



**LABORATORY AND LOOP STUDIES ON
CHEMICAL METHODOLOGIES FOR DECONTAMINATION
OF BWR COOLANT SYSTEM SURFACES**

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Abstract

Laboratory powder dissolution studies have been carried out on moderately sintered α -Fe₂O₃ (haematite) in citric acid - EDTA - ascorbic acid (CEA) mixtures of different compositions to identify the role of each component and arrive at an optimum composition to effect fast and quantitative dissolution. Experiments involving other reducing agents (in place of ascorbic acid) and chelating agents (in place of EDTA) revealed that there are no better substitutes for these two reagents. Samples prepared by heating ferrous hydroxide at different temperatures from 373 - 1073 K exhibited vastly different dissolution behaviour. Chromium substituted iron oxides prepared by heating the coprecipitated mixture of the two hydroxides at high temperature in the required proportions were having low solubility in the CEA mixtures. Pretreatment of these by alkaline permanganate (AP) rendered them somewhat more soluble, particularly in CEA mixtures containing higher ascorbic acid concentrations. Comparative evaluation of the efficacy of single and multi-step AP-CEA and AP-LOMI processes has been made by carrying out experiments on decontamination of contaminated specimens of oxide coated SS-304 surfaces from the reactor water clean-up circuit piping of Tarapur Atomic Power Station (TAPS) BWRs both in once through and closed loop circulation modes. A methodology has been worked out for compaction of the radwastes arising from chemical decontaminations employing AP-CEA and AP-LOMI processes - this involves simply mixing of the AP and CEA or LOMI effluents in proper proportions and digesting at 363 K when MnO₂ precipitates out carrying with it more than 99% of the radioactivity.

1 INTRODUCTION

In all types of water cooled nuclear power reactors viz. BWRs, PWRs and PHWRs corrosion products which are generated as a result of structural material - primary coolant interactions get transported to the core where they can deposit on the

fuel surfaces and become activated by neutron irradiation. The activated corrosion products are released back into the circulating coolant and eventually get deposited on the out - of - core surfaces resulting in build up of radiation fields in areas where personnel access is required for maintenance and servicing. Over a period of time this results in relatively high occupational doses which must be controlled to ensure compliance with statutory requirements.

There are many possible ways of reducing the radiation doses received by personnel in nuclear power plants such as improvement in reactor design in terms of choice of proper materials of construction and operation with improved coolant chemistries which are conducive to minimising in-core deposition of corrosion products. But in recent years chemical decontamination methodology which involves the dissolution of radioactive deposits from the surfaces of structural materials in the primary coolant circuit without causing undue corrosion to the base metal has evolved as a practical solution to the problem of high radiation fields on out-of-core surfaces.

The radionuclides in the system get incorporated in the oxide layers on the inner side of pipework and components. These oxides are complex in composition and vary between reactor types and also between different surfaces even in the same reactor depending on the materials of construction, coolant pH, dissolved oxygen concentration and temperature. In all the above reactor types iron bearing alloys are the main constructional materials in the primary coolant circuit. Hence oxide compositions ranging from haematite, nickel ferrite, magnetite, Ni and Cr substituted ferrites and the underlying iron chromite are observed on surfaces exposed to BWR coolant containing higher dissolved oxygen (thicker oxide layer) whereas in the PWR coolant under reducing chemistry conditions one observes magnetite, iron chromite and high chromium and nickel substituted ferrites (thinner oxide layer) [1]. In PHWR coolant circuits magnetite is the principal oxide deposit. Any chemical decontamination methodology has therefore to be addressed to dissolution of such oxides. A number of detailed laboratory studies on the dissolution of iron oxides and mixed oxides containing iron, nickel and chromium have been reported in the literature [2-17].

2 BACKGROUND AND OBJECTIVES OF THE RESEARCH PROJECT

Indian nuclear power programme comprises of two operating 200 MWe BWR units at Tarapur (TAPS) and two operating 220 MWe PHWR units each at Rawatbhatta (RAPS), Kalpakkam (MAPS), Narora (NAPS) and Kakrapara (KAPS). Concerned with the

gradually increasing radiation fields on the out-of-core coolant surfaces (largely carbon steel) of the four earlier PHWR units, our group has developed the dilute chemical decontamination technology for these reactors and this was successfully employed in MAPS Unit #1 in Dec 1993, MAPS Unit #2 in April 1995 and again in MAPS Unit #1 in Nov 1997. The present project is aimed at developing a suitable methodology for the chemical decontamination of the primary coolant system surfaces (stainless steel) of the TAPS BWRs. The work under the project involved : (i) preparation of different types of iron oxides representative of reactor system surfaces ; (ii) study of their dissolution behaviour in different reagent systems ; (iii) decontamination experiments on specimen pieces cut from the primary coolant circuit piping of an operating BWR and (iv) experiments aimed at compaction of radioactive wastes arising from chemical decontamination.

3 TECHNICAL APPROACH

3.1 Preparation of different iron oxides

Ferrous hydroxide was precipitated from 1 mol m⁻³ FeSO₄ solution by adding 50% NaOH in an inert atmosphere and heated in air for 6 hrs at various temperatures ranging from 373 - 1073 K. After heat treatment the samples were characterised by chemical analysis and powder X-ray diffraction (XRD). It was found that crystalline α -Fe₂O₃ (haematite) was formed on heat treatment at temperatures > 773 K. The sample heated at 673 K showed less developed peaks of α -Fe₂O₃. At lower temperatures the samples were less crystalline in nature and from their powder XRD patterns they were identified as defect inverse spinel oxides. The oxide prepared by heating ferrous hydroxide at 873 K for 6 hrs is referred to as 'moderately sintered haematite'. For preparing Cr-substituted haematites, the Fe(II) and Cr(III) ions corresponding to different initial ratios were coprecipitated as hydroxides at room temperature under inert atmosphere and the precipitate was digested for 6 hrs on a steam bath also under inert atmosphere. From the Differential Thermal analysis (DTA) studies of these coprecipitated hydroxides in air the temperature corresponding to the formation of the single phase oxides was determined to be 1073 K. The coprecipitated hydroxides were then heated in air for 4 hrs at this temperature. The oxides, thus prepared gave sharp and symmetric XRD peaks confirming the presence of single phase species.

