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ÉNERGIE ATOMIQUE
DU CANADA LIMITÉE

**DECONTAMINATION EFFECTIVENESS OF MIXTURES OF
CITRIC ACID, OXALIC ACID AND EDTA**

**EFFICACITÉ DES MÉLANGES D'ACIDE CITRIQUE,
D'ACIDE OXALIQUE ET D'EDTA COMME AGENTS DE DÉCONTAMINATION**

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January 1990 janvier

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by

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*A shortened version of this paper was published in the
Proceedings of the Conference on Water Chemistry for
Nuclear Reactor Systems 5, British Nuclear Energy
Society, London, 1989.*

System Chemistry and Corrosion Branch
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RÉSUMÉ

On a effectué une étude expérimentale sur l'efficacité des mélanges d'acide citrique, d'acide oxalique et d'EDTA comme agents de décontamination afin de déterminer s'il était possible de supprimer l'acide oxalique des solutions de décontamination pour réduire au minimum la corrosion. Au cours d'essais en boucle, des échantillons radioactifs provenant de deux réacteurs à eau bouillante et d'un réacteur à eau sous pression ont été mis en suspension dans des solutions contenant soit un seul acide, soit un mélange de réactifs, à des concentrations de réactif totales inférieures à 0,1 % en poids, dans des conditions similaires à celles rencontrées lors de la décontamination des réacteurs. Les constantes de vitesse pour la dissolution des oxydes et les facteurs de décontamination ont été mesurés. Les résultats obtenus ont permis de conclure que, dans certaines conditions, l'acide oxalique était le réactif le plus efficace pour la dissolution des oxydes. Cependant, on a également établi que les conditions dans lesquelles on obtenait une dissolution efficace dans des solutions d'acide oxalique ou d'acide citrique, étaient difficiles à déterminer et à contrôler. L'EDTA s'est révélé un réactif efficace pour la dissolution des oxydes, les vitesses de dissolution obtenues dans les solutions à base d'EDTA, à 117°C, ayant été comparables aux vitesses de dissolution dans des solutions à base d'acide oxalique. @ 90°C, l'EDTA agit en synergie avec l'acide oxalique, la vitesse de dissolution des oxydes dans des solutions mixtes d'acide citrique, d'acide oxalique et d'EDTA ayant été supérieure à celle mesurée dans des solutions d'acide citrique et d'EDTA. L'addition d'ions ferriques (60 mg/kg) diminue considérablement à vitesse de dissolution des oxydes dans les solutions acide citrique/acide oxalique, acide citrique/EDTA et acide citrique/acide oxalique/EDTA.

On en conclut qu'il est possible de décontaminer efficacement les filières BWR et PWR à l'aide de mélanges d'acide citrique et d'EDTA.

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Janvier 1990

DECONTAMINATION EFFECTIVENESS OF MIXTURES OF
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ABSTRACT

An experimental study of the decontamination effectiveness of citric acid, oxalic acid and EDTA mixtures was conducted to assess whether oxalic acid could be removed from decontamination solutions to minimize corrosion. In loop experiments, radioactive specimens from two boiling water reactors and one pressurized water reactor were suspended in solutions of single acids or in mixtures of reagents at total reagent concentrations of less than 0.1 wt% under conditions similar to those used to decontaminate reactor systems. Rate constants for dissolution of oxides and decontamination factors were measured. Based on the results, it was concluded that under certain conditions, oxalic acid was the most effective reagent for dissolution of oxides. It was also found, however, that conditions under which effective dissolution occurred in solutions of oxalic acid and/or citric acid were difficult to define and control. EDTA was found to be an effective reagent for dissolution of oxides such that rates of dissolution in EDTA containing solutions at 117°C were comparable to rates in oxalic acid containing solutions. At 90°C, EDTA acted synergistically with oxalic acid such that the rate of dissolution of oxides in citric-acid/oxalic-acid/EDTA solutions was higher than in citric-acid/EDTA solutions. The rates of dissolution of oxides were significantly reduced when 60 mg/kg of ferric ion was added to the citric-acid/oxalic-acid, citric-acid/EDTA and citric-acid/oxalic-acid/EDTA solutions.

It was concluded that effective decontaminations of BWR and PWR systems could be achieved with mixtures of citric acid and EDTA.

System Chemistry and Corrosion Branch
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1990 January

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1. INTRODUCTION

During normal operation of nuclear reactors, metal oxide films containing activated corrosion products such as Co-60 are deposited on inside surfaces of out-of-core components such as recirculating pipes in boiling water reactors (BWRs) and steam generators in pressurized water reactors (PWRs). Considerable effort over many years has been directed at characterizing BWR and PWR oxides, at assessing various reagents for use in dissolving corrosion products and at determining the mechanisms of metal oxide dissolution in various reagents. The oxides which contain most activation products are typically nickel ferrites (NiFe_2O_4) in the case of type 304 stainless steel BWR piping [1,2], and high nickel and chrome oxides, probably also spinels, in the case of Inconel-600 steam generator tubes in PWRs [2,3]. Oxide films formed on type 304 stainless steel specimens under PWR conditions were reported to be two-layer, with an $(\text{Fe,Cr})_2\text{O}_3$ inner layer and spinels of the type NiFe_2O_4 in the outer layer [4]. These oxides are more difficult to dissolve than the magnetite (Fe_3O_4) formed in carbon steel systems, such as CANDU pressurized heavy water reactors, and on the secondary side of the steam generators [5,7].

While a large number of reagents have been assessed for oxide dissolution, citric acid, oxalic acid and EDTA, or mixtures of these acids, have been studied in considerable detail. Several decontamination processes using oxalic acid in combination with either citric acid or citric acid and EDTA have been developed, patented in some cases, and used in field decontaminations [8-14]. Oxalic acid has been generally regarded as one of the most effective reagents for dissolution of oxides and mechanisms for dissolution of magnetite have been postulated [1,5,15-19]. The mechanism is postulated to involve adsorption of oxalate ions at ferric ion sites in the oxide lattice [16,18]. After an induction period in which ferrous ions build up in solution, reductive dissolution occurs in which an electron transfer takes place between a ferrous oxalate species adsorbed on the oxide from solution and the ferric oxalate species in the oxide lattice [16]. Once the ferric ion in the oxide lattice is reduced, it is more readily dissolved in the bulk solution. In carbon steel systems, an autoreductive dissolution, in which base metal reacts with ferric ions in the oxide lattice, can predominate under conditions of low oxalate concentration [18].

Citric acid has been regarded as not very effective in dissolving metal oxides [1,15,20] but has been added to decontamination solutions as a pH buffer, to provide increased Fe^{3+} solubility, and to reduce the quantity of ferrous oxalate precipitates that form on carbon steel surfaces [15].

Conflicting evidence exists in the literature as to the role and effectiveness of EDTA in decontamination solutions. While EDTA has proved to be an effective reagent for dissolution of magnetite under some conditions [20-23] and is used in secondary-side steam-generator cleaning solutions in the nuclear industry [24,25], some data suggests that it is not an effective reagent for dissolution of magnetite or the nickel- and chromium-containing oxides found in BWRs and PWRs. At temperatures less

than 80°C and pHs less than 7, adsorption of EDTA on magnetite [5] and hematite [20] surfaces has been postulated to stabilize surfaces resulting in low rates of dissolution. At higher temperatures, about 120°C for hematite, a dramatic increase in dissolution rate of hematite was noted. In experiments carried out with nickel ferrite at 80°C, dissolution rates were relatively low with complete dissolution taking about 5 h even at relatively high EDTA concentrations of 0.1 mol/L [26].

In other work, addition of EDTA to phosphoric acid was reported to have no effect on rate of dissolution of nickel ferrite [27]. In experiments carried out with BWR samples, where about 90% of the Co-60 was incorporated in nickel ferrite, only 52% of the Co-60 was released into a 0.1 mol/L solution of EDTA at 90°C in 56 h, while 80-90% of the Co-60 was released into 0.03-0.26 mol/L solutions of oxalic acid at 90°C within 0.3-6 h [1]. Anstine concluded that no benefits were observed by addition of EDTA to decontamination solutions [1]. In contrast, other work using BWR and PWR specimens indicated that EDTA was an effective reagent for dissolution of oxides at 180°C [28,29]. At 120°C, which is closer to temperatures typically used in reactor decontaminations, oxalic acid dissolved oxides faster than any other reagent tested [29]. Some studies have indicated that dissolution of metal oxides by EDTA occurs by reductive dissolution as a result of transfer of electrons from ferrous-EDTA complexes [23,30] as described previously for ferrous oxalate and in the literature for vanadous picolinate [7]. There are few reports of the role of EDTA in mixtures of EDTA with either citric acid or oxalic acid where synergistic effects may occur. In experiments using magnetite and mixtures of oxalic acid and EDTA, oxalic acid was postulated to adsorb at ferric ion sites in the oxide lattice and assist in dissolution of the oxide, while EDTA was postulated to assist in removal of ferrous ion from oxide surfaces by complexation in solution [18].

The solvents and conditions used during decontamination must be aggressive enough to dissolve Co-60-containing surface oxide films without causing significant corrosion damage to the underlying metals. Recently, there have been concerns that some decontamination solvents may cause intergranular attack (IGA) in sensitized 304 stainless steel (SS), and perhaps may increase the susceptibility of the stainless steel to stress corrosion cracking [31,32]. In view of the concerns, an experimental study was undertaken to study the corrosiveness of mixtures of citric acid, oxalic acid and EDTA to sensitized 304SS and other reactor materials of construction, 304SS, 410SS, carbon steel (CS) A366 and A508, and heat-treated Inconel-600. Results of the autoclave and loop experiments showed that of the three reagents considered, oxalic acid was most likely to cause IGA in sensitized 304SS [33-36]. The results also suggested that removal of oxalic acid from decontamination solutions would lower the corrosiveness of solutions to sensitized 304SS [33-35] and to other nuclear reactor materials, particularly 304SS and 410SS [36]. A considerable benefit, then, could be obtained in terms of lowering corrosiveness by removing oxalic acid from decontamination solutions. Since oxalic acid has been shown to be one of the most effective reagents for dissolution of oxides, and since conflicting

evidence exists as to the effectiveness of EDTA as a decontamination reagent, the present study was undertaken.

To assess whether removal of oxalic acid from solvents would affect decontamination effectiveness, experiments were carried out using radioactive specimens from two BWRs and one PWR. The results of the decontamination experiments are reported in this paper. In the experiments, the reactor specimens were suspended in mixtures of reagents: citric-acid/oxalic-acid, citric-acid/EDTA and citric-acid/oxalic-acid/EDTA, or in solutions of single acids or in deionized water. Experiments were done in loops under conditions similar to those used to decontaminate reactor systems. In particular, the temperatures used in these experiments, 90°C and 117°C, are close to typical and maximum temperatures, respectively. Two flow rates were used with linear velocities through test sections of 6 cm/s or 250 cm/s to simulate a range of flows that might occur in reactor contaminations. During reactor decontaminations, dissolution of the oxide film results in an equilibrium concentration of 30-50 mg/kg of ferric ion before base metal is exposed [37,38]. Some of the experiments reported here were carried out with addition of ferric ion to simulate the effects of ferric ion in field decontaminations. No detailed assessment of the effects of ferric ion addition on the effectiveness of decontamination solutions has been reported in the literature.

2. EXPERIMENTAL

Active samples of approximate size 15 mm x 15 mm x 5 mm were prepared by cutting pieces from pipes of two BWR recirculation systems and from one PWR steam generator man-way cover. Scanning electron microscopy (SEM) examinations of the BWR specimens showed that the oxide morphology was similar to that of specimens characterized by Anstine [1]. Typical micrographs of one BWR sample are shown in Figure 1. The oxide morphology and particle sizes (0.2-0.6 μm for smaller particles) illustrated in Figure 1a are similar to the morphology of the inner layer and particle sizes described by Anstine [1], suggesting that the oxides are NiFe_2O_4 -type spinels. In the BWR oxides characterized by Anstine, the tightly adherent inner layer of NiFe_2O_4 contained about 90% of the Co-60, with about 10% of the Co-60 contained in the loosely adherent outer layer. Examination of Figure 1b confirms that the amount of loosely adherent corrosion products (large particles, 2-3 μm) on the specimens used in this work was very low, such that the crevice pattern due to IGA in the underlying metal is observed. As described by Anstine, in cases where the amounts of loosely adherent corrosion products were high, the crevice pattern was covered by deposited particles.

