

Boehmite Sorbs Perrhenate and Pertechnetate

Peng-Chu Zhang*, James L. Krumhansl, and Patrick V. Brady

MS-0750, Sandia National Laboratories

Albuquerque, New Mexico 87185

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Abstract

Boehmite and Al-oxyhydroxide gels sorb ReO_4^- , a non-radioactive analogue of TcO_4^- from NaNO_3 solutions. Sorption appears to be substantially electrostatic (though there appears to be a specific preference for ReO_4^- over NO_3^-) and is most effective at $\text{pH} < 8$. Measured K_d 's lie between 5 and 105 ml g^{-1} , depending on the solid, pH, and ionic strength. ReO_4^- and TcO_4^- are both partially removed from high pH Hanford-type acid waste simulants upon neutralization and formation of Al-rich sludges. We therefore propose that sequestration of Tc by boehmite limits dissolved Tc levels in some Hanford tanks, and that boehmite might be relied on as a backfill, or reactive barrier, to limit environmental transport of Tc.

* Corresponding author phone: (505) 844 2669; fax: (505) 844 7354; email: pzhang@sandia.gov

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Introduction

Technetium is a common component of nuclear wastes and is of environmental concern because it is generally mobile in groundwaters and has a relatively long half life (2.1×10^5 years). In near surface environments, Tc typically exists in its oxidized form as pertechnetate, TcO_4^- . Because of its relatively large ionic radii and small negative charge density, TcO_4^- , negatively charged soil matrices rarely attract and retard TcO_4^- (1-3). Moreover, TcO_4^- forms no insoluble solids (1) that would limit transport in nature.

Recent studies of tank sludges at the Hanford Reservation indicate high levels of solids-associated Tc (4) suggesting formation of insoluble, or strongly sorbed, Tc. One possibility is that organic components in the tank fluids reduce TcO_4^- to insoluble TcO_2 (2). However, the high nitrate and ferric iron content of the tank fluids point to oxidizing conditions, and instead suggest that some sludge component sorbs TcO_4^- . Tank sludges are predominantly composed of hydrous oxy-hydroxides of iron and aluminum. Except for inner sphere complexes of PO_4^{3-} , CrO_4^{2-} , SeO_3^{2-} , and AsO_4^{3-} , iron oxy-hydroxides are not known to sorb anions. Al hydroxides, however, are known to attract anions, though uptake is apparently non-specific and is greatest at pH's less than 9.2, the point of zero charge in dilute fluids (5). Anions sorb to aluminum hydroxide gels in roughly the order: phosphate > carbonate > sulfate > chloride = nitrate (6-9).

We hypothesize that aluminum oxyhydroxide and boehmite [$\text{AlO}(\text{OH})$] removed pertechnetate from the waste storage tank solutions. We confirm this by measuring

adsorption of ReO_4^- , a non-radioactive analogue for TcO_4^- (possessing similar charge, radius and structure), on well crystalline boehmite or an amorphous aluminum oxyhydroxide. Subsequent confirmation of appreciable uptake was made with TcO_4^- . We therefore propose that aluminum hydroxides in general, and boehmite in particular, should be considered as reactive components of engineered chemical backfills and reactive barriers designed to limit the transport of pertechnetate into the environment.

Materials and Methods

Pertechnetate adsorption on aluminum hydroxides was measured on two phases: a well crystalline boehmite [$\text{AlO}(\text{OH})$] and an aluminum gel. Boehmite was prepared by heating a commercial aluminum hydroxide [$\text{Al}(\text{OH})_3 \cdot n\text{H}_2\text{O}$] (Fisher Scientific), which has a typical gibbsite structure as demonstrated by its XRD pattern (Figure 1a), in an oven at 240°C for 24 hours. The only mineral identified by XRD from the heated aluminum hydroxide (which lost about 20% of its original weight from water during the period of heating) was a well crystallized boehmite as shown by the characteristic peaks (Figure 1b). Before use the mineral was passed through a 200 mesh (pore diameter = 0.043 mm) sieve.

Aluminum gel was prepared by titrating a 1.0 N NaOH solution into a 0.1 N $\text{Al}(\text{NO}_3)_3$ solution to pH 9 under vigorous stirring. After the pH stabilized, the suspension was aged in an incubator at 90°C for two days. The pH of the suspension was periodically checked and adjusted as necessary during incubation. The suspension was subsequently dialyzed in a dialysis tube in a deionized water bath. The water was

changed daily until the dialysis solution was free of NO_3^- as measured by a nitrate test strip.

A $0.001 \text{ mol L}^{-1} \text{ ReO}_4^-$ stock solution was prepared by dissolving 0.289 g of KReO_4 in 1.00 L of deionized water. Re in solution was measured using a directly coupled plasma spectrophotometer (DCP). Rhenium DCP standards were prepared from dilution of 1010 mg L^{-1} standard atomic absorption Re solution (Fisher Scientific).