3.2 Powder dissolution studies

The dissolution experiments on oxide powders prepared as above were performed in a magnetically stirred cylindrical glass vessel provided with a thermostatic water jacket (Fig. 1). 200 cm³ of the dissolution mixture with the required concentration of the components (viz. citric acid, EDTA and ascorbic acid - referred to as CEA) was deaerated for 60 min by purging with argon. Oxide powders of weight corresponding to 22 mol m⁻³ Fe were used for the dissolution experiments. This quantity of oxide corresponds to dissolving a coating thickness of about 5 microns of oxide in a system having surface area/volume ration of 67 m⁻¹ taken in a solution volume of 200 cm³. The initial pH was adjusted to 2.8 with nitric acid. Experiments were performed under inert atmosphere by keeping a steady flow of oxygen-free argon gas through the mixture throughout the duration of the experiment. Samples were periodically withdrawn, centrifuged and filtered through 0.2 µm pore size membrane filter. Iron concentrations in the filtrate were determined spectrophotometrically by the standard o-phenanthroline method and Cr content was analysed by AAS. Treatment with alkaline permanganate (KMnO₄ in NaOH) was also carried out in the same apparatus, but without inert gas purging.

3.3 Coupon decontamination experiments

Test coupons of dimensions 26 mm x 26 mm x 6 mm thick cut from a section of the 100 mm OD SS-304 piping removed from the reactor water clean-up system circuit of TAPS Unit #1 were used in the experiments. These coupons had oxide coating of approx. 2 µm thickness on the curved inner surface which had been exposed to the BWR coolant environment (553 K, 70 Kg/cm², pH 6.2, DO 200 ppb) over about 20 years of operation and their radioactivity content was ~ 7 µCi cm⁻², the surface dose rate being ~ 1000 mR/hr. The solutions (volume ~ 600 cm³) with which these were treated at ~340 K for 4-5 hrs either singly or sequentially one after the other are : (i) AP (alkaline permanganate) - 0.3% KMnO₄ in 1.5% NaOH, (ii) CE - 1% citric acid and 0.3% Na₂EDTA and (iii) CEA - 2 mol m⁻³ with respect to each of citric acid, EDTA and ascorbic acid adjusted to pH 2.8 and (iv) LOMI - 4 mol m⁻³ in V(HCO₂)₂, 13 mol m⁻³ in HCOOH and 24 mol m⁻³ in picolinic acid. The treatment was carried out by suspending the coupons in the appropriate solution in a glass flask with arrangement for purging with inert gas to make the solutions oxygen-free and maintain an inert atmosphere (this was done only in the case of treatments with CEA

