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Kinetics of Chromate and Phosphate Sorption by Oxide Minerals and Soils.

David S. Burden

Louisiana State University and Agricultural & Mechanical College

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Kinetics of chromate and phosphate sorption by oxide minerals and soils

Burden, David S., Ph.D.
The Louisiana State University and Agricultural and Mechanical Col., 1989
KINETICS OF CHROMATE AND PHOSPHATE SORPTION
BY OXIDE MINERALS AND SOILS

A DISSERTATION

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Agronomy

by

David S. Burden
B.S., Harding University, 1980
M.S., Louisiana State University, 1985
December 1989
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ABSTRACT

A nonlinear multireaction model was used to describe kinetic retention data sets for chromate, phosphate, arsenate, borate, fluoride, molybdate, selenite, and silicate by goethite, an iron oxide mineral, and selected soils. These data sets were obtained from laboratory batch experiments with time up to 24 h. Either a three-parameter version of the model consisting of one nonlinear reversible and one first order irreversible reaction, or a five-parameter version consisting of two nonlinear reversible and one first order irreversible reactions was capable of predicting anion sorption by goethite. A mechanistic model consistent with the nonlinear multireaction approach was also proposed in order to account for the adsorption of inorganic oxyanions onto oxide surfaces. The retention of chromate by goethite as a function of pH showed equilibrium constants to decrease with increasing pH. This was supported by the rate equations derived from the mechanistic model which predicted the pseudo rate coefficients for ligand exchange to be pH dependent.

Two equilibrium type models, namely the Freundlich and two-site Langmuir were found to adequately describe the sorption (after 24 h of reaction) of chromate, phosphate, arsenate, selenite, and silicate by goethite. Both the Freundlich model and the multireaction model were found to be consistent in establishing an affinity sequence for anion adsorption by goethite. The data suggested the following affinity sequence: arsenate > selenite > phosphate > molybdate > chromate > fluoride > borate > silicate.
The retention of chromate by six soils having different soil chemical properties were well described by either the three- or five-parameter versions of the multireaction model. Soils with high iron oxide contents and low pH were capable of retaining chromate to a greater degree than soils low in iron oxides and high pH. It was also found that significant amounts of chromate were incapable of being adsorbed by amorphous aluminum oxide and humic acid.

The data sets generated for chromate and phosphate retention by goethite and various soils, as well as the models used for the prediction of their behavior, are a prerequisite for the quantification of their amounts remaining in the soil solution and thus susceptible to transport to the groundwater.
INTRODUCTION

For numerous years man has been applying waste materials and chemicals to the soil with little regard to the long term effects this may have upon the quality of the soil, neighboring watersheds, or underlying groundwater. Of great concern today is the deterioration of groundwater in many areas throughout the United States. Numerous factors that have been identified as possible and/or probable causes of the deterioration of groundwater quality include, the improper disposal of pesticides and toxic waste chemicals, municipal sludge application on farms and landfills, the excess application of fertilizers, and the movement of toxic metals from surface to groundwater by diffusion and percolation through soils (Scott, 1987).

Recently, trace metals have received increased attention with regard to accumulation in soils, uptake by plants, and contamination of groundwater. Trace metals receiving the most attention include chromium, cadmium, copper, mercury, nickel, lead, and zinc.

Of near equal concern has been the impact of the application of excess fertilizers and land application of wastewater containing high concentrations of phosphorus. Since the eutrophication of lakes and streams can be accelerated by the addition of nutrient rich water, an understanding of the interaction of phosphorus and soil constituents would be useful.

Chromium and phosphorus are similar in some respects in that they both can exist as oxyanions and both form inner-sphere complexes. Chromium and phosphorus also differ in some respects in that phosphorus forms many minerals of low solubility in soils and chromium can exist in
cationic and anionic forms and can change oxidation states. The cationic Cr(III) species is generally insoluble and hence relatively immobile in soils, whereas the anionic Cr(VI) species is very mobile. Some of the more common inorganic oxyanions found in the aqueous phases of soils are \( \text{B(OH)}_4^- \), \( \text{CO}_3^{2-} \), \( \text{NO}_3^- \), \( \text{H}_3\text{SiO}_4^- \), \( \text{PO}_4^{3-} \), \( \text{SO}_4^{2-} \), \( \text{AsO}_4^{3-} \), \( \text{SeO}_3^{2-} \), \( \text{MoO}_4^{2-} \) and when the oxyanion is multivalent, some of the protonated forms may be present (Sposito, 1984).