Methods:

1. Adsorption on Boehmite

a. Effect of pH on adsorption

One liter (1.00 L) of boehmite suspension, with a solid concentration of 30.0 g L^{-1} , was made by combining 0.50 L of the Re stock solution ($0.001 \text{ mol Re L}^{-1}$), 0.50 L of 0.001 N NaNO_3 solution, and 30.0 g of boehmite. The suspension was stirred with a magnetic bar while the pH was adjusted with a 0.1 N HNO_3 solution. The pH range tested in this study was 5.0 to 9.6. When the desired pH was obtained, two 20.0 ml of suspension were taken and placed into two 40 ml covered polyethene bottles. The suspensions in the bottles were then agitated on a shaker at the rate of 100 rpm for 18 hours. The pH in each suspension was measured after shaking. The final pH's generally shifted less than 0.5 units from the starting pH. The solids from the suspension were then separated using a $0.1 \mu\text{m}$ membrane and syringe apparatus. Filtrates were analyzed for Re and the amount of Re removed is calculated from the difference between initial Re concentration, $5 \times 10^{-4} \text{ mol L}^{-1}$, and the concentration in the filtrate.

b. Effect of ionic strength on adsorption

In a parallel series of tests, the ionic strength was adjusted with a 1.0 N NaNO_3 solution to 0.0005, 0.001, 0.005, 0.05 and 0.10 M. The initial pH was adjusted at 5.8 for all tested samples and the final pH values almost uniformly shifted to the range of 6.2-6.4. The ReO_4^- concentration was $5 \times 10^{-4} \text{ mol L}^{-1}$. Duplicates were run and Re uptake determined as described above.

c. Effect of solid/liquid ratios on adsorption

Boehmite concentrations of 1.0, 5.0, 15.0, 30.0 and 60.0 g L^{-1} were used and Re uptake measured from a $5 \times 10^{-4} \text{ mol L}^{-1}$ Re solution. The ionic strength was 1×10^{-3} M and the pH was in the range of 5.7 (initial) to 6.0 (final).

2. ReO_4^- Adsorption on Aluminum Gel

An aliquot of dialyzed aluminum gel was pipetted into a 25 ml polyethene bottle containing a 0.001 M KReO_4 solution. Suspension pHs were adjusted with 0.1 N HNO_3 and 0.1 N NaOH solutions. After 18 h shaking, the suspensions were centrifuged and the liquid phase passed through a 0.1 μm membrane. For some suspensions, the ultrafiltration membrane cones (Micon) were used to separate solid and liquid under centrifugation. The solid concentration was determined from the dry weight of 10 ml of the aluminum gel.

Results and Discussion

1. Adsorption of ReO_4^- on Boehmite Surface

Adsorption of ReO_4^- on boehmite is pH dependent and decreases with increasing pH (See figure 2). Approximately 80% and of the added ReO_4^- ($5 \times 10^{-4} \text{ mol L}^{-1}$, or 93 mg Re L^{-1}) was removed from the liquid phase at pH 5.4. Adsorption of ReO_4^- gradually decreases with pH and at pH 9, adsorption is minimal. Although the point of zero charge (PZC) of boehmite was not measured, the PZC of boehmite and pseudo-boehmite has been reported to be about 8.7 - 9.2 (10). The ReO_4^- adsorption isotherm observed in this study is broadly consistent with previously observed anion uptake reported in literature.

The distribution coefficient (K_d , ml g^{-1}), which is widely applied in models for contaminant transport in subsurface, is the ratio of concentrations of solute sorbed on the surface and in the liquid phase and can be calculated from:

$$K_d = (C_{\text{ini}} - C_{\text{eq}})V / (SC_{\text{eq}}) \quad (1)$$

where C_{ini} is the initial ReO_4^- concentration, C_{eq} is the ReO_4^- concentration at equilibrium, V is the volume of suspension (ml) and S is the amount of boehmite solid in the suspension (g). Measured K_d values are plotted in Figure 3. The high K_d values at the slightly acidic and neutral pH conditions indicate a high capacity of boehmite to retard ReO_4^- . On the basis of electrostatic considerations, one might also expect even greater pertechnetate uptake under the same conditions since TcO_4^- has a slightly smaller ionic radii and higher charge density which should allow more ready access to the positively charged boehmite surface.

Nitrate ion competition with ReO_4^- is significant, and is shown in Figure 4a. Under identical initial ReO_4^- concentration ($5 \times 10^{-4} \text{ mol L}^{-1}$), solid concentration (30 g L^{-1}), and pH - 6.2(± 0.2), the amount of ReO_4^- adsorbed on boehmite decreases from

8.10(± 0.25) to 2.22(± 0.18) $\mu\text{mol g}^{-1}$ when $[\text{NO}_3^-]$ changes from 1.00×10^{-3} to 0.1 mol L^{-1} . Correspondingly, the K_d decreases from 31.64(± 1.97) to 5.13(± 0.47) ml g^{-1} .

