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Journal of Nuclear Materials 299 (2001) 271–273

journal of nuclear materials

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Letter to the Editors

# High temperature application of EDTA solvents for iron oxide removal

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Received 15 August 2001; accepted 21 August 2001

**Abstract**

The sludge dissolution kinetics and corrosion of materials were quantitatively evaluated when iron oxide removal solvents containing EDTA were applied at temperatures ranging from 93 to 150 °C. Periodic ventilation and excessive EDTA concentration were evaluated as alternatives to enhance the sludge dissolution kinetics. Magnetite dissolution was drastically accelerated as the temperature was raised up to 150 °C, while the amount of corrosion was well controlled within an allowable limit. © 2001 Elsevier Science B.V. All rights reserved.

## 1. Introduction

Corrosion products from feed line systems are accumulated as sludge on the secondary side of nuclear steam generators, mainly on top of the tube sheet. Sludge causes various types of corrosion and distorts eddy current signals from steam generator tubes. Therefore, chemical cleaning is a very effective method for mitigating outer diameter degradation of the tubes.

The generic iron oxide removal chemical cleaning process using ethylenediaminetetraacetic acid (EDTA) as a chelate was developed [1,2] and commercially applied at many nuclear power plants [3–6]. The solvent is maintained at 93 °C and is recirculated by external recirculation equipments. It has been suggested recently, however, that faster and more effective cleaning can be achieved by applying a higher solvent temperature without external heat-up and recirculation systems. Several field applications of these high temperature processes have been reported [7–10]. However, technical data to compare the high temperature processes with the 93 °C standard process in detail are limited. In this paper, therefore, quantitative data were produced on the sludge dissolution kinetics and corrosion of materials when the solvent was applied at temperatures up to 150 °C.

## 2. Experimental procedures

A Type 316 stainless steel autoclave with one gallon capacity was used as a test vessel. Sampling through a sampling line with a cooling jacket was periodically undertaken to analyze the dissolved iron content. A vent line with a cooling jacket was attached to evaluate the effect of solvent boiling on the dissolution efficiency. Ventilation was performed every hour for 30 s, which resulted in a pressure drop of about 10 psi (~70 kPa) below the saturation pressure.

The solvent chemistry of the iron removal process used is as follows [2]: 10–20% EDTA, 1% $N_2H_4$, 1% CCI-801, [1] pH 7.0 (adjusted with $NH_4OH$). All tests were conducted using an EDTA concentration of 10% with the exception of where special notes are given.

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[1] CCI-801 is a trade name of a corrosion inhibitor manufactured by Petrolite Corporation [11].

0022-3115/01/$ - see front matter 
PII: S0022-3115(01)00689-4

The amount of sludge loaded in each run was 20.7 g $Fe_3O_4$/l (15 g Fe/l). Two types of magnetite sludge were used: the powder as it was, and small pellets obtained by pressing and baking the powder. The procedures are described in detail elsewhere [2]. The pellets were put into a sludge cup made of Alloy 600 tubing with one end open, in order to simulate hard sludge consolidated to piles inside the dense tube bundle where access of the fresh solvent is hindered.

Uniform corrosion 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.

## 3. Results and discussion

### 3.1. Sludge dissolution behavior

Fig. 1 illustrates the dissolution behavior of magnetite powder at different temperatures, showing that the sludge dissolution rate is drastically increased with solvent temperature. The dissolution efficiency was only 68% during a 9 h test period for the conventional 93 °C process. However, 97% of the sludge loaded was dissolved in 7 h for the 130 °C process and all the sludge was completely dissolved within half an hour for the 150 °C process.

It should be noted that an increase of the EDTA concentration from 10% to 20% at 130 °C accelerated the dissolution kinetics, resulting in a reduction of the cleaning time to a third. That is, all the sludge was dissolved after only 2 h in the 20% EDTA solvent, while in the 10% EDTA solvent 97% of the sludge was dissolved in 7 h. It is, therefore, suggested that the excessive EDTA concentration in the solvent is very effective for dissolving sludge.

The dissolution rate of hard sludge in the sludge cup was, as expected, significantly lower compared to that of powder sludge, as shown in Fig. 2. The amount of hard sludge dissolved was only 46% in 49 h for the 93 °C process, 82% in 24 h for the 130 °C process, and finally 65% in 8 h for the 150 °C process. This clearly shows that dissolution of hard sludge accumulated inside the dense tube bundle would be very difficult.