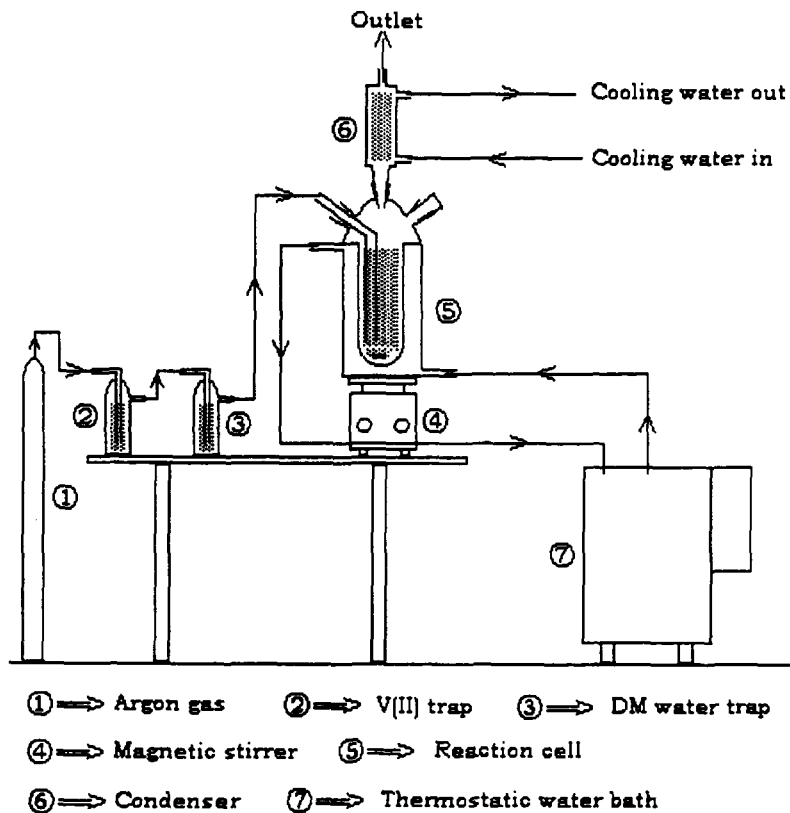


Fig. 1 : Experimental set up for powder dissolution experiments

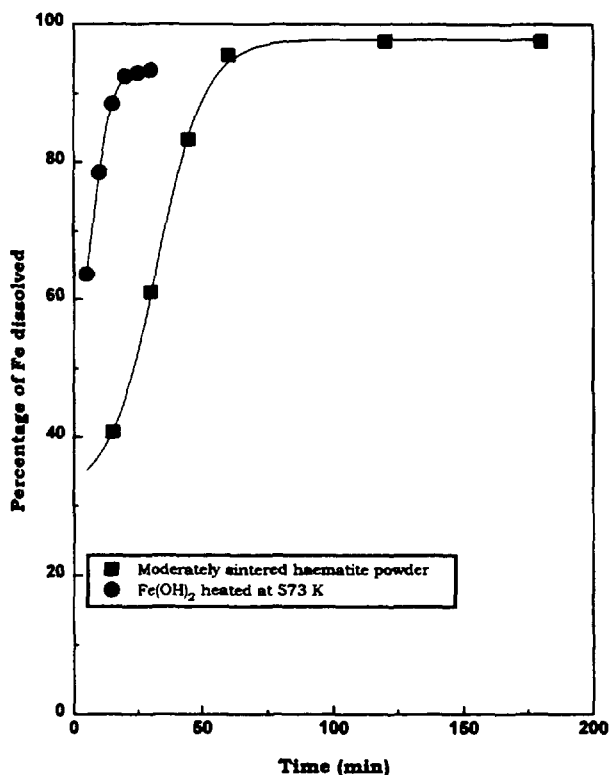


Fig. 2 : Typical plots of dissolution of iron oxides in CEA 11:44:4 mol m⁻³ mixture at 353 K

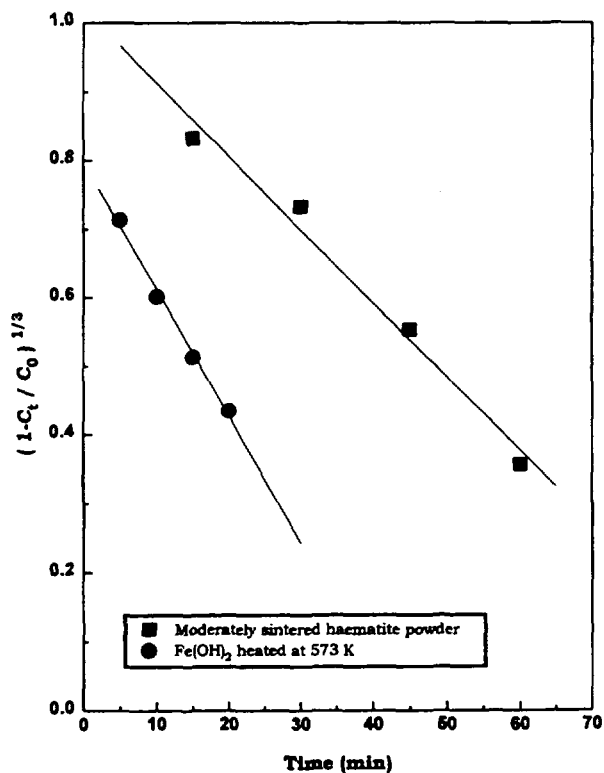


Fig. 3 : Typical inverse cubic rate law plots for dissolution of iron oxides in CEA 11:44:4 mol m⁻³ mixture at 353 K

and LOMI solutions). Solution analyses for Fe and Cr were carried out as described in section 3.2. Standard methods were employed for measurement of solution radioactivity and radiation fields on specimen surfaces.

3.4 Loop experiments with spool piece

The loop experimental set up is shown in Fig. 4. This consisted of SS-304 spool pieces of dimensions 500 mm long x 100 mm NB cut from the reactor water clean-up system of TAPS-BWR (the same from which coupons were cut for experiments described in section 3.3) and, SS-304 solution preparation and circulation tanks connected as shown with circulating pump, valves, joints etc. using flexible tubing. The contents of solution preparation and circulation tanks could be purged with inert gas in the case of experiments with LOMI and CEA reagents. The entire system was maintained at 343 K employing external electrical heating. The dissolution reagents