Although NO_3^- competition measurably decreases ReO_4^- adsorption, the competition is not stoichiometric (See figure 4b). Instead, ReO_4^- uptake is preferred. Note that a 2 order of magnitude increase in nitrate levels causes less than a factor of 7 decrease in ReO_4^- K_d 's (Adsorption of NO_3^- was not actually measured, partially because a HNO_3 solution was used to adjust pH).

Increasing the boehmite to solution ratio increases the amount of ReO_4^- sorbed (see Figure 5a). ReO_4^- adsorption, calculated on a per gram of boehmite basis, actually decreases though. One explanation may be that the maximum adsorption capacity of the boehmite was not reached in the experiments. This conclusion can be drawn indirectly from Figure 5b which shows that K_d 's decrease with increasing solid/liquid ratio. In the low solid concentration system, there is less likelihood of solid particle aggregation, and there is more opportunity for aggregated solids to separate. Therefore, the surface area per unit weight of boehmite exposed to the solution is likely to be larger at low solids concentration, which would enhance ReO_4^- adsorption. The opposite effect is expected in the higher solid system. In fact, K_d 's are not that sensitive to the solid/liquid ratio when the solid concentration is equivalent to, or higher than, 15 g L^{-1} .

II. Sorption of ReO_4^- on Aluminum Oxyhydroxide Gel

From our measurements it is impossible to unambiguously identify a ReO_4^- sorption mechanism for Al-O gels. The Al-O gel did not have distinguishable particle characteristics; tended to dissolve at $\text{pH} < 5$; formed a new phase at $\text{pH} > 8$; and was

almost impossible to separate from solution by filtration (instead high speed centrifugation was used). Because of the accumulated experimental uncertainties, we will only discuss sorption in a semi-quantitative fashion without attributing the sorption to any specific mechanism. Table 1 gives ReO_4^- K_d 's for Al-O gels.

Table 1. Sorption of ReO_4^- on the Aluminum Oxyhydroxide Gel, pH = 7.1-7.3, background electrolyte $\text{NaNO}_3 = 0.001 \text{ mol L}^{-1}$.

Solid/Liquid	Re sorbed (mg g^{-1})	Total Volume (ml)	Final Re Conc. (mg L^{-1})	K_d (mL g^{-1})
2/150	0.51	15	20.3	23.6
2/150	0.44	15	20.9	20.8
1/100	0.71	10	32.9	21.9
1/100	0.74	10	32.6	22.7
1/500	1.45	50	13.1	110.7
1/500	1.40	50	13.2	106.1

III. Application to Tank Sludges

The Re uptake results outlined above strongly suggest that sorption onto Al-oxyhydroxides may be one cause for the high Tc content of Hanford tank sludges. They also point to reliance on Al-oxyhydroxides as a potential method for immobilizing Tc in natural groundwater systems. To further test the tank immobilization hypothesis, five synthetic tank sludges were made by neutralizing the five Hanford-type simulant acidic reprocessing fluids (4). Prior to neutralization the fluids were individually doped with

ReO_4^- (40.0 ppm Re), TcO_4^- (1.0 ppm Tc) and SeO_4^{2-} (40.0 ppm Se). Because Al and Fe are the principal sludge components the recipes are tabulated as molar ratios in Table 2 (although the high pH dictates that an appreciable fraction of the Al remained in the solution).

(Insert Table 2 here)

Two things are immediately evident from Table 2, the most important being that TcO_4^- behavior mirrors, at least semiquantitatively, that of ReO_4^- . It is also evident that significant anion removal only occurs in the synthetic sludges rich in aluminum. X-ray diffraction confirmed that boehmite was the principal component of the high pH aluminum sludges.

From the ReO_4^- results described earlier one might also infer that both the high pH and nitrate content of the fluids would preclude retaining sorbed anions in the final fluids. However, the Al-oxy-hydroxide precipitates formed as the solutions changed from being mildly acidic to slightly basic. In this pH range there is a significant potential for anion sorption and subsequent occlusion. We hypothesize that SeO_4^{2-} , ReO_4^- and TcO_4^- sorbed onto freshly formed surfaces at this time and were occluded by further Al-O-OH precipitation, and thus prevented from subsequently desorbing into high pH solutions.

