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Dissolution of Nickel Ferrite and Rare Earths Containing Magnetites in Citric Acid – EDTA – Gallic Acid (CEG) Formulation

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Abstract

It has been shown by us earlier that gallic acid can be used as a reductant in dilute chemical decontaminant formulations containing EDTA as chelant. The results on the dissolution of magnetite in such a formulation were quite promising. Moreover, the superior radiation stability of gallic acid vis-à-vis other reductants such as ascorbic acid or oxalic acid is another plus point for this formulation. Besides having an inherent stability against radiation degradation, it is able to protect even EDTA against radiation induced decomposition to a great extent unlike the case of ascorbic acid. In an extension of that work, dissolution experiments have now been carried out on nickel ferrite and magnetites containing rare earths like La, Ce and Zr. This is to simulate the presence of fission product oxides in magnetite resulting from a possible phase of operation with leaky fuel. The rate constants have been determined using the inverse cubic rate law. In the case of nickel ferrite, although there is an initial induction period, the rate constants for the dissolution were determined to be at 1.6×10^{-2} and $3.6 \times 10^{-3} \text{ min}^{-1}$ at 353 K and 333 K respectively. Presence of Ce in particular either alone or in combination with Zr/La at a level of 1 at.% equivalent each in magnetite is seen to increase the surface area of the oxide. The rate constants for the dissolution at 353 K in a 11:44:4 mM CEG formulation taken with magnetite and rare earth containing magnetites equivalent to yielding 22 mM Fe upon complete dissolution are as follows: $5.09 \times 10^{-2} \text{ min}^{-1}$ (magnetite), $7.06 \times 10^{-2} \text{ min}^{-1}$ (Ce_2O_3 containing magnetite), $6.33 \times 10^{-2} \text{ min}^{-1}$ (Ce_2O_3 , ZrO_2 containing magnetite), $1 \times 10^{-1} \text{ min}^{-1}$ (Ce_2O_3 , ZrO_2 , La_2O_3 containing magnetite). The presence of Ce, Zr and La at 1 at.% level each has not resulted in any turbidity in solution at the end of magnetite dissolution suggesting chemical dissolution of these rare earth oxides in the formulation. Simple magnetite (worth 0.4 mM Fe upon complete dissolution) taken in a 1.4:1.4:1.7 CEG formulation yielded a rate constant of $7.55 \times 10^{-2} \text{ min}^{-1}$. It is concluded that the presence of rare earths in magnetite at low amounts has not affected the dissolution characteristics of magnetite in CEG formulation. This conclusion corroborates a similar observed behaviour in Citric acid-EDTA-Ascorbic acid (CEA) formulation. The main advantage of CEG formulation over CEA formulation seems to be its stability towards radiation induced decomposition, a consideration important when chemical decontamination is planned under a short shutdown period (a few days) of the reactor.

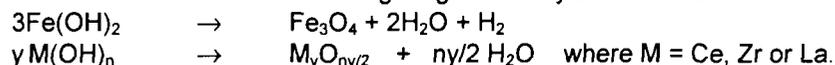
Introduction

Dilute Chemical Decontamination (DCD) formulations used for dissolving iron oxides in the primary coolant system of water cooled nuclear reactors employ a chelant, a reductant and a buffering agent.⁽¹⁻²⁾ Ethylene Diamine TetraAcetic acid (EDTA) and Picolinic acid (PA) and Oxalic acid⁽³⁾ have been extensively used as chelants. Citric acid(CA) is generally employed as a buffering agent. Among reductants, oxalic acid, ascorbic acid⁽⁴⁾ have been employed. The use of these reductants has certain associated disadvantages. While ascorbic acid (AA) is very prone to aerial oxidation in aqueous solutions at higher temperatures (353 K), oxalic acid (OA) has the potential to cause susceptibility to intergranular attack. Moreover, both of them are susceptible to radiation degradation due to their high reactivity with radiolytic species produced from water radiolysis. Consequently there is a loss in the efficiency of the formulations containing ascorbic acid or oxalic acid for dissolving magnetite after receiving a high radiation dose of 1-10 KGy (100-1000 Krad).⁽⁵⁾ Hence, an alternative suitable organic reductant which is quite stable in aqueous solution and good radiation stability was looked for. Of course, the new organic reductant should satisfy other conditions such as good solubility, thermal stability and appropriate ion-exchange behaviour i.e., it should not get sorbed on the cation exchanger while the decontamination process is going on and should be removed by the anion exchanger at the completion of decontamination. Gallic acid (GA) which is a very good reductant is found to satisfy all these conditions and the results of magnetite dissolution studies as well as radiation stability studies with the Citric acid- EDTA-Gallic acid (CEG) formulation have earlier been reported from this laboratory.⁽⁶⁾ It may be noted that the cost of GA is