Aluminum, iron, and manganese oxides, oxyhydroxides, and hydroxide minerals are among the most abundant minerals in the lithosphere due to their low solubility in the normal pH range of soils. Among the iron oxide minerals, goethite is the most prevalent in soils. Goethite is a major component responsible for anion retention in soils in addition to the fact that chemical properties of goethite can be directly applied to soils. Thus, a comprehensive study involving the interaction of goethite with some of the commonly occurring and environmentally important inorganic oxyanions would seem to be in order. Moreover, a general purpose multireaction model capable of describing and/or predicting the retention of anions in the soil environment would be of significant value. The objectives of this study were:

(i) to study the kinetics of chromate and phosphate retention and exchange on synthetic goethite under varying experimental conditions;
(ii) to describe the kinetics of chromate and phosphate retention and exchange on synthetic goethite using a nonlinear multireaction model;
(iii) to describe the kinetics of chromate retention on synthetic goethite in the presence of other major oxyanions;
(iv) to describe the kinetics of chromate retention on several soils of different pH; and
(v) to relate the experimental rate equations of the multireaction model to mechanistic rate equations for ligand exchange on oxide surfaces.
LITERATURE REVIEW

Classical thermodynamic studies predict substances will react until they reach their most stable states. However, many reactions proceed at a very slow rate and, thus, do not immediately lead to their most stable state. The mechanisms and rates of ionic reactions in minerals and soils are not disclosed through thermodynamic investigations. To assist in understanding and modeling elemental reactions in minerals and soils, a knowledge of kinetics should be employed. Chemical kinetics deals with chemical reaction rates and how these rates can be explained in terms of reaction mechanisms (Laidler, 1965). The retention of the soil ions by soil particles does not occur only by simple exchange reactions, but instead involves many different reactions. Many investigators including Griffin and Jurinak (1974), Zasoski and Burau (1978), and Harter and Smith (1981) have suggested kinetic approaches should be used in studying adsorption reactions in soils.

The discovery of cation exchange by H. S. Thompson (1850) and the sharing of his idea with J. Thomas Way marked the beginning of one of the most important aspects of soil chemistry. Way, considered by many as the patriarch of soil chemistry, introduced the theory that many of the ion exchange reactions were rapid and instantaneous. This idea led Thompson and Way to devise methods to study these exchange reactions, thus the batch and miscible displacement techniques were conceived. Over the years these two techniques have prevailed with new variations constantly being tested.

The batch technique has seen the widest use over the years involving studies with soils and soil constituents. Basically this technique
involves placing a given initial amount of an element of interest in a stirred suspension of a known amount of soil, mineral, humic material or other solid phase soil component in a batch reactor in which experimental conditions can be controlled and/or monitored. At periodic intervals the suspension is sampled, the solid and liquid phases are separated by centrifugation or filtration, and the solution phase is analyzed for the elemental species of interest. The batch reaction method has been successfully used to study the kinetics of numerous reactions in soil systems (Zasoski and Burau, 1978; Harter and Lehman, 1983; Amacher and Baker, 1982) and will be used in this study.