Acknowledgements

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Table 2. Sequestration of Tc by Simulated Hanford Tank Sludge

Waste	Al/(Al+Fe)	Fe/(Al+Fe)	Zr/(Al+Fe)	Bi/(Al+Fe)	Cr/(Al+Fe)	Ni/(Al+Fe)	% Re	% Tc	% Se
Stream							Sorbed	Sorbed	Sorbed
Bi-phosphate	0.72	0.28	2.6×10^{-3}	0.1	2.7×10^{-2}	1.4×10^{-2}	0	0	0
U-recovery	0	1.0	0	0	7.0×10^{-2}	3.5×10^{-2}	0	0	0
REDOX	0.96	0.04	0	0	6.1×10^{-2}	3.5×10^{-2}	20	33	29
Purex-Al clad	0.87	0.13	3.3×10^{-3}	0	8.7×10^{-2}	1.1×10^{-2}	40	28	35
Purex-Zr clad	0	1.0	2.5	0	8.5×10^{-2}	3.7×10^{-2}	0	0	0

Title of Figures

Figure 1. XRD patterns for: a. Aluminum hydroxide or gibbsite; b. Boehmite [$\text{AlO}(\text{OH})$]; and c. Synthetic aluminum oxyhydroxide gel. The aluminum oxyhydroxide gel has a structure of poorly crystallized boehmite.

Figure 2. Removal of perrhenate by boehmite under various pH's.

Figure 3. Distribution coefficient (K_d) of perrhenate in the boehmite suspension as a function of pH.

Figure 4. Effect of NO_3^- (as a competing anion) concentration on removal of perrhenate by boehmite (a) and K_d (b).

Figure 5. Effect of boehmite solid concentration on removal of perrhenate (a) and K_d (b).