comparable to that of AA. Earlier we had studied the dissolution of magnetite with GA as the reductant and employing EDTA, Picolinic acid and Pyridine dicarboxylic acid (PDCA) as chelants apart from reporting the radiation stability of gallic acid containing formulation⁽⁶⁾. In this present paper we report the dissolution of nickel ferrite, an important corrosion product formed in the primary coolant system of Pressurized Heavy Water Reactors (PHWRs), in Citric Acid-EDTA-Gallic Acid (CEG) formulation. In addition, we report here the dissolution characteristics of magnetite containing fission product oxides like Ce₂O₃, ZrO₂ and La₂O₃ in minor amounts in this CEG formulation, a simulated situation where earlier operation with failed fuel in the core could have resulted in the release of some of these fission products to the coolant.

Experimental

a) Preparation of fission product (f.p.) (Ce, Zr and La) containing magnetites and the dissolution experiments: All the chemicals employed in this study were of AnalaR quality. The Fe(II) and M, where M = Ce(III), Zr(IV), La(III) (using ferrous ammonium sulphate, La₂O₃, Ce₂(SO₄)₃·8H₂O and Zr(SO₄)₂ dissolved in dilute H₂SO₄), in an initial molar ratio with M corresponding to 1 at.% of iron in magnetite lattice, were co-precipitated as hydroxides by using 40% w/v KOH at a pH of 10.5 under deoxygenated condition. The precipitate was filtered, washed, transferred in a Pt boat to a furnace. The precipitate was dried at 373 K for ~ 2 h under iolar-2 N₂ atmosphere. The heating was continued at the rate of 13.5 K per minute to reach 1073 K. The temperature was held at 1073 K for 4 h and then the furnace was cooled to room temperature. The oxide obtained was characterized by X-ray diffraction (XRD), Fourier Transform Infra-red (FT-IR), Transmission Electron Microscopy and elemental analysis for iron by Atomic Absorption Spectrophotometry. The general equation for the formation of M containing magnetite may be written as



Though the XRD and FT-IR patterns were found to possess only the peaks characteristic of magnetite lattice, nevertheless formation of a solid solution of oxides of M with Fe₃O₄ can be ruled out based on ionic size considerations. Hence, these fission product oxides are expected to be present as separate phases along with magnetite. Table-1 shows the various fission product containing magnetites prepared along with their BET surface area.

Table-1: Fission product containing magnetites (equivalent to 1 at. % in magnetite lattice) prepared

Oxide	Initial Fe(II)/M ratio	Sp.surface area (m ² /g)
Magnetite	-	3
Ce-magnetite	99	7
Ce,Zr-magnetite	98	7
La, Ce, Zr-magnetite	97	7

Dissolution experiments were carried out in 11:44:4 mM Citric acid:Na₂EDTA:Gallic acid mixture. The dissolution experiments were performed at 353 K in a magnetically stirred glass vessel provided with a thermostatic water jacket. The dissolution mixture of 200 ml was deoxygenated by bubbling iolar-2 N₂ gas, then 340 mg Fe₃O₄ (corresponding to 22 mM Fe upon complete dissolution), 340 mg Ce₂O₃ containing magnetite (corresponding to 21.6 mM Fe + 0.217 mM Ce on complete dissolution), 352 mg of ZrO₂, Ce₂O₃ containing magnetite (corresponding to 22 mM Fe + 0.224 mM Ce + 0.224 mM Zr upon complete dissolution) and 360 mg La₂O₃, ZrO₂, Ce₂O₃ containing magnetite (corresponding to 22.4 mM Fe + 0.231mM La + 0.232 mM Zr + 0.231 mM Ce upon complete dissolution) were introduced. The initial pH was adjusted to 2.8 with dilute HNO₃. Periodic samples of the dissolution mixture were withdrawn, filtered through 0.2 μm membrane filter and the filtrate was analysed spectrophotometrically for Fe using the O-phenanthroline method. Absorbance of the Fe(II)-O-phenanthroline complex was measured at 510 nm using a Hitachi 2U-2001 UV-VIS spectrophotometer.