The large 2-3 μm crystallites were analyzed by an Energy Dispersive X-ray (EDX) technique and the oxide was found to have an elemental composition of about 92% Fe, 5% Cr and 3% Ni, a composition close to that of the loosely adherent outer oxide, $\alpha\text{-Fe}_2\text{O}_3$, characterized by Anstine (95% Fe, 2% Cr, 3% Ni). The inner oxide (0.2-0.4 μm particles) was analyzed by EDX

in-situ and found to have an elemental composition of about 75% Fe, 13% Cr and 12% Ni. The values for chromium and nickel are close to the average of values for the underlying metal (18% Cr, 8% Ni) and values for inner oxide given by Anstine (1-9% Cr, 15-20% Ni), suggesting that "shine" from the underlying metal was affecting the in-situ measurements.

SEM examination of the PWR stainless specimens showed that crystallites were not resolved even at 12 000X magnification. Figure 2 shows a sparse population of large particles as reported for Inconel-600 steam-generator specimens [2]. The PWR man-way specimens were analyzed by EDX and the oxide was found to be significantly enriched in chromium and nickel compared to the underlying stainless steel with an oxide elemental composition of about 40% Cr, 21% Ni and 38% Fe. These results are similar to those reported for Inconel-600 specimens [2].

Samples were gamma-counted before and after experiments. In all cases, Co-60 was the major radionuclide and initially was present in concentrations of about 10-15 $\mu\text{Ci}/\text{sample}$ in the case of BWR-1 specimens, about 20-30 $\mu\text{Ci}/\text{sample}$ in the case of BWR-2 specimens, and about 15-25 $\mu\text{Ci}/\text{sample}$ in the case of PWR samples. The PWR samples were pre-treated before decontamination experiments by stirring for 30 minutes in a concentrated alkaline permanganate (AP) solution (30 g/L KMnO_4 , 100 g/L NaOH) at 85°C. As in the case of dilute AP pretreatments in PWR steam generator decontaminations, such a pretreatment is intended to oxidize Cr^{3+} in the PWR oxide to Cr^{6+} and make the oxide more soluble in the decontamination solution. As confirmed by gamma-counting the specimens after the AP pretreatment, no Co-60 was removed from the specimens during the pretreatment. In preliminary experiments using PWR samples, negligible amounts of Co-60 were removed when PWR samples had not been pretreated with AP.

Active specimens were suspended in mixtures of reagents, citric-acid/oxalic-acid, citric-acid/EDTA and citric-acid/oxalic-acid/EDTA, or in solutions of single acids, or in deionized water, in either of two stainless steel loops with differing flow rates and temperature. In the first test loop (TL#1), illustrated in Figure 3, about 2 L of solution was circulated at $(117 \pm 4)^\circ\text{C}$, with a linear velocity through the test section of 6 cm/s, for 22 h. Solution from the main loop was circulated through 100 mL of IRN-77 cation exchange resin to regenerate reagents and remove corrosion products. To ensure that solution composition remained constant over the 22 h experiments, TL#1 was operated in a feed and bleed mode. This results in the total loop volume being replaced every 2 h with fresh decontamination solution.

In the second test loop (TL#2), about 7 L of solution was circulated at $(90 \pm 3)^\circ\text{C}$, with a linear velocity through the test section of 250 cm/s, for 5 h. Solution from the main loop was circulated through 125 mL of IRN-77 cation exchange resin to regenerate reagents and remove corrosion products.

Solutions were prepared with reagent grade oxalic acid ($C_2O_4H_2 \cdot 2H_2O$, MW = 126.07 g/mol), citric acid ($C_6O_7H_8 \cdot H_2O$, MW = 210.14 g/mol), EDTA ($C_{10}O_8N_2H_{11}$, MW = 292.25 g/mol) and deoxygenated in the loops by bubbling nitrogen through the solutions at 90°C for 1 h. Loop system pressures were maintained during experiments at 30 psi (200 kPa) using nitrogen as a cover gas. Ferric ion concentrations were adjusted by substituting ferric citrate ($FeC_6H_5O_7 \cdot 5H_2O$, MW = 335.03 g/mol) for citric acid. Solutions were analyzed for Fe^{2+} and Fe^{3+} during loop runs using a Beckman Model 2 spectrophotometer and o-phenanthroline as the colouring agent. Analyses for citric-acid, oxalic acid and EDTA were carried out for selected loop runs using a high-performance liquid chromatographic technique developed for this purpose [39].

Some typical conditions for loop runs are shown in Table 1, where the pH of solutions averaged 2.9 ± 0.2 for the loop runs, as established by appropriate selection of reagent concentrations and by corrosion of materials used to assess corrosivity of decontamination solutions. This can be compared with average pHs of 2.7 ± 0.1 for three citric-acid/oxalic-acid runs and 2.9 ± 0.1 for two citric-acid/EDTA runs. As reported in ref.6, dissolution of $Ni_{0.6}Cr_{0.6}Fe_{1.8}O_4$ by proton attack is only significant below a pH of 2.5. In view of these results, the effects on dissolution of oxide caused by small variations in pH from the average value of 2.9 in this work were considered to be negligible.

Approximately 30 loop experiments were carried out with active specimens. Active specimens were initially placed in the loop test section in deoxygenated water at room temperature, and when the loop conditions were reached, the test section was valved in. The fraction of oxide dissolved as the experiment progressed was determined by on-line gamma counting of the active specimen.

3. RESULTS

The decontamination effectiveness of the various solutions was assessed using BWR samples at 117°C and 90°C by measuring rate constants for dissolution of oxides and decontamination factors (DFs). The effect of adding ferric ion on the decontamination effectiveness of solutions was also assessed at 117°C using BWR specimens. For PWR specimens, experiments were carried out at 90°C to assess the effectiveness of various solutions. The results are discussed in turn below.

3.1 Dissolution Behaviour of BWR Oxides

As indicated previously, experiments at 117°C were carried out by exposing BWR-1 and BWR-2 specimens in aqueous solutions of citric acid, oxalic acid, EDTA and in mixtures of reagents citric-acid/oxalic-acid, citric-acid/EDTA, citric-acid/oxalic-acid/EDTA, for 22 h with linear velocities over the specimens of 6 cm/s. Experiments at 90°C were carried out with BWR-2 specimens in mixtures of reagents circulated at 250 cm/s for 4-5 h. Typical conditions for selected loop runs at 117°C are shown in

Table 1, where runs 1-12 were carried out using BWR-1 specimens, while runs 13-16 were carried out using BWR-2 specimens. Note that for BWR-1 runs 7-10, where mixtures of two reagents were used, concentrations of citric acid were about 273 mg/kg and concentrations of oxalic acid or EDTA were 210 mg/kg. For BWR-2 runs 14 and 15, where mixtures of two reagents were used, concentrations of citric acid were still 273 mg/kg, but concentrations of oxalic acid or EDTA were 400 mg/kg. Runs 17-20 were carried out at 90°C using BWR-2 samples and reagent concentrations similar to those used in runs 13-16.

Figures 4 and 5 show selected plots of fraction of oxide dissolved at 117°C versus time for BWR-1 specimens, and Figure 6 shows plots for BWR-2 specimens at 90°C. As noted previously, on-line gamma counting of specimens was used to assess fraction of oxide dissolved. Anstine [1] showed that rates of release of Fe and Co-60 from oxides were comparable. Examination of plots for single reagents in Figure 4 shows that BWR-1 oxide dissolved most rapidly at 117°C in oxalic acid such that 80% of the oxide was removed within 1.0-1.5 h, compared with 2.0-2.5 h for EDTA. Several hours were required to dissolve the BWR-1 oxide in citric acid. The results for mixtures of reagents are illustrated in Figure 5. As shown, the rates of dissolution of BWR-1 oxide at 117°C in the mixtures containing EDTA, that is, citric-acid/EDTA and citric-acid/oxalic acid/EDTA, were comparable to rates observed for EDTA alone, and significantly higher than rates observed for citric acid. In contrast, the rate of dissolution of oxide in the citric-acid/oxalic-acid mixture was significantly lower than the rates observed for oxalic-acid alone and comparable to rates observed for citric-acid. As shown in Figure 6 for dissolution of BWR-2 oxides at 90°C, the relative ranking of solvents is approximately the same as that observed for oxide dissolution at 117°C, except that at 90°C, rates of oxide dissolution were no longer equal in citric-acid/EDTA and citric-acid/oxalic-acid/EDTA mixtures. The fact that rates, at 90°C, were higher in mixtures of three acids suggests that oxalic acid and EDTA act synergistically in a way that was obscured or not active at higher temperatures. As shown in Figure 5, the BWR-2 oxide dissolved within about 1.5-2 h in the citric-acid/oxalic-acid/EDTA mixture at 90°C, compared with 4 h in a citric-acid/EDTA mixture, where the concentration (by weight) of EDTA in the citric-acid/EDTA mixture equalled the sum of the concentrations of oxalic acid and EDTA in the mixture of three acids. The combination of oxalic acid and EDTA is so effective at 90°C that the rates of dissolution of BWR-2 oxide are comparable to rates of dissolution of inner oxide (nickel ferrite) obtained in a solution of oxalic acid five times as concentrated (reported in ref.1 for specimens obtained from the Nine Mile Point reactor).

The results at 90°C can also be used to highlight differences in dissolution behaviour which were not as pronounced at higher temperatures. As illustrated in Figure 6, dissolution of oxide in the citric-acid/EDTA and citric acid solutions was preceded by an induction period such that the dissolution curves were S-shaped. As summarized in Table 2, induction periods were observed most frequently, though not exclusively, in solutions containing citric acid or EDTA where the induction time decreased (to zero

in some cases) with increasing temperature and reagent concentration. In the cases where the induction period was eliminated, dissolution plots were parabolic. As illustrated in Figure 5, in the cases of oxalic acid and citric-acid/oxalic-acid solutions, plots were parabolic over the first part of the curve. Such parabolic dissolution was reported to be typical of BWR oxides by Anstine [1], where the decrease in rate of dissolution with time was attributed to a lowering of the available particle surface area. Diggle concluded that electrolyte properties predominate in parabolic type dissolutions while properties of the oxides (e.g., solid defect structure) predominate in S-shaped type dissolution [40].

3.2 Dissolution Rate Constants

To define the dissolution characteristics of various decontamination solutions more precisely, rate constants were calculated by fitting data using the equation:

$$(1-\alpha)^{1/3} = 1 - k_{\text{obs}}t$$

where $k_{\text{obs}} = \frac{k}{r_{\text{op}}}$, with r_{op} = initial particle radius and p = oxide density. The equation corresponds to the shrinking core model of dissolution [6], where in the work reported here the fraction of oxide dissolved, $1-\alpha$, was determined by on-line gamma counting of specimens with time, t . As shown in Figure 7 for BWR-1 specimens, plots of $(1-\alpha)^{1/3}$ versus time are linear, where values of k were calculated from slopes of these plots. An interesting feature of all plots was a change in slope which typically occurred at values of $(1-\alpha)^{1/3}$ of 0.58 ± 0.08 , corresponding to fractions of oxides dissolved of 0.8. (Note that in a minority of cases, a slope change also occurred at $(1-\alpha)^{1/3}$ values of about 0.8, as illustrated in Figure 7 for oxalic acid and citric-acid/EDTA solutions. This change was usually associated with high rate constants and, as discussed later, is probably related to a kinetic limiting process, e.g., by-product transport.) The change in slope at $(1-\alpha)^{1/3}$ values of 0.58 suggests that one type of oxide containing about 80% of the Co-60 dissolves at a faster rate than a second type of oxide containing about 20% of the Co-60. These results are consistent with Anstine's characterization of BWR nickel ferrites (NiFe_2O_4) as type 1 and 2, where species 1 nickel ferrite containing 80% of the Co-60 in the tightly adherent layer had a low chromium content (1%), while species 2 nickel ferrite containing 20% of the Co-60 had a high chromium content (9%). The high chromium oxides were shown to be less soluble in 0.05 mol/L nitrilotriacetic acid than the low chromium oxides [1]. The rate constants reported in this work are for dissolution of the more easily dissolved fraction, in that the major fraction of Co-60 was removed by dissolution of this oxide.