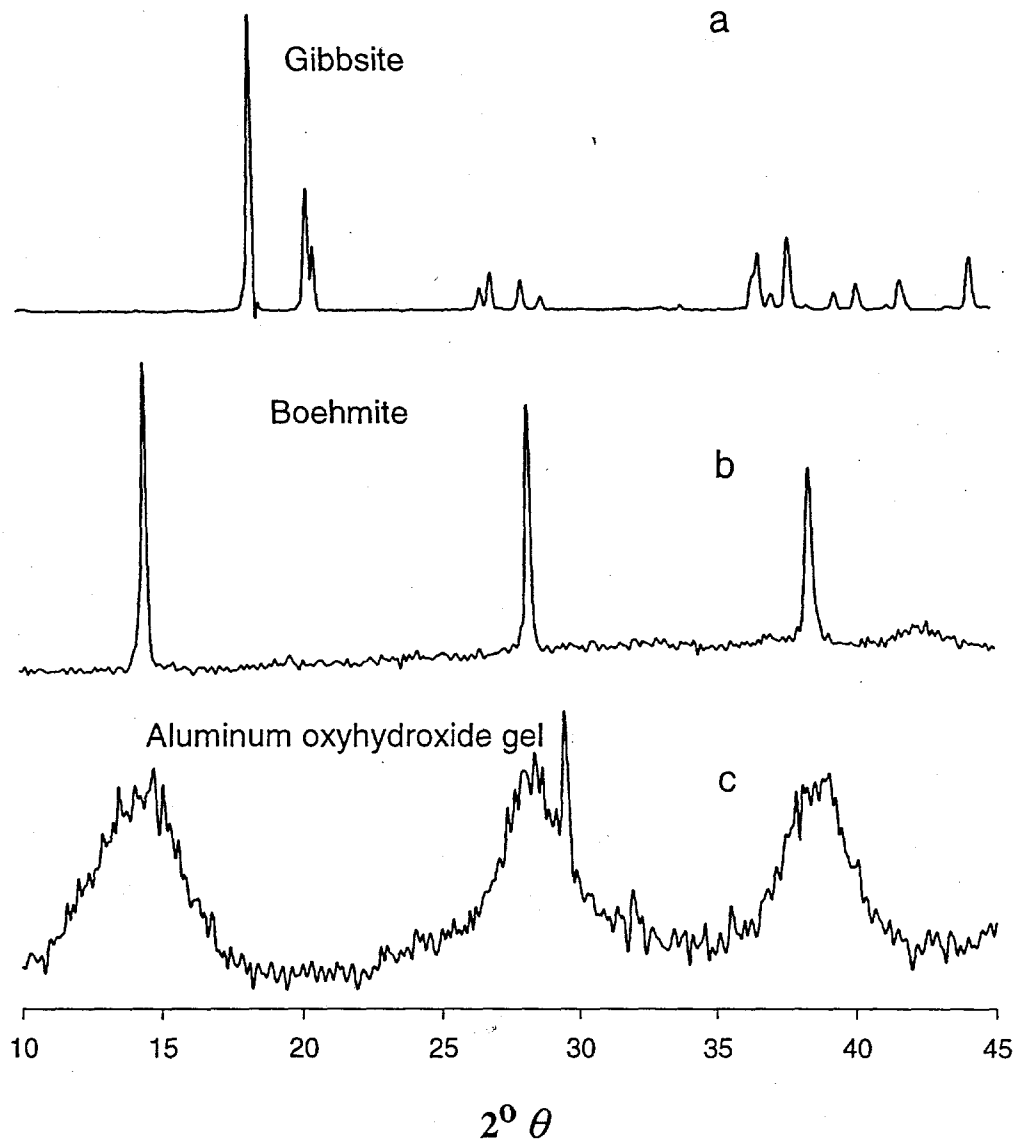


Figure 1

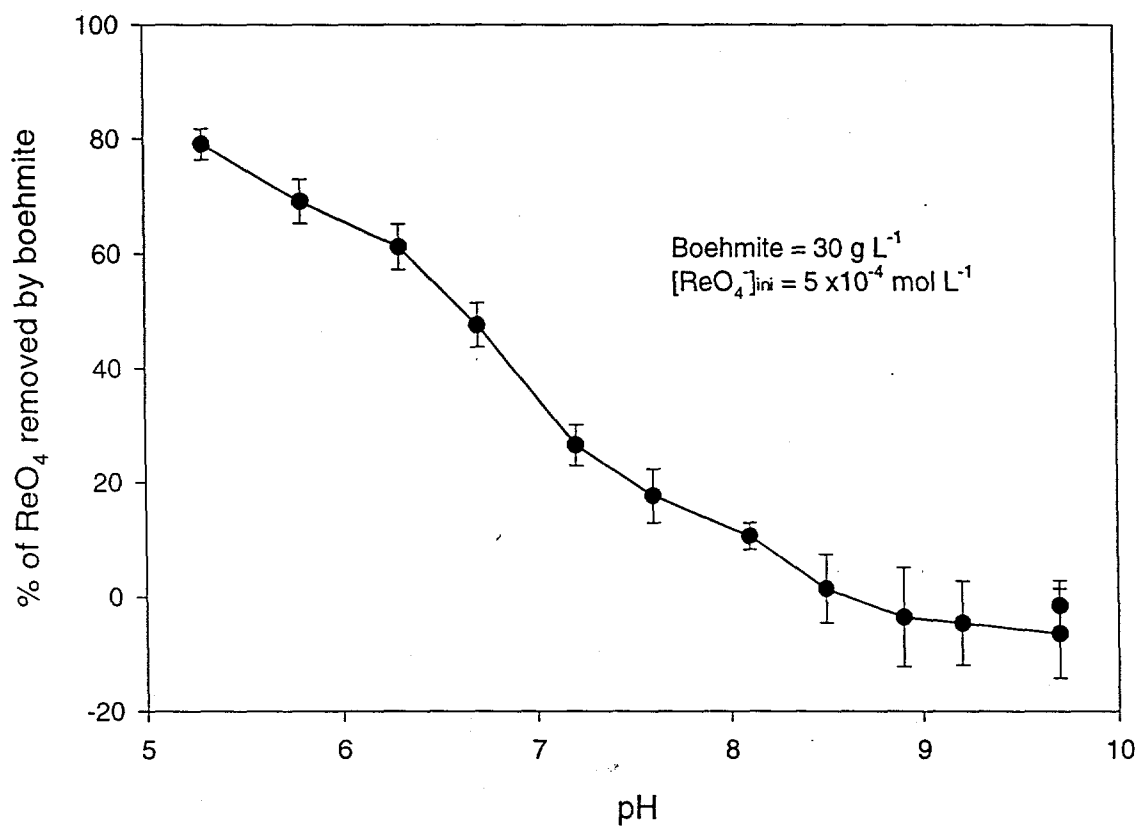


