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DISSOLUTION OF VARIOUS METAL OXIDES IN DIFFERENT FORMS IN DILUTE ORGANIC COMPLEXANTS

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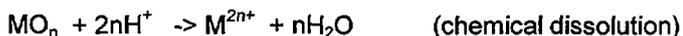
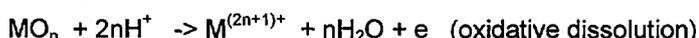
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Abstract

The dissolution of iron containing metal oxides is of importance in various power plant industries from the point of crud and scale removal for efficient operation and better performance of plant. The removal of these oxides has to be accomplished with minimum corrosion to the structural material, with minimum cost and removal duration and also with minimum waste generation for easy disposal. Activity build-up due to pick up of Co^{60} and fission products occurs on PHT system surfaces of nuclear power plants. The dissolution kinetics of these oxides are influenced by pH, redox potential, chelating strength, concentration and temperature of the solution, constitution of oxides, and the physical form of existence of oxides. In this paper the influence of the existence of different forms of iron oxides on the ability of the dissolution characteristics of the different formulations have been brought out. How the change in dissolution characteristics can be ingeniously used to characterize both qualitatively and quantitatively the mixtures of oxides have been brought out. How the magnetite dissolution behaviour varies for base metal unaided condition in different formulation in static condition, in regenerative mode is also brought out. The OCP values and iron release behaviour for magnetite coated CS surface and magnetite pellet were also described.

Introduction

Magnetite invariably exists within the coolant circuits both in the form of mobile particulates and adherent layers on the metal surfaces. The protective oxide film formed in the primary coolant circuit in most nuclear reactors develop radiation fields due to the incorporation of neutron activated corrosion product in the film[1]. In order to understand the dissolution of radioactive oxide film from the metal surface and also the dissolution of the oxide constituent in the absence of metal substrate detailed electrochemical studies were carried out on magnetite coated coupons and magnetite pellet besides simple dissolution kinetic studies. Depending on the chemical nature of the oxide, the chelants and the reagents used, dissolution can take place by the following three processes.



For the iron/iron oxide system, metal surface itself acts as a reductant especially in the case of carbon steel system. The process is known as auto reduction.

The dissolution kinetic studies on mixture of iron oxides like α and γ - Fe_2O_3 , Fe_3O_4 , NiFe_2O_4 also helped to understand that besides the formulation ability to dissolve the oxides, the various constituents of iron oxides present also determine the decontamination efficiency. The individual components of mixture of oxides were quantitatively determined based on dissolution kinetic behaviour.

Nickel ferrite is one of the corrosion products in the pipeline surfaces of water-cooled nuclear reactors. Since nickel is present as a ferrite in the corrosion product along with magnetite in the nuclear reactors, it is of interest to investigate its dissolution behaviour by using dilute chemical decontamination formulation.

Specifically, the present study deals with the leaching of iron and nickel from the nickel ferrite prepared by the solid-state method. The dissolution studies are performed in PDCA, NTA and EDTA based formulations at 85°C. The effects of reductant AA and Fe(II)-L complex have been studied to understand the mechanism of dissolution.

The dissolution kinetics of magnetite (powder) under regenerative conditions is cost effective since the quantity of chemicals to be used is less, less corrosive to the structural materials there by helping the plant life extension concept by achieving lower man-rem to the maintenance people and also the amount of waste generated in this process and to be disposed on a mixed bed is less. This is generally done by using ion exchange resins. In the dilute chemical decontamination process, the formulation used has to be regenerated for further oxide layer dissolution. the interaction of metal complexes with cation exchange resin releases the H⁺ from the resin to the solution [2]. This cleavage of metal-complex bond is dependent on the complex stability, ion exchange selectivity coefficient and the pH of the solution. As the stability constant of the complex increases, the cleavage of the metal – complexant bond becomes difficult and the pickup of the metal ion by the cation exchange resin decreases and thereby affects the regeneration of the formulation. In the actual system decontamination, the process is carried out in regenerative mode where the complex formed during dissolution should be broken up by the cation exchange resin. This is possible only if the complex formed is of intermediate stability.

The choice of complexing agent for decontamination is not based on the stability constant of metal-ligand alone. The complexing agents should not be picked up by the cation exchange resin. The protonated amino group of aminopolycarboxylic acid is responsible for their pick up in the cation exchange resin. To accomplish this, the complexant is so chosen that its complex with Fe(II) / Fe(III) ions formed during reductive dissolution, gets picked up on the cation exchange resin liberating equal amount of H⁺ ions which together with the anion of the complexant come out of the cation exchange column. Thus the complexant continuously gets regenerated and the free concentration of the complexant in the formulation is kept available for further oxide dissolution in the reaction vessel.

Experimental

The dissolution behaviour of Iron oxide powders, Ferrites and Nickel ferrites individually and as mixture of oxides were carried out in a round bottomed 1L flask by taking different dilute chemical decontamination formulations like EDTA, NTA, PDCA with reductants like AA, Fe(II)-L and organic acid like CA both in static mode and in regenerative mode using cation ion exchange column. The Electrochemical open circuit potential measurements and E vs I measurements on magnetite coated metal specimen (carbon steel) and on magnetite pellet were measured using Calomel electrode as reference electrode and Pt/graphite as counter electrode. These measurements are carried out at different temperatures like 28°, 60° and 85° C.

Results and Discussion

Individual Iron oxide dissolution

α -Fe₂O₃ (1.37mM) dissolution only to the extent of 5 to 7% was observed in 4 hours in Ethylene Diamine tetra acetic acid (EDTA (1.37mM)), Pyridine 2,6-Dicarboxylic acid (PDCA (2.75mM)) and Nitrilo triacetic acid (NTA (2.75mM)) formulations containing ascorbic acid (AA (1.7mM)) or oxalic acid (OA) as reductant and Citric acid (CA (1.4)) at 60°C. In absence of reductant ~ 2% dissolution was observed in all the above formulations. The k_{obs} obtained based on cubic rate law was ~1*10⁻⁴ min⁻¹ both in presence and absence of reductant. Dissolution of γ -Fe₂O₃ to the extent of ~ 80% over a period of 3 to 4 h was observed at identical conditions in presence of reductant and 5 to 7% in the absence of reductant in these formulations. In presence of reductant, the dissolution kinetics is faster both in PDCA and NTA (k_{obs} ~10⁻³ min⁻¹) than in EDTA (k_{obs} ~ 6* 10⁻⁴ min⁻¹). OA as reductant was not as effective as AA in γ - Fe₂O₃ dissolution. The difference in the rate of dissolution between α -Fe₂O₃ and γ - Fe₂O₃ can be attributed to the structural stability of the hexagonal close packed (hcp) α -Fe₂O₃ as compared to cubic close packed (ccp) γ -Fe₂O₃. The dissolution of magnetite to the extent of ~ 90 % over a period of 2 to 4 hours in presence of AA and 75 to 90 % in absence of AA in these formulations was observed. The k_{obs} both in presence and absence of AA is of the order of 10⁻² min⁻¹ and in presence of OA ~ 10⁻³ min⁻¹ in different formulations.