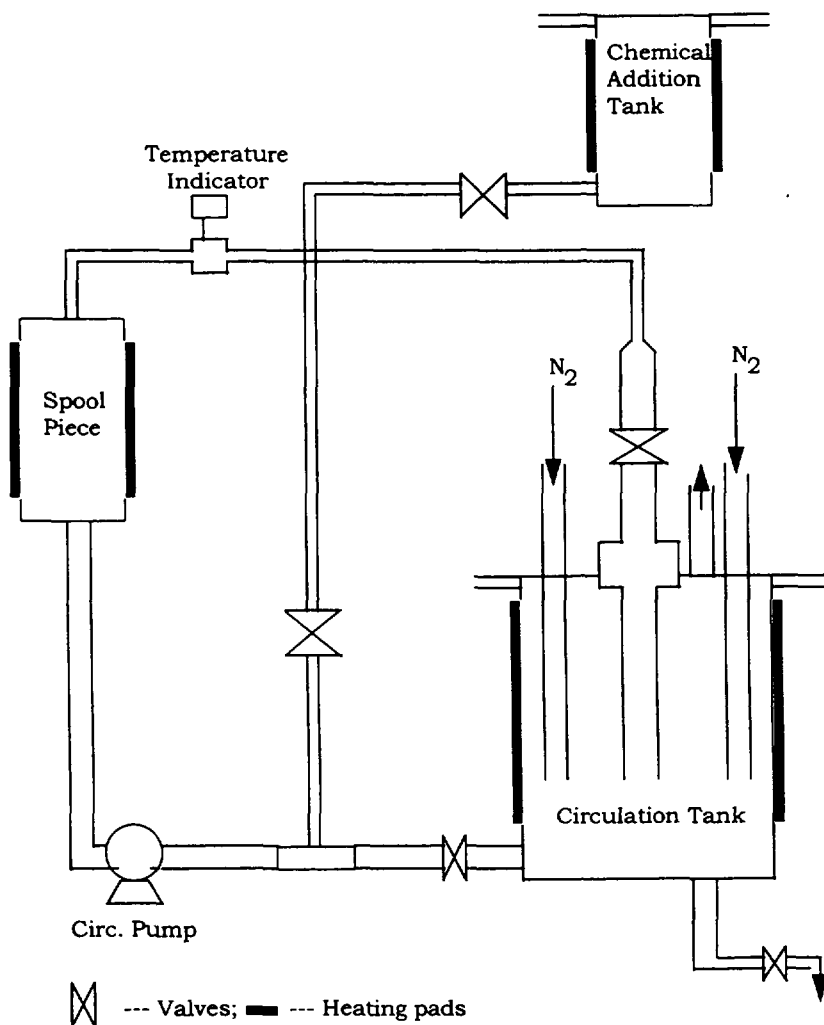


Fig. 4 : Schematic diagram of spool piece decontamination loop

used were the same as described in section 3.3. Solution analyses for Fe and Cr, and radioactivity and radiation field measurements were as described in section 3.3.

4 ACCOMPLISHMENTS

Typical plot of iron released as a function of time for the dissolution of moderately sintered haematite in 11:44:4 mol m⁻³ CEA mixture is given in Fig. 2, from which it is seen that there is rapid initial dissolution, the rate falling off with time and reaching a plateau (saturation) due to decrease in surface area of the particles as inferred by earlier workers [13,17]. This trend would suggest that the reaction occurs at the surface of the particles and the rate is proportional to the instantaneous surface area. The dissolution data were analysed according to the 'grain model' proposed by Segal et al.^[17] : $(1-C_t/C_0)^{1/3} = 1 - k_{obs} t$, where k_{obs} (dissolution rate constant) is given by : $k/r.\rho$, C_t and C_0 being the respective instantaneous and final concentrations of metal ion released, and 'r' and 'ρ' the particle radius and density respectively. Figure 3 illustrates representative inverse cubic rate law plots. The slope of the initial linear region of such plots gives k_{obs} . Linearity was observed upto about 75% dissolution in all cases.

Citric acid and EDTA individually were unable to dissolve moderately sintered haematite even when present in stoichiometrically excess concentration with respect to the oxide. Dissolution data in different CEA mixtures are summarised in Table 1. There was no appreciable increase in the maximum percentage dissolution with increase in citric acid concentration (11 mol m⁻³ - 66 mol m⁻³), when the concentrations of EDTA and ascorbic acid were maintained constant at 2 and 4 mol m⁻³ respectively, whereas the dissolution rate constant increased upto 33 mol m⁻³ citric acid concentration beyond which it decreased. The decrease may be due to the formation of less soluble iron-citrate complex and also adsorption of citric acid on active sites on the oxide. In presence of stoichiometric/excess of EDTA and minimum concentration of ascorbic acid, citric acid initially enhanced the dissolution rate due to the availability of additional H⁺ ions which contribute to the acid assisted dissolution route. Citric acid also helps to control the pH during the dissolution process (Table 2). Since adsorption of ligands is maximum at pH 2-3, it is preferable to maintain almost a constant pH of ~ 3 throughout the dissolution period. As seen in Table 2 if the initial pH is not adjusted to 2.8 the dissolution rate constant decreases leading to lesser percentage dissolution. The role of citric acid in controlling the pH becomes more important at lower EDTA concentrations where the pH changes are more pronounced.

**TABLE 1 : Dissolution of moderately sintered haematite at 80° C
in different CEA mixtures**

Mixture concentration (mol m ⁻³)			Percentage dissolution in 4 hrs	Time for complete dissolution	Dissolution rate constant k _{obs} x 10 ³ (min ⁻¹)
C	E	A			
Citric acid variation					
11	02	04	36	> 8 hrs (43%)	1.3
22	02	04	39	> 8 hrs (47%)	1.5
33	02	04	37	> 8 hrs (41%)	2.2
44	02	04	49	> 8 hrs (54%)	2.2
55	02	04	42	> 8 hrs (51%)	1.7
66	02	04	43	> 8 hrs (55%)	1.4
00	22	04	89	6 hrs	5.2
02	22	04	97	3-4 hrs	5.8
11	22	04	92	3-4 hrs	8.0
22	22	04	93	3-4 hrs	4.2
00	44	04	96	3-4 hrs	5.7
11	44	04	97	3-4 hrs	9.9
EDTA variation					
02	00	04	06	> 8 hrs (09%)	1.6
02	11	04	54	> 8 hrs (56%)	4.0
02	22	04	97	3-4 hrs	5.8
02	33	04	95	3-4 hrs	6.3
02	44	04	95	3-4 hrs	7.3
02	55	04	96	3-4 hrs	9.0
Ascorbic acid variation					
00	00	80	18	> 8 hrs (28%)	1.2
02	02	04	18	> 8 hrs (20%)	1.9
02	02	10	22	> 8 hrs (28%)	2.0
02	02	25	29	> 8 hrs (34%)	1.7
02	02	40	36	> 8 hrs (44%)	1.7
02	02	60	45	> 8 hrs (57%)	1.7
02	02	80	54	> 8 hrs (68%)	1.6

(C : Citric acid ; E : EDTA ; A : Ascorbic acid)

Although stoichiometrically excess EDTA alone was unable to bring about any dissolution, it was very effective in presence of ascorbic acid. Complete dissolution was observed in 3-4 hrs in the presence of minimum amount of ascorbic acid. On varying EDTA concentration in the presence of 2 mol m⁻³ citric acid and 4 mol m⁻³ ascorbic acid, the dissolution rate increased linearly as the concentration of EDTA was increased (Table 1). There was no dissolution in mixtures containing only citric acid and EDTA. With varying ascorbic acid concentration at constant citric acid and EDTA concentrations (2 mol m⁻³), the percentage dissolution in 4 hrs increased from 18-54%. In presence of stoichiometric or excess EDTA with respect to Fe, minimal

concentrations of citric and ascorbic acids were sufficient to bring about rapid dissolution. Ascorbic acid acts as an initiator for the dissolution process by initially reducing the lattice Fe(III) ions to Fe(II) ions which are then released into solution by complexation with EDTA. The Fe(II)-EDTA complex being a good reducing agent accelerates the dissolution.