Figure 2

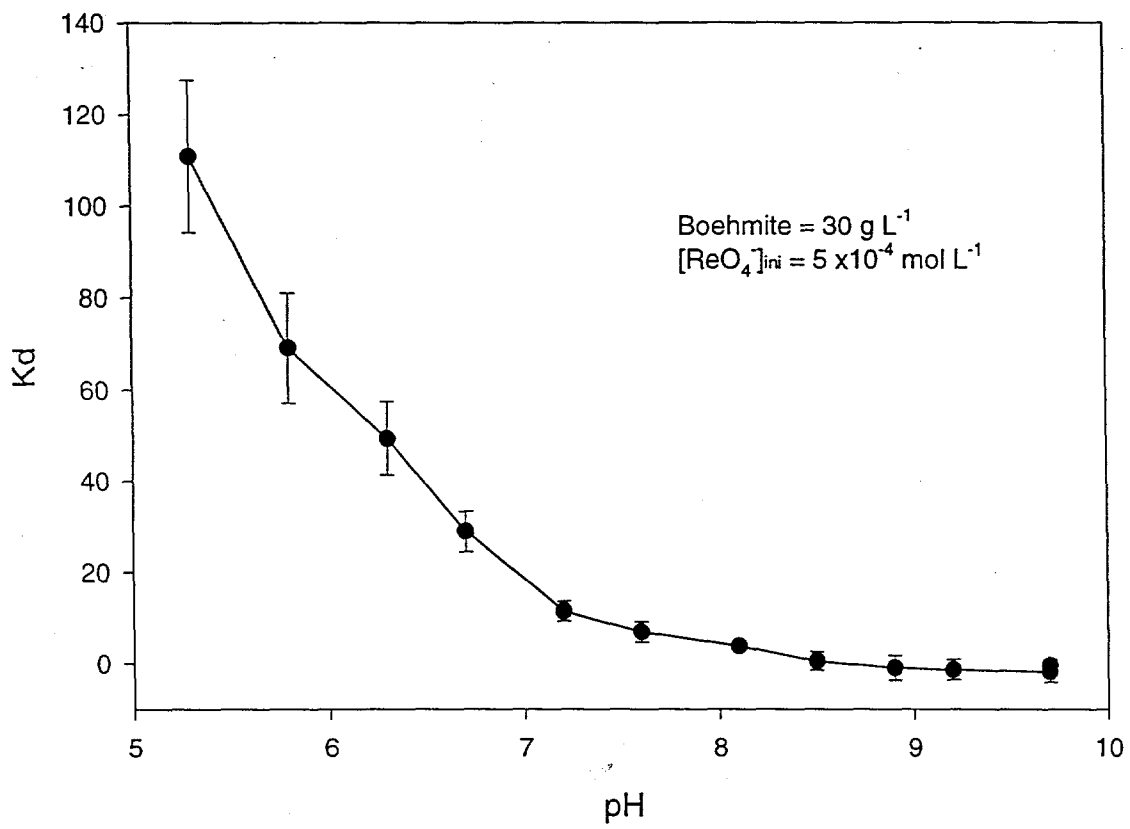


Figure 3