Rate constants obtained using BWR-1 and BWR-2 specimens at 117°C and 90°C are shown in Table 3: for single acids the rate constants for dissolution of BWR-1 low Cr oxides at 117°C were initially highest in 210-500 mg/kg of oxalic acid (1.3 h^{-1}) and a factor of about four lower in 210-500 mg/kg

of EDTA (0.30-0.37). As illustrated in Figure 7 and given in Table 4, the observed rate constants (k) changed after 0.1 h for oxalic acid and after 0.5-1.0 h for EDTA solutions, such that rate constants were 0.21-0.25 h^{-1} for oxalic acid and 0.11-0.18 h^{-1} for EDTA. The net effect of the ten-fold decrease in k for oxalic acid solutions after only six minutes of oxide dissolution was that complete dissolution of the low Cr BWR-1 oxide took almost as long in oxalic acid as EDTA. As illustrated in Figure 4, the low Cr nickel ferrite (species 1) is assumed to be completely dissolved at a fraction of oxide dissolved of about 0.8, where dissolution of high Cr nickel ferrite is assumed to predominate at fractions of oxide greater than 0.8. In most cases, maximum values for fraction dissolved stabilized between 0.85 and 0.90, as established by background Co-60 counts. Typically, then, dissolution of about 30-50% of the high Cr nickel ferrite could be monitored by on-line gamma spectrometry. While times to reach 95% dissolution of the high Cr oxide could be estimated by extrapolating plots similar to those in Figure 7 to $(1-\alpha)^{1/3}$ values of 0.2, it was considered more accurate to estimate times using existing data. In this paper, time to reach complete dissolution of oxide refers to the time taken to reach a fraction of oxide dissolved of 0.8.

Initial rate constants for dissolution of BWR-1 oxides in citric acid ranged from a relatively high value of 0.5 h^{-1} in the 273 mg/kg citric acid solution to a relatively low value of 0.05 h^{-1} in the more concentrated 700 mg/kg citric acid solution. In both cases, rate constants changed to lower values of about 0.02 h^{-1} (Table 4), with the result that complete dissolution of low Cr oxide took over 10 h (Figure 4).

Initial values of k for dissolution of BWR-1 oxide in citric-acid/EDTA and citric-acid/oxalic-acid/EDTA were intermediate and comparable to values obtained in EDTA solutions, about 0.3-0.4 h^{-1} , and while rate constants changed to lower values after 0.5-1.0 h in the case of citric-acid/EDTA mixtures (Table 4), the effects were insignificant since 75-85% of the low Cr oxide was already dissolved. As shown in Figure 5, complete dissolution of low Cr oxide took about 1.5-2.0 h in EDTA-containing solutions.

The rate constant for dissolution of BWR-1 oxide in citric-acid/oxalic-acid was unusually low, 0.09 h^{-1} , especially when compared with the rate constants for components of the mixture; 1.3 h^{-1} for 210 mg/kg oxalic acid, and 0.5 h^{-1} for 273 mg/kg citric acid. That the rate constant for mixtures of citric acid and oxalic acid could potentially be higher was suggested by one of three results obtained using citric-acid/oxalic-acid mixtures and BWR-2 samples at 117°C. As shown in Table 3, an initial value of k of 3.3 h^{-1} was obtained in one experiment, compared to an average value of 0.18 for repeat experiments. Except for the value of 3.3 h^{-1} , which was an exceptionally high rate constant, the relative ranking of the constants for dissolution of BWR-2 oxide for various solutions was the same as for BWR-1 oxides, but k values for BWR-2 oxides were about twice those for dissolution of BWR-1 oxide, suggesting that BWR-2 oxide was more easily dissolved. Note that negligible amounts of BWR-2 oxide were dissolved in the control experiment using just H_2O and that BWR-1 and BWR-2 results for

citric-acid/oxalic-acid and citric-acid/EDTA mixtures are not directly comparable, since concentrations of oxalic acid or EDTA were 400 mg/kg in BWR-2 runs compared with 210 mg/kg in BWR-1 runs. Note, however, that in the case of the citric-acid/EDTA run and in two of three runs for citric-acid/oxalic-acid, the rate constants were only doubled even though concentrations of reagents were higher. The fact that the rate constants for dissolution of BWR-2 oxide in citric-acid/oxalic-acid and citric-acid/EDTA solutions were only twice those for BWR-1 oxide, even though the concentrations of oxalic-acid or EDTA were doubled, is consistent with previous results: for dissolution of BWR-1 oxide in oxalic acid, the rate constant did not increase from 1.3 h^{-1} as the concentration of oxalic acid was increased from 210 mg/kg to 500 mg/kg. Similarly, for dissolution of BWR-1 oxide in EDTA, the rate constant only increased from 0.30 h^{-1} to 0.37 h^{-1} as the concentration of EDTA was increased from 210 mg/kg to 500 mg/kg. These results suggest, in the case of oxalic acid or EDTA, that once a threshold concentration is reached, there is not much benefit in increasing the reagent concentrations. The minimal dependence of rate constants with reagent concentrations is consistent with postulates that oxalic acid and EDTA act by adsorption, then by binding oxide iron, after which iron-oxygen bonds in the crystal lattice break [20,26]. Once the oxide surface is covered at a particular concentration of reagent, no benefit can be obtained by increasing the concentration of reagent in the bulk solution unless a supply of uncomplexed reagent is required. In a dilute regenerative decontamination, oxalic acid and EDTA can be regenerated using iron-exchange resin [9,10,11].

As shown in Table 3, and as expected, the rate constants for dissolution of BWR-2 oxide at 90°C were significantly lower than those obtained at 117°C . The relative ranking of rate constants for BWR-2 specimens at 90°C for various solutions was approximately the same as that observed for BWR-1 and BWR-2 specimens at 117°C , with the exception of results obtained in citric-acid/oxalic-acid/EDTA mixtures. In this case, the rate constant observed at 90°C , 0.42 h^{-1} , was only 16% less than the rate constant, 0.5 h^{-1} , observed at 117°C . This compares with four-fold decreases in values of k observed for citric-acid/oxalic-acid and citric-acid/EDTA solutions. Approximate activation energies (E_a) were estimated from the rate constant data for BWR-2 oxide at 90°C and 117°C using the Arrhenius equation: for the citric-acid/oxalic-acid/EDTA solution, the E_a value was 2 kcal/mol compared with values of E_a of 14 kcal/mol for the citric-acid/EDTA solution and 16 kcal/mol for the citric-acid/oxalic-acid solution. These numbers confirm that oxalic acid and EDTA act synergistically in the dissolution of nickel ferrite. In experiments using magnetite and mixtures of oxalic acid and EDTA, Shoesmith postulated that oxalic acid adsorbed at ferric ion sites in the oxide lattice and assisted in dissolution of the oxide, while EDTA assisted in the removal of ferrous ion from oxide surfaces by complexation in solution [18].

3.3 Decontamination Factors

Decontamination factors (DFs), calculated by dividing the initial Co-60 activity on samples by the final activity on samples after exposure to decontamination solutions, are given in Table 5 for BWR-1 and BWR-2 specimens. As shown, DFs varied by as much as a factor of four for duplicate runs. DFs are dependent on time of exposure to solution, and to the initial amount of Co-60 on specimens. Since rate constants (given in Table 3) are independent of time and the initial amount of Co-60 on specimens, and since results were reproducible to within $\pm 0.07 \text{ h}^{-1}$ for duplicate runs, the rate constant data were regarded as a more reliable estimate of decontamination effectiveness than DFs. In general, while there was a good correlation between rate constants and DFs such that highest values for DFs were obtained where rate constants were highest, the DF numbers were not as sensitive to solution composition; for example, rate constants for BWR-1 specimens in oxalic acid and EDTA solutions at 117°C were a factor of four different (Table 3), while DFs were approximately the same. As expected, highest values for DFs were obtained with higher temperature and exposure time.

3.4 Effects of Ferric Ion Addition

As illustrated in Figures 8-10, the addition of 60 mg/kg of Fe^{3+} to citric-acid/EDTA, citric-acid/oxalic-acid and citric-acid/oxalic-acid/EDTA solutions resulted in significant decreases in the rate of dissolution of BWR-1 oxide at 117°C , such that complete dissolution took about 5-6 h in the cases of citric-acid/EDTA and citric-acid/oxalic-acid/EDTA solutions with Fe^{3+} , compared with 2 h without Fe^{3+} . For the citric-acid/oxalic-acid solution, complete dissolution was not achieved even after 22 h in the presence of added Fe^{3+} , where complete dissolution took about 5 h without added Fe^{3+} . An S-shaped curve shown in Figure 8 was found only for dissolution in the citric-acid/EDTA mixture with Fe^{3+} , where dissolution was preceded by the characteristic induction period. In the case of the citric-acid/oxalic-acid/EDTA/ Fe^{3+} curve shown in Figure 10, mixed behaviour was observed. During the first 0.5 h, dissolution behaviour was similar to that observed in the citric-acid/oxalic-acid solution, but after 2 h, dissolution behaviour was similar to that in the citric-acid/EDTA/ Fe^{3+} solution. These results are consistent with Fe^{3+} being initially complexed by EDTA, leaving uncomplexed citric acid and oxalic acid for oxide dissolution. After the initial period of dissolution, the dissolution mechanism was dominated by citric-acid/EDTA/ Fe^{3+} , perhaps, as discussed later, as a result of buildup of dissolution byproducts, such as $\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)^+$ or $\text{Fe}^{\text{II}}(\text{C}_2\text{O}_4)$, in solution or on the oxide surface.

As shown in Table 6, rate constants for dissolution of BWR-1 oxide were lower (by factors ranging from four to nine) in solutions to which 60 mg/kg of Fe^{3+} was added. DFs decreased only in the case of the citric-acid/oxalic-acid solution, in that the rate constant was so low that complete dissolution of the BWR-1 oxide did not occur even after 22 h. In the cases of citric-acid/EDTA and citric-acid/oxalic-acid/EDTA mixtures,

even though rate constants decreased by factors of four and five, complete dissolution of oxide occurred within 15 h.

Loop samples were analyzed for Fe^{3+} during loop runs. While 60 mg/kg of Fe^{3+} was added to each of the citric-acid/oxalic-acid, citric-acid/EDTA and citric-acid/oxalic-acid/EDTA solutions, only 5 mg/kg, 30 mg/kg and 20 mg/kg of Fe^{3+} , respectively, was found by analysis in loop samples.

3.5 Dissolution of PWR Oxides

Experiments with PWR samples were carried out at 90°C by exposing specimens in solutions of citric acid, and in mixtures of reagents citric-acid/oxalic-acid, citric-acid/EDTA and citric-acid/oxalic-acid/EDTA for 5 h with linear velocities through the test section of 250 cm/s. Decontamination results for the PWR specimens are shown in Table 7. As noted previously, a preliminary experiment was carried out by exposing an "as-received" PWR sample in a citric-acid/EDTA solution. As expected, and as given in Table 7, no Co-60 was removed from the specimen during the experiment. In subsequent experiments, specimens which had been pretreated with alkaline permanganate to oxidize Cr^{3+} were used.

The rate constants for dissolution of PWR oxide at 90°C in citric acid and citric-acid/EDTA solutions were comparable to rate constants for BWR oxide dissolution at 117°C. Dissolution of oxide is complete within about 1 h. The rate constant for removal of PWR oxide was highest, 6 h^{-1} , in the citric-acid/oxalic-acid solution, and removal of oxide was complete within five minutes. As in the case of BWR specimens, there was a correlation between high rate constants and high DFs for the PWR specimens.