A dissolution experiment in which the amount of (Ce,Zr,La)-substituted magnetite was only about 6 mg in 200 ml of a dilute EGC formulation containing 300 mg of citric acid (1.4 mM), 400 mg of EDTA (1.4 mM) and 300 mg of GA (1.7 mM) dissolved in 1 litre of DM water to give a total amount of 1g/l of the DCD components was also carried out.

b) Nickel Ferrite dissolution experiments in CEG formulation:

The nickel ferrite was prepared through the co-precipitation route as described in elsewhere.⁽⁷⁾ Dissolution experiments were carried out with 3 mg of nickel ferrite in 100 ml volume of formulations of a fixed concentration of 1.4 mM CA, 1.4 mM EDTA and 1.7 mM GA. This amount of nickel ferrite when fully dissolved would yield an iron concentration of 0.26 mM in solution. Iolar grade nitrogen was passed through the solution at the rate of 100 ml/min to maintain an oxygen free atmosphere as well as to stir the solution. After the completion of the dissolution experiment, the solution was filtered through a Whatmann No. 542 filter paper and the volume made up to 100 ml. The iron in the solution was estimated by the O-phenanthroline method as before.

Results and Discussion

a) Dissolution of fission product containing magnetites in CEG formulation:

Fig.1a shows the dissolution profiles of fission product containing magnetites in comparison with simple

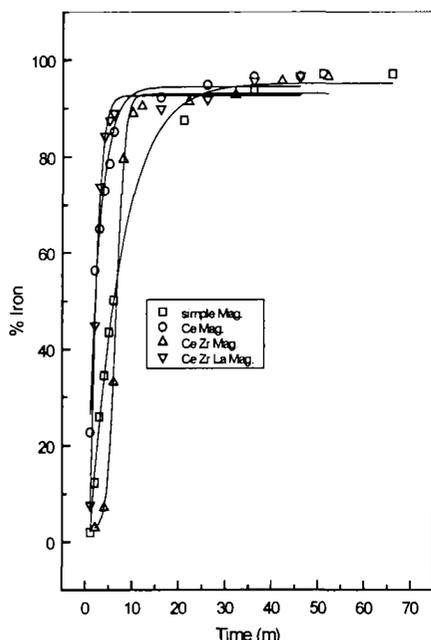


Fig.1 Dissolution Ce, Zr and La containing magnetite in CEG (11:44:4) mM mixture.

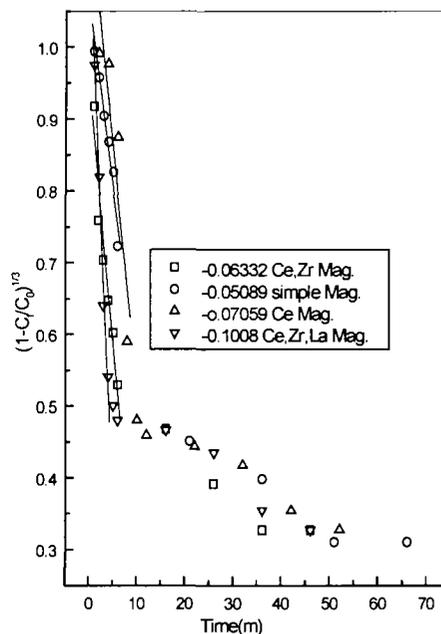


Fig.2 Inverse cubic rate law plot for the dissolution of Ce, Zr and La containing magnetite in CEG (11:44:4)mM mixture.

