

# High temperature dissolution of chromium substituted nickel ferrite in nitrilotriacetic acid medium



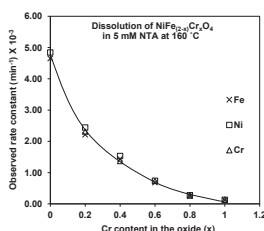
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## HIGHLIGHTS

- Dissolution of  $\text{NiFe}_{(2-x)}\text{Cr}_x\text{O}_4$  was remarkably increased at 160 °C in NTA medium.
- The dissolution was significantly decreasing with the increase in Cr content in the oxide.
- Dissolution rate is dependent on the lability of metal-oxo bonds.
- The rate of dissolution was not significantly reduced in the presence of  $\text{N}_2\text{H}_4$ .
- NTA at high temperature is effective for decontamination of stainless steel surfaces.

## GRAPHICAL ABSTRACT



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## ABSTRACT

High temperature (HT) dissolution of chromium substituted nickel ferrite was carried out with relevance to the decontamination of nuclear reactors by way of chemical dissolution of contaminated corrosion product oxides present on stainless steel coolant circuit surfaces. Chromium substituted nickel ferrites of composition,  $\text{NiFe}_{(2-x)}\text{Cr}_x\text{O}_4$  ( $x \leq 1$ ), was synthetically prepared and characterized. HT dissolution of these oxides was carried out in nitrilotriacetic acid medium at 160 °C. Dissolution was remarkably increased at 160 °C when compared to at 85 °C in a reducing decontamination formulation. Complete dissolution could be achieved for the oxides with chromium content 0 and 0.2. Increasing the chromium content brought about a marked reduction in the dissolution rate. About 40 fold decrease in rate of dissolution was observed when chromium was increased from 0 to 1. The rate of dissolution was not very significantly reduced in the presence of  $\text{N}_2\text{H}_4$ . Dissolution of oxide was found to be stoichiometric.

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## 1. Introduction

To reduce the radiation exposure hazard to the maintenance personnel of nuclear power reactors, radiation field on the out of core surfaces has to be reduced. This is achieved by periodic chemical decontamination of coolant systems of nuclear power

reactors. The oxide layer formed on the reactor coolant system surfaces by the interaction of high temperature coolant water over a period of reactor operation acts as the host for radioactive nuclides, which leads to the constant radiation field build up around the coolant circuits. Decontamination is done by dissolving the oxide layer along with the impregnated radio-nuclides in suitable chemical formulations and removing them on ion exchange resins. The success of the process depends on the effectiveness of the formulation in dissolving the oxide deposit along with the radio nuclides. The low temperature dilute chemical decontamination

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(DCD) process is effective in dissolving magnetite, the main oxide formed under alkaline and reducing chemistry conditions on carbon steel surfaces of the primary heat transport system (PHT) of Pressurized Heavy Water Reactors (PHWRs) [1–4]. Many Indian PHWRs have been decontaminated using the DCD process at 85 °C and satisfactory decontamination factors (DF) were obtained on carbon steel surfaces [5]. However, in Indian PHWRs, where monel-400 (Cu-Ni alloy) is used as the steam generator tube material, the main corrosion product oxide formed on the tube surface is nickel ferrite [6], whereas in PHWRs, where incoloy-800 is used as the steam generator tube material, the corrosion product oxide layer is composed of mixed ferrites and chromites. In the case of Pressurized Water Reactors (PWRs) and Boiling Water Reactors (BWRs), stainless steel (SS-316 and 304 respectively) is the major coolant system structural material. PWRs are operated under hydrogen water chemistry (HWC) conditions (reducing and alkaline chemistry), while BWRs are operated under either normal water chemistry (NWC) conditions (neutral pH and relatively high dissolved oxygen level) or under HWC conditions. The corrosion product oxide formed on the PHT system surfaces of PWRs consists of fine-grained chromium rich spinel (inner layer) and a nickel rich spinel (outer layer) [7,8]. The inner oxide layer is formed by Fe-Cr-Ni oxide with spinel structure [9]. Practically found elemental compositions of the inner oxide layer correspond to  $(\text{Ni}_{0.2}\text{Fe}_{0.4}\text{Cr}_{0.4})_3\text{O}_4$  [10] or  $(\text{Ni}_{0.1}\text{Fe}_{0.5}\text{Cr}_{0.4})_3\text{O}_4$  [11] or  $(\text{Ni}_{0.1}\text{Fe}_{0.45}\text{Cr}_{0.45})_3\text{O}_4$  [12]. The inner layer is formed by the topotactic replacement of majority of Fe and Ni atoms in the steel lattice. The outer oxide layer is Ni-doped magnetite. It can be considered as almost similar to an ideal solid solution of  $\text{Fe}_3\text{O}_4$  and  $\text{NiFe}_2\text{O}_4$  [9]. In BWRs that are operated under NWC conditions, the inner oxide layer is composed of nickel ferrite and chromium rich nickel ferrite and the outer layer is loosely adherent hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) [7,8]. In BWRs, which are operated under HWC conditions, the outer oxide layer is composed of ferrites. These corrosion product oxides formed on stainless steel and other non-carbon steel surfaces are not that easy to dissolve in low temperature formulations [13]. Normally, chromium rich oxides are effectively dissolved in multi-step multi-cycle process involving alternate oxidation and reduction processes. This multi-step multi-cycle process is time consuming besides generating large volume of radioactive waste. Hence, an effective process is imperative for dissolving nickel and chromium containing mixed ferrites formed on stainless steel surfaces thereby to achieve good DFs and low volume of radioactive waste. Also, study on the development of an effective decontamination process assumes importance from the point of view of decontamination for decommissioning of retired reactors where complete removal of radioactivity from the surface is required for unrestricted release of the materials. By increasing the process temperature, it would be possible to dissolve the difficult oxides. Several studies, including our own, have been reported on the application of high temperature process for enhancing the dissolution of oxides and cleaning of stainless steel surfaces [8,14–18].