TABLE 2 : pH variation in the dissolution of moderately sintered haematite in different CEA mixtures at 80°C.

Mixture concentration (mol m ⁻³)			pH		Dissolution rate constant k _{obs} x 10 ³ (min ⁻¹)	Time for complete dissolution
C	E	A	Initial	Final		
00	22	04	2.8	4.7	5.2	6 hrs
02	22	04	2.8	4.1	5.8	3-4 hrs
11	22	04	2.8	3.6	8.0	3-4 hrs
00	44	04	2.8	4.0	5.7	3-4 hrs
02	44	04	2.8	3.3	7.3	3-4 hrs
11	44	04	2.8	3.15	9.9	3-4 hrs
02	55	04	2.8	3.0	9.0	3-4 hrs
11	44	04*	3.1	3.8	8.5	3-4 hrs
02	55	04*	3.3	5.2	3.8	> 4 hrs (67%)

(C : Citric acid ; E : EDTA ; A : Ascorbic acid)

* Initial pH of the mixture not adjusted to 2.8

TABLE 3 : Dissolution of moderately sintered haematite in 11:44:4 mol m⁻³ CEA mixture at different initial pHs.

pH	Percentage dissolution in 4 hrs
6.0	24
5.0	43
4.0	67
3.0	100
2.0	Complete dissolution in 2-3 hrs*
1.0	Complete dissolution in 2-3 hrs*

* EDTA precipitation occurs

In order to find out the effect of pH on the dissolution, experiments were performed in 11:44:4 mol m⁻³ CEA mixture at different initial pHs from 1 - 6. From the results (Table 3) it is seen that a very rapid dissolution occurs at low pHs, whereas above pH 3.0 dissolution is appreciably slower. The faster dissolution at lower pHs is due to contribution of the acid assisted dissolution of the oxide.

From the results of studies using different reducing agents in solutions containing 11 mol m⁻³ citric acid and 44 mol m⁻³ EDTA (Table 4) it is seen that the dissolution of moderately sintered haematite is very fast, complete dissolution occurring in 3-4 hrs when ascorbic acid is used as the reducing agent. In the case of thioglycolic acid as the reductant it is ~ 49% and with hydrazine <4%, and no dissolution at all was observed in 4 hrs when sodium dithionite, oxalic acid and formic acid were used as reductants. It is obvious that there is no correlation between the extent of dissolution and reduction potential, and other factors such as adsorption of the reductant on the oxide surface which is also pH dependent may also have to be taken into account.

Dissolution data for different chelating ligands in solutions containing 11 mol m⁻³ citric acid and 4 mol m⁻³ ascorbic acid along with the stability constants of the Fe(II) complexes formed with these ligands are given in Table 5. Complete dissolution occurs in 4 hrs when EDTA and DTPA are used as the chelating ligands, whereas in the case of HEDTA and NTA it is ~ 79% and ~ 39% respectively. In the case of IDA there is practically no dissolution in the initial stages but there is ~ 22% dissolution in 4 hrs. Fe(II)-DTPA and Fe(II)-EDTA complexes have very high stability constants and this makes them strong reductants capable of accelerating the dissolution process. Stability constants of complexes of Fe(II) with other ligands are much lower and these are ineffective in dissolving α -Fe₂O₃ at appreciable rate. The data in Table 5 reflect these trends.

Dissolution behaviour of iron oxides prepared by heating Fe(OH)₂ in air at different temperatures are given in Table 6. Complete dissolution in 3-4 hrs was observed in the case of samples heated at 773 K and above. The samples heated at 673 K dissolved completely in 2 hrs and in the case of those heated at 573, 473 and 373 K, the dissolution was very rapid with complete dissolution occurring in less than 30 mins. Samples heated at low temperatures are less crystalline in nature as compared to those heated at higher temperatures. The ferrous hydroxide precipitated

TABLE 4 : Effect of different reducing agents on the dissolution of moderately sintered haematite in citric acid - EDTA mixtures at 80°C

Reducing agent (4 mol m ⁻³)	Redox potential E ⁰ (vs NHE)	Percentage dissolution in 4 hrs.	k _{obs} × 10 ³ (min ⁻¹)
Ascorbic acid	+0.412 V	100	9.9
Thioglycolic acid	-0.23 V	49	2.3
Hydrazine	-1.15 V	<4	-
Sodium dithionite	-0.40 V	No dissolution	-
Oxalic acid	-0.23 V	No dissolution	-
Formic acid	-0.056 V	No dissolution	-

*(Citric acid 11 mol m⁻³; EDTA 44 mol m⁻³)

TABLE 5 : Effect of different complexing agents on the dissolution of moderately sintered haematite in citric acid - ascorbic acid mixtures at 80°C.