magnetite. In all the dissolution profiles, there is a significant dissolution ($\approx 90\%$) in the initial stage (in first 10-15 minutes) beyond which the dissolution falls off with time. The closeness of the dissolution profiles shows similar dissolution behaviour in these oxides. The slow rate during the later stages may be due to the reduction in the surface area to volume ratio. All the dissolution profiles could be fitted to a sigmoidal function. These dissolution curves have been analyzed using the inverse cubic rate law: $(1-C_t/C_\infty)^{1/3} = 1-k_{obs}t$ where C_t is the concentration of iron in solution at any time 't', C_∞ is the concentration of iron at the end of dissolution and k_{obs} is the rate constant of dissolution.

Fig.1b shows the plot of $(1-C_t/C_\infty)^{1/3}$ against 't'. The straight line behaviour with a higher negative slope during the initial stage of dissolution wherein maximum dissolution occurs is used for evaluating the rate constant of dissolution.

Table 1: Dissolution rate constants for the dissolution of magnetite, Ce_2O_3 magnetite Ce_2O_3 , ZrO_2 magnetite, and Ce_2O_3 , ZrO_2 , La_2O_3 magnetite in CEG (11:44:4)mM formulation at 353 K.

Formulation	Initial concentration mM	Temp. (K)	Oxide	$k_{obs} \times 10^2$ (min^{-1})
C:E:G	11:44:4	353	Fe_3O_4	5.089
C:E:G	11:44:4	353	Fe_3O_4 containing Ce_2O_3	7.059
C:E:G	11:44:4	353	Fe_3O_4 containing Ce_2O_3 , ZrO_2	6.332
C:E:G	11:44:4	353	Fe_3O_4 containing Ce_2O_3 , ZrO_2 , La_2O_3	10.082
C:E:G	1.4:1.4:1.7	353	Fe_3O_4	7.55

C: Citric acid, E: Na_2 EDTA, G: Gallic acid

Table-1 shows the rate constants obtained for f.p. containing magnetites vis-à-vis simple magnetite. It is seen that f.p. containing magnetites show a somewhat higher k_{obs} of around $7 \times 10^{-2} min^{-1}$ than that shown by simple magnetite, $k_{obs} = 5.1 \times 10^{-2} min^{-1}$. This increased rate of dissolution of f.p. containing magnetites could be due to the larger surface area of these powders compared to that of simple magnetite powder. Presence of Ce

in particular either alone or in combination with Zr / La at a level of 1 at.% equivalent in magnetite lattice, seems to increase the surface area of the particles as seen in Table-2.

Table-2 - The surface area characteristics and dissolution of the fission product containing magnetites employed.

Oxides (M = 1 at.% each)	Initial Fe(II) / M ratio	Specific surface area (m ² / g)	Dissolution in CEG formulation (11-44-4) mM
Fe ₃ O ₄	-	3	cd
Ce-magnetite	99.0	7	cd
Zr, Ce-magnetite	98.0	7	cd
La,Zr,Ce-magnetite	97.0	7	cd

*M: Ce, Zr, La; cd: complete dissolution

The reductive mechanism of dissolution while operating on the magnetite, is not expected to act in the same way on the f.p. oxides such as Ce₂O₃, La₂O₃ and ZrO₂. The appearance of a clear solution at the end of dissolution suggests that at 1 at.% level, these fission products are soluble chemically and hence no turbidity is observed. In studies with Citric acid-EDTA-Ascorbic acid formulation, we have observed the generation of a greyish-green turbidity if the f.p content is > 3 at.% equivalent in magnetite lattice either individually or together.

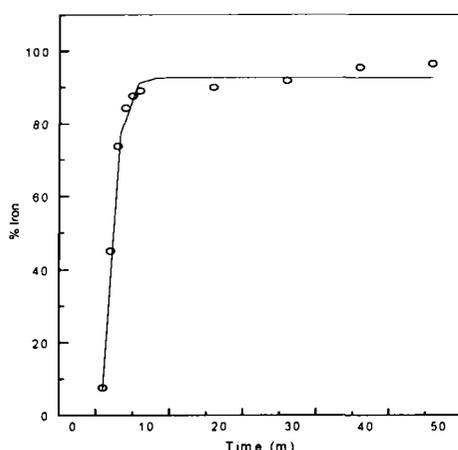


Fig 3 Dissolution of Ce Zr La Mac. in CEG (11 44 4) Mixture.

