



Comparative Dissolution of Natural Goethite Samples in HCl and HNO₃

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ABSTRACT: The dissolution of goethite samples in mineral acids from to extreme parts of Nigeria (Osogbo and Kaduna) have been investigated. The rate of dissolution was found to be slightly faster in HCl than HNO₃. The higher rate of dissolution in HCl could be attributed to the complexing ability of Cl⁻ in addition to the H⁺ effect while lowering effect by NO₃⁻ was attributed to adsorption of NO₃⁻ on to the goethite surface. Mononuclear complexes, especially bidentate of oxyanion are found to accelerate dissolution as opposed to binuclear complexes. A binuclear bidentate surface complex formation between NO₃⁻ and Fe³⁺ was therefore proposed to account for the inhibition observed. The possible formation of Fe—Cl reduces both the surface positive charge and the repulsion between the oxide surface and protons in solution. This produced accelerated proton dissolution. The effect of temperature on the initial dissolution rate fit into Arrhenius equation, with Kaduna goethite exhibiting higher rate than Osogbo type in both acids. The activation energies for Kaduna goethite sample are 66.11 and 82.43 kJmol⁻¹ in 0.1M HCl and 0.1M HNO₃ respectively while for Osogbo goethite sample are 54.60 and 76.32 kJmol⁻¹ in 0.1M HCl and 0.1M HNO₃ respectively. The frequency factors of 8.4 x 10⁻⁴ & 11.17 x 10⁻⁴ and 5.0 x 10⁻⁵ and 3.09 x 10⁻³ for Kaduna and Osogbo goethite samples were obtained. @JASEM

Iron, Manganese and Aluminum oxides and hydroxides are common features of many acid soils submerged soils and their clay fractions. Among the hydrous oxides, goethite (α - FeOOH), a more acidic substance, is a good sorbent material in natural environment. Goethite exhibits amphoteric behavior in solution due to the ability of the surface OH groups to take up or release protons depending on the pH of the solution. This will often give rise to surface charge resulting in proton transfer reactions.

It is evident from the previous works that the chemistry of micronutrients availability to plants is influenced by goethite. The chemistry of goethite dissolution is imperative in many respects: (i) goethite dissolution in soil solutions will release incorporated ions in its lattice structure and which may be essential for plant growth; (ii) the ions so released may also react or interact with other micronutrients, thereby modifying their availability to plants; (iii) the dissolution products will have less quantity of goethite, thereby reducing its effective potential as a sorbent material and (iv) it influences the magnetic susceptibility of soils and geochemical prospecting.

The conventional methods of removing heavy metals from liquids include chemical precipitation, electroflotation, ion exchange, reverse osmosis and adsorption on to activated carbon (Kadrivehi and Namasivayam, 2003). These methods are not cost effective and that gave rise to research on commonly available substrate with competitive adsorptive properties. The recent prolific research works on synthetic goethite as shown by the number of experimental studies in the recent past complement this assertion (Manning et al, 1998, Moyes et al, 2000;

Lehmann et al , 2001; Chin-Hsing et al 2002. The adsorptive properties have been utilized in water treatment plants Johnson, 1990 in toxic metals remediation of industrial liquids and soils Chin-Hsing et al 2002) and in the nuclear plants (Moyes et al, 2000). Most of these research works have been devoted to modeling the adsorption processes in order to identify likely surface reactions on the goethite, the influence of some physical parameters such as temperature, pH, adsorbate and adsorbent concentrations, and recently, desorption of heavy metals from goethite for possible reuse. Regeneration of goethite is important on account of cost saving and reduction of contamination originating from disposal of spent goethite. The quest for regeneration must be balanced with the geo-structural stability of goethite in common acid media that are commonly used for such regeneration.

Early studies on dissolution of goethite dealt with mechanism of dissolution and effect of crystal morphology on dissolution. There could be varying degree of substitution of Al for goethite-Fe in terrestrial weathering environments, Fe_{1-x}Al_xOOH (where x < 1.0).The level of substitution alters crystal size, texture, surface area, morphology and other structural properties that influence the rates and mechanisms of goethite dissolution. It was reported that low Al substitution for Fe in goethite leads to a decrease in proton – and ligand – promoted reductive dissolution because of an increase in disorder of crystal within the interdomains and leading to fewer structural defects that promote abiotic dissolution (Cervini-Silva and Sposito, 2002) Generally less attention has been given to studies of natural goethite and its dissolution process and mechanism is not an exception. The extent of co-existing ions in the outer

or inner sphere of goethite crystallography may enhance or inhibit the release of Fe (III) into solution in acid medium. The present study is concerned with acid dissolution of two goethite samples from two different geographical weathering locations in Nigeria and the relationship between the dissolution rates and crystal morphologies.