Iron oxide minerals have been identified as the more important soil constituents responsible for anion retention in soils. A review of the soil chemistry of Fe minerals is therefore in order. The iron present in magmatic rock is primarily bound in silicates in the reduced (Fe$^{2+}$) state. However, as the weathering of this rock proceeds to soils, the iron is released through hydrolytic and oxidative reactions. Within the normal pH range of soils Fe$^{3+}$ oxides have a very low solubility, thus as Fe$^{2+}$ is released through dissolution, Fe$^{3+}$ will be precipitated as an oxide or hydroxide. Under anaerobic soil conditions microorganisms may utilize Fe$^{3+}$ oxides as final electron acceptors to carry out oxidative decomposition of organic matter. In turn Fe$^{3+}$ is reduced to the more soluble Fe$^{2+}$, accelerating the dissolution of the oxide. The chemical nature and high specific surface area of iron oxides in particles and as coatings on other particles, make them efficient sinks for anions such as phosphate, molybdate, and silicate, as well as trace elements like copper, lead, vanadium, zinc, cobalt, chromium, and nickel (Schwertmann and Taylor, 1977). Some of the more common iron oxide minerals found in
soils include goethite, hematite, lepidocrocite, maghemite, and ferrihydrite. The most frequently occurring iron oxide form found in soils is goethite. Thermodynamically, it has the greatest stability under most soils conditions and is known to occur in about every soil type and climatic region (Schwertmann and Taylor, 1977). Goethite distribution may occur as concentrated accumulations in certain horizons or it may be evenly distributed throughout the soil. Synthetic goethite usually assumes an acicular formation and in soils the morphology is usually poorly developed (Schwertmann and Taylor, 1977).

Iron oxides are important buffer systems in soils and exert a significant control on the concentration of trace metals in soil solution (Jenne, 1968). The most important pH-dependent mechanism used to account for the binding of trace metals by iron oxides in the range of pH 3 to 8, has been specific adsorption (Gadde and Laitinen, 1974; Kinniburgh and Jackson, 1982; Barrow, 1986).

Hingston et al. (1974) conducted experiments to determine some of the factors involved in the desorption of specifically adsorbed anions (phosphate, selenite, and fluoride) on goethite. The effects of time, ionic strength, and pH on the anion desorption were examined. Results indicated desorption of the anions varied between complete reversibility to almost complete irreversibility. Surface charge measurements were made, revealing that when the isotherm was irreversible, OH⁻ was desorbed in preference to the desorption of the specifically adsorbed anion. Moreover, when the isotherm was reversible the specifically adsorbed anion was desorbed. Surface adsorption complexation appeared to be the mechanism involved with the irreversible reaction of anions. Formation of monodentate ligands favored the reversible reactions,
whereas multidentate ligands favored irreversibility.

Bruemmer et al. (1988) studied the reaction of several trace metals (nickel, zinc, and cadmium) with goethite and found the adsorption of metals to increase with pH, reaction time, and temperature. Results also indicated the initially rapid adsorption of metals within a few hours was followed by a much faster reaction linearly related to time$^{1/2}$. This in turn was interpreted as diffusion-controlled penetration of goethite. High amounts of trace metals have been associated with natural iron oxides bound to surface sites and occluded inside the oxide particles (Suarez and Langmuir, 1976; Schwertmann and Taylor, 1977). Bruemmer et al. (1988) concluded that the adsorption of heavy metals by goethite to be determined by three different steps: adsorption on external surfaces, diffusion into the goethite particles, and adsorption and fixation at positions inside the particles. In addition, diffusion from external to internal binding sites increased with time, temperature, and metal concentration.

One of the elements chosen for detailed study is chromium (Cr) because it can exist as an oxyanion in soils and be retained by soil iron oxides. A review of the soil chemistry of Cr is therefore presented next.

Chromium is an interesting element that is prevalent in rocks and soils naturally and as a result of environmental contamination. Natural Cr concentrations in magmatic rocks have been reported to range from 4 ppm to as high as 3400 ppm and in sedimentary rocks from 5 to 120 ppm have been reported. Soils derived from mafic and volcanic rocks show the highest Cr concentration, while soils lowest in Cr are typically sandy and Histosols. Through the years Cr and chromium based chemicals
have found uses in the textile and tanning industry, wood preservation, production of paints, dyes, and fungicides, and as corrosion inhibitors in steel, iron, aluminum, copper, brass, and related alloys. However, because of its widespread use in many products over the years, contamination of soils and groundwater are becoming more widespread. The Environmental Protection Agency (EPA) has set a limit of 1 umol L\(^{-1}\) (50 ppb) Cr for domestic water supplies and 2 umol L\(^{-1}\) for freshwater aquatic life (U. S. EPA, 1976). Naturally occurring Cr\(^{6+}\) concentrations in groundwater exceeding EPA limits have been found (Robertson, 1975). Stollenwerk and Grove (1985) reported Cr\(^{6+}\) concentrations of as much as as 12.5 umol L\(^{-1}\) as a result of groundwater contamination.