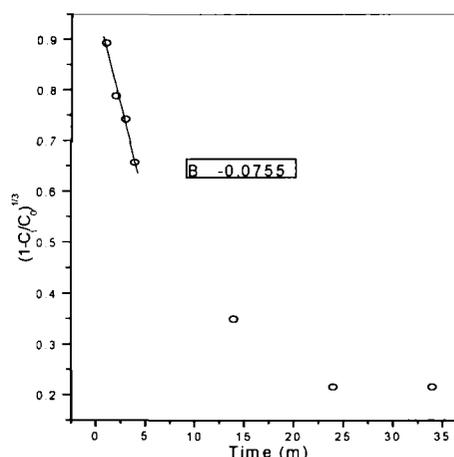


Fig 4 Inverse cubic rate law plot for the dissolution of Ce Zr La Magnetite in CEG mixture (1.4:1.4:1.7) mM.

Dissolution of La-Zr-Ce containing magnetite at a level of ≈ 0.4 mM Fe on complete dissolution in a CEG mixture of 1.4mM:1.4mM:1.7mM (Figs.2a&2b) yielded a rate constant of $7 \times 10^{-2} \text{ min}^{-1}$. This shows that as long as proper ratio of iron to be dissolved from magnetite to the formulation concentration is kept the dissolution behaviour is predictable.

b) Dissolution of nickel ferrite in CEG formulation:

It has been shown by us earlier⁽⁶⁾ that gallic acid can be used as a reductant in dilute chemical decontaminant formulations in place of ascorbic acid for dissolution of magnetite. The superior radiation stability of gallic acid vis-à-vis other reductants such as ascorbic acid or oxalic acid is a plus point in its favour. As aromatic compounds have inherent stability against radiation degradation, it is able to protect even EDTA in the formulation to a great extent. In an extension of that work, dissolution experiments have now been carried out on nickel ferrite.

Plots of percentage Fe dissolved vs time at 333 K and 353 K during the dissolution of nickel ferrite in CEG (although sometimes referred to as EGC) formulation are shown in Fig 3-a and 4-a respectively. At 353 K, 100% of nickel ferrite dissolved in 60 minutes while at 333 K it took 4 hrs for 86% dissolution. Under the same conditions viz., at 353 K, 3 mg nickel ferrite and 100 ml of formulation, it took 40 minutes for complete dissolution in EDTA (1.4 mM)/ascorbic acid (1.7 mM)/ citric acid (1.4 mM) formulation or in 2.6 pyridine diacetic acid (2 mM)/ascorbic acid (2 mM) formulation.⁽⁶⁾ Thus, gallic acid containing formulation is little slower in dissolving nickel ferrite as compared to the above formulations. The plots of $(1-C_t / C_0)^{1/3}$ vs. time at the two temperatures are shown in Figs. 3-b and 4-b at 333 K and 353 K respectively. The rates of dissolution were estimated to be $3.6 \times 10^{-3} \text{ min}^{-1}$ and 1.6×10^{-2} at 333 K and 353 K respectively.