EXPERIMENTAL

Sampling: Two goethite samples from locations with different weathering conditions were collected. The locations are Osogbo – south western and Kaduna – northern part of Nigeria samples were sufficiently air-dried. Combinations of techniques previously characterized these samples: IR, XRF, XRD and optical microscopy. The percentage goethite was found to be 63.60 (Kaduna) and 78.20 (Osogbo). The goethite samples were ground with pestle and mortar and the fraction passing 90 μ m was used for further studies.

Dissolution: 0.5g – goethite sample was used for 25.0 cm³ of the various acids and contacted for a maximum period of 10 hours under simple mechanical agitation using a regulated orbital shaker. In all experiments, 0.1, 0.5 and 1.0 M HCl and HNO₃ concentrations were variously used. The limitation of these concentrations was based on the practical need of using any of the acids for goethite regeneration and desorption experiments. The temperature effect on the dissolution rates at laboratory temperature (~

30^oC), 40, 50 and 60 \pm 1^oC was done, keeping goethite: acid concentration ratio constant and for contact time of 90 minutes. The kinetic runs were carried out in a 3 – neck round bottom flask fitted with a refluxing condenser and a thermometer with constant shaking. 1g- goethite: 150 cm³ acid concentrations were used at 5 different temperatures between 30 and 60^oC. Clear aliquot samples were withdrawn from the suspension with a 5 ml plastic syringe at intervals over a period of 180 and 240 minutes for Osogbo and Kaduna respectively and filtered into plastic vials. The aqueous Fe³⁺ in the filtrates was analyzed by atomic absorption spectroscopy. Control experiments under the same dissolution conditions were done with de – ionized water.

RESULTS AND DISCUSSIONS

All control experiments showed practically no presence of dissolved Fe. The influences of acid concentrations and temperatures on the two goethite samples are compared in Table 1. The release of Fe³⁺ was generally low for all acid concentrations and temperatures. There was a general increase in the amount of goethite dissolved with increasing temperature. There is a sharp but un - linear increase in dissolved Fe³⁺ between 0.1 and 0.5M while the effect slowed down between 0.5 and 1.0M acid concentrations.

Table1: Influence of concentration and temperature on dissolution of Osogbo and Kaduna goethite

HNO ₃ concentration	Temperature (^o C)	Osogbo goethite	Kaduna goethite
		% dissolved/g- goethite	% Fe dissolved/g- goethite
0.1M	30	0.15	0.11
	40	0.48	0.42
	50	0.60	0.50
	60	0.64	0.55
0.5 M	30	0.52	0.50
	40	1.12	1.12
	50	1.73	1.56
	60	2.58	1.98
1.0 M	30	0.73	0.61
	40	1.15	1.10
	50	2.19	1.92
	60	3.38	2.89

The goethite dissolution can only be justified by proton – promoted dissolution process. This involves protonation of an oxide or hydroxide ion adjacent to

the removable Fe complex. When this happens, the Fe-Fe linkage is polarized and the bond weakens. Consequently, the Fe adjacent to protonated Fe

breaks off from the surface. The increase in dissolution with increase in acid concentration, therefore, is due to increased proton activity. The overall proton promoted dissolution can be represented thus:

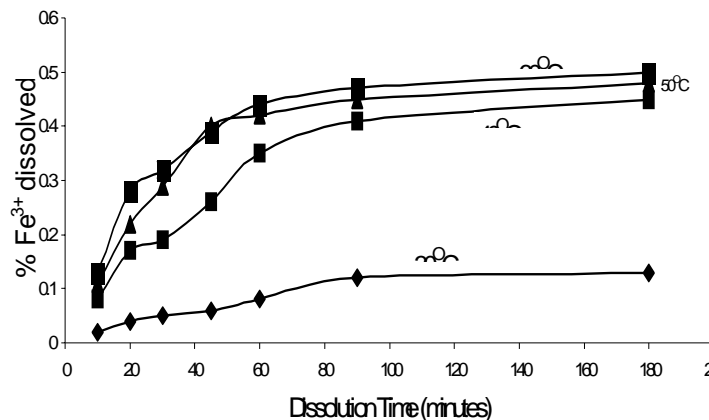
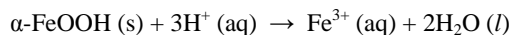