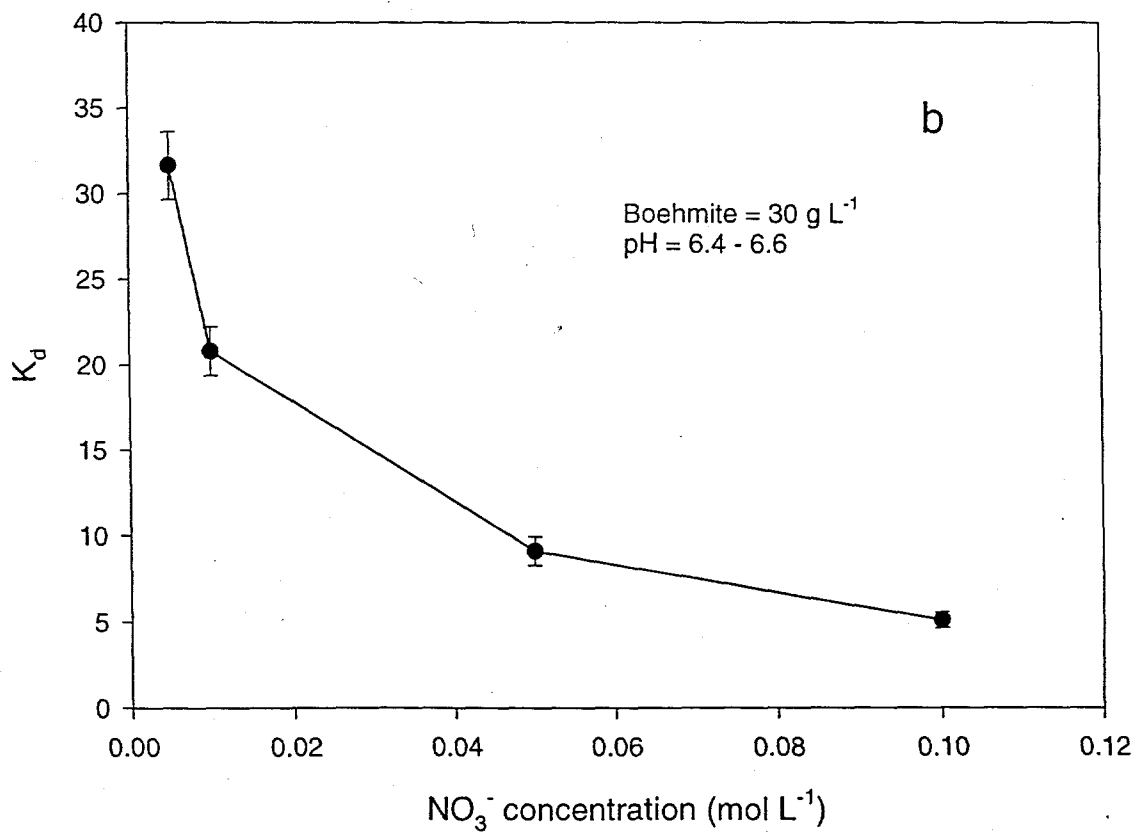
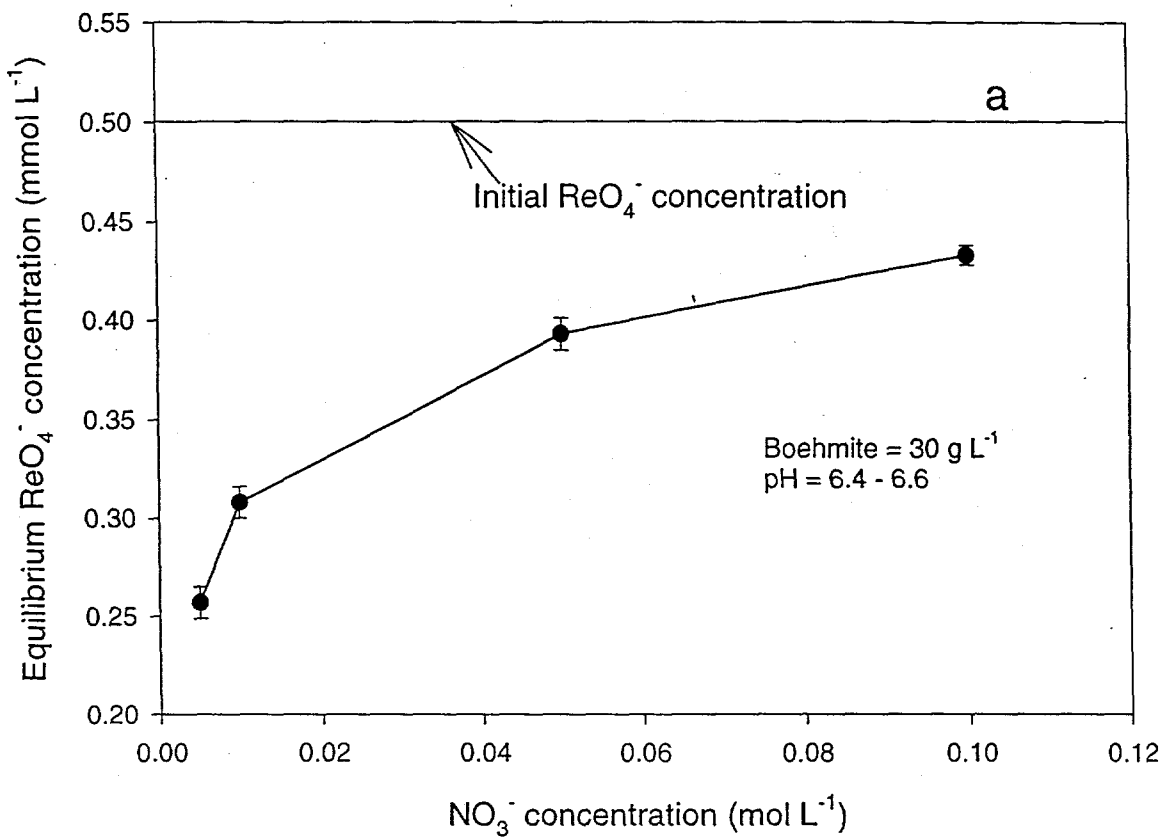