Dissolution of Binary mixtures

Binary mixtures of Fe_3O_4 , $\alpha\text{-Fe}_2\text{O}_3$ and $\gamma\text{-Fe}_2\text{O}_3$ in the mole ratio of 80:20, 50:50 and 20:80 were taken for dissolution studies in all the three formulations in presence of reductant only. In EAC formulation for $\alpha\text{-Fe}_2\text{O}_3$ and Fe_3O_4 mixture the dissolution varied between 45 to 85% over a period of 4 h with k_{obs} in the range $0.35 - 2.45 \times 10^{-2} \text{ min}^{-1}$. In PDCA formulation for $\alpha\text{-Fe}_2\text{O}_3$ and Fe_3O_4 mixture (Fig.1) the dissolution varied between 26 to 82% over a period of 4 h with k_{obs} in the range 1.6 to $8.1 \times 10^{-3} \text{ min}^{-1}$. In NTA formulation for $\alpha\text{-Fe}_2\text{O}_3$ and Fe_3O_4 mixture the dissolution varied between 22 to 82% over a period of 4 h with k_{obs} in the range 1.1 to $7.2 \times 10^{-3} \text{ min}^{-1}$. The higher dissolution of $\alpha\text{-Fe}_2\text{O}_3$ in EDTA formulation can be attributed to the influence of Fe (II) released by magnetite acting as a powerful Fe (II)-EDTA reductant in reducing Fe (III) of $\alpha\text{-Fe}_2\text{O}_3$. Due to this reason enhancement in rate of dissolution was also observed.

In EAC formulation for $\gamma\text{-Fe}_2\text{O}_3$ and Fe_3O_4 mixture the dissolution was $\sim 85\%$ over a period of 2 hrs for all the mixtures with k_{obs} in the range 0.48 to $2.48 \times 10^{-2} \text{ min}^{-1}$. In PDCA formulation for $\gamma\text{-Fe}_2\text{O}_3$ and Fe_3O_4 mixture the dissolution varied between 76 to 85% over a period of 2 h with k_{obs} in the range 0.43 to $1 \times 10^{-2} \text{ min}^{-1}$. In NTA formulation for $\gamma\text{-Fe}_2\text{O}_3$ and Fe_3O_4 mixture the dissolution was $\sim 85\%$ over a period of 2 hrs with k_{obs} in the range 0.56 to $1.1 \times 10^{-2} \text{ min}^{-1}$. The dissolution rate and the % dissolution is almost same in all the formulations. This is attributed to the ease with which $\gamma\text{-Fe}_2\text{O}_3$ undergoing dissolution in various formulations in presence of Fe (II) -L is same and $\gamma\text{-Fe}_2\text{O}_3$ having the same structure as Fe_3O_4 (ccp) devoid of Fe^{2+} ions in the crystal lattice.

In EAC formulation for $\alpha\text{-Fe}_2\text{O}_3$ and $\gamma\text{-Fe}_2\text{O}_3$ mixture the dissolution varied between 20 to 52% over a period of 4 hrs with k_{obs} in the range 0.4 to $1.6 \times 10^{-3} \text{ min}^{-1}$. In PDCA formulation for $\alpha\text{-Fe}_2\text{O}_3$ and $\gamma\text{-Fe}_2\text{O}_3$ mixture the dissolution varied between 20 to 61% over a period of 4 h with k_{obs} in the range 0.5 to $2 \times 10^{-3} \text{ min}^{-1}$. In NTA formulation for $\alpha\text{-Fe}_2\text{O}_3$ and $\gamma\text{-Fe}_2\text{O}_3$ mixture the dissolution varied between 17 to 67% over a period of 4 h with k_{obs} in the range 0.3 to $2.9 \times 10^{-3} \text{ min}^{-1}$. The percentage dissolution of this binary mixture is the same in all the formulations with a marginal difference in k_{obs} . This is due to the variation in the kinetic ability of AA to act as reductant in presence of various chelant.

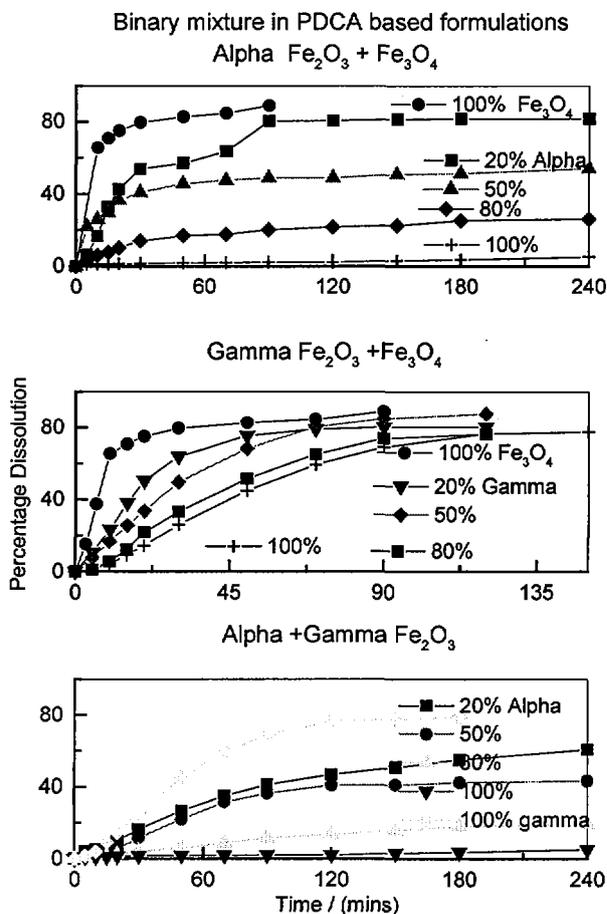


Fig.1

Ternary mixture oxide dissolution studies In PDCA Formulation

The formulation containing the reductant dissolves maximum quantity of Fe_3O_4 (82.5%) in 50 mins while only $\sim 2\%$ of $\alpha\text{-Fe}_2\text{O}_3$ gets dissolved. The reductant was ineffective in the case of $\alpha\text{-Fe}_2\text{O}_3$ while it was playing a moderate role in the case of $\gamma\text{-Fe}_2\text{O}_3$ (44.1%) In the absence of reductant, only Fe_3O_4 dissolved significantly. Both α and $\gamma\text{-Fe}_2\text{O}_3$ did not show any significant dissolution in 50 min. These differences in the rates of dissolution due to either the reductant or the nature of the oxide are utilised in the quantification of oxides from a physical mixture.