Fig1: Percentage of Fe³⁺ dissolved versus dissolution time for Osogbo goethite in 0.1M HCl

The rate of dissolution was studied with 0.1M HCl and 0.1M HNO₃ for 5 temperatures ranging between 30 and 60°C. The plots of Fe³⁺ leached versus dissolution time are shown in Figures 1 & 2 and 3 & 4 for Osogbo and Kaduna goethite samples respectively. There is initial sharp release of Fe³⁺ within the 20 minutes of the experiment. The Fe may have been from an amorphous impurity or partly due to effect of increased surface area (fine particles of << 0.09 mm) (Salami and Adekola, 2002). The increased dissolution rate of goethite in HCl than HNO₃ under the same experimental conditions could

be attributed to Cl ion concentration. This ion has the tendency to accelerate dissolution due to possible Fe---Cl complex formation on the oxide surface. This will reduce the surface positive charge and the repulsion between the oxide surface and protons in solution. Furthermore, such complex formation induced polarization of bonds between metal and oxygen atoms in the mineral lattice. The polarization weakens the attractive forces between Fe³⁺ and O²⁻ in Fe-O bond, thus lowering the energy barrier for the dissolution of Fe (Duckworth and Martin, 2001).

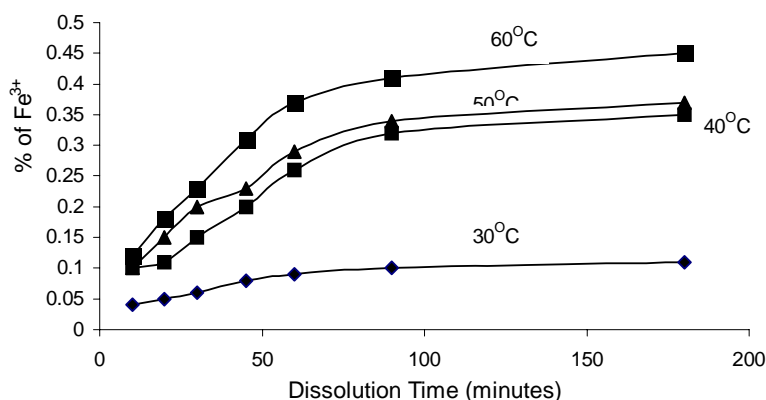


Fig.2: Percentage of Fe³⁺ dissolved versus dissolution time for Osogbo goethite in 0.1M HNO₃

There is either formation of passive oxide and metal films by strong O – containing acid such as HNO₃, which prevent interaction of protons with Fe³⁺ on the goethite surface or adsorption of NO₃ on the surface which inhibit dissolution of Fe oxide as predicted for hematite (Biber et al, 1994). There is a possibility of strong surface – metal oxyanion pairing with Fe³⁺ which result in the precipitation of insoluble Fe – NO₃ phase. Adsorption of anion extends the cross – link of the solid goethite thereby increasing resistance to proton - dissolution. Consequently, the dissolution effect is reduced when compared with HCl dissolution effect. It was similarly observed (Chiarizia and Horwitz, 1991) that higher HNO₃ concentration than HCl was necessary to bring about

comparable dissolution of synthetic goethite. This behaviour of HNO₃ can be compared with phosphate (PO₄) and arsenate (AsO₄) pairing with Fe³⁺ of goethite leading to formation of insoluble Fe(PO₄, AsO₄) phases (Eick et al, 1999). Although, oxyanions can inhibit or accelerate proton dissolution, depending on the type of surface complex formed and the bond strength. Previous spectroscopic evidences showed that bidentate-mononuclear complexes accelerate proton dissolution while binuclear surface complexes formations inhibit it (Eick et al, 1999). On account of the trend of dissolution results obtained, a binuclear surface complex formation is suggested for the adsorption of NO₃ on to the surface (Fig. 5).

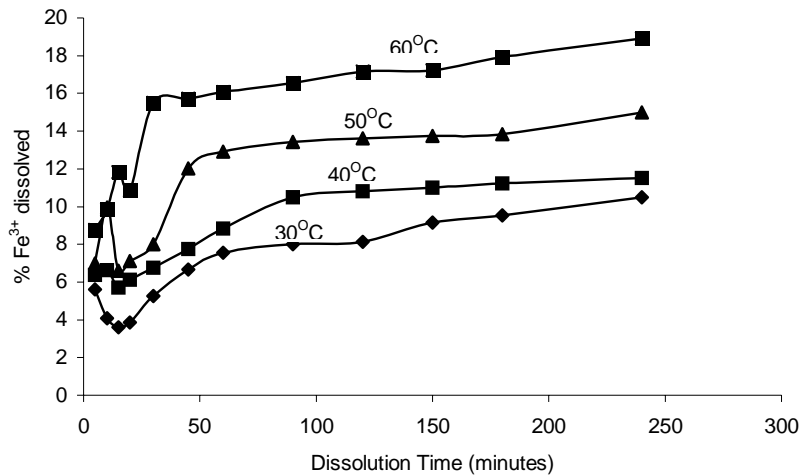


Fig.3: Percentage of Fe³⁺ dissolved versus dissolution time for Kaduna goethite in 0.1M HCl

The degree of dissolution of the goethite samples is also related to the relative stability of chloride or nitrate ions with Fe³⁺. The p_k value for FeCl²⁺ and FeNO₃²⁺ are 1.5 and 1.0 respectively, which conferred higher stability for NO₃⁻ on the goethite surface. When the Cl⁻ ion concentration in the aqueous phase increases, the pH is lowered and the acidity strength of the solution increases. This favours dissolution of goethite in HCl than HNO₃. The initial rapid release of Fe³⁺ is followed by a linear and constant dissolution. The dissolution rates were calculated from this portion of the curves (Eick et al, 1999). The kinetic behavior of proton – promoted of crystalline Fe (III) is thermodynamically controlled. When the solution approaches thermodynamic equilibrium, the dissolution rate decreases until it approaches zero (Liu et al, 2001). This account for the portion of the curves, which are almost horizontal to the time axes. There was no

appreciable increase in dissolution between 50°C and 60°C in Fig.1 and between 40°C and 50°C in Fig.2. Similar trend was not observed in Figs. 3 and 4. This difference may be attributed to the poor structural crystallinity of Kaduna goethite as revealed in an earlier characterization of the goethite samples (Ho and Ng, 2001). The macroscopic dissolution rate, k, depends on several microscopic rates, r_i,

$$K = \sum r_i \dots\dots\dots 1$$

While r_i depends on both the dissolution conditions in the reactor and the surface morphology of goethite structure. The micro – heterogeneity of goethite surface and consequently the heterogeneity of surface site energies are summed up in the macroscopic dissolution rate, k. The relationship between dissolution rate and temperature for goethite was described by the Arrhenius equation

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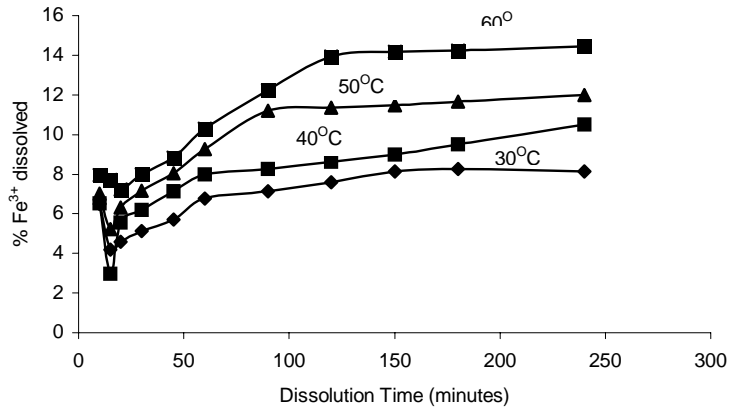


Fig. 4: Percentage of Fe³⁺ dissolved versus dissolution time for Kaduna goethite in 0.1M HNO₃

$$k = Ae^{-E_a/RT} \dots\dots\dots 2$$

Linearization of equation 2 gives

$$\ln k = \ln A - E_a/RT \dots\dots\dots 3$$

Where k = dissolution rate, A = frequency factor, E_a = activation energy, T = absolute temperature and R = gas constant. The value of E_a and A were calculated from the slope and intercept of ln k versus 1/T plots for each goethite sample. Figures 6 - 9 represent the Arrhenius plots.

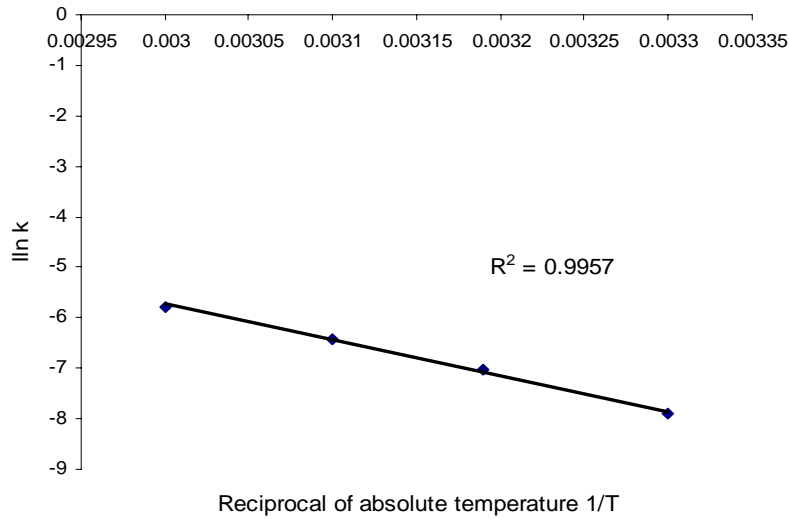


Fig 6. The plot of ln K against 1/T of 0.1M dissolution (Ogbomoso)

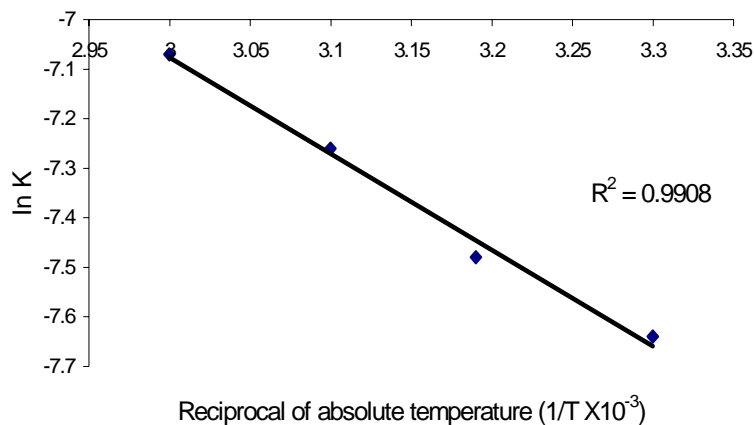
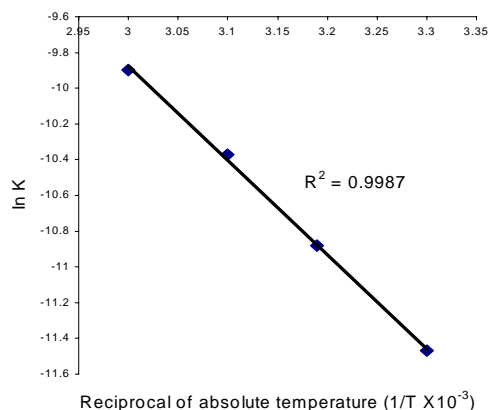


Fig 7. The plot of $\ln K$ against $1/T$ of 0.1M dissolution (Ogbomoso)



There are differences in the activation energy, E_a , values obtained for the different acid media and different further are the E_a values calculated for each goethite samples under similar experimental conditions. The E_a values of 66.11 and 82.43 kJmol^{-1} for Kaduna goethite in HCl and HNO_3 respectively were obtained while E_a values of 54.60 and 76.32 kJmol^{-1} obtained for Osogbo goethite in HCl and HNO_3 respectively. Differences in activation energy are generally related to bond strengths and in this case may be due to the relative weakness of the Fe^{3+} - O bond in goethite. Other contributing factors may include acid concentration, the number of reactive site on goethite, Cl/NO_3 adsorption factor, elemental substitution (Al) for Fe and impurity associated with each goethite sample. The E_a and A values for Osogbo and Kaduna goethite samples are given in Table 2.

Table2: Activation energies and frequency factors for Osogbo and Kaduna goethite in HCl and HNO_3 .

Sample	Acid	E_a kJ/mol	$A \times 10^{-4}$
Osogbo	0.1M HCl	13.05	5.0
Kaduna	0.1M HCl	15.80	8.50
Osogbo	0.1M HNO_3	18.24	30.9
Kaduna	0.1M HNO_3	19.70	11.17

Conclusion: The Nigerian goethite dissolution in HCl and HNO_3 at concentrations level studied was found to be a simple chemical process. The HCl produces accelerated dissolution than HNO_3 under the same experimental conditions. In case these acids are needed for regeneration or desorption experiments, the concentrations used are mild enough and will produce minimal loss of goethite samples based on the percentage of Fe^{3+} dissolved per g- goethite.

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