The oxidation states of Cr ranges from 2+ to 6+ and can form complex anionic and cationic ions. The two most naturally occurring Cr compounds have valences of 3+ (chromic) and 6+ (chromate). The mineral chromite (FeCr\(_2\)O\(_4\)), the most commonly occurring form of Cr in soils, is resistant to weathering and thus accounts for most of the Cr in residual material. Trivalent Cr closely resembles Fe\(^{3+}\) and Al\(^{3+}\) in ionic size and in geochemical properties with ionic radii of 0.63, 0.51, and 0.64 Å, respectively. Under progressive oxidation, it has been shown that Cr forms the chromate ion (CrO\(_4^{2-}\)) which is readily mobile and is also easily sorbed by clays and hydrous oxides (Kabata-Pendias and Pendias, 1984). Most of the soil Cr occurs as Cr\(^{3+}\) and is within the mineral structures of forms of mixed Cr\(^{3+}\) and Fe\(^{3+}\) oxides. Only in very acid media is Cr\(^{3+}\) mobile, however Cr\(^{6+}\) is mobile in both acid and alkaline soils. Studies conducted by Griffin et al. (1977) on Cr adsorption from landfill leachate revealed that adsorption by clays is highly pH dependent. Adsorption of Cr\(^{6+}\) decreased as pH increased, while Cr\(^{3+}\) adsorp-
tion increased as pH increased. In addition, results suggested that landfill disposal of Cr\(^{6+}\) wastes poses a potential pollution hazard due to its high mobility in earth materials and safe disposal may require conversion of Cr\(^{6+}\) in wastes to Cr\(^{3+}\). Chromium behavior in soils may also be modified by organic complexes of Cr, it has been found that the dominant effect of organic matter is the stimulation of the reduction of Cr\(^{6+}\) to Cr\(^{3+}\) (Kabata-Pendias and Pendias, 1984). Effective methods of reducing chromate toxicity in Cr polluted soils include liming, phosphorus application, and organic matter (Grove and Ellis, 1980).

In an extensive review by Mertz (1969) on the occurrence of Cr in biological systems, low levels of Cr have been found to be essential in human nutrition. With respect to its essentiality in plants, Huffman and Allway (1973) have shown Cr to be non-essential, however, Pratt (1966) reported Cr to be beneficial to plants. Typically, higher Cr contents are observed in roots than in leaves or shoots, whereas the lowest concentration is in grains (Kabata-Pendias and Pendias, 1984). Common levels of Cr found in plant material are on the order of 0.02 to 0.2 ppm (dry weight) (Kabata-Pendias and Pendias, 1984). Chromium toxicity symptoms in plants appear as wilting of tops and root injury, in addition chlorosis in young leaves and chlorotic bands on cereals may be present.

Bartlett and Kimble (1976a) studied effects of pH, organic matter, and phosphorus on the chemical behavior of Cr\(^{3+}\) in soils and found Cr\(^{3+}\) solubility to decrease as the solution pH was raised above 4 and complete precipitation occurred at pH 5.5. The amount of NH\(_4\)OAc extractable Cr\(^{3+}\) decreased in the presence of phosphorus, moreover phosphorus had no effect on NaF extractable Cr\(^{3+}\). The behavior of Cr\(^{3+}\) was found
to be quite similar to that of aluminum in response to varying amounts and sequences of applied lime and phosphorus. In a study of the hexavalent forms of Cr by Bartlett and Kimble (1976b), it was reported that the presence of soil organic matter produced spontaneous reduction of Cr\(^{6+}\) to Cr\(^{3+}\) at pH values above 7. In the presence of orthophosphate, adsorption of Cr\(^{6+}\) did not occur due to competition of adsorption sites. The researchers concluded that Cr\(^{6+}\) behavior is similar to that of orthophosphate, however, in contrast to phosphate, Cr\(^{6+}\) can be reduced by soil organic matter. In addition, Bartlett and Kimble (1976b) concluded if the Cr\(^{6+}\) concentration exceeds both the adsorbing and the reducing capacities of the soils, then it will remain mobile. Bartlett and James (1979) have attributed the oxidation of Cr\(^{3+}\) to Cr\(^{6+}\) in soils to oxidized soil Mn.