Dissolution experiments under inert conditions at 60°C in a dilute chemical formulation containing an organic chelant just sufficient to complex the entire amount of iron present in various forms of iron oxides, (determined separately by estimating the total iron) a reductant sufficiently in excess to reduce the Fe (III) to Fe (II) and an organic acid to maintain the pH were carried out for binary mixtures of these oxides and the percentage dissolution of iron at a fixed time say 50 mins in PDCA based formulation (time can vary depending

on the strength of the chelant) was plotted against composition of the binary mixture. The plot obtained was found to be linear for the entire range from 100 to 0 % of the components for all the three binary mixtures of α - Fe_2O_3 , γ - Fe_2O_3 and Fe_3O_4 oxides. This observation suggested that there is no appreciable chemical interaction between the components in solution during dissolution.

Encouraged by the meaningful results, a dissolution process was attempted for a three-component mixture. Based on the percentage dissolution of individual components at 50 min both in presence and absence of reductant, a ternary component "dissolution diagram" was constructed. Conceptually the treatment is similar to that of three-component phase diagram in an ideal case. Concentrations of the three components are plotted on an equilateral triangle. Each apex of the triangle is taken as 100% of the component with which it is designated. This is constructed with increasing % dissolution component from left to right. The sides of the triangle represent various proportions of constituents in two-component systems. (AB- α + γ - Fe_2O_3 , AC- α - Fe_2O_3 + Fe_3O_4 , BC- γ - Fe_2O_3 + Fe_3O_4). The line a'b' represents the variation in percentage dissolution of iron for a binary mixture of pure α - Fe_2O_3 (a') and pure γ - Fe_2O_3 (b') in presence of reductant. Similarly the lines b'c' and a'c' represent the dissolution behaviour for γ - Fe_2O_3 + Fe_3O_4 and α - Fe_2O_3 + Fe_3O_4 binary mixtures respectively in presence of reductant. The curve a'b'c' represent the dissolution behaviour of a ternary mixture of α - Fe_2O_3 , γ - Fe_2O_3 and Fe_3O_4 in presence of reductant. In absence of reductant ascorbic acid, the lines a''b'', b''c'' and a''c'' give the dissolution behaviour of binary mixtures of α - and γ - Fe_2O_3 , γ - Fe_2O_3 and Fe_3O_4 and α - Fe_2O_3 and Fe_3O_4 respectively. The curve a''b''c'' represents the dissolution behaviour of the ternary mixture in absence of reductant.

A tertiary mixture (60 Fe_3O_4 ; 20 α - Fe_2O_3 ; 20 γ - Fe_2O_3) was prepared for testing this hypothesis. 62.6% of iron dissolution was observed in 50 min in PDCA formulation with reductant and 11.44% only in the absence of reductant during 50 min at 60°C. Since the dissolution of α - Fe_2O_3 was negligible both in the presence and absence of reductant, the total iron found in the solution arises mainly from Fe_3O_4 and γ - Fe_2O_3 . In the absence of reductant the contribution from γ - Fe_2O_3 was also negligible and as a result the amount of iron found in solution correspond to that of Fe_3O_4 only.

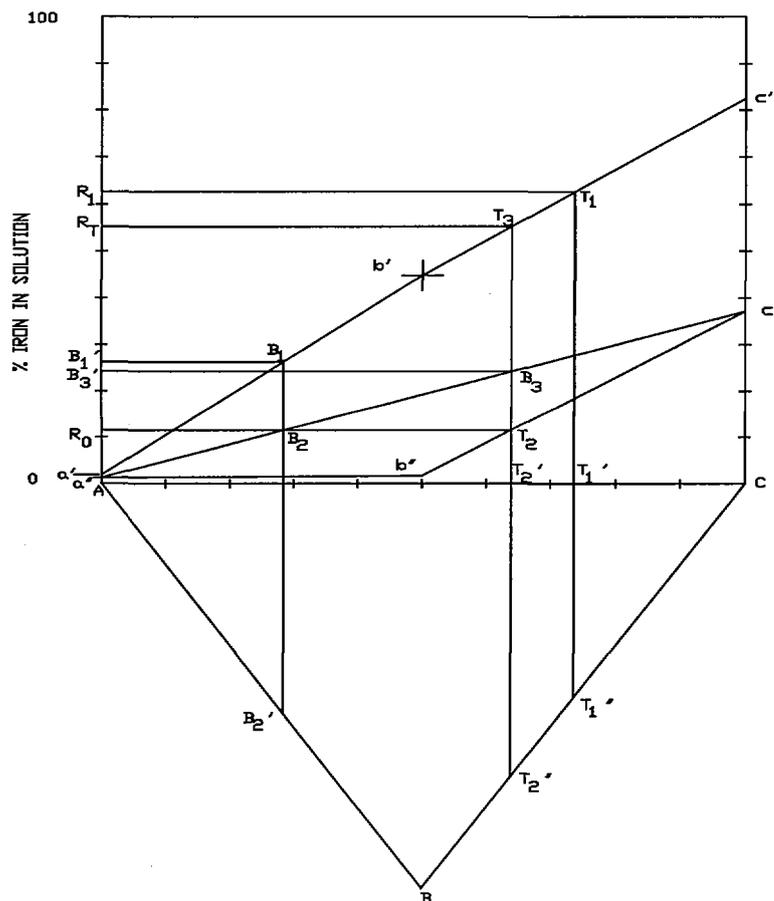


Fig.2 Ternary component diagram in PDCA based formulation:

In the ternary dissolution diagram, if a line is drawn parallel to the y axis for 62.6% (R_1T_1) of total iron dissolution it intersects the sides of the equilateral triangle in the dissolution diagram to give compositions of 73.6 % Fe_3O_4 + 26.4 % $\alpha-Fe_2O_3$ on AC (T_1') or 47.2 % Fe_3O_4 + 52.8 % $\gamma-Fe_2O_3$ on BC (T_1''). This implies that Fe_3O_4 composition can vary between 47 and 74% , $\alpha-Fe_2O_3$ composition can vary between 0 and 27% and $\gamma-Fe_2O_3$ composition can vary between 0 and 53%.

For 11.44% of total iron dissolution (R_0T_2) in the absence of reductant when a line is drawn parallel to the y axis it intersects the sides of the equilateral triangle in the dissolution diagram to give compositions of 63.8 % Fe_3O_4 and 36.2 % $\alpha-Fe_2O_3$ on AC (T_2') or 27.6 % Fe_3O_4 and 72.4 % $\gamma-Fe_2O_3$ on BC (T_2''). Since in the absence of reductant, the contributions by $\alpha-$ and $\gamma-Fe_2O_3$ for the dissolved iron in the solution were negligible, the composition of Fe_3O_4 in the tertiary mixture corresponds to ~63.8 % as determined by the intersecting point on AC. This value is also within the region of percentage distribution for Fe_3O_4 in presence of reductant ($T_1'T_1''$). Since both in the presence and in the absence of reductant the contribution by $\alpha-Fe_2O_3$ was negligible, the difference in iron dissolution with and without reductant could be attributed to $\gamma-Fe_2O_3$. This value based on the ternary diagram corresponds to 19.60% [$2*(T_1'-T_2') = (T_1''-T_2'')$]. The remaining amount of 16.6% corresponds to $\alpha-Fe_2O_3$. These observed results can be improved further to a first approximation by subtracting the contributions to the percentage dissolution from $\alpha-Fe_2O_3$ in presence of reductant and from both $\alpha-$ and $\gamma-Fe_2O_3$ in absence of reductant based on the estimated percentage distribution of these components. Thus the corrected percentage distribution of these components are 63.3 % Fe_3O_4 , 19.9 % $\gamma-Fe_2O_3$ and 16.8 % $\alpha-Fe_2O_3$. While the theoretical value of the percentage of the different components was 60:20:20, the computed value based on the measurement of dissolution turned out to be 63:20:17.

How to distinguish between a binary mixture and a tertiary mixture of these oxides? In absence of reductant 11.44% of iron in solution was observed. Had it been a binary mixture of Fe_3O_4 and $\alpha-Fe_2O_3$ or Fe_3O_4 and $\gamma-Fe_2O_3$ or $\alpha-Fe_2O_3$ and $\gamma-Fe_2O_3$ dissolution of 26.2 % (B_1'), 55.2 % (RT) and 26.2 % (B_1'') of the total iron respectively should have been observed in the presence of reductant. A line parallel to AC on R_0 can never cut a"b". Hence $\alpha+\gamma$ binary mixture is ruled out. Since it is not the case, simple binary mixtures is ruled out because of the incompatibility of data in the presence and absence of reductant. The argument for Fe_3O_4 content to be in the region 47-63 % (less than 63%) does not hold good since this could have resulted in lowering of the amount of iron dissolved in absence of reductant. If the remaining amount of 37.19% corresponds to only $\alpha-Fe_2O_3$, then the % dissolution of total iron would have been different both in presence and absence of reductant. For example if the remaining 37.19% contribution comes only from $\alpha-Fe_2O_3$ then in presence and absence of reductant the total iron found in the solution should have been 55.21% (R_1T_3) and 24.14% (B_3B_3') respectively. This clearly indicates that the presence of $\alpha-Fe_2O_3$ and $\gamma-Fe_2O_3$ together with Fe_3O_4 suppresses the dissolution of iron from magnetite in absence of reductant. Even the percentage distribution between $\alpha-$ and $\gamma-Fe_2O_3$ can be calculated based on the extent of suppression in the amount of iron dissolved in the absence or presence of reductant in a ternary mixture by comparing with the expected value if all the Fe_2O_3 is of either α or γ -form. The more the contribution by $\gamma-Fe_2O_3$ relative to the $\alpha-Fe_2O_3$ in a ternary mixture for a fixed percentage of Fe_3O_4 , higher is the percentage dissolution of iron in presence of AA.

In NTA Formulation

The ternary component diagram was constructed based on the % Fe in solution at 50 mins for individual component dissolution both in presence and absence of reductant in NTA formulation (Table 3.3.2). Similar to PDCA case, in NTA formulation also with reductant Ascorbic acid, the plot obtained for 50 mins dissolution was found to be linear for the entire range from 100 to 0 % of the components for all the three binary mixtures of $\alpha-Fe_2O_3$, $\gamma-Fe_2O_3$ and Fe_3O_4 oxides (Fig 3.3.29).

A ternary mixture of composition 40:25:35% of Fe_3O_4 , $\alpha-Fe_2O_3$ and $\gamma-Fe_2O_3$ was taken for estimation. By fitting the value of percentage iron in solution for the same 50 mins duration for the ternary mixture both in presence (41.72%) and absence of reductant (13.09%) in the ternary component diagram, (Fig. 3) the composition arrived for the mixture 36% Fe_3O_4 , 27% $\alpha-Fe_2O_3$ and 37% $\gamma-Fe_2O_3$. In this example, the ternary component diagram is disseminated as follows; in presence of reductant the dissolution of both Fe_3O_4 and $\gamma-Fe_2O_3$ can take place. The line drawn corresponding to percentage iron in solution intersects the $\alpha-Fe_2O_3$ and $\gamma-Fe_2O_3$ axis in a ratio determined by the % $\alpha-Fe_2O_3$ and % ($\gamma-Fe_2O_3 + Fe_3O_4$). In absence of reductant the line drawn corresponding to the percentage iron in solution intersect the $\gamma-Fe_2O_3$ and Fe_3O_4 axis in a ratio

determined by the percentage distribution between them in the mixture. Similar arguments and explanations as in the PDCA based formulation case, holds good also for NTA based formulation.

Ternary Components Dissolution
Diagram In NTA based Formulation

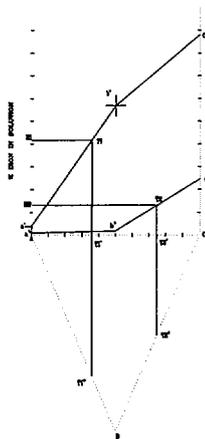


Fig.3

The attempt to resolve the ternary mixture by using oxalic acid as reductant is not satisfactory because very little dissolution of individual components of α -Fe₂O₃ and γ -Fe₂O₃ was observed both in presence and absence of reductant. Thus in this method of quantification, the choice of complexant, reductant and duration of dissolution are to be optimised for accurate results.

Dissolution studies on Nickel Ferrite

The dissolutions of nickel ferrite in PDCA, NTA and EDTA formulation are influenced by the presence of reductants in the formulation. The addition of Fe (II) (0.46 mM) in the formulation greatly enhances the dissolution. The preferential dissolution of nickel over iron in all the formulation indicates that the ferrite prepared

by solid-state route contains particles with nickel-rich surface layers. This conclusion is in agreement with the results obtained from XPS surface analysis of the nickel ferrite layers. Ascorbic acid (AA) was found to be a better reductant than Fe(II)-L in PDCA and NTA formulation for the dissolution of nickel ferrite, since this dissolution required more of Fe(II)-L in solution which can be achieved by the presence of AA. The initial rate constant

of the dissolution was increased by the addition of Fe(II)-L in all the three formulation. The EDTA formulation along with Fe(II)-EDTA as reductant was found to be a better formulation for the dissolution of nickel ferrite.

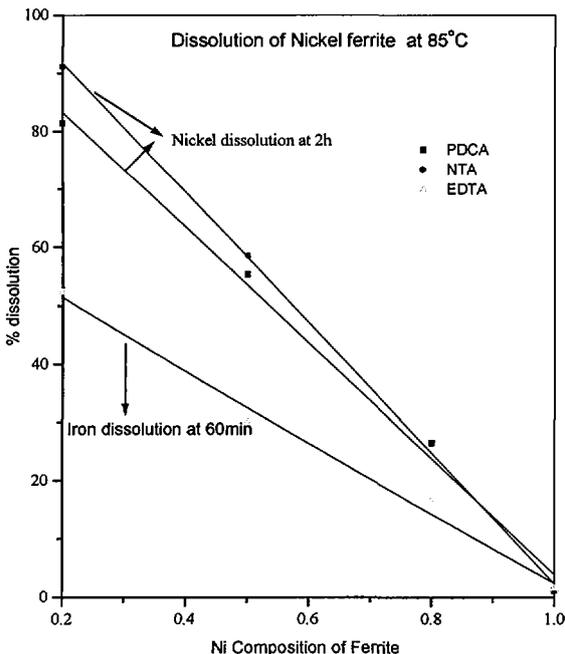


Fig.4

A linear relationship was observed between the composition of nickel ferrite and time of dissolution (Fig.4). The calibration graph drawn will be helpful in finding out the unknown composition of nickel ferrite based on the dissolution studies. Dissolution kinetic studies also helped to distinguish a mixture of Fe_3O_4 and NiFe_2O_4 and pure $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$.

Dissolution of Fe_3O_4 in regenerative mode in PDCA, NTA and EDTA formulations

The combined effect of regeneration by ion exchange and ascorbic acid was evaluated by carrying out dissolution studies of magnetite powder in PDCA, NTA and EDTA based formulations. In one set of experiments, no regeneration was used while in another set regeneration with cation exchange resin was employed for removing the dissolved iron. After exposure of the oxide with the formulation for 5-7 hours, the results are compared.

Under non-regenerative condition, the powder dissolution was essentially controlled by the strength of the complexes formed by EDTA, PDCA or NTA. The ascorbic acid did not contribute to the reductive dissolution in the case of EDTA. The extent of dissolution was comparable between the formulations though the rate of dissolution is subject to the stability of the Fe (II)-L and Fe (III) complexes. Under regenerative condition, the regeneration of the complexant PDCA, which is not picked up in the IX column, resulted in higher percentage dissolution and kinetics. In NTA case though the regeneration of the formulation has taken place in the regenerative mode, the pick up of the chelant on the IX column made it less efficient as compared to PDCA. In both PDCA and NTA based formulations AA served as an effective reductant in reducing Fe (III)-L to Fe (II)-L. The continuous presence of Fe (II)-L with regeneration of the formulation enhanced the dissolution rate. The cation IX column pick up behaviour in PDCA+ CA case also showed that Fe (III)-PDCA can be broken up on the column releasing free PDCA. In EDTA formulation in presence of AA, one third of total iron dissolved was picked up on the IX column. Two thirds of iron corresponding to Fe (III)-EDTA was not split up on the IX column to regenerate the formulation. Since AA could not reduce the Fe (III) EDTA in solution, the Fe (II)-L aided further dissolution could not take place. After 2-3 h, the IX inlet and outlet iron concentration remained same. In EDTA + CA case, only ferric EDTA was observed in solution (probably due to oxygen ingress). So very little pick up on the IX column was observed (<1 %). Hence EDTA could not be regenerated. This situation did not occur in NTA and PDCA media. As a consequence of the above, percentage dissolution and k_{obs} of Fe_3O_4 in PDCA formulations were observed to be very high. (Fig.5)

Salient Observations

1. The PDCA formulation is found to be better for the dissolution of Fe_3O_4 in both static and regenerative mode in the presence of reductants than NTA and EDTA.

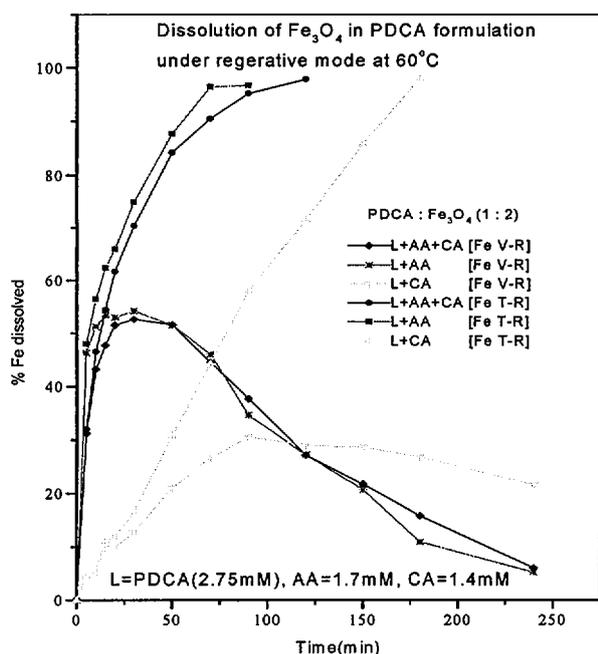


Fig.5

2. The hindrance caused by citric acid (CA) in PDCA formulation was found to be less pronounced in dynamic mode than in static mode. The presence of CA does not have an adverse effect in NTA and EDTA formulation.

3. The presence of reductants helps the oxide dissolution rate in PDCA and NTA formulation.

4. There is no adsorption of PDCA on the cation exchange resin and it is being fully regenerated, where as NTA and EDTA are getting adsorbed on the cation exchange resin.

5. The dissolution kinetics obeyed the cubic rate law for higher percentage dissolution in regenerative mode than in static mode.

6. The k_{obs} was found to be higher in the case of regenerative mode than in the static mode in PDCA based formulations, comparable in NTA based formulation, and lower in EDTA based formulations.

7. Based on the above observation the dissolution capability of the complexing agents under regenerative conditions for base metal unaided magnetite dissolution can be written in the following order.

PA > PAC > NAC > PC > NA ≈ EAC > EA > EC > NC

Electrochemical studies on magnetite coated coupons and pellets

It is also reported that the open circuit potential measurements on magnetite film dissolution in citrate and EDTA solutions under various pH and temperature conditions have shown three potential regions [3]. In region I, (> -125 mV) the film did not dissolve. In region II, (-125 to -500 mV) cathodic oxide dissolution accompanied by the anodic dissolution of the exposed base metal through the pores in the base layer of magnetite (auto reduction). In region III, (< -500 mV) proton reduction dominates over cathodic oxide dissolution. In a complexing medium, the dissolution of magnetite pellet produces a mixed flux of Fe^{2+} and Fe^{3+} species. The composition of the mixed flux varies as a function of potential. If the potential decreased to more negative values, the rate of Fe^{2+} release increased. The size of the pores and the rate at which they were formed via auto reduction control the observed potential. Variations in the pore size of the magnetite layer control the surface area of exposed metal and hence the extent of polarization and the rate of metal dissolution.

Gorichev et al [4] have reported that in the dissolution of free magnetite powder, the additives that shift the solution potential to more negative values can increase the dissolution rate. Shailaja et al [5] reported that nonuniformly coated CS spiral specimens showed lower percentage of oxide dissolution. The time taken to attain the "negative potential" shift is again not easily reproducible due to varying nature of oxide film (different pore density, micro cracks etc.) According to Hickling and Ives [6] a $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox system in the solid state is established and produces a potential-determining exchange current.

$$E = E' - 0.059\text{pH} - 0.059\log(a_{\text{Fe}^{2+}}(\text{solution}))$$

Magnetite coated coupons obtained from a high temperature engineering facility for testing PHT pumps and magnetite pellet prepared from hydrothermally synthesized magnetite were used for electrochemical studies of OCP and E Vs I measurements. These experiments helped to understand the electrochemical processes and mechanisms involved in the dissolution process of magnetite. The parameters studied were 1) The presence and absence of base metal CS 2) Different chelants 3) and different temperatures (28°C and 60°C). The magnetite coated specimens were found to have ~ 14 μm oxide thickness when descaled with Clark's solution.

Magnetite coated coupon

E Vs Time measurements

The coated coupon when immersed in 2mM EDTA solution at 28°C and 60°C for open circuit potential measurements with reference to a saturated calomel electrode, the potential changed over a period of 20 hours from -0.438 V immediately after immersion to -0.590 V at 28°C and the ocp varied from -0.450 V immediately after immersion to -0.650 V in 6 hours at 60°C . Though the anodic base metal dissolution continued to exist, the cathodic oxide dissolution was found to be more at 60°C . From the weight loss measurements, descaling of the exposed coupon and the total iron present in solution, the base metal corrosion rate was found to be 0.235 $\mu\text{m}/\text{hr}$ and only 30% of magnetite coating dissolved in 20 hrs at 28°C and at 60°C the base metal corrosion rate was found to be ~ 0.83 $\mu\text{m}/\text{hr}$ and the oxide dissolution increased to 72% in 6 hours. The corrosion rate of blank CS was observed to be 0.3 $\mu\text{m}/\text{hr}$ at 28°C . The slopes of metal release rate curve at 28°C between polished metal coupon and magnetite coated coupon matched well.

Magnetite coated coupon when immersed in 4mM PDCA (pH 2.49) formulation at 28°C and 60°C , the open circuit potential changed from -0.184 V immediately after immersion to -0.635 V in 18 hours at 28°C and from -0.251 V immediately after immersion to -0.644 V at 60°C in 7 hours. The cathodic oxide dissolution rate increased significantly at 60°C (86% in 7 hours) as compared to at room temperature (77% in 18 hours) with little change in anodic metal dissolution rate at both temperatures (0.175 $\mu\text{m}/\text{h}$ at 28°C and 0.225 $\mu\text{m}/\text{h}$ at 60°C). The addition of AA (1.7mM) shifted the ocp value immediately after immersion to more negative value -0.363 at 28°C and -0.367 V at 60°C . However the addition of CA (1.4mM) to PDCA +AA formulation did not result in any additional shift of OCP at 28°C or 60°C immediately after immersion. In presence of AA the base metal corrosion rate of 0.234 $\mu\text{m}/\text{h}$ at 28°C with 66% magnetite dissolution and 0.30 $\mu\text{m}/\text{h}$ at 60°C with 36% magnetite dissolution was observed. In presence of both AA and CA (pH 2.42) the base metal corrosion rate of 0.45 $\mu\text{m}/\text{h}$ at 28°C with 9% (in 21 hrs) magnetite dissolution and 0.16 $\mu\text{m}/\text{h}$ at 60°C with 23% (in 24 hrs) magnetite dissolution was observed. The observed higher corrosion rate of the base metal in presence of CA at 28°C can be due to its ability to act more as a surface ligand by adsorption than as a solution ligand leading to higher corrosion.

E Vs I measurements

Magnetite coated coupon under impressed potential condition using thin platinum foil as counter electrode at a scan rate of 20 mV/min showed monotonous decrease in current after an initial increase for the potential region 500 mV to -750 mV. The observed initial increase in current at more positive applied potentials can be assigned to release of Fe (III)-EDTA subsequent to chelant adsorption. The change of iron concentration with potential plot showed that the total metal release rate at 28°C matched with that occurring when the impressed potential did not exist. However at 60°C the rate of iron release with impressed potential was higher marginally, probably due to enhanced anodic reaction. The potential of zero current in both cases approached the ocp value of the base metal.

The E vs. I behavior for magnetite coated coupon in all PDCA based formulations showed monotonous change from anodic current to cathodic current for the applied potential region 500 mV to -700mV. At 28°C the addition of reductant AA shifts the OCP (potential at zero current) to -0.490 V from -0.520 in PDCA alone possibly due to the suppression of base metal dissolution. The addition of CA to PDCA+AA in solution shifts the OCP to -0.530 V suggesting the enhanced anodic base metal dissolution. At 60° C the OCP in PDCA alone shifts to -0.590 V and in PDCA+AA and in PDCA+AA+CA OCP ~-0.570 was observed. These results suggests that under the influence of the applied potential at 60°C, the anodic base metal dissolution is more resulting in the shift of OCP value to more negative values

Magnetite pellet

E Vs Time measurement

The magnetite pellet when immersed in 2mM EDTA for ocp measurements over a period of 24 hrs showed double hump behaviour at 28°C (Fig 3.4.14). While the first hump can be attributed to the release of Fe (III)- EDTA in to solution after the adsorption of (Y²⁻) form of EDTA on magnetite pellet. This is confirmed by ocp measurements on r-Fe₂O₃, which contained only Fe (III) ions. For this oxide after an initial increase in OCP, the potential remained constant for 20 hours. The second hump in magnetite case can be attributed to the Fe (II)-EDTA present in solution aiding the reductive dissolution of magnetite as reported by Mancy et al [7] that the reductive species present in solution when aids the dissolution shifts the potential to more positive values.

The magnetite electrode senses the solution redox potential during the course of the experiment. The redox components are Fe²⁺ and Fe³⁺ either in complexed or free state. The Nernst equation of relevance at 28°C for single e⁻ reaction should be

$$E = E^0 - 0.059 \log \text{Fe (II)/Fe (III)}$$

Based on this equation as Fe (II) increases E becomes more negative, while it should become more positive when there is only a release of Fe (III) to solution. When compared with r-Fe₂O₃ dissolution, it can be said that stoichiometric dissolution of magnetite has occurred at 28°C. This is further supported by an independent open circuit potential measurements of Fe²⁺, Fe³⁺ (1mM each) and together in PDCA solution. The potential observed for the mixture of iron ions (152.4mV) lying in between that for Fe³⁺ (249.3mV) and Fe²⁺ (72.5mV).

When the temperature is increased to 60°C, dissolution rate was enhanced. The first hump was not observed due to the preferential release of Fe²⁺ as normally reported in literature. Similar to the observation at 28°C, the reductive species present in solution aiding the dissolution shifts the potential to more positive value.

The iron analysis data showed that after an initial increase in iron concentration up to 3 hours did not show any further increase up to 15 hours at 28°C. However at 60°C, there was a marginal increase in iron content from 3 to 15 hours. After this period of inertia, which corresponds to the initial decrease followed by an increase in potential from 3 to 15 hrs, the iron content present in solution showed a steep increase after 15 hours.

The magnetite pellet when immersed in 4mM PDCA, the OCP values show some initial variation between +100 to +200 mV and later stabilise at a particular value. In PDCA the OCP stabilises at 168 and 145 mV at 28 and 60°C respectively. Stoichiometric dissolution is favored. In the presence of AA the separation between OCPs at 28°C (33 mV) and 60°C (154 mV) increases sharply as a consequence of reductive dissolution altering stoichiometric dissolution. In the presence of AA and CA, the trend with respect to temperature is reversed between 28°C (175 mV) and 60°C (117 mV). Though AA provides the reducing environment, the CA hinders the adsorption of PDCA to a larger extent.

E Vs I measurements

Magnetite pellet under impressed potential condition in 2mM EDTA showed a linear variation in I in the applied potential region 500 to -500 mV at 28°C with change in anodic current to cathodic current occurring ~ 80 mV (Potential of zero current-OCP). At 60°C, the behaviour was similar to at 28°C from 500 to -380 mV with the change in anodic current to cathodic current occurring at more positive potentials ~ 170 mV (OCP) due to increased temperature favoring the higher rate of release of Fe²⁺ species. The rotating disc electrode experiment on magnetite pellet carried out by Mancy et al [7] showed that under the influence of the applied potential, the relative flux of the Fe²⁺ (cathodic) and Fe³⁺ (anodic) influence the observed potential at zero current. The iron release from the pellet was found to be almost identical for applied potential regions both at 28°C and 60°C. Total iron released and iron release rates are also found to be much lower than that occurring in the oxide coated specimens.

The E vs. I behavior of magnetite pellet in PDCA based formulations at 28°C and 60°C showed a monotonous change from anodic to cathodic current as the potential applied shifted from 500mV to -600 mV. Due o the relatively higher rate of release of Fe²⁺ contributing to the cathodic current at 60°C ocp value (potential at zero current) increased to a more +ve value. The OCP values obtained in presence of AA both at 28°C and 60° C are more +ve with respect to that obtained in PDCA alone. In PDCA +AA +CA formulation both at room temperature and at 60°C the OCP values observed were 0.07 and 0.13 V respectively. But the OCP value at 28°C in presence of CA is less positive as compared to that with AA. At 60°C the reducing ability of AA for Fe (III)-citrate could have increased or the surface adsorption of citrate decreased at higher temperature leading to the shift of OCP value to more +ve value.

Table-1. Dissolution behaviour of magnetite coated film in PDCA based formulation

Formulation	% Magnetite dissolution		Corrosion rate (µm/h)		OCP values (V)	
	28°C	60°C	28°C	60°C	28°C	60°C
PDCA	77in 18h	86 in 7h	0.18	0.23	-0.18	-0.25
PDCA+AA	66	36	0.23	0.30	-0.36	-0.37
PDCA+AA+CA	9	23	0.45	0.16	-0.36	-0.37

Table-2. Dissolution behavior of magnetite coated film in NTA based formulation

Formulation	% Magnetite dissolution		Corrosion rate (µm/h)		OCP values (V)	
	28°C	60°C	28°C	60°C	28°C	60°C
NTA	27	64	0.24	0.48	-0.25	-0.32
NTA+AA	~1	~1	0.26	0.34	-0.22	-0.29
NTA+AA+CA	~1	33	0.45	0.50	-0.33	-0.41

Table-3. OCP values for E vs. I on magnetite coated coupon

Formulation	OCP values (V)		Formulation	OCP values (V)	
	28°C	60°C		28°C	60°C
PDCA	-0.52	-0.59	NTA	-0.49	-0.55
PDCA+AA	-0.49	-0.57	NTA+AA	-0.55	-0.49
PDCA+AA+CA	-0.53	-0.57	NTA+AA+CA	-0.51	-0.61

Table-4. OCP values for E vs. I on magnetite pellet

Formulation	OCP values (V)		Formulation	OCP values (V)	
	28°C	60°C		28°C	60°C
PDCA	-0.14	-0.09	NTA	0.29	0.01
PDCA+AA	0.11	-0.03	NTA+AA	0.17	0.13
PDCA+AA+CA	0.07	0.13	NTA+AA+CA	0.17	0.09

Comparison of the formulations based on iron release behaviour

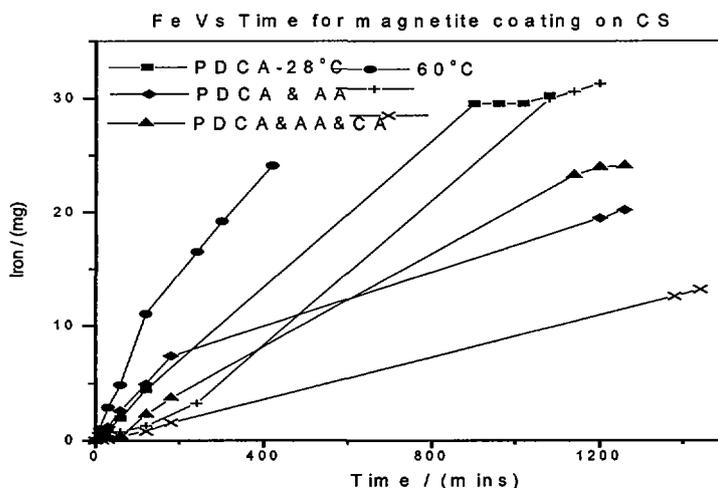


Fig 6

Magnetite coated coupon

For magnetite-coated specimen for the E Vs Time measurements the iron release followed the order

PDCA > EDTA > NTA at 28° C

PDCA ~ EDTA > NTA at 60° C

PDCA being a tridentate ligand in comparison with EDTA (hexa dentate) and NTA (tetra dentate) has less steric hindrance to act as a surface ligand at 28° C.

For this reason more dissolution of magnetite in PDCA was observed. At 60°C, the higher temperature favoured the dissolution followed by complexation and surface ligand behaviour gets reduced leading to comparable iron release in PDCA and EDTA, though in PDCA still the magnetite dissolution was observed to be more. In presence of AA, the observed iron release behaviour was

PDCA > NTA at 28° C and 60° C.

AA being a bidentate ligand can act as a better surface ligand resulting in lower iron release and lower magnetite dissolution compared to the case where chelant don't contain it since base metal already acts as a reductant. In presence of AA+ CA the release was observed to be PDCA~ NTA at 28° C. In this case also, further lowering of dissolution of magnetite was observed since besides AA, CA being a tridentate ligand can compete with PDCA and NTA there by favoring base metal iron release than the iron from magnetite. At 60° C, the iron release behaviour was observed to be NTA>PDCA. The solution ligand behaviour of NTA was found to be better due to its tetra dentate nature in comparison to PDCA which acts as a tridentate ligand competing with another tridentate ligand CA.

Magnetite pellet

For magnetite pellet for the E Vs Time measurements the iron release followed the order

PDCA > NTA > EDTA at 28° C

NTA > PDCA > EDTA at 60° C

In the absence of the base metal aided dissolution, the iron release behaviour showed that NTA acts as a better surface ligand than EDTA. In the case of NTA, two aquo molecules complete the hexa dentate co-ordination. As a result, it can approach the surface better than the bulkier EDTA (steric hindrance). At 60°C the

extent to which the decrease in surface ligand behaviour of PDCA occurred was more leading to the reversal in the trend. In presence of AA, the iron release was observed to be PDCA ~ NTA at 28°C reflecting that the surface ligand nature of bidentate AA decide the iron release. At 60° C, the observed behaviour was PDCA >NTA.

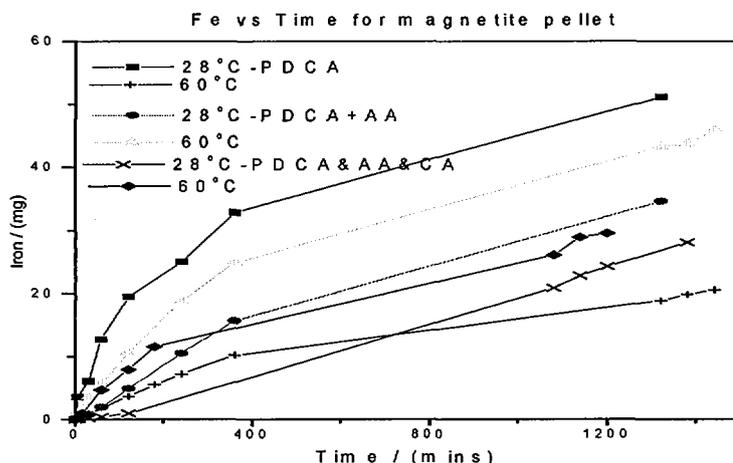


Fig 7

This behaviour in contrast to the observed trend for iron release in absence of AA showed that the reductive nature of AA for Fe (III)-PDCA was higher than for Fe (III)-NTA. In presence of AA and CA, the iron release followed the order

PDCA ~ NTA at 28° C

NTA > PDCA at 60° C

The iron release behaviour was similar to that observed for magnetite coated coupons.

In order to understand the dissolution behaviour of magnetite either from compact pellet or from a coated surface (with underlying active metal), electrochemical measurements are quite useful. The open circuit potential reflects primarily the solution redox potential arising out of the presence of relative amounts of Fe²⁺ and Fe³⁺. OCP also reflects the zero current state where the sum of anodic and cathodic current negates each other.

In a dissolution process, the concentration in solution varies widely. The rates of such processes are affected by complexation, adsorption and reduction. The present investigations were meant for arriving at a correlation between OCP and the dissolution by the complexant and reductant.

In general, it can be concluded that when an oxide film is coated over an active metal, the electron provided by the free metal is able to reduce Fe³⁺ substantially. Nevertheless, this reduction occurs only when the formulation gets access to the base metal, which means the pores should open up. Hence after the initial incubation period, the reductive dissolution dominates. No other reductant like Fe (II) EDTA from solution or ascorbic acid is able to compete. The nature of the complexing ligand ranging from EDTA, PDCA and NTA to citric acid also does not play a significant role.

In the case of a pellet, this dominant feature of metal reduction is absent. It will also be true for thick oxide coatings over metal surfaces and in cases where the underlying metal is inert. In these cases, one mechanism for dissolution is surface adsorption followed by complexation at the surfaces and release. An alternative to this is reduction after surface adsorption followed by release. In both these steps, adsorption as well as release is highly sensitive to temperature. Depending on the nature of the adsorption, it can be aided by temperature increase or suppressed. Hence in the cases of pellet dissolution, the OCP measured using pellet electrode reflects the solution potential. The chemical and physical environment dominates the mechanism. In the presence of PDCA at low temperature, surface adsorption and release is quite dominant making it a more attractive formulation for low temperature dissolution of magnetite than the well-established EDTA based formulation. The ability of EDTA to complex on the surface is lessened because of the geometry of the iron-EDTA complex.

Conclusions

These studies demonstrated how the dissolution studies on various iron oxides can be used for characterization of mixture of oxides both qualitatively and quantitatively. These studies also indicate the dissolution efficiency of various chelant for the mixture of these iron oxides. The dissolution studies on magnetite powder in regenerative mode indicate the efficiency of formulation in base metal unaided dissolution. The electrochemical studies on magnetite coated coupon (carbon steel) and on magnetite pellet in various dilute chemical decontamination formulation establish the efficiency of the formulation based on both OCP values and on total iron release behaviour. The observation of more negative initial open circuit potential for magnetite coated specimen on CS in comparison to the free magnetite pellet suggests that all the magnetite layers grown on metal substrate contain a number of micro cracks at the base of which additional anodic reactions take place.

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