Chelating agents (44 mol m ⁻³)	Log K	Percentage dissolution in 4 hours	k _{obs} × 10 ³ (min ⁻¹)
DTPA	16.4	100	6.2
EDTA	14.3	100	9.9
HEDTA	12.2	79	5.2
Oxalic acid	9.4	59	2.1
NTA	8.3	39	1.2
IDA	5.8	22	0.3

(Citric acid 11 mol m⁻³; Ascorbic acid 4 mol m⁻³)

TABLE 6 : Dissolution behaviour of iron oxides* in CEA 11:44:4 mol m⁻³ mixture at 80°C

Temperature (K) of heat treatment	k _{obs} × 10 ³ (min ⁻¹)	Time for complete dissolution
373	46.7	< 30 mins
473	31.2	< 30 mins
573	20.0	< 30 mins
673	12.5	2 hrs
773	10.3	3-4 hrs
873	09.9	3-4 hrs
1073	06.6	3-4 hrs

* Prepared by heating Fe(OH)₂ in air at different temperatures for 6 hrs.

at ambient temperature has a porous structure, and on heating at low temperatures these pores may not coalesce to any significant extent to form a compact phase. This in turn will cause weaker binding between the crystallites thus facilitating better access to the solution mixture and hence faster dissolution. Increase in treatment temperature renders stronger binding between the crystallites and increases the crystallinity (less porosity) of the sample prepared by heating at 1073 K. In highly crystalline samples the compact nature of the lattice hinders the reduction of the lattice Fe(III) ions by the reducing agent and hence the release of the reduced Fe(II) ions into the solution by complexation with the chelating agent would be rather slow.

α -Fe₂O₃ prepared by heating Fe(OH)₂ at 1073 K showed near identical dissolution behaviour as the moderately sintered sample prepared at 873 K. The chromium substituted oxides prepared by heating at 1073 K, were more difficult to dissolve in CEA mixture as compared to α -Fe₂O₃ prepared at 1073 K (Table 7) suggesting that replacement of part of Fe(III) ions by Cr(III) ions in the spinel lattice increases the stabilization of the lattice, thereby hindering dissolution. It has been reported ^[1] that in the case of oxides especially spinels and inverse spinels containing chromium, an oxidative pre-treatment using alkaline permanganate (AP) is required to solubilise the Cr as CrO₄⁻², after which the chromium depleted iron oxides can be readily dissolved in a reductive - complexing formulation. However it was observed that when the Cr substituted haematites prepared by heating at 1073 K were treated with 0.3 -1% KMnO₄ in 1.2% NaOH at 353 K, chromium was not appreciably released from the oxides. On the other hand simple Cr₂O₃ prepared under the same conditions dissolved completely in this medium. It would appear that the hexagonal lattice of Cr substituted haematites has a high degree of lattice stabilization which makes the oxidation of Cr(III) in the host lattice very difficult. Such chromium substituted haematites also do not readily dissolve in any of the CEA mixtures.

In the case of low chromium containing haematite sample (3.5%) complete dissolution in CEA mixture was observed only at higher concentrations of the reducing agent (Table 7), the mechanism being reductive - complexation of Fe as in the case of unsubstituted haematites and simple complexation of Cr. When the low chromium containing oxide was first treated with 0.3% KMnO₄ in 1.2% NaOH there was no significant amount of chromium or iron released on subsequent treatment with 11:44:4 mol m⁻³ CEA mixture, but when KMnO₄ concentration was increased to 0.6%, there was considerable dissolution in this CEA mixture. Even at higher KMnO₄ concentrations only a fraction of the Cr(III) present in the lattice seems to get oxidised.

TABLE 7 : Dissolution behaviour of chromium substituted spinel oxides in different CEA mixtures and the effect of alkaline permanganate pre-treatment

Sample	Fe %	Cr %	Treatment	Percentage Dissolved*	
				Fe	Cr
Fe _{1.93} Cr _{0.07} O ₃	96.5	3.5	CEA 11:44:4 mol m ⁻³	ND	ND
Fe _{1.93} Cr _{0.07} O ₃	96.5	3.5	AP (0.3%KMnO ₄ + 1.2% NaOH)	ND	L
			CEA 11:44:4 mol m ⁻³	ND	ND
Fe _{1.93} Cr _{0.07} O ₃	96.5	3.5	AP (0.6%KMnO ₄ + 1.2% NaOH)	ND	L
			CEA 11:44:4 mol m ⁻³	69	51
Fe _{1.93} Cr _{0.07} O ₃	96.5	3.5	CEA 11:44:11 mol m ⁻³	70.5	61.5
Fe _{1.93} Cr _{0.07} O ₃	96.5	3.5	AP (0.6%KMnO ₄ + 1.2% NaOH)	ND	L
			CEA 11:44:11 mol m ⁻³	CD	CD
Fe _{1.93} Cr _{0.07} O ₃	96.5	3.5	CEA 11:44:22 mol m ⁻³	CD	CD
Fe _{1.9} Cr _{0.1} O ₃	95	5.0	AP (0.6%KMnO ₄ + 1.2% NaOH)	ND	L
			CEA 11:44:11 mol m ⁻³	12	5
Fe _{1.9} Cr _{0.1} O ₃	95	5.0	AP (1%KMnO ₄ + 1.2% NaOH)	ND	L
			CEA 11:44:11 mol m ⁻³	43	19.5
Fe _{1.9} Cr _{0.1} O ₃	95	5.0	CEA 11:44:22 mol m ⁻³	66	23.5
Fe _{1.9} Cr _{0.1} O ₃	95	5.0	AP (1%KMnO ₄ + 1.2% NaOH)	ND	L
			CEA 11:44:22 mol m ⁻³	80	42
Fe _{1.9} Cr _{0.1} O ₃	95	5.0	CEA 11:44:44 mol m ⁻³	80	44.5
Fe _{1.85} Cr _{0.15} O ₃	92.5	7.5	CEA 11:44:44 mol m ⁻³	61	27.5
Fe _{1.85} Cr _{0.15} O ₃	92.5	7.5	AP (1%KMnO ₄ + 1.2% NaOH)	ND	L
			CEA 11:44:22 mol m ⁻³	58	51
Fe _{1.8} Cr _{0.2} O ₃	90	10	CEA 11:44:44 mol m ⁻³	15	10.5
Fe _{1.8} Cr _{0.2} O ₃	90	10	AP (1%KMnO ₄ + 1.2% NaOH)	ND	L
			CEA 11:44:22 mol m ⁻³	31	19.5
Fe _{1.75} Cr _{0.25} O ₃	87.5	12.5	AP (1%KMnO ₄ + 1.2% NaOH)	ND	L
			CEA 11:44:22 mol m ⁻³	14	6
Fe _{1.75} Cr _{0.25} O ₃	87.5	12.5	CEA 11:44:44 mol m ⁻³	ND	ND
Fe _{1.75} Cr _{0.25} O ₃	87.5	12.5	AP (1%KMnO ₄ + 1.2% NaOH)	ND	L
			CEA 11:44:44 mol m ⁻³	41.5	24.5