The present study was aimed at to examine the efficiency of a formulation at high temperature in dissolving the chromium substituted nickel ferrite that would be formed on stainless steel surfaces. Chromium substituted nickel ferrite with varying concentration of chromium ( $\text{NiFe}_{(2-x)}\text{Cr}_x\text{O}_4$ ) was synthetically prepared and characterized by XRD and Raman spectroscopy. The dissolution of these oxides was studied in Nitrotriacetic acid (NTA) based formulation at 160 °C. The effect of variation in chromium concentration in the oxide lattice on the dissolution behaviour of chromium substituted nickel ferrite was studied. The effect of the presence of hydrazine in NTA solution on high temperature dissolution of the oxide has also been studied. The results are discussed in detail in this paper.

## 2. Experimental

### 2.1. Materials and methods

All chemicals used were of analytical reagent (AR)/guaranteed reagent (GR) grade. Thermo UV–Visible Double beam Spectrophotometer (Model Evolution-500) was used for absorbance measurements for the estimation of dissolved iron (Fe) as Fe(II)-phenanthroline complex. Horiba Jobin Yvon (Model: Ultima-2) Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) was used for the estimation of dissolved chromium (Cr) and nickel (Ni). Characterization of synthesized oxide powder was done using Philips X-Ray Diffractometer (Model: Xpert Pro), which uses  $\text{Cu K}_\alpha$  (1.5406 nm) line as the X-ray source and NaI(Tl) scintillation counter as the detector. Jobin Yvon micro-Raman spectrometer (Model: LABRAM 800HR) with an argon ion laser at 514.5 nm was used for recording Raman spectra of oxide powder. The laser beam was focused using 100× objective lens and laser power was optimized to ~1 mW on the sample surface. Ultra-pure water of conductivity <0.1  $\mu\text{S}/\text{cm}$  was used for all experimental purposes.

### 2.2. Analytical procedures

#### 2.2.1. Determination of iron

Dissolved iron concentration was determined spectrophotometrically by o-phenanthroline method. Absorbance of the Fe(II)-o-phenanthroline complex, formed by the addition of o-phenanthroline, hydroxylamine hydrochloride and acetic acid-sodium acetate buffer of pH 5.0, was measured against the reagent blank at 510 nm using 1 cm quartz cell. Minimum detection limit for Fe by this spectrophotometric method is about 20  $\mu\text{g}/\text{L}$ .

#### 2.2.2. Determination of chromium and nickel

Dissolved Cr and Ni were determined by ICP-AES. Emission lines used for the determination of Cr and Ni were 267.716 and 231.604 nm respectively. At times, concentration of dissolved iron also was measured by ICP-AES at the emission line 238.204 nm. Metal standard solutions, certified by National Institute of Standards and Technology (NIST) were used for the calibration. The minimum detection limit for Fe, Cr and Ni by ICP-AES at the above emission lines was determined by aspirating blank (Ultra-pure water) and standard solutions and the value was found to be about 1  $\mu\text{g}/\text{L}$ .

### 2.3. Preparation of chromium substituted nickel ferrite

#### ( $\text{NiFe}_{(2-x)}\text{Cr}_x\text{O}_4$ )

Chromium substituted nickel ferrites of composition  $\text{NiFe}_{(2-x)}\text{Cr}_x\text{O}_4$ , ( $x = 0, 0.2, 0.4, 0.6, 0.8, 1.0$ ), were prepared by combustion route [19], i.e. six oxides of composition  $\text{NiFe}_2\text{O}_4$ ,  $\text{NiFe}_{1.8}\text{Cr}_{0.2}\text{O}_4$ ,  $\text{NiFe}_{1.6}\text{Cr}_{0.4}\text{O}_4$ ,  $\text{NiFe}_{1.4}\text{Cr}_{0.6}\text{O}_4$ ,  $\text{NiFe}_{1.2}\text{Cr}_{0.8}\text{O}_4$  and  $\text{NiFeCrO}_4$  were prepared. The solution of metal nitrates ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) in their stoichiometry was prepared in ultra-pure water containing citric acid. The molar ratio of citric acid to total moles of nitrate ions was 1:3. The solution was neutralized using ammonia solution. This solution was evaporated to dryness by heating at temperature of 100 °C until it became a very viscous gel and on further heating, the gel burnt completely in a self-propagating combustion manner to form a loose powder. Finally, the burnt powder was calcined in air at temperature of 1000 °C for 1 h to obtain spinel phase. In these ferrites, the tetrahedral sites are occupied by  $\text{Fe}^{3+}$  ions, half of the octahedral sites are occupied by  $\text{Ni}^{2+}$  ions and the other half is shared by  $\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$ . The structural characterization of all the synthesized oxide powder samples was done by XRD and Laser

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