, the magnetite dissolution rate is lower than at a higher temperature process. The other solvent formula was 2–6% nitrilotriacetic acid (NTA), 1–2 g/l N₂H₄, pH 9.5 (adjusted with NH₄OH) since its first application in 1986 [4]. Presently, this process is also applied mainly by using EDTA instead of NTA as a chelate agent [5], because EDTA has more dissolving capacity and less corrosive property than NTA [1,6]. It should be noted that this process is applied above 140 °C, and thus faster and more effective cleaning is achievable [5,7]. In this case, the process temperature is maintained by using the heat flux from the primary to secondary side of the steam generators. Therefore no external heat-up and recirculation equipments are required.

The goal of chemical cleaning is to maximize the dissolution effectiveness and simultaneously minimize the corrosion of the steam generator construction materials. To apply the solvent formulae EDTA, N₂H₄, NH₄OH and inhibitor used at 93 °F to higher temperatures, it is necessary to optimize the solvent chemistry with this in mind. However, proprietary technical data have not been published and the available data are too limited to evaluate critical parameters, safety aspects

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¹ CCI-801 is a trade name of a corrosion inhibitor manufactured by Petrolite Corporation [2].

and effectiveness at higher temperatures. In this paper, the effects of hydrazine, pH and inhibitor concentration on the dissolution effectiveness and material corrosion were evaluated to find out the optimum solvent chemistry at 150 °C.

2. Experimental procedures

A titanium autoclave with 1 l capacity was used as a test vessel. The solvent chemistry for the iron removal process used was as follows: 10% EDTA, 0–4% N₂H₄, pH 5–9 (adjusted with NH₄OH) and 0–1% CCI-801 corrosion inhibitor. Magnetite powder was loaded stoichiometrically, assuming that one molecule of EDTA in the solvent can react with one iron ion. That is, for 10% EDTA solution, the amount of magnetite powder loaded was 20.7 g Fe₃O₄/l, corresponding to 15.0 g Fe/l. All tests were conducted at 150 °C for 3 h under static condition.

The corrosion rate during the magnetite dissolution tests was measured from weight loss of corrosion coupons. The coupons were polished with #600 SiC papers, ultrasonically cleaned in acetone, and weighed. Then they were put on Teflon hangers to insulate them electrically from the autoclave body. The coupon surface-to-solvent volume ratio was maintained at the same value of 0.093 cm²/l for all tests.

3. Results and discussion

Fig. 1 shows the effect of the hydrazine content on magnetite dissolution and corrosion in 10% EDTA + 1% corrosion inhibitor solvent at pH 7. The solvent pH was adjusted with NH₄OH. The dissolved iron concentration was only about 7 mg/ml without hydrazine, whereas the iron concentration increased to about 13 mg/ml by addition of 1% hydrazine. The dissolution effectiveness was not affected by further addition of hydrazine. On the other hand, the corrosion rate in hydrazine free solvent was about 3 times higher than for a concentration of 1% hydrazine, and it increased with further addition of hydrazine. As one molecule of magnetite dissolves in the solvent, one ferrous ion and two ferric ions are formed [1]. The ferric ions cause corrosion of base materials by the following reaction,



In the absence of hydrazine, therefore, high corrosion rates are expected due to this ferric ion corrosion. Since ferric ion is effectively reduced to harmless ferrous ion by hydrazine, corrosion is decreased by addition of 1% hydrazine. However, because hydrazine acts as a corrodant as well as a reducing agent [8], further addition

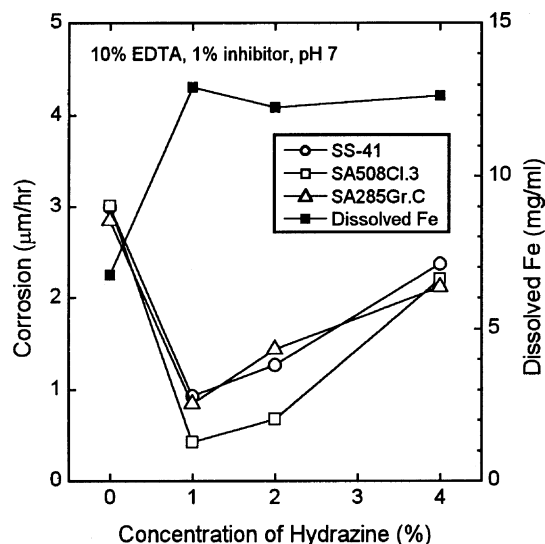


Fig. 1. Effect of hydrazine concentration on magnetite dissolution and corrosion in 10% EDTA + 1% inhibitor + pH 7 solvent at 150 °C for 3 h.

would accelerate corrosion. The obtained results also indicate that both the corrosion resistance and the dissolution efficiency are deteriorated as the content of hydrazine is depleted to zero by the reaction with ferric ion and due to thermal decomposition.