Studies conducted by Turner and Rust (1971) on the effects of Cr on growth and mineral nutrition of two soybean varieties showed Cr concentrations as low as 0.5 ppm in nutrient culture and 10 ppm in soil culture significantly reduced dry-matter yields. At the smallest Cr additions of 5 ppm in the soil culture study, there appeared to be an interference with the accumulation of Ca, K, Mg, P, B, and Ca by soybean tops, with little or no effect on Fe, Mn, and Zn uptake.

Cary et al. (1977a,b) studied the adsorption and translocation of Cr in numerous crops. Results indicated that leafy vegetables (i.e. spinach, turnip leaves, etc.) that tend to accumulate Fe appeared to be the most effective in translocating Cr to the edible tops of the plant. Leafy vegetables such as head lettuce and cabbage that do not accumulate high concentrations of Fe in their leaves were substantially less effective in translocating Cr to the leaves. There was very little
indication of Cr transport into seeds of beans, peas, corn, and wheat. The mechanism most likely responsible for low Cr availability to plants is the conversion of soluble Cr$^{6+}$ to insoluble Cr$^{3+}$.

Amacher and Baker (1982) studied the redox reactions of Cr so that Cr reactions could possibly be used as a general model for plutonium (Pu) reactions in soil. Results of their study revealed the redox chemistry to be controlled by organic matter, minerals containing Fe$^{2+}$, and manganese oxides. Results of chemical fractionation disclosed that when Cr was present in soils as a result of sewage sludge application, or from other organic sources, it remained in the soil in the reduced state associated with organic matter or as organo-Cr complexes sorbed to iron oxides and was not oxidized by manganese oxides. Inorganic sources of Cr were oxidized in soil, however, complete oxidation was not observed if the Mn$^{4+}$ sites at manganese oxide mineral surfaces were filled. Thus, Mn$^{2+}$ blocked further access of Cr$^{3+}$ to Mn$^{4+}$ beneath the mineral surface. Conditions of low temperature and pH slowed the oxidation reaction. In the presence of fulvic acid, the reduction of Cr$^{6+}$ was found to be slow and was rapid only at low pH values. They concluded immediate Cr availability is controlled through oxidation by manganese oxides while long-term availability is controlled through reduction by organic matter.

James and Bartlett (1983) found Cr$^{6+}$ adsorption by two A and two B horizon soils to be less when added with sulfate and phosphate, with the greater effect being exerted by phosphate. In addition, soils that had been limed adsorbed less Cr$^{6+}$ and less was available in exchangeable or non-exchangeable forms. Major groundwater anions reduce chromate adsorption on amorphous iron oxyhydroxide by competing for binding
sites, consequently increasing chromate mobility (Zachara et al., 1987). Cations have been shown not to have a significant effect upon chromate adsorption. Zachara et al. (1987) found chromate adsorption to be greatest in low pH soils enriched in kaolinite and crystalline iron oxides. Subsoil chromate adsorption was similar to that observed for pure-phase oxides.

Recently, Ainsworth et al. (1989) investigated the adsorption of chromate on three different goethite preparations varying in specific surface area and aluminum substitution over a range in pH, sorbate and sorbent concentrations and ionic strength. Results indicated that chromate is preferentially adsorbed by iron sites. Moreover, aluminum substitution on the goethite does reduce chromate adsorption due to difference in the acid-base nature of aluminum and iron sites and the consequent reactions of these sites with background electrolyte anions in solution.

The other element chosen for detailed study is phosphorus (P). It too exists as an oxyanion in soils and can be retained by soil iron oxides. Phosphorus, a known major nutrient element, is essential for plant growth and applications to agricultural land often improves crop production. While phosphate is not toxic, excessive application of phosphate fertilizers may produce detrimental effects in both terrestrial and aquatic environments. Surface and subsurface runoff is effective in transporting phosphorus from the terrestrial to aquatic environment, resulting in the deterioration in water quality from accelerated eutrophication.

Several trace elements, such as arsenic, cadmium, chromium, lead, and vanadium occur naturally in phosphate rock and are not eliminated
during the manufacture of phosphate fertