

## HETEROGENEOUS Fe(II) OXIDATION AND ZETA POTENTIAL

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### Abstract

Zeta potential was used as a tool alongside kinetic experiments to delineate between three plausible mechanisms for the heterogeneous oxidation of Fe(II) by dissolved oxygen. One of these mechanisms is dependant on the positive surface charge that exists on Fe(III)oxyhydroxide surfaces at pH values below the Iso-Electric Point (IEP). However, this mechanism can be disputed as, in the presence of bicarbonate alkalinity typical of many UK mine waters, catalysis is still observed at pH 6.5 despite an IEP shift from pH 8 to 4. As well as an IEP shift an overall reduction of the zeta potential is observed that may have beneficial effects to particle coagulation, settling and permeability characteristics in passive mine water treatment systems.

### Introduction

The abiotic oxidation of Fe(II) by dissolved oxygen can proceed along two parallel pathways, firstly homogeneous oxidation in a solution containing no surfaces and secondly via heterogeneous oxidation in a suspension. In a homogeneous solution the Fe(II) oxidation rate greatly increases with hydrolysis of the Fe(II) ion due to an increase in the reduction potential (see Table 1). For this reason the rate of homogeneous oxidation is highly pH dependant, (Millero, 1985; Wherli, 1990).

**Table 1. Second order rate constants and redox potentials for Fe(II) species (after Wherli, 1990).**

Fe(II) <sub>i</sub> Species	pH range at which rate dominated by species	E° (V)	2 <sup>nd</sup> order rate constant (k <sub>i</sub> ) M <sup>-1</sup> sec <sup>-1</sup>	Composite homogeneous rate Law
Fe <sup>2+</sup>	<3.5	0.771	7.9x10 <sup>-6</sup>	$R = \frac{d[\text{Fe(II)}]}{dt} = (\sum k_i [\text{Fe(II)}]_i)[\text{O}_2]$
FeOH <sup>+</sup>	3.5 – 5	0.34	25.1	
Fe(OH) <sub>2</sub>	>5	-0.02	7.94x10 <sup>+6</sup>	

[ ] is the molar (M) concentration, R is the Fe(II) oxidation rate in M sec<sup>-1</sup>, k<sub>i</sub> is the 2<sup>nd</sup> order rate constant for the oxidation of Fe(II) by O<sub>2</sub> in M<sup>-1</sup> sec<sup>-1</sup>, t denotes the time in sec and E° is the standard reduction potential.

In a heterogeneous suspension, Fe(III)oxyhydroxide surfaces are well known to catalyse the oxidation of Fe(II), (Tamura et al., 1976; Sung and Morgan, 1980; Tufekci and Sarikaya, 1996; Park and Dempsey, 2005). However, the mechanisms behind the observed catalytic behaviour are not fully understood; three reaction models have been presented in the literature and are described below.

1) Counter-ion mechanism (Tufekci and Sarikaya, 1996): Fe(III)oxyhydroxide surfaces are amphoteric in nature and carry a surface charge dependant on specifically chemisorbed ions. Electric Double Layer (EDL) theory describes how this charge generates an electrostatic potential in contact with a solution that declines rapidly away from the surface. EDL theory also assumes that an excess of counter-ions (ions of opposite charge) exist near the surface (Langmuir, 1997). Below a pH of about 8, Fe(III)oxyhydroxides typically have a positive surface charge (Dzombak and Morel, 1990). Therefore an elevated concentration of OH<sup>-</sup> counter-ions will form near the surface, locally shifting the Fe(II) speciation equilibrium in favour of the faster oxidising FeOH<sup>+</sup> and Fe(OH)<sub>2</sub><sup>0</sup> species.

2) Reactive surface species mechanism (Tamura et al., 1976; Wherli, 1990; Liger et al., 1999): Chemisorption of Fe(II) at the Fe(III)oxyhydroxide surface enhances its reactivity in electron transfer reactions in the same way that hydrolysis promotes electron transfer in dissolved Fe(II).

3) Semiconductor mechanism (Park and Dempsey, 2005 and references therein): Fe(III)oxyhydroxide can act as a semiconductor in the presence of adsorbed Fe(II) due to electron transfer with the underlying Fe(III). The surface then acts as an electrode where surface sites with strongly adsorbed Fe(II) become electron rich (anodes) and sites without adsorbed Fe(II) become electron-poor (cathodes). O<sub>2</sub> is thus reduced at anode sites whilst Fe(II) is oxidized at cathode sites. In this mechanism both dissolved and adsorbed Fe(II) is required to produce a catalytic effect and the adsorbed portion of the Fe(II) remains un-reacted.

The aim of this study is to distinguish between the applicability of each of these mechanisms via kinetic and zeta potential (ζ) analysis. ζ is the potential drop that exists within the EDL between the shear plane and the bulk solution, (Eckenfelder, 2000). Due to a number of assumptions that must be invoked and problems with results

interpretation,  $\zeta$  can not be directly related back to the magnitude of the surface potential (Dzombak and Morel, 1990) but in most cases gives a definite measure of its sign and the pH of the Point of Zero Charge (pHPZC) or Iso-Electric Point (IEP). It was decided to use zeta potential ( $\zeta$ ) as a tool in this investigation because the counter-ion mechanism described above is dependant on the sign and possibly the magnitude of the surface charge.

## Method

Kinetic experiments were undertaken to compare homogeneous and heterogeneous Fe(II) oxidation rates. Oxidation experiments were run in 1L Pyrex water jacketed reaction vessels and the reaction temperature maintained at 25°C  $\pm$  0.1°C. pH and temperature were monitored throughout the oxidation run and logged automatically via a PC. Dissolved O<sub>2</sub> was maintained at 8.5 mg/L ( $\pm$  0.5 mg/L) via gas bubbling with a balance of N<sub>2</sub> and CO<sub>2</sub>, pH buffering was achieved using a HCO<sub>3</sub><sup>-</sup> / CO<sub>2(g)</sub> buffer system and was maintained to  $\pm$  0.05 pH units by carefully adjusting the flow of CO<sub>2</sub> and N<sub>2</sub>. In heterogeneous experiments 200 mg/L of synthetic goethite (Bayferrox 930, Lanxess, Germany) was added to the reaction mixture. An oxidation experiment was initiated by adding an aliquote of anoxic Fe(II) stock solution. Samples were withdrawn at predetermined intervals and analysed spectrophotometrically for dissolved and total Fe(II) in accordance with a previously published method (Park and Dempsey, 2005). By subtracting the dissolved Fe(II) portion from the total Fe(II) portion it was then possible to ascertain a theoretical adsorbed Fe(II) concentration. Pseudo 1<sup>st</sup> order rates were observed for [Fe(II)<sub>dissolved</sub>] at constant [O<sub>2</sub>] and pH in accordance with equation 1.

$$R = -d[\text{Fe(II)}_{\text{dissolved}}]/dt = k'[\text{Fe(II)}_{\text{dissolved}}] \quad (1)$$

where [ ] is the molar (M) concentration, R is the Fe(II) oxidation rate in M sec<sup>-1</sup>, k' is the pseudo 1<sup>st</sup> order rate constant in sec<sup>-1</sup> and t denotes the time in sec. Values of k' were determined from the slopes of first order plots in which the natural logarithm of the [Fe(II)<sub>dissolved</sub>] at t = n over [Fe(II)<sub>dissolved</sub>] at t = 0 is plotted against time.

Running in parallel to this laboratory based study has been the development of a Vertical Flow ochre accretionary Reactor (VFR) at the Taff Merthyr mine water treatment scheme in South Wales (UK). The VFR is a passive mine water treatment system in which effluent is passed through an ochre bed. It accomplishes highly efficient iron removal due to self filtration of suspended particles and by heterogeneous oxidation of Fe(II) (see Sapsford et al., 2007). For this reason it was decided to compare field and synthetic Fe(III)oxyhydroxides. Zeta potential ( $\zeta$ ) titrations were carried out on samples of field Fe(III)oxyhydroxide collected from the Taff Merthyr site and also samples of Bayferrox 930 (see Table 2). The Bayferrox had been previously washed with 0.1 M NaOH and HNO<sub>3</sub> before rinsing several times to remove any specifically adsorbed contaminants. Samples were titrated with 0.1 M HNO<sub>3</sub> in 500 ml polyethylene beakers and pH was monitored with a Mettler Toledo Seven multi meter and combination glass electrode. At the required pH, samples were removed for determination of the  $\zeta$  using a Malvern Instruments Zeta Sizer Nano.

**Table 2. Solids characterisation.**

	Method	Units	Field Ochre	Bayferrox 930
Mineralogy	XRD		2-line Ferrihydrite	Goethite
Expected stoichiometry			Fe <sub>2</sub> O <sub>3</sub> ·0.5(H <sub>2</sub> O)	FeOOH
Formula weight		g/mol	169	89
Surface area	BET	m <sup>2</sup> /g	244 <sup>a</sup>	14
pH IEP	Electrophoresis	pH	8.29 <sup>a</sup>	8
Elemental analysis – HF + HCl + HNO <sub>3</sub> digest				
Fe	ICP-OES	% w/w	82.86 as Fe <sub>2</sub> O <sub>3</sub>	94.36 as FeOOH
SiO <sub>2</sub>	ICP-OES	% w/w	13.39	5.57
CaO	ICP-OES	% w/w	2.09	0.06

<sup>a</sup>Liger et al (1999)

Bayferrox 930 was first titrated in indifferent NaNO<sub>3</sub> electrolytes (0.1, 0.01 and 0.001 M) and  $\zeta$  readings were taken at 0.25 pH unit intervals. A further group of tests were carried out to see the effect of HCO<sub>3</sub><sup>-</sup> on the  $\zeta$  of the Bayferrox sample; to do this fixed pH spot  $\zeta$  measurements were taken in a 0.006 M NaHCO<sub>3</sub> solution and pH was kept constant via CO<sub>2</sub> bubbling. Field Fe(III)oxyhydroxide was titrated unwashed in water collected from the same site with the mean chemical composition as shown in Table 3. The minewater is characterised by high

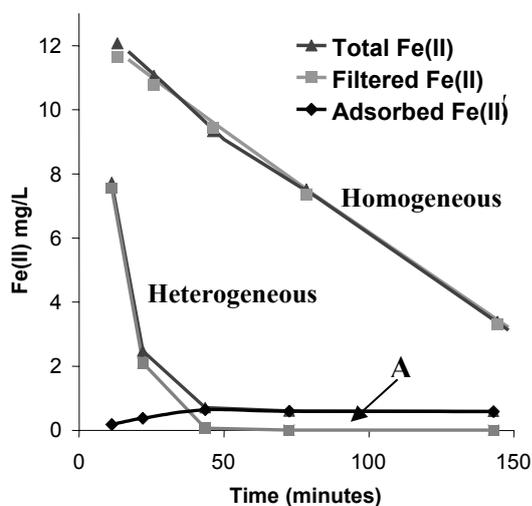
bicarbonate alkalinity and fairly high sulphate, Ca and Mg concentrations typical of many circum-neutral discharges.

**Table 3. Typical Taff Merthyr mine water composition.**

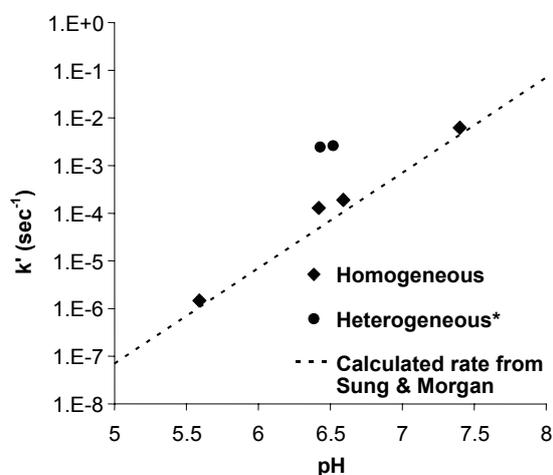
Analyte	Units	Concentration
pH		6.7
Conductivity	$\mu\text{S/cm}$	880
Alkalinity	mg/L (as $\text{HCO}_3^-$ )	528
Fe(II)	mg/L	7.3
Ca	mg/L	100
Mg	mg/L	42
K	mg/L	12.5
Na	mg/L	12.7
Si	mg/L	4.4
$\text{SO}_4^{2-}$	mg/L	220
Cl	mg/L	10

## Results and Discussion

Figure 1 compares the reaction profile of homogeneous and heterogeneous iron oxidation in the presence of 8.5 mg/L  $\text{O}_2$  at 25°C, pH 6.5 and with 200 mg/L Fe(III)oxyhydroxide solids in the heterogeneous run. Heterogeneous oxidation is significantly faster and this is reflected in the order of magnitude difference in  $k'$  displayed in Figure 2 for homogeneous ( $1.9 \times 10^{-4} \text{ sec}^{-1}$ ) and heterogeneous ( $2.5 \times 10^{-3} \text{ sec}^{-1}$ ) oxidation. Also evident from Figure 1 is the residual surface-bound Fe(II) (point A, Figure 1) that appears to be an unsuitable reducing agent for  $\text{O}_2$ . Experimental homogeneous rates are in good agreement with Sung and Morgan's (1980) empirically derived rate constant in the circum neutral pH range (see Fig. 2).



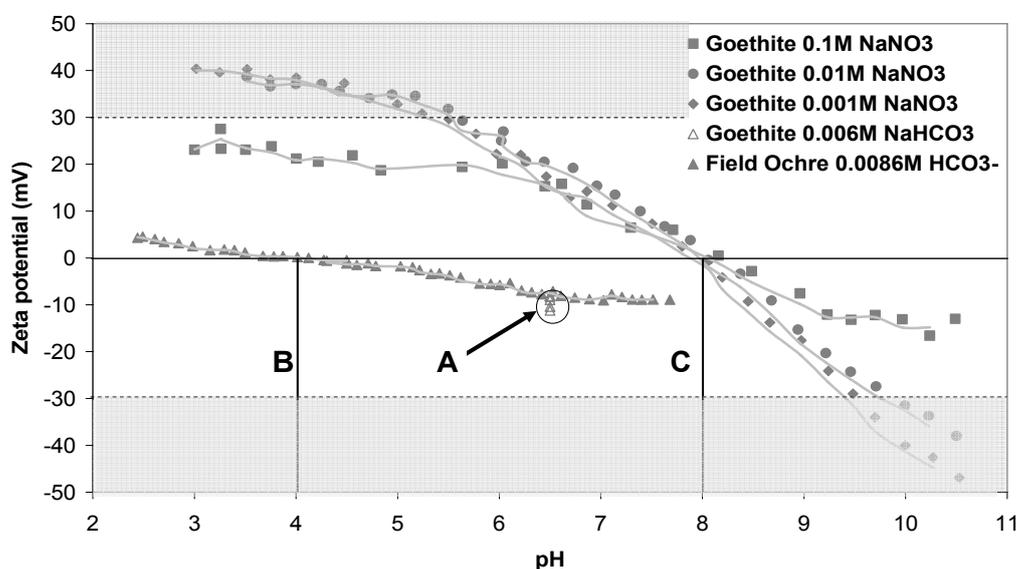
**Figure 1. Reaction profile for heterogeneous and homogeneous oxidation at 25°C, pH 6.5, 8.5 mg/L  $\text{O}_2$  and 200 mg/L Fe(III) in heterogeneous experiment.**



**Figure 2. Pseudo 1<sup>st</sup> order rate constants calculated for the oxidation of Fe(II) at 25°C and 200 mg/L Fe(III) in the heterogeneous experiments. Dotted line indicates homogeneous rate predicted using Sung and Morgan (1980) rate constant.**

The results of the kinetic experiments are consistent with the results of Park and Dempsey (2005), which show a portion of residual Fe(II) remaining on the surface and therefore support the semiconductor model. However, Zhang et al. (1992) found evidence for two surface Fe(II) species ( $\equiv\text{FeOFe}^+$  and  $\equiv\text{FeOFeOH}$ ) of which Liger et al. (1999) found only the  $\equiv\text{FeOFeOH}$  species to be an effective reducing agent for U(VI). If this is the same for the reduction of  $\text{O}_2$  then it would be expected that a residual  $\equiv\text{FeOFe}^+$  species would remain un-reacted on the surface. If surface equilibrium is presumed to be rapid it would be expected that residual surface Fe(II) would be quickly cycled through the reactive  $\equiv\text{FeOFeOH}$  species and diminish. However, Dzombak and Morel (1990)

state that there are both strong and weak sites for the adsorption of divalent cations, significant hysteresis may be observed in the cycling of strong site  $\equiv\text{FeOFe}^+$  through the weak site  $\equiv\text{FeOFeOH}$  reactive species. Preliminary modelling using PHREEQC geochemical software in the present study has shown that at pH 6.5 the  $\equiv\text{FeOFeOH}$  species makes up only 10% of the total adsorbed Fe(II) with strong site  $\equiv\text{FeOFe}^+$  making up 60%. Therefore the adsorbed Fe(II) detected in this study and in the study by Park and Dempsey (2005) may be an artefact of the strong site  $\equiv\text{FeOFe}^+$  species thus supporting the reactive surface species mechanism. These results equally support the counter-ion mechanism if it is assumed that all chemisorbed Fe(II) is un-reactive and that all oxidation proceeds in the near surface EDL. Therefore, using these results alone it is not possible to discount any of the above models. By employing  $\zeta$  measurements it has been possible to get a better understanding of the counter-ion model. Point A on Figure 3 shows the  $\zeta$  measured for Bayferrox under reaction conditions of the heterogeneous kinetic experiments. The results show that the  $\zeta$  is -10 mV. As a positive  $\zeta$  is required for the counter-ion mechanism this evidence effectively discounts the mechanism as plausible under these experimental conditions. It should also be noted that the field Fe(III)oxyhydroxide titrated in Taff Merthyr mine water had an IEP of pH 4 (see point B on Fig. 3) discounting the possibility of the counter-ion mechanism operating in the VFR.



**Figure 3. The variation in  $\zeta$  with pH for field ochre and synthetic goethite.**

Titration of the washed Bayferrox in an indifferent electrolyte gave both a Common Intersection Point (CIP) and the IEP at pH 8 (see Fig. 3, point C), 4 pH units higher than the field Fe(III)oxyhydroxide. It is also assumed that the Bayferrox titrated in 0.006 M  $\text{NaHCO}_3$  solution also shares a similar IEP to the field Fe(III)oxyhydroxide.  $\text{NaHCO}_3$  seems to be responsible for the shift in IEP for the Bayferrox and it can be assumed that the high  $\text{HCO}_3^-$  concentration in the Taff Merthyr mine water (see Table 3) may also be responsible for the low IEP of the field Fe(III)oxyhydroxide.

$\zeta$  values greater than  $\pm 30$  mV are generally taken to give stable sols. The sol becomes increasingly unstable and the likelihood of coagulation and settling increases as  $\zeta$  approaches zero. These stability regions have been marked in Figure 3 by light grey shading. It is evident from Figure 3 that the  $\zeta$  for Bayferrox in 0.006 M  $\text{NaHCO}_3$  is lowered to within the instability region. Dempsey (1995) demonstrated, although in an oversimplified view (see Bullen, 2006), that in active mine water treatment using the High Density Sludge (HDS) process, that the lowest density sludge is often produced when  $\zeta$  is closest to zero and the primary precipitate is destabilised forming dendritic flocs. In passive treatment however a low  $\zeta$  will enhance coagulation and settling rate in a traditional settling lagoon but will also help to maintain a high surface area and bed permeability in a VFR system.

## Conclusions

This study has shown that heterogeneous catalysis is apparent in the absence of a positive surface charge making the diffuse layer mechanism unlikely under the conditions of this laboratory study and at the Taff Merthyr site.

However, this mechanism is still feasible under conditions where a positive surface charge would occur e.g. under acidic pH and where the chemisorption of Fe(II), which the alternative mechanism depend on, is negligible.

Mine water chemistry has a large impact on both the magnitude of the  $\zeta$  and its IEP. The current results have shown that the Taff Merthyr mine water, typical of many circum neutral discharges significantly lowers the pH of the IEP and also suppresses the  $\zeta$  of the field Fe(III)oxyhydroxide. The shift in the IEP is likely due to the specific adsorption of the potentially determining  $\text{HCO}_3^-$  ion.

Suppression of the  $\zeta$  of particulate Fe(III)oxyhydroxide by typical circum-neutral mine waters may be beneficial to passive treatment enhancing coagulation and settling in typical settling lagoons and by maintaining high surface area and bed permeability in VFR systems. For these reasons, the measurement of  $\zeta$  and the IEP should be included as a useful tool in the characterisation of mine discharges to help in the design of future treatment schemes.

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