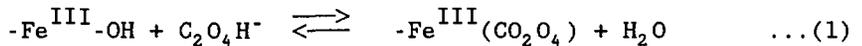
4. DISCUSSION

The decontamination effectiveness of various mixtures of citric acid, oxalic acid and EDTA with and without the addition of ferric ion will be discussed.

4.1 Solutions of Oxalic Acid and/or Citric Acid

The results given in Tables 3-7 and illustrated in Figures 4-6 show that, under certain conditions, oxalic acid is the most effective reagent for dissolution of nickel ferrite of the three reagents: citric acid, oxalic acid and EDTA. Note, however, that the conditions under which effective dissolution occurs in the presence of oxalic acid and/or citric acid are difficult to define and control. For example, as shown in Table 3, of the three experiments carried out with BWR-2 samples in a citric-acid/oxalic-acid solution at 117°C, two of the rate constants were similar, averaging 0.18 h^{-1} , while the third rate constant was 20 times higher, 3.3 h^{-1} . In addition, as shown in Table 4, while rate constants for dissolution of oxides in oxalic acid or citric-acid/oxalic-acid solutions were initially high at 1.3 h^{-1} and 3.3 h^{-1} , respectively, after a relatively

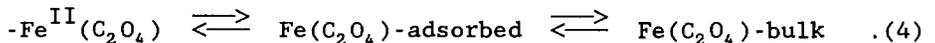
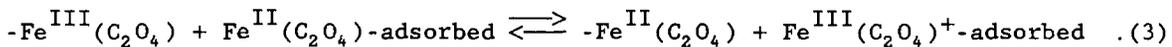
short time of 0.1 h, the rate constants changed to low and similar values of 0.21-0.25 h⁻¹. As shown in Table 4, similar changes in rate constants were observed for citric acid solutions, but after a longer period of time of 0.5-2.5 h. As described below, it is possible to rationalize most of the results for oxalic acid and citric acid on the basis of several competing reactions which are rate limiting under different sets of conditions. The reactions proposed by Shoesmith [18] and by Baumgartner [16] are described below, where -Fe indicates that this species is part of the solid. In the first step, surface -OH groups are replaced by oxalate.



Direct dissolution can occur slowly according to reaction 2.



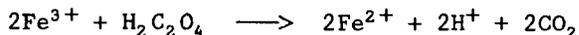
Note that reaction 2 predominates when the concentration of Fe^{II} in the bulk solution is negligible. At higher concentrations of Fe^{II} (e.g., 30 mg/kg for dissolution of magnetite at 30°C), fast dissolution was proposed to occur by a reductive mechanism described by reactions 3 and 4, where either of 3 or 4 could be rate determining.



Some evidence supports the premise that the high observed rate constants for dissolution of BWR-1 at 117°C in oxalic acid containing solutions, 1.3 h⁻¹, are due to dissolution by reaction 3. As shown in Table 8 for runs 3 and 4, the amount of Fe²⁺ present in oxalic acid solutions when the test section was valved in was about 34-37 mg/kg as a result of corrosion of the loop materials of construction. This is a similar concentration to the 30 mg/kg used to eliminate the induction period during dissolution of magnetite at 30°C [16]. It is not clear why the rate constants decreased to 0.32-0.25 h⁻¹, after only 0.1 h, particularly since the average concentrations of Fe²⁺ in the loop were 36 mg/kg and 44 mg/kg during the loop runs. The dissolution of oxide was probably limited by reaction 2 or 4, where locally high concentrations of Fe^{II}(C₂O₄) or Fe^{III}(C₂O₄)⁺ in the bulk solution reduced the rate of desorption of adsorbed species from the oxide surface or the rate of byproduct removal as dictated by diffusion of Fe^{II}(C₂O₄) or Fe^{III}(C₂O₄)⁺ from the oxide surface. The possibility that the buildup of dissolution

byproducts limits diffusion of fresh reagent HC_2O_4^- to the oxide surface, and hence limits reaction 1, cannot be excluded.

The premise of a limiting process is supported by data for dissolution of BWR-2 oxide at 117°C in citric-acid/oxalic-acid solutions, as shown in runs 14a and 14b, Table 8. In run 14a, the rate constant, 3.3 h^{-1} , decreased to 0.21 h^{-1} after 0.1 h, while in run 14b only a single rate constant of 0.24 h^{-1} was observed after an induction time of 0.25 h. It is not clear why the rate constant in run 14a was initially high while an induction period was observed in run 14b, in that the amounts of Fe^{2+} found by analysis of loop solution were 3 mg/kg at valve-in in both experiments. The fact that corrosion rates for carbon steel specimens (adjacent to and upstream of the BWR specimens) were higher in run 14a compared with run 14b suggests that local concentrations of Fe^{2+} in run 14a were at the critical value necessary for reductive dissolution. The fact that amounts of Fe^{2+} in run 14b were not high enough for reductive dissolution according to reaction 3 and hence not enough to limit dissolution by reaction 4 suggests that dissolution was occurring by the mechanism and rate limiting step described in reaction 2. Even though BWR-2 oxide was more readily dissolved than BWR-1 oxide in citric acid and citric-acid/oxalic-acid/EDTA (Table 3), rate constants for dissolution of BWR-2 oxide in runs 14a and b had limiting values of 0.21-0.24 h^{-1} . These k values for BWR-2 oxide are close to the final values obtained for BWR-1 oxide, 0.21-0.25 h^{-1} , and suggest that a similar limiting process occurred after initial rapid dissolution by reaction 3. Data for run 14b suggest that the limiting reaction is 2 and relates to desorption or diffusion of $\text{Fe}^{\text{II}}(\text{C}_2\text{O}_4)^+$ from the oxide surface. That the rate of dissolution of oxide is sensitive to the concentration of Fe^{3+} in solution is shown clearly in Figure 9 and Table 6, where the addition of 60 mg/kg of Fe^{3+} to a citric-acid/oxalic-acid solution resulted in a nine-fold reduction in rate constant for dissolution of BWR-1 oxide. Based on the data, it is not possible to say definitely that the effects of Fe^{3+} addition are not due to Fe^{2+} , as described below. While 60 mg/kg of Fe^{3+} was added to the solution of citric-acid/oxalic-acid (run 8), only 5 mg/kg of Fe^{3+} was found in loop samples by analysis. Loss of Fe^{3+} probably occurred by reaction of Fe^{3+} with metal and oxalic acid:

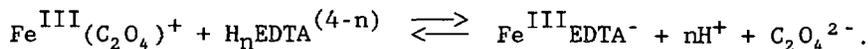
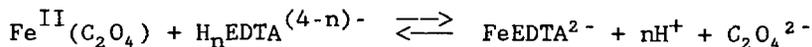


or, as described in ref.16, by photolysis of $\text{Fe}(\text{C}_2\text{O}_4)_3$. The possible mechanisms by which relatively high concentrations of Fe^{2+} affect rate of oxide dissolution are described below.

Evidence of buildup of $\text{Fe}^{\text{II}}(\text{C}_2\text{O}_4)$ and of the limiting effects of such buildup on dissolution of oxides was observed in all other experiments carried out with citric acid and/or oxalic acid. As shown in Table 8, the

corrosion rates for carbon steel specimens (adjacent to and upstream of the BWR specimens) were an order of magnitude higher in runs 14c, 7, 18, 21, 1 and 2, compared with runs 3, 4, 14a and 14b. In the latter cases, a protective film of ferrous oxalate probably formed on the surfaces of the carbon steel specimen, as has been described previously [15,33,41]. In the former cases, the higher corrosion rates resulted in significant concentrations of Fe^{2+} and hence of $\text{Fe}^{\text{II}}(\text{C}_2\text{O}_4)$ in the vicinity of the BWR specimens. The Fe^{2+} analyses for loop samples were not elevated in the runs with high corrosion rates, suggesting that precipitation of ferrous oxalate occurred during loop runs - as was observed visually on loop and corrosion coupon surfaces. The consequences of the relatively high concentrations of Fe^{2+} are twofold. In the first case, the locally high concentrations of $\text{Fe}^{\text{II}}(\text{C}_2\text{O}_4)$ could reduce the rate of desorption or of diffusion of $\text{Fe}^{\text{II}}(\text{C}_2\text{O}_4)$ from the oxide surface, resulting in a reduction in the rate of dissolution of oxide by inhibition of reaction 4. In addition, precipitation of $\text{Fe}^{\text{II}}(\text{C}_2\text{O}_4)$ would result in a decrease in the amount of oxalic acid in solution, and hence would affect the rate at which oxalate anions sorb to oxide surfaces, and hence the rate at which reaction 1 occurs. As suggested by the data in Table 8, the same mechanisms are occurring in solutions of citric acid as have been described for oxalic acid.

The benefits of EDTA addition in mitigating the effects of Fe^{2+} and Fe^{3+} in citric-acid/oxalic-acid solution are considerable. Comparison of data in Table 3 and Table 6 for citric-acid/oxalic-acid and citric-acid/oxalic-acid/EDTA solutions and comparisons of curves 7 and 11 in Figure 5, and curves 18 and 20 in Figure 6, shows clearly that addition of EDTA to the citric-acid/oxalic-acid solutions results in significant increases in the dissolution rates of BWR oxides. The effects are most pronounced at 90°C where, as described previously, oxalic acid and EDTA act synergistically. As postulated by Shoesmith [18], oxalic acid adsorbs at ferric ion sites in the oxide lattice and assists in dissolution of the oxide, while EDTA assists in the removal of ferrous and ferric ions from oxide surfaces by ligand exchange and complexation in solution:



The rate limiting steps imposed by high concentrations of $\text{Fe}^{\text{II}}(\text{C}_2\text{O}_4)$ and $\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)^+$ at oxide surfaces are therefore replaced by other limiting reactions, perhaps ligand exchange.

The results for dissolution of oxides in solutions containing EDTA are discussed below.

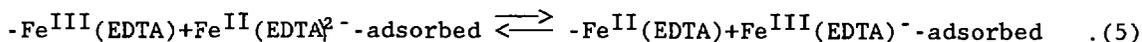
4.2 Solutions Containing EDTA

The results for dissolution of oxide in EDTA-containing solutions are given in Tables 3-7, and illustrated in Figures 4-6. As deduced by comparison of curves 5 and 6 in Figure 4 with curves 9 and 11 in Figure 5, dissolution of BWR-1 oxide in EDTA containing solutions at 117°C appears to be dominated by EDTA even in the presence of oxalic acid and citric acid. Note in particular that addition of EDTA to the citric-acid/oxalic-acid solution (compare curves 7 and 11 in Figure 5) resulted in a significant increase in dissolution rate of BWR-1 oxide, while addition of oxalic acid to the citric-acid/EDTA solution (compare curves 9 and 11) resulted in a slight decrease in the dissolution rate compared with the citric-acid/EDTA solution. As given in Table 3, the negative effects of oxalic acid addition are more pronounced in the case of BWR-2 samples where, at 117°C, the value of k was lowered from 0.8 h^{-1} to 0.5 h^{-1} upon addition of oxalic acid to the citric-acid/EDTA solution.

At 90°C, and as illustrated by comparing curves 18 and 19 in Figure 6 with curve 20, EDTA acts synergistically with oxalic acid, where oxalic acid has been postulated to adsorb on the oxide surface in preference to EDTA. The rate constant for dissolution of oxide in citric-acid/EDTA solution at 90°C is a factor of two less than the constant for dissolution in the citric-acid/oxalic-acid/EDTA solution.

The results obtained for EDTA-containing solutions at 90°C and 117°C using BWR specimens (nickel ferrite) are consistent with results reported for magnetite [5] and hematite [20] where at low temperatures, 25°C-100°C, adsorbed EDTA was postulated to block the oxide surface and retard dissolution. When the temperature was raised to 120°C in the case of hematite, dissolution of oxide was significant as sufficient activation energy became available above a critical temperature.

As proposed by Blesa et al. [23], the mechanisms for dissolution of oxide in EDTA-containing solutions are analogous to those for dissolution in EDTA. It is probable that the rate limiting step for dissolution is initially:



where Fe^{II} builds up in solution to a critical concentration during the induction period. As indicated in Table 3, rate constants ranged from 0.3 in experiments with BWR-1 specimens to 0.8 in experiments with BWR-2 specimens.

As in the case of solutions containing oxalic acid and/or citric acid, rate constants changed after a period of time to lower values (Table 4),

probably as a result of build-up of corrosion and dissolution byproducts on the oxide surface.

Evidence of the limiting effects on dissolution of oxides of such buildup was observed in experiments with added Fe^{3+} . As shown in Table 6 and illustrated in Figures 8 and 10, additions of Fe^{3+} to solutions containing EDTA resulted in four- to five-fold decreases in rate constants. Blesa et al. [23] and Matijevic [20] have reported results for magnetite and nickel ferrite where additions of an oxidant, NO_3 , resulted in significant reductions in rate of oxide dissolution in EDTA solutions. In these experiments, Fe^{2+} present in solution is oxidized to Fe^{3+} and is complexed by EDTA. As demonstrated by Blesa et al. [23] for magnetite, adsorption of EDTA in the presence of Fe^{3+} is significantly reduced, suggesting that addition of Fe^{3+} affects oxide dissolution by suppressing:



(charges on H_nEDTA have been omitted for clarity).

The effects of Fe^{2+} addition on oxide dissolution in EDTA solutions were considerably less pronounced than were the effects of Fe^{3+} addition. As shown in Table 3, the rate constant for dissolution of BWR-1 oxide in 500 mg/kg of EDTA at 117°C was 0.37 h^{-1} , compared with 0.33 h^{-1} with dissolution in 500 mg/kg of EDTA, to which 80 mg/kg of Fe^{2+} was added. These results are consistent with those of Blesa et al. [23] in that magnetite dissolved too rapidly in Fe^{II} -EDTA solutions by reaction 5 for adsorption measurements to be obtained. The results for the experiment with 80 mg/kg of Fe^{2+} do confirm, however, that dissolution in other EDTA and citric-acid/EDTA runs occurred by reductive dissolution (reaction 5).

The rate constants for dissolution of PWR oxide at 90°C in citric acid and citric-acid/EDTA shown in Table 7 were comparable to rate constants for BWR oxide at 117°C . Mechanisms for dissolution of PWR oxide are assumed to be similar to those described for BWR oxide. In the case of the citric-acid/oxalic-acid solution, the rate constant for removal of PWR oxide was higher, 6 h^{-1} , than any observed in this work, such that removal of oxide was complete within five minutes. While it is possible that dissolution was occurring by reduction dissolution, the data were not recorded at short enough intervals to discount the possibility that the oxide was only partially dissolved and undercut and released to the solvent as particulates.

5. SUMMARY AND CONCLUSIONS

In view of recent concerns that some decontamination solvents may cause intergranular attack (IGA) in sensitized 304SS, an experimental study was previously undertaken to study the corrosiveness of mixtures of citric

acid, oxalic acid and EDTA to nuclear reactor materials of construction. Results of the experiments reported in refs.33-36 showed that of the three reagents, oxalic acid was most likely to cause IGA in sensitized 304SS but only under extreme conditions of temperature, exposure time and level of sensitization. To assess whether removal of oxalic acid from solvents would affect decontamination effectiveness, experiments reported here were carried out using actual radioactive specimens from BWRs and a PWR. Based on the results of the experiments, the following conclusions can be drawn about the decontamination effectiveness of mixtures of citric acid, oxalic acid and EDTA:

- (1) Under certain conditions, oxalic acid was the most effective reagent for dissolution of nickel ferrite of the three reagents tested. For the range of reagent concentrations tested, 200-700 mg/kg, the conditions under which effective dissolution occurs in solutions of oxalic acid and/or citric acid were difficult to define and control. Under conditions of elevated ferrous and ferric ion concentrations, the rate constants for dissolution of nickel ferrite were lowest in solutions of oxalic acid and/or citric acid. The retarding effects of elevated ferrous and ferric ion concentrations were mitigated by addition of EDTA to citric-acid/oxalic-acid solutions.
- (2) EDTA, and under certain conditions citric acid, were effective for dissolution of oxides. Rates of dissolution of nickel ferrite in EDTA-containing solutions at 117°C were comparable to rates in oxalic acid containing solutions. This result suggests that decontaminations carried out at 120°C (the approximate maximum used in the field) should be carried out using solutions of EDTA or citric-acid/EDTA to minimize the possibility and extent and depth of IGA in sensitized 304SS.
- (3) At 90°C, EDTA acted synergistically with oxalic acid such that the rate of dissolution of nickel ferrite in citric-acid/oxalic-acid/EDTA solutions was higher than in citric-acid/EDTA and citric-acid/oxalic-acid solutions. At 90°C, where the possibility of causing IGA in sensitized 304SS is reduced and the extent and depth of attack would be negligible, more effective decontaminations will result with mixtures of the three acids. An effective decontamination at 90°C, with negligible risk of causing IGA in sensitized 304SS, can be effected with a citric-acid/EDTA solution in a longer time.
- (4) The rates of dissolution of nickel ferrite were significantly reduced when ferric ion was added to citric-acid/oxalic-acid, citric-acid/EDTA and citric-acid/oxalic-acid/EDTA solutions. Concentrations of ferric ion, then, should be minimized during decontamination to ensure an effective decontamination in a minimum time.

6. ACKNOWLEDGEMENTS

The author would like to thank P.A. Burchart and K. Kanhai for their help in obtaining the experimental results, and LN Technologies Corporation, Columbia, South Carolina, for providing BWR and PWR samples.

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TABLE 1: SUMMARY OF ANALYSES FOR SELECTED LOOP RUNS*.

RUN #	SOLUTION COMPOSITION (mg/kg)			SOLUTION pH	AMOUNT OF Fe ²⁺ (mg/kg)		TEMP. °C	LINEAR VELOCITY IN TEST SECTION (cm/s)	RUN TIME (h)	BWR SPECIMEN USED
	Citric Acid	Oxalic Acid	EDTA		At Valve-In	Average				
1	273	-	-	3.1	10	10	117	6	22	1
2	700	-	-	3.0	3	6	117	6	22	1
3	-	210	-	3.0	37	36	117	6	22	1
4	-	500	-	2.7	34	44	117	6	22	1
5	-	-	210	3.1	7	6	117	6	22	1
6	-	-	500	2.8	5	6	117	6	22	1
7	273	210	-	3.2	3	25	117	6	22	1
8▲, ▼	273	210	-	2.7±0.1	4±3	12±6	117	6	22	1
9**	273	-	210	2.9±0.1	4±2	7±6	117	6	22	1
10▼	273	-	210	3.0	3	16	117	6	22	1
11**	273	210	210	2.6±0.3	1	20±3	117	6	22	1
12▼	273	210	210	2.2	4	8	117	6	22	1
13	700	-	-	3.0	3	7	117	6	22	2
14▲	273	400	-	2.8	9±10	40±14	117	6	22	2
15	273	-	400	2.8	1	1	117	6	22	2
16	273	210	210	2.9	0	23	117	6	22	2
17	700	-	-	3.1	7	15	90	250	5	2
18	273	400	-	2.7	5	32	90	250	5	2
19	273	-	400	2.9	0	3	90	250	5	2
20	273	210	210	2.7	0	4	90	250	5	2

*Results reported are averages of about 10 analyses carried out during loop runs.
Approximate σ for average of pH and Fe analyses are ± 0.06 pH units and ± 7 mg/kg.

**Numbers are averages of results from two experiments.

▲Numbers are averages from three experiments.

▼60 mg/kg of Fe³⁺ added.

TABLE 2: APPROXIMATE INDUCTION TIMES FOR DISSOLUTION OF BWR OXIDES.

SOLUTION COMPOSITION (mg/kg)			INDUCTION TIME (h)		
Citric Acid	Oxalic Acid	EDTA	BWR-1	BWR-2	
			117°C 6 cm/s	117°C 6 cm/s	90°C 250 c/m
273	-	-	0.1	-	-
700	-	-	0	0	3.0
-	210	-	0	-	-
-	500	-	0	-	-
-	-	210	0.25	-	-
-	-	500	0	-	-
273	210,400*	-	0 (0)**	0,0,0.25 [▲]	0
273	-	210,400*	0,0.25 [▲]	0 (0.25)**	1.0
273	210	210	0,0.25 [▲]	0	0.5

*Concentrations of oxalic acid and EDTA were 210 mg/kg in experiments using BWR-1 samples, but were 400 mg/kg in experiments using BWR-2 samples.

**Experiments were carried out at a temperature of about 90°C.

[▲]Experiments carried out in duplicate and triplicate.

TABLE 3: RATE CONSTANTS FOR DISSOLUTION OF BWR OXIDES.

SOLUTION COMPOSITION (mg/kg)			RATE CONSTANTS FOR OXIDE DISSOLUTION (h ⁻¹)		
Citric Acid	Oxalic Acid	EDTA	BWR-1	BWR-2	
			117°C 6 cm/s	117°C 6 cm/s	90°C 250 cm/s
-	-	-	-	0.002	-
273	-	-	0.50	-	-
700	-	-	0.05	0.08	0.04
-	210	-	1.30	-	-
-	500	-	1.30	-	-
-	-	210	0.30	-	-
-	-	500	0.37 [0.33] ^{▲▲}	-	-
273	210,400*	-	0.09 (0.03)**	3.3 [▲] , 0.24, 0.15	0.04±0.04
273	-	210,400*	0.38 ± 0.05	0.8 (0.22)**	0.21
273	210	210	0.29 ± 0.07	0.5	0.42

*Concentrations of oxalic acid and EDTA were 210 mg/kg in experiments using BWR-1 specimens, but were 400 mg/kg in experiments using BWR-2 specimens.

**Experiments were carried out at a temperature of about 90°C.

[▲]Results for the three experiments were significantly different.

^{▲▲}Experiment was carried out with addition of 80 mg/kg of Fe²⁺ where Fe²⁺ was added as iron powder.

TABLE 4: CHANGES IN RATE CONSTANTS DURING LOOP EXPERIMENTS.

SOLUTION COMPOSITION (mg/kg)			RATE CONSTANTS FOR OXIDE DISSOLUTION (h ⁻¹)					
Citric Acid	Oxalic Acid	EDTA	BWR-1			BWR-2		
			Initial	Final	Time** (h)	Initial	Final	Time** (h)
-	210	-	1.30	0.21	0.1	-	-	-
-	500	-	1.30	0.25	0.1	-	-	-
273	210,400*	-	0.09	-	-	3.30	0.21	0.1
-	-	210	0.30	0.11	1.0	-	-	-
-	-	500	0.37	0.18	0.5	-	-	-
273	-	210,400*	0.38	0.16	1.0	0.80	0.18	0.5
273	-	-	0.50	0.02	0.5	-	-	-
700	-	-	0.05	0.02	2.5	0.08	0.03	1.7

*Concentrations of oxalic acid and EDTA were 210 mg/kg in experiments using BWR-1 specimens, but were 400 mg/kg in experiments using BWR-2 specimens. All experiments carried out in TL#1 at 117°C and 6 cm/s linear velocity.
 **Time at which change in rate constant occurs.

TABLE 5: DECONTAMINATION FACTORS FOR BWR SPECIMENS.

SOLUTION COMPOSITION (mg/kg)			DECONTAMINATION FACTORS		
Citric Acid	Oxalic Acid	EDTA	BWR-1	BWR-2	
			117°C, 6 cm/s 22 h	117°C, 6 cm/s 22 h	90°C, 250 cm/s 5 h
-	-	-	-	1.2	-
273	-	-	30	-	-
700	-	-	3	25	1.1, 1.3
-	210	-	115	-	-
-	500	-	14	-	-
-	-	210	120	-	-
-	-	500	25	-	-
273	210,400	-	30	300, 3	3, 2
273	-	210,400	30, 130	45	4, 5
273	210	210	90, 170	60	2

TABLE 6: EFFECT OF FERRIC ION ADDITION ON DECONTAMINATION EFFECTIVENESS FOR BWR-1 SPECIMENS*.

SOLUTION COMPOSITION (mg/kg)			RATE CONSTANTS FOR OXIDE DISSOLUTION, h ⁻¹		DECONTAMINATION FACTORS	
Citric Acid	Oxalic Acid	EDTA	No Fe ³⁺	Fe ³⁺ Added (60 mg/kg)	No Fe ³⁺	Fe ³⁺ Added (60 mg/kg)
700	-	-	0.05 / 0.02	-	3	-
273	210	-	0.09	0.01 ± 0.01	30	1.6, 3, 6**
273	-	210	0.38 ± 0.05	0.07	30, 130**	90
273	210	210	0.29 ± 0.07	0.07	90, 170**	110

*Experiments were carried out in TL#1 at 117°C and with a linear velocity in the test section of 6 cm/s.

**Experiments carried out in duplicate or triplicate.

TABLE 7: DECONTAMINATION RESULTS FOR PWR SPECIMENS*.

SOLUTION COMPOSITION (mg/kg)			RATE CONSTANT (h ⁻¹)	DECONTAMINATION FACTORS (after 5 h)
Citric Acid	Oxalic Acid	EDTA		
-	-	-	0.07	4
700	-	-	0.1, 0.7	20, 60
273	400	-	6 ± 2	70, 430
273	-	400	0.5	50
273	210	210	**	130
273	-	400 [▲]	**	1

*Experiments lasting about 5 h were carried out in TL#2 at 90°C and with a linear velocity in the test section of 250 cm/s.

**No on-line counting available, so rate constants could not be calculated.

[▲]In this experiment, PWR specimen was not AP pretreated.

TABLE 8: SUMMARY OF DATA FOR CITRIC ACID AND OXALIC ACID RUNS.

RUN	SOLUTION COMPOSITION (mg/kg)		BWR SAMPLE USED	AMOUNT OF Fe (mg/kg)		CARBON STEEL CORROSION RATE ($\mu\text{m}/\text{h}$)	RATE CONSTANT (h^{-1})
	Citric Acid	Oxalic Acid		At Valve-In	Average		
3	-	210	1	37	36	0.6	1.3/0.21
4	-	500	1	34	44	<0.1	1.3/0.25
14a	273	400	2	3	28	1.2	3.3/0.21
14b	273	400	2	3	35	0.7	0.24
14c	273	400	2	20	56	6.7	0.15
7	273	210	1	3	25	4.6	0.09
18*	273	400	2	5	32	6.1	0.04
21*	273	210	1	2	9	6.4	0.03
1	273	-	1	10	10	4.4	0.5/0.02
2	700	-	1	3	6	7.6	0.05/0.02

*Run temperature was 90°C. Temperature for all other runs was 117°C.

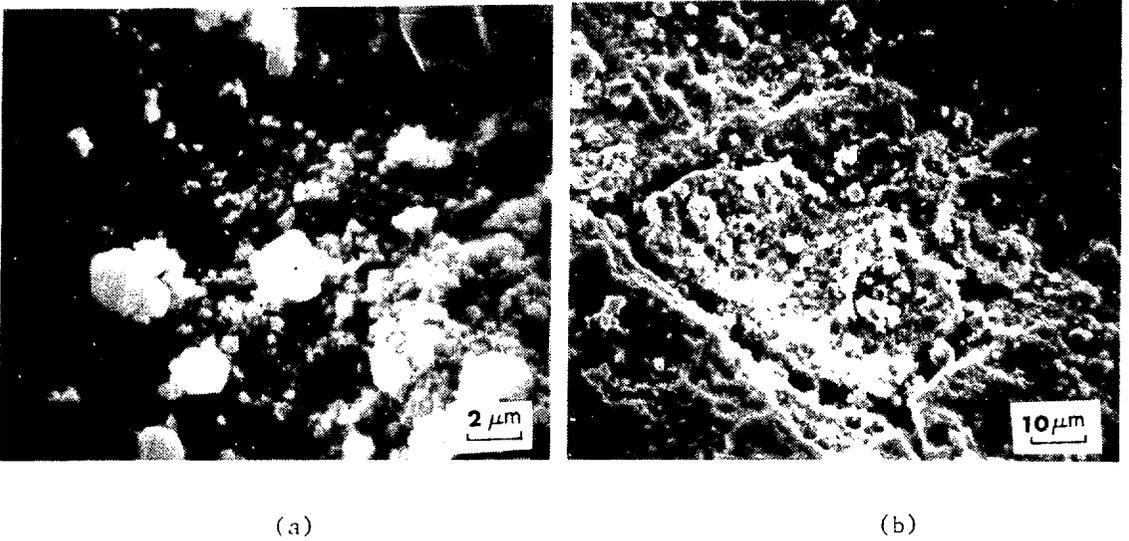


FIGURE 1. Scanning electron micrograph of BWR-1 specimen.

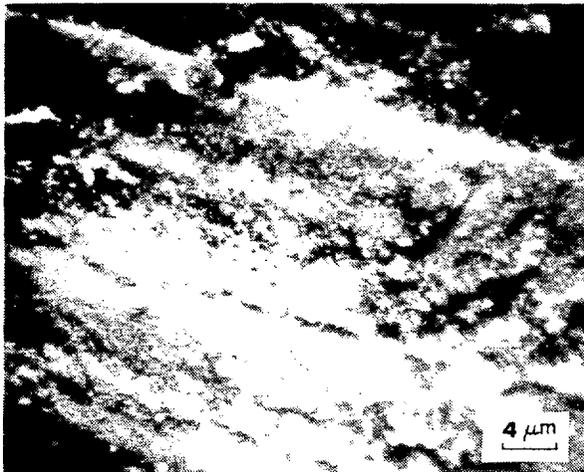


FIGURE 2. Scanning electron micrograph of PWR specimen.

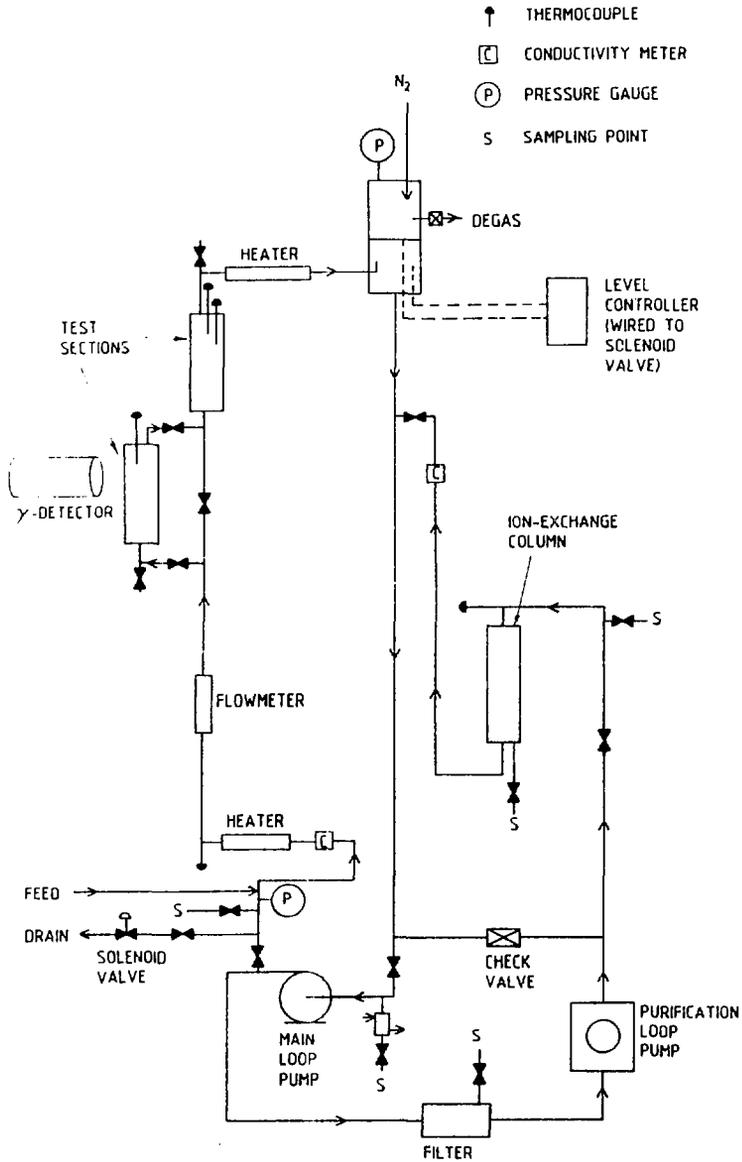


FIGURE 3. Illustration of test loop used in decontamination experiments.

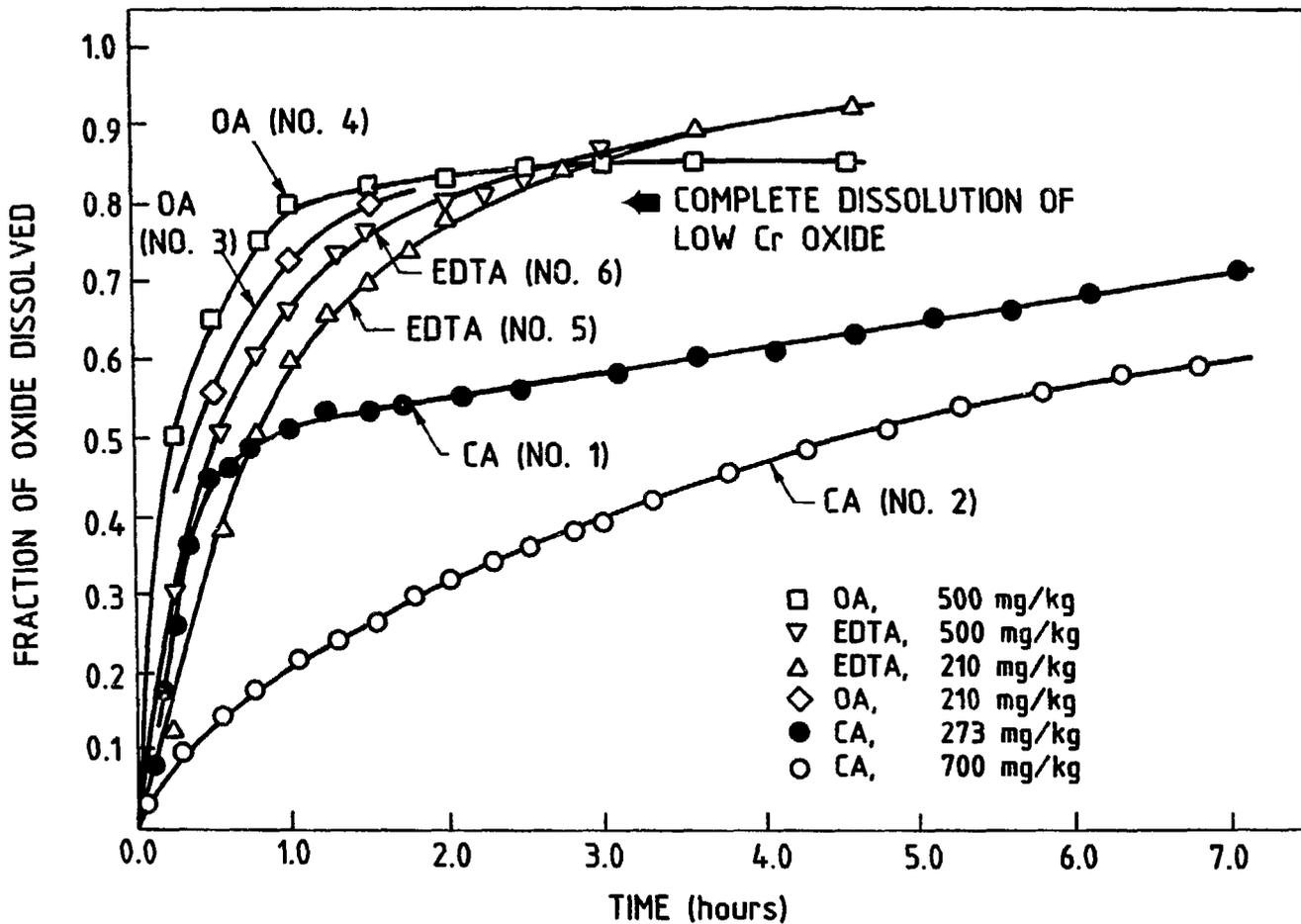


FIGURE 4. Dissolution of BWR-1 oxide in citric acid, oxalic acid or EDTA solutions at 117°C.

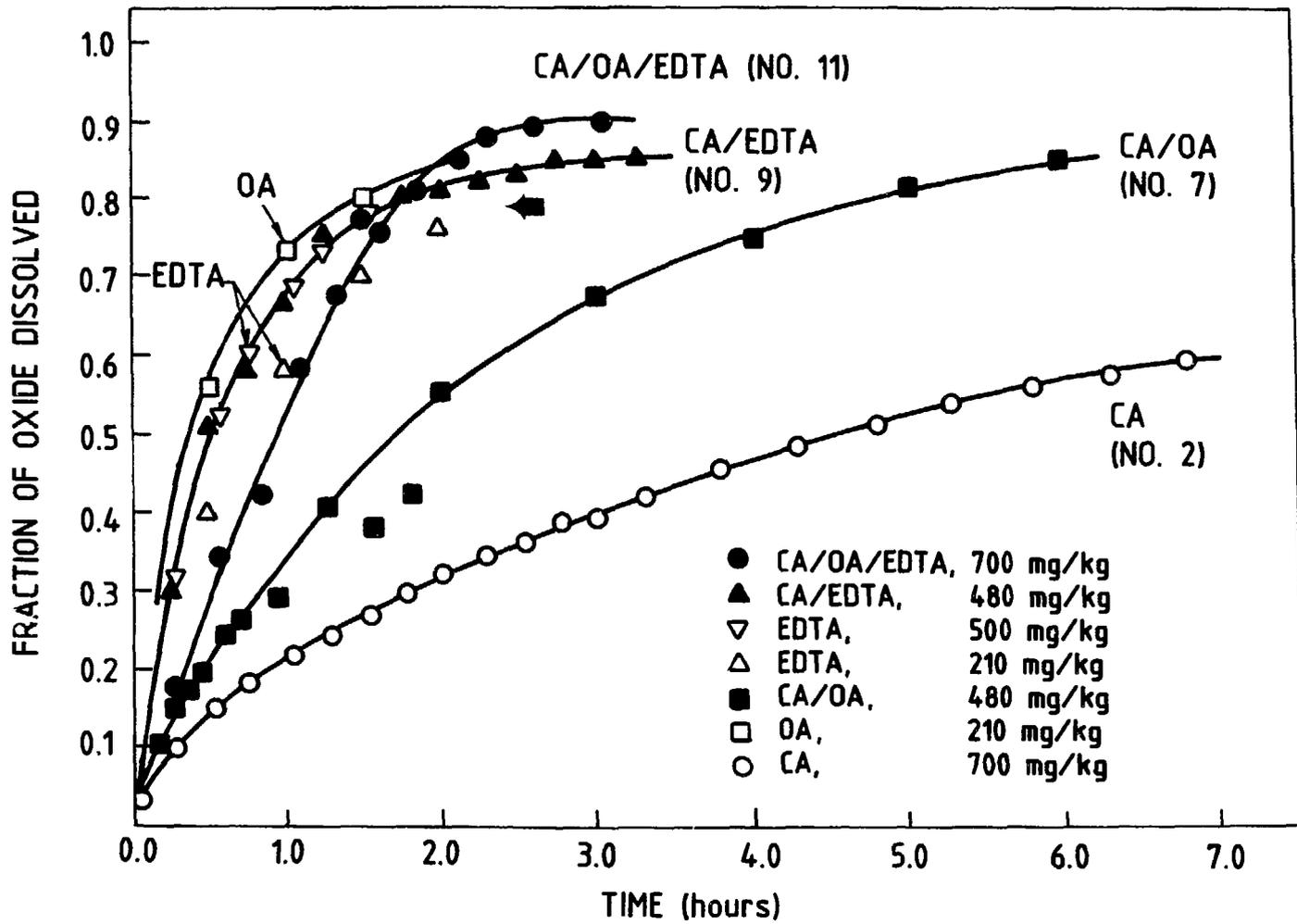


FIGURE 5. Dissolution of BWR-1 oxide in mixtures of citric acid, oxalic acid and EDTA at 117°C.

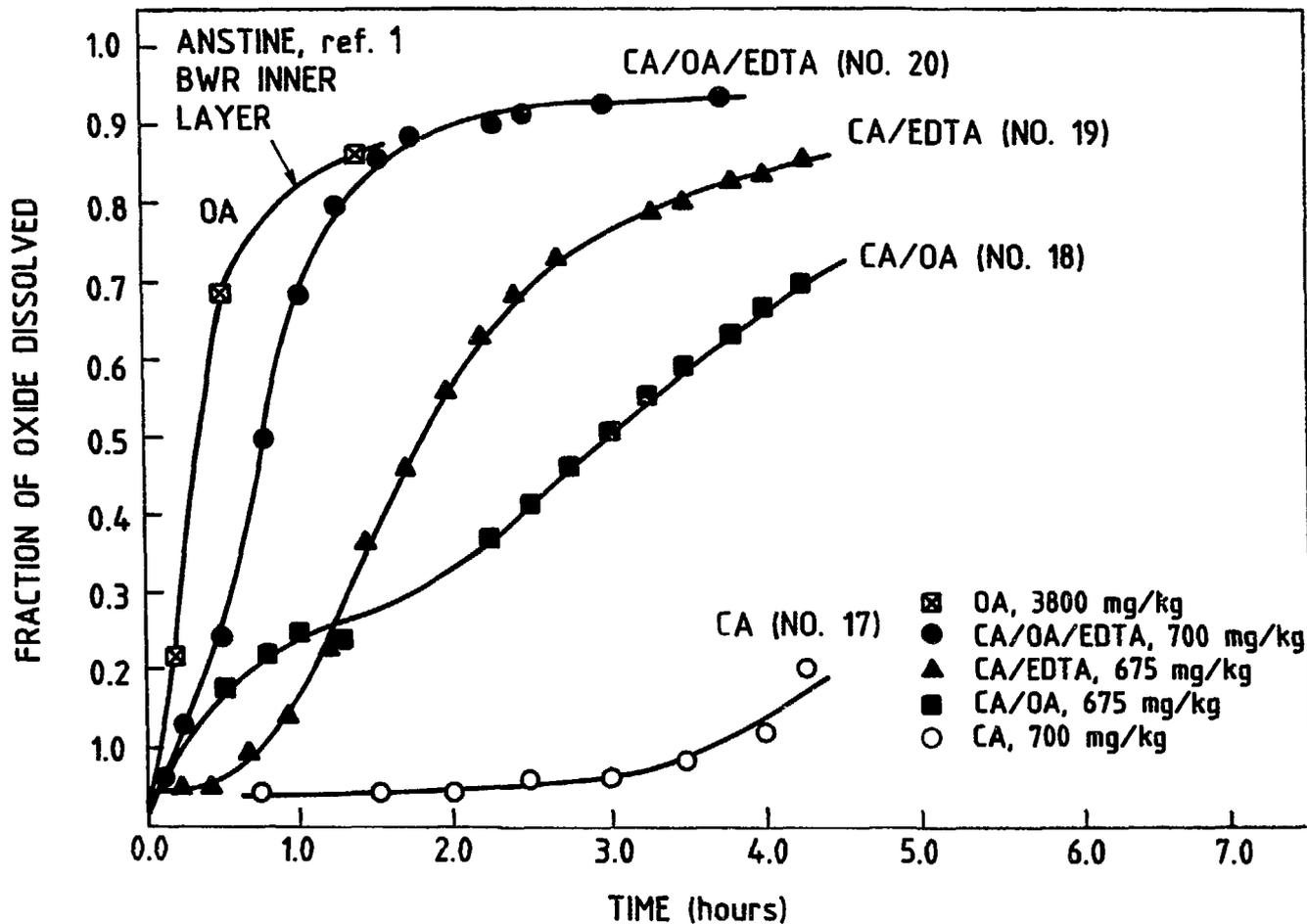


FIGURE 6. Dissolution of BWR-2 oxide in mixtures of citric acid, oxalic acid and EDTA at 90°C.

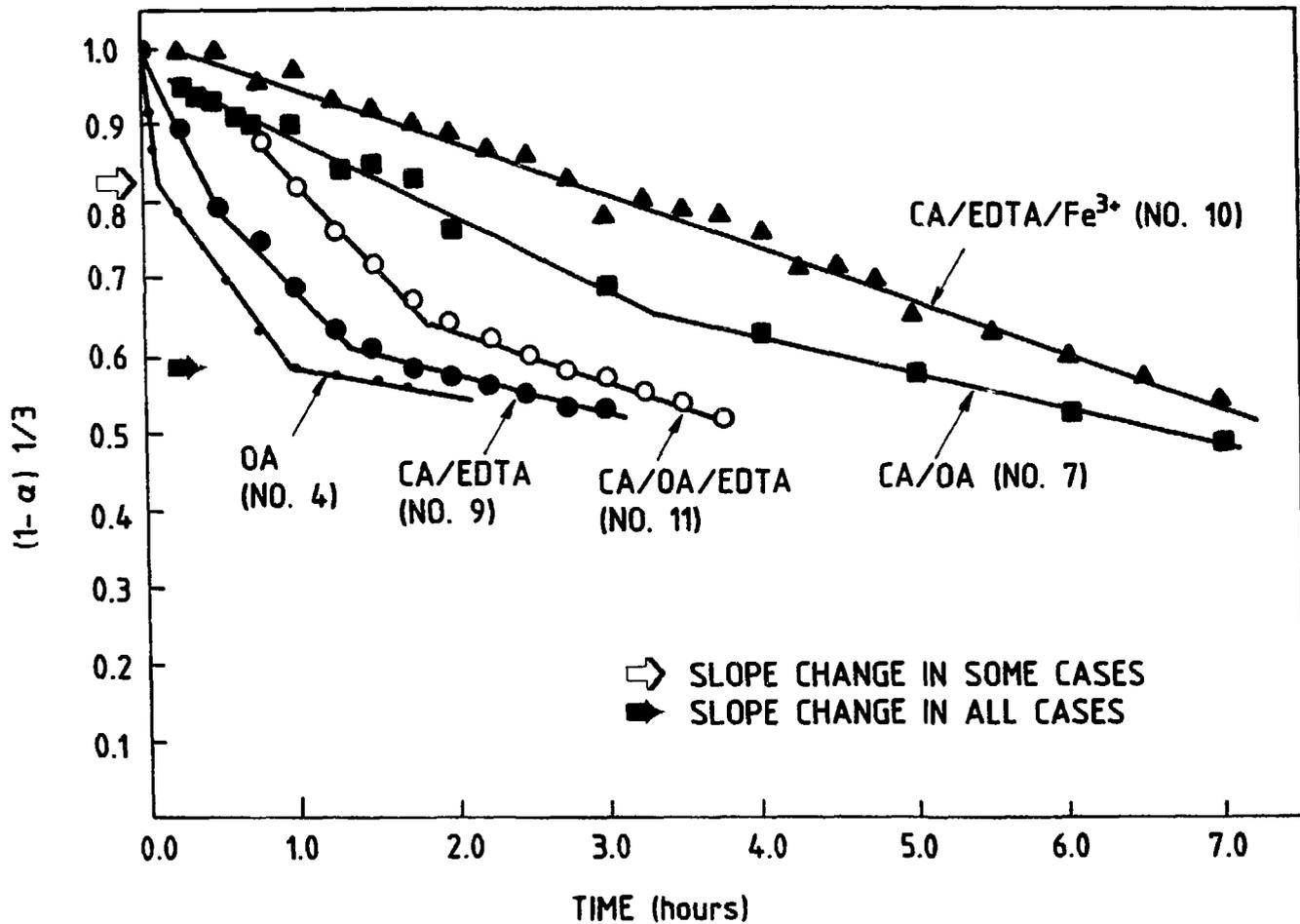


FIGURE 7. Plots of $(1-\alpha)^{1/3}$ versus time for dissolution of BWR-1 in mixtures of citric acid, oxalic acid and EDTA.

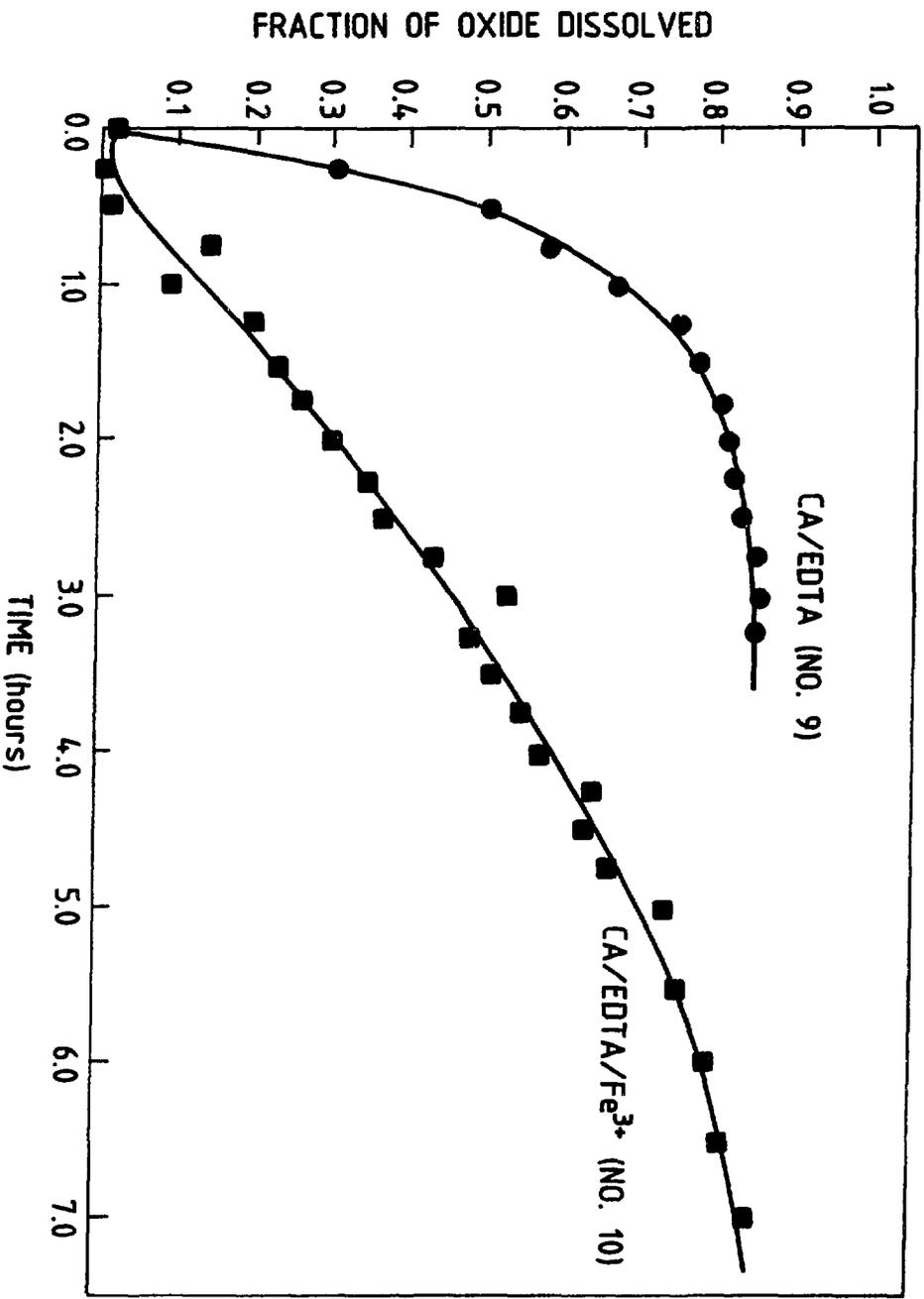


FIGURE 8. Effect of ferric ion addition on dissolution of BWR-1 oxide in citric-acid/EDTA mixture.

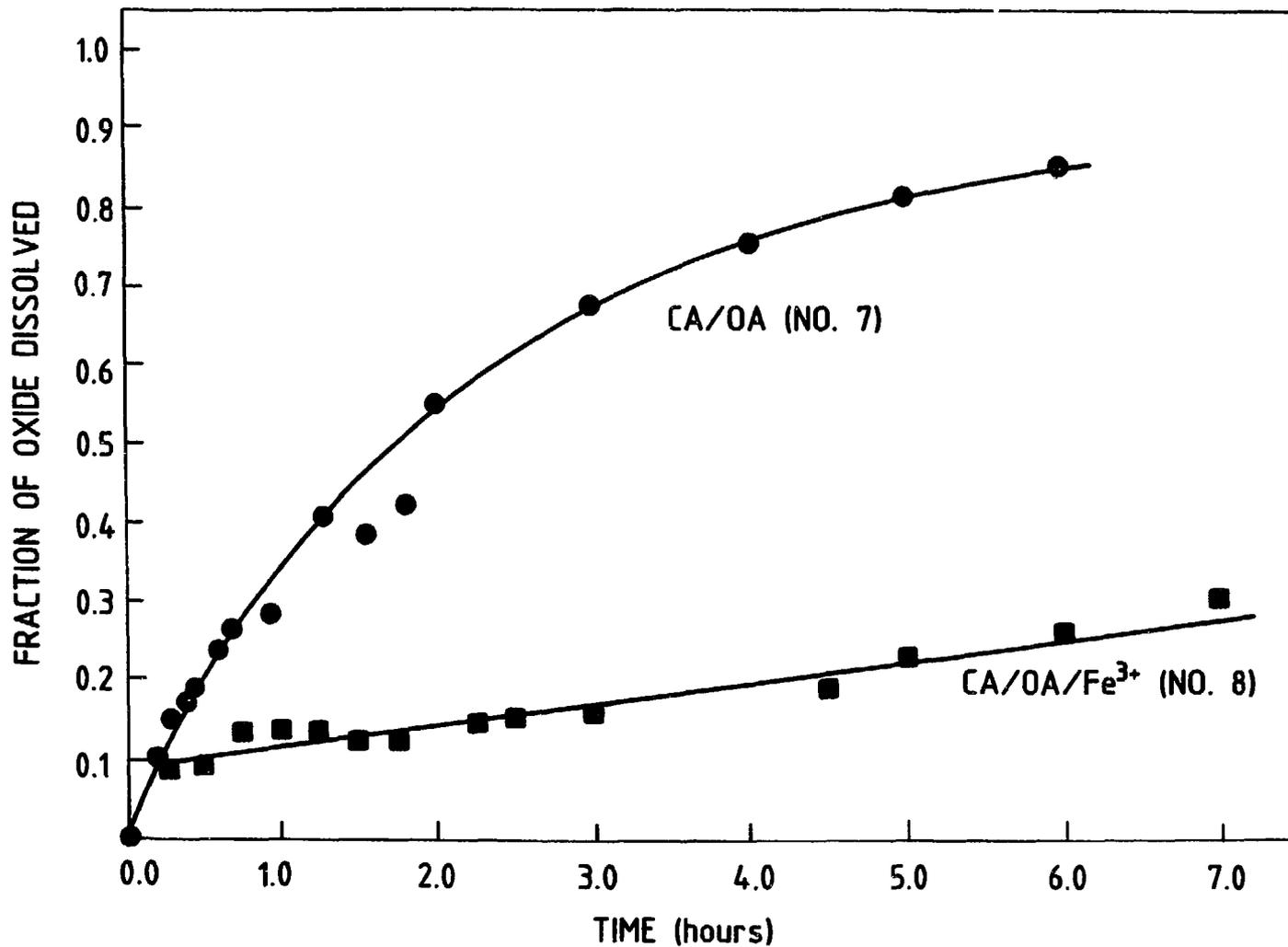


FIGURE 9. Effect of ferric ion addition on dissolution of BWR-1 oxide in citric-acid/oxalic-acid/mixture.

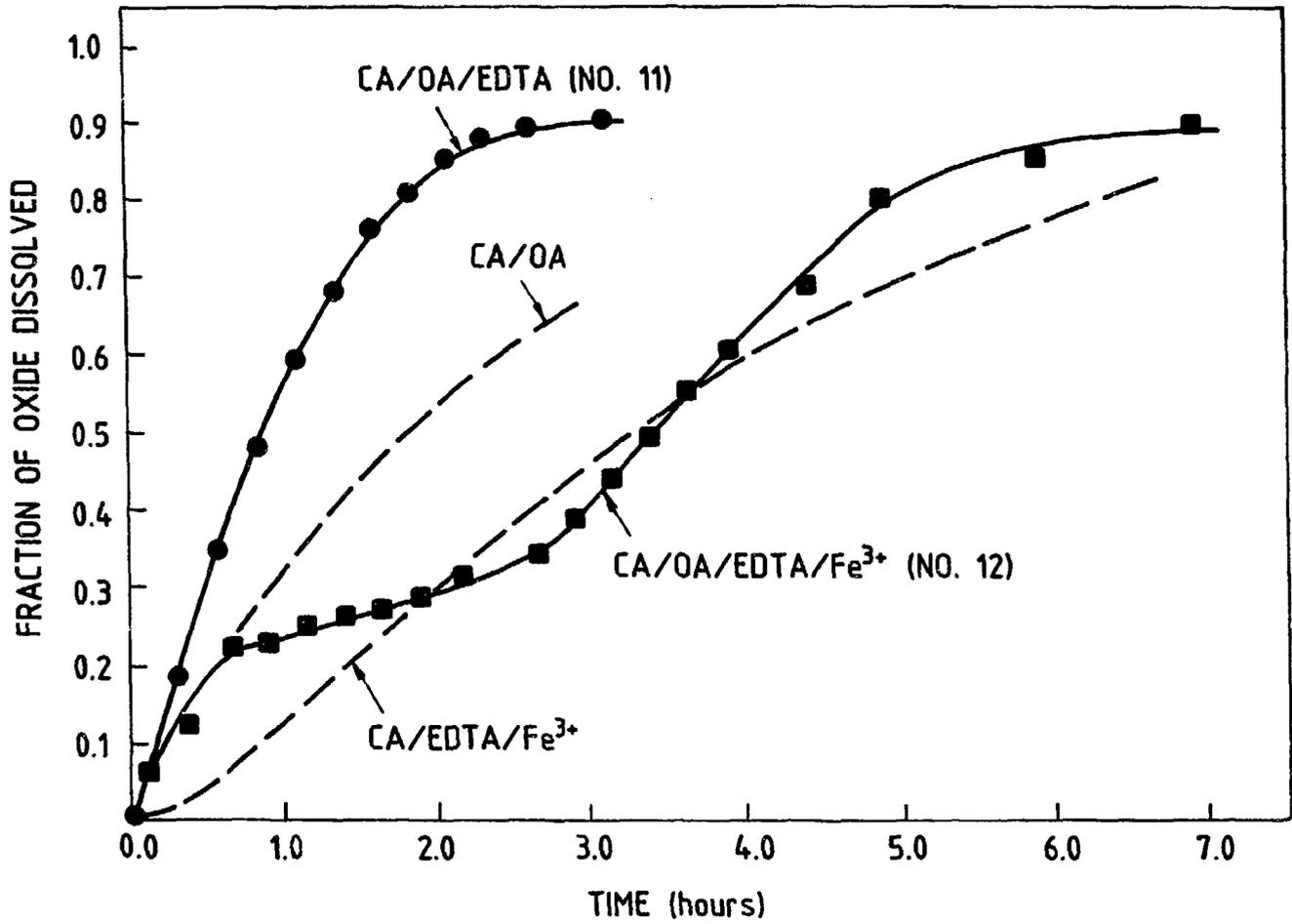


FIGURE 10. Effect of ferric ion addition on dissolution of BWR-1 oxide in citric-acid/oxalic-acid/EDTA mixture.

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