* In 8 hrs

L : Low dissolution (3-5%)

ND : No significant dissolution (i.e. < 2-3 ppm Fe or Cr in solution)

CD : Complete dissolution

This slight disturbance of the lattice could facilitate the access of the reducing agent to the Fe(III) ions in the lattice in the subsequent treatment with the reductive - complexing formulation. Thus though there is no appreciable release of chromium in the AP pre-treatment step, it plays a definite role in facilitating the dissolution in the CEA mixture.

As the chromium content of the oxide increases it tends to become hard and a progressively higher concentration of the reducing agent is required to bring about some dissolution. Here also pre-treatment with a higher concentration of KMnO₄

followed by treatment with the CEA mixture resulted in higher extent of dissolution as compared to what was observed in the absence of pre-treatment. When the chromium content is above 10%, treatment with CEA alone using even very high concentration of the reducing agent (11:44:44 mol m⁻³) was ineffective indicating the high degree of lattice stabilization of the oxide. However when this oxide was pre-treated with 1% KMnO₄ in 1.2% NaOH and subsequently treated with 11:44:44 mol m⁻³ CEA formulation there was some dissolution. This behaviour of chromium substituted haematites is quite different from what has been reported in the literature in the case of chromium substituted ferrites [1].

The results of coupon decontamination experiments are given in Table 8. These were primarily aimed at comparative evaluation of CEA as a reductive - complexing solvent with the known LOMI reagent for the specimens from the BWR coolant system piping. Whereas either of these formulations by themselves were not able to effect any

Table 8 : Results of Coupon Decontamination Experiments

Treatment*	Step DF	Cumulative DF
AP	1.4	-
AP-1	1.0	2.6
LOMI-1	2.6	
AP-2	1.2	2.5
LOMI-2	2.1	
AP/CE	-	1.1
AP/CEA-1	-	1.6
AP/CEA-2	-	2.2
		6.5
		3.4

(* Solution compositions are given in text, p 5)

decontamination of the specimens, on pre-treatment with alkaline permanganate there was appreciable decontamination in the subsequent treatment step with LOMI or CEA formulations - the DFs observed in the case of AP-LOMI being appreciably higher than in the AP-CEA case. In either case, the DF in the AP pre-treatment step was only marginal, the actual decontamination occurring in the subsequent LOMI or CEA step. It is also seen that citric acid - EDTA mixture with no reductant (ascorbic acid) present is not able to bring about any decontamination even after the preoxidation with AP. These observations are also supported by the results of spool piece decontamination experiments (Tables 9-10). There was appreciable Cr release only in the AP step, but not in the subsequent LOMI or CEA step. On the other hand large amounts of Fe and radioactivity release occurred in the latter step. The spool piece experiments conclusively showed that AP-LOMI procedure leads to higher DFs as compared to AP-CEA, at least at the low concentration of CEA mixture (2:2:4 mol

TABLE 9 : Metal and radioactivity release during 2-cycle AP-LOMI decontamination of spool piece

Time (hr)	Metal concentration in solution (mg/Kg)			Gross radioactivity in solution (nci/ml)
	Filtrate			Filtrate
	Fe	Ni	Cr	
1st AP step				
1	0.30	0.20	1.27	0.23
2	0.27	0.14	1.56	0.06
3	0.33	0.20	1.68	0.06
4	0.30	0.20	1.90	0.07
1st LOMI step				
1	28.01	2.90	0.44	198
2	30.50	3.45	0.85	239
3	32.27	4.22	1.33	257
4	34.04	5.07	1.77	269
2nd AP step				
1	0.18	0.13	0.65	0.10
2	0.27	0.16	0.52	0.05
3	0.15	0.16	0.67	0.06
4	0.12	0.13	0.76	0.06
2nd LOMI step				
1	6.22	0.57	-	15.7
2	9.39	0.72	-	23.2
3	12.98	1.07	-	26.1
4	19.06	1.13	-	28.3

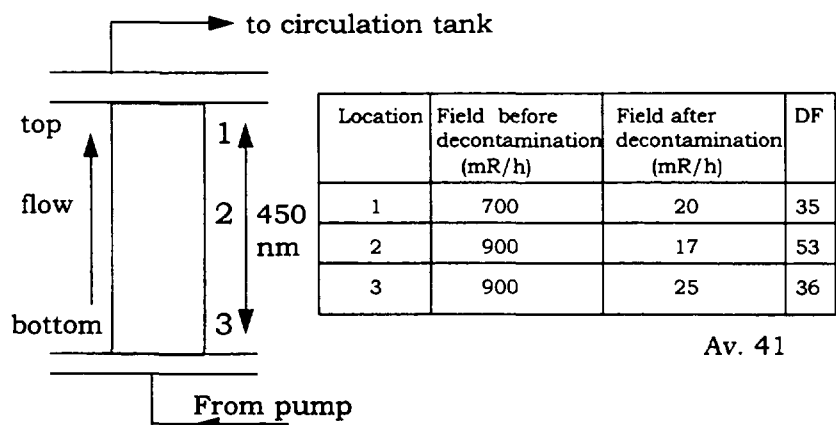
TABLE 10 : Metal and radioactivity release during 2-cycle AP-CEA decontamination of spool piece