Figure 4

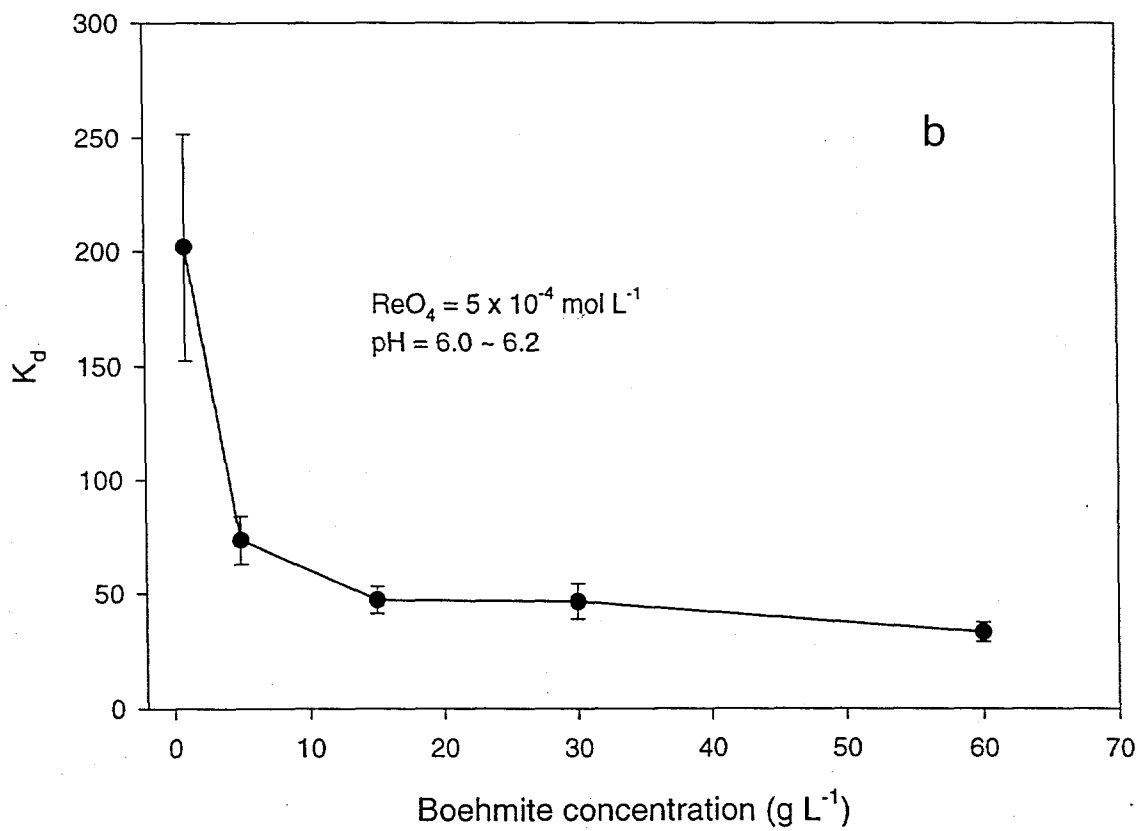
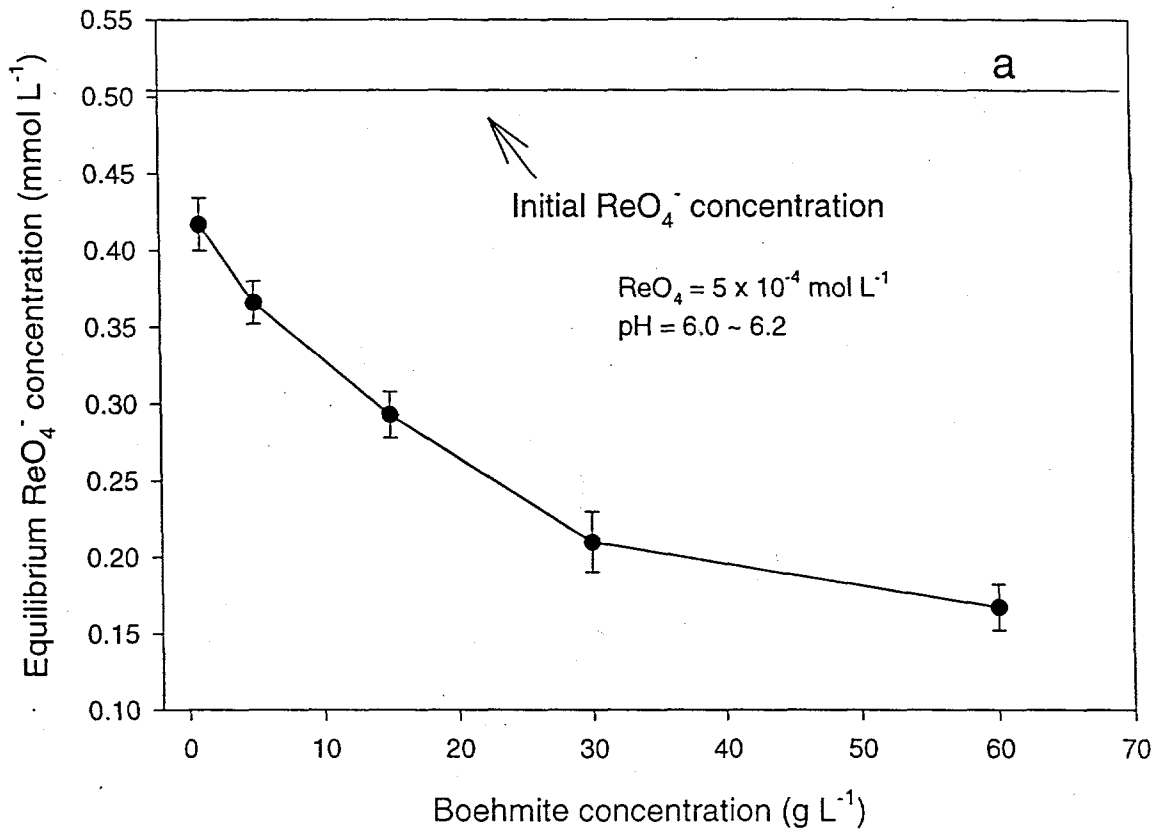


Figure 5