Fig. 2 shows the effect of the solvent pH on magnetite dissolution and corrosion in 10% EDTA + 1% corrosion inhibitor solvent without hydrazine. The concentration

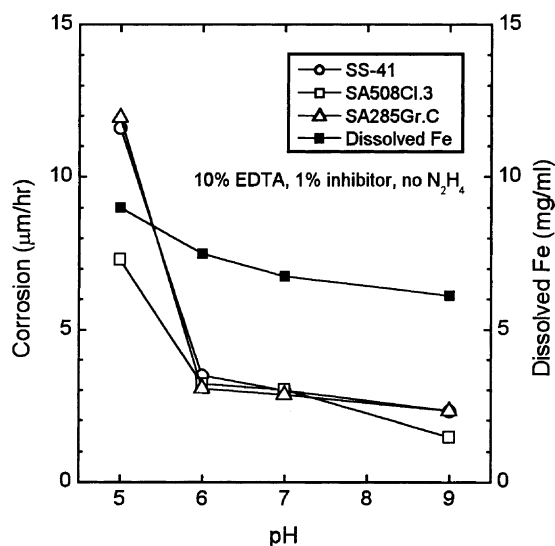


Fig. 2. Effect of pH on magnetite dissolution and corrosion in 10% EDTA + 1% inhibitor solvent at 150 °C for 3 h.

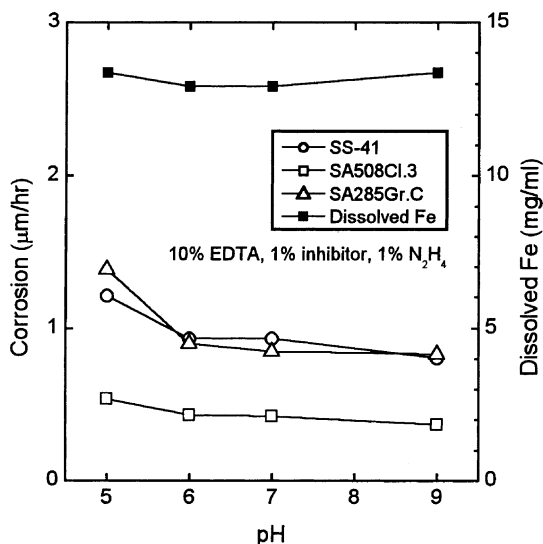


Fig. 3. Effect of pH on magnetite dissolution and corrosion in 10% EDTA + 1% N_2H_4 + 1% inhibitor solvent at 150 °C for 3 h.

of dissolved iron decreases with the solvent pH. The corrosion rate at a pH of 5 is about 2–3 times higher than at pH 6 and then it slightly decreases as the pH increases from 6 to 9.

Fig. 3 shows the effect of the pH on magnetite dissolution and corrosion in 10% EDTA + 1% corrosion inhibitor solvent with 1% hydrazine. In this case, the effectiveness of magnetite dissolution was not varied by the solvent pH. The corrosion rate decreased slightly with increasing pH. Comparing Figs. 2 and 3, the amount of dissolved magnetite was increased by addition of 1% hydrazine in the pH range of 5–9, while corrosion was decreased, similar to the result in Fig. 1 obtained at pH 7. Therefore, it is clear that the pH should be kept above 6 and is preferably at 7. It can also be concluded that a proper concentration of hydrazine is 1% based on the results shown in Figs. 1–3. These values are similar to those for the conventional 200 °F (93 °C) process.

Fig. 4 shows the effect of inhibitor concentration. It is clear that the inhibitor has no effect on the magnetite dissolution behavior. The corrosion rate was only slightly decreased as the inhibitor concentration increased from 0.2% to 1%. However, it was 6–20 times higher depending on the material when no inhibitor was added. Therefore, an inhibitor concentration of 1% is recommended since it will provide a sufficient margin of corrosion safety against local inhibitor depletion for high temperature application.

In summary, the optimum EDTA solvent chemistry for application at 150 °C was found to be similar to that for the conventional 200 °F (93 °C) process. It has

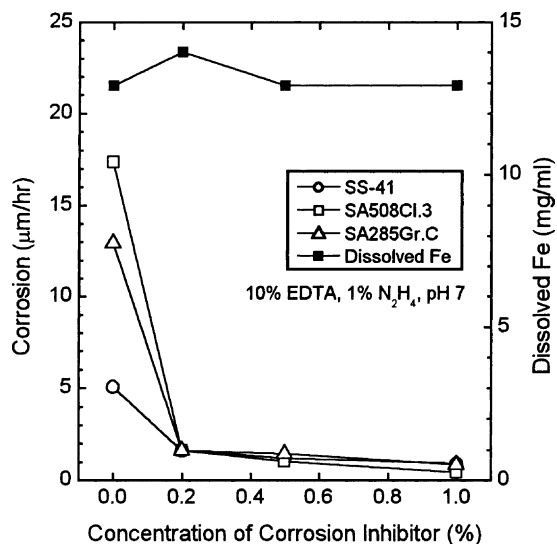


Fig. 4. Effect of corrosion inhibitor concentration on magnetite dissolution and corrosion in 10% EDTA + 1% N_2H_4 + pH 7 solvent at 150 °C for 3 h.

previously been reported that magnetite dissolution is drastically accelerated as the temperature is increased up to 150 °C [7]. The amount of material corrosion is also well controlled within an allowable limit during the high temperature processes [5,7]. Therefore, it can be concluded that the high temperature cleaning process using EDTA-based solvent can be applied effectively and safely.

4. Summary

The influence of hydrazine, pH and CCI-801 corrosion inhibitor concentration contained in EDTA solvent for an iron oxide removal process were parametrically evaluated in order to apply the solvent at a higher temperature than 93 °C. The optimum EDTA solvent chemistry for application at 150 °C was found to be 1% N_2H_4 , pH 7 and 1% corrosion inhibitor. This formula is quite similar to that for the conventional 93 °C process.

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