Time (hr)	Metal concentration in solution (mg/Kg)			Gross radioactivity in solution (nci/ml)
	Filtrate			
	Fe	Ni	Cr	Filtrate
1st AP step				
1	0.24	0.24	2.50	0.94
2	0.21	0.27	2.36	0.60
3	0.29	0.31	2.50	1.10
4	0.32	0.31	2.64	0.70
1st CEA step				
1	15.09	0.37	0.15	7.2
2	21.95	0.64	0.20	21.9
3	26.52	1.08	0.12	40.0
4	29.88	1.55	0.25	68.5
2nd AP step				
1	0.40	0.14	1.86	0.20
2	0.38	0.20	1.79	0.09
3	0.44	0.17	1.97	0.09
4	0.47	0.20	2.05	0.10
2nd CEA step				
1	4.24	0.24	0.10	8.2
2	6.17	0.41	0.12	17.8
3	17.36	0.72	0.10	35.9
4	23.53	1.10	0.15	55.2

m⁻³) used in these experiments (Fig. 5). Use of such low concentrations was necessitated from the point of view of keeping the chemical contents in the waste effluents as low as possible. It was also observed during these experiments that although AP-LOMI procedure is superior from the point of giving higher DFs, in practical use it requires very stringent dissolved oxygen control during its preparation, storage and circulation, whereas CEA mixture is less sensitive to oxygen.

Although in decontamination campaigns it is the common practice to compact the radioactive waste solutions by use of ion exchangers, we have investigated an alternative possibility. Since the AP effluent is alkaline and contains a strong oxidant and the CEA or LOMI effluent (carrying the radioactive nuclides) is acidic and contains a strong reductant, mixing the two and digesting can be expected to bring

2-cycle AP-LOMI Process



2-cycle AP-CEA Process

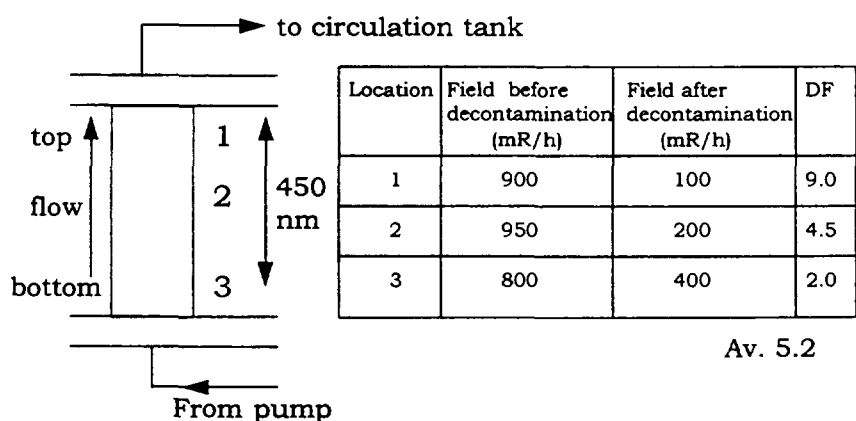


Fig 5 : Results of two cycle AP-LOMI and AP-CEA decontamination of spool piece.

about their neutralisation and reduction of MnO_4^- to the Mn^{4+} stage and precipitation of the latter as MnO_2 which could trap the radioactive nuclides. Experiments in this direction showed that it is possible to trap more than 99% radioactivity in the MnO_2 precipitate when the two effluents are mixed in equal volumes and digested at $\sim 90^\circ C$ for 1 hr.

5 SUMMARY AND CONCLUSIONS

The overall conclusions of the present investigations are as follows :-

⇒ The dissolution of moderately sintered haematite in CEA mixtures involves ligand assisted reductive complexation process in which the different components have specific roles. Citric acid alone is not effective for the dissolution, but in presence of EDTA and ascorbic acid it aids the dissolution process. The role of ascorbic acid is to

reduce the lattice Fe(III) ions to Fe(II) which are then complexed by EDTA thus solubilising the oxide.

⇒ Amongst the various reducing agents employed, ascorbic acid is the most effective one. EDTA and DTPA are the most effective chelating agents. The dissolution decreases at pHs above 3.0 whereas at $\text{pH} \leq 2.0$ there is problem of EDTA precipitation although dissolution is not hampered.

⇒ Heat treatment of iron oxides significantly affects their dissolution in CEA mixtures - the higher the treatment temperature, the more difficult it is to solubilise the oxide.

⇒ Substitution of part of Fe(III) ions by Cr(III) ions in the haematite makes it more difficult to dissolve in the CEA mixture. When the chromium content is low ($< 3.5\%$), complete dissolution is possible irrespective of whether or not an oxidative pre-treatment with alkaline KMnO_4 is carried out. The effectiveness of the dissolution of the oxides by the CEA mixture decreases as the chromium content of the oxides increases. Higher concentration of reducing agent or a pre-oxidation step with alkaline permanganate helps to some extent in dissolving high Cr containing oxides.

⇒ Both static and dynamic loop studies on specimen pieces cut from the Reactor Water Clean-up system piping of TAPS-BWR showed that a two cycle AP-LOMI process is capable of giving higher decontamination factors as compared to a two cycle AP-CEA process. However the former requires very stringent control on dissolved oxygen.

⇒ The radioactive LOMI or CEA effluents arising from decontamination using either the AP-LOMI or AP-CEA process can be mixed with the relatively inactive AP effluent and digested at $\sim 90^\circ\text{C}$ when MnO_2 precipitates out carrying with it all the radioactivity; this is envisaged as a simple way for radwaste disposal.

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