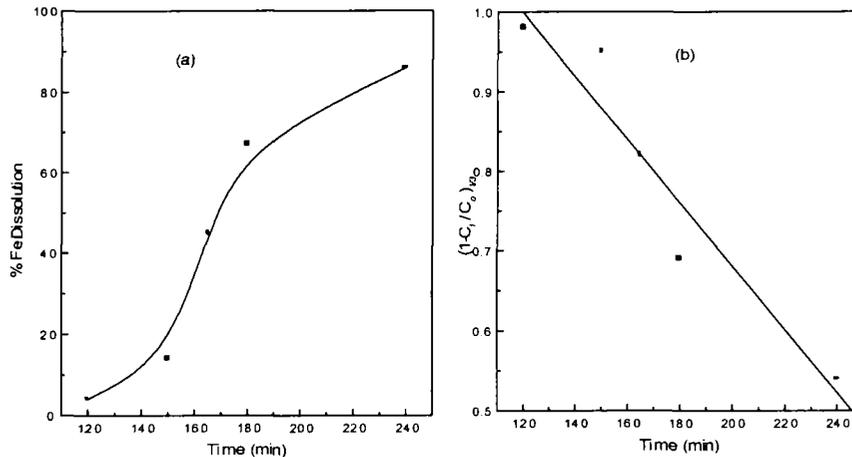


Fig.3: Nickel Ferrite Dissolution in EGC formulation at 333 K

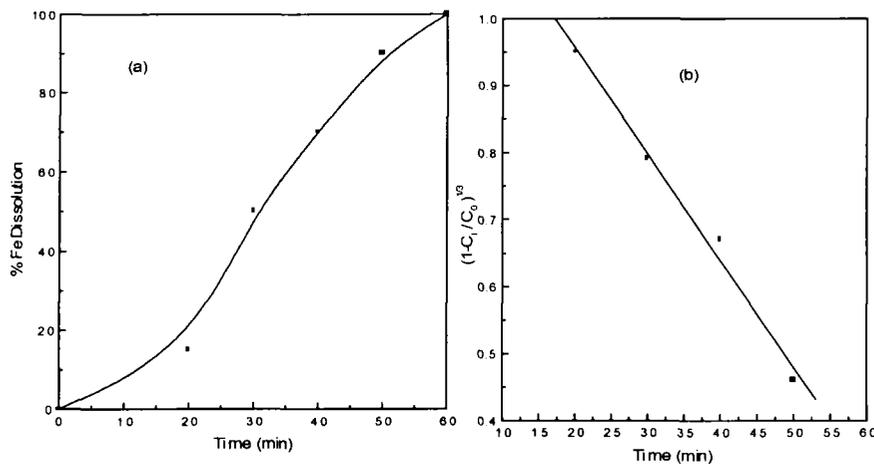


Fig.4: Nickel Ferrite Dissolution in EGC formulation at 353 K.

Unlike the dissolution of fission product containing magnetites, the dissolution of nickel ferrite in CEG formulation shows an initial induction period. Its duration seems to depend critically on the temperature : at 333 K - 2 h , at 353 K - < 0.3 h. Such induction periods were observed in the dissolution of Cr substituted hematites and magnetites in CEA formulations.⁽⁹⁾ The stability of the oxide lattice of nickel ferrite being higher than that of magnetite (stronger Ni(II)-O bond as compared to Fe(II)-O bond) could be the reason for the observed induction period. The slow buildup of the Fe(II)-EDTA complex in the solution is indicated by this induction period. Baumgartner et al., observed an induction period of 1 h in their dissolution studies involving magnetite powders in oxalic acid solutions at 303 K.⁽¹⁰⁾ The lower rate constant of dissolution of nickel ferrite at 353 K ($1.6 \times 10^{-2} \text{ min}^{-1}$) as compared to that of magnetite or fission product containing magnetites ($\approx 6.5 \times 10^{-2} \text{ min}^{-1}$) in the CEG formulation at the same temperature shows that the Fe(II)-EDTA driven autocatalytic mechanism of dissolution is hindered by the stability of the nickel ferrite lattice. Manjanna et al., have observed a rate constant value of $3.1 \times 10^{-2} \text{ min}^{-1}$ for the dissolution of fission product substituted magnetites in CEA formulation.⁽¹¹⁾ When one compares this rate constant value with that of $6.5 \times 10^{-2} \text{ min}^{-1}$ observed in CEG formulation in the present work, then it appears that CEG is better than CEA formulation for the dissolution of magnetites. When one considers the better radiation stability of CEG over CEA, then using CEG looks to be advantageous.

Conclusions

The earlier studies in our laboratory showed that the radiation stability of gallic acid was much better than that of ascorbic acid and it even prevented the radiation induced decomposition of EDTA. The present study has revealed that the fission product containing magnetites dissolved as freely as magnetite in CEG formulation. From the magnetite dissolution point of view this formulation appears to be better than CEA formulation for the decontamination of the primary system of PHWRs.

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