The effect of periodic ventilation on the sludge dissolution rate in the 130 °C process is also shown in Fig. 2. Sludge dissolution was significantly accelerated by ventilation, and completed within only 4 h, in contrast to the dissolution efficiency of 82% in 24 h without ventilation. This result is attributed to vigorous boiling due to a pressure drop during ventilation, which breaks up the hard sludge and supplies fresh solvent inside the sludge cup. As a result, it is expected that periodic

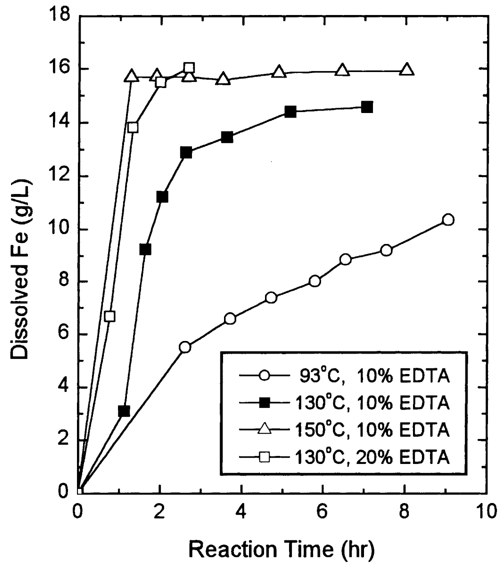


Fig. 1. Effect of temperature and EDTA concentration on the powder sludge dissolution behavior.

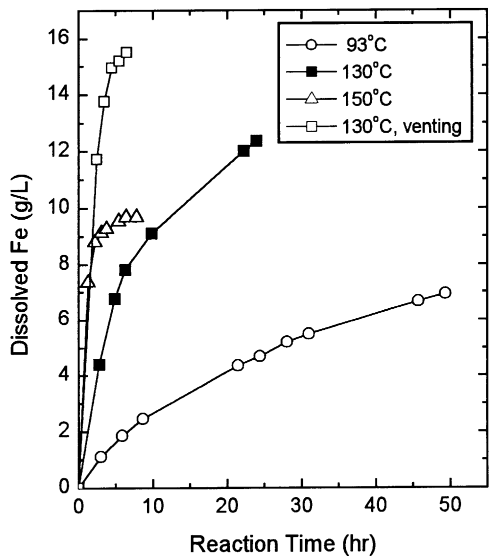


Fig. 2. Effect of temperature and venting on the hard sludge dissolution behavior.

ventilation would be a very effective alternative for dissolving hard tube sheet sludge piles and packed tube support plate crevices in steam generators.

### 3.2. Corrosion

Table 1 summarizes the corrosion of coupons obtained from weight loss after each sludge dissolution test. All the corrosion rates showed far lower values than

Table 1
Corrosion results from corrosion coupons

| Test conditions (°C) | Corrosion coupons (μm/day) | | |
|---|---|---|---|
| | SA 508 Cl.3 | SA 516 Gr.70 | SA 285 Gr.C |
| 93[a] | 1.23 | 1.39 | NT[d] |
| 130[a] | 2.92 | 7.90 | NT |
| 150[a] | 12.27 | 25.65 | NT |
| 130[b] | NT | NT | 6.60 |
| 130[c] | NT | NT | 13.23 |

[a] 10% EDTA, 1% $N_2H_4$, 1% CCI-801, pH 7.0, powder sludge.
[b] 20% EDTA, 1% $N_2H_4$, 1% CCI-801, pH 7.0, powder sludge.
[c] 10% EDTA, 1% $N_2H_4$, 1% CCI-801, pH 7.0, hard sludge, venting.
[d] Not tested.

the EPRI guideline [12], 254 μm (10 mil), although they were increased with increasing temperature. Similarly, it was reported that corrosion was sufficiently low during the high temperature processes [8,13]. These results indicate that the high temperature chemical cleaning process using EDTA solvents can be applied very safely and effectively.

## 4. Conclusions

The sludge dissolution rate was significantly accelerated when the iron removal solvents containing EDTA were applied at high temperatures up to 150 °C, while the amount of corrosion can be controlled well within an allowable limit. It is expected that periodic ventilation and excessive EDTA concentration in the solvent would be very effective in dissolving hard tube sheet sludge piles and packed tube support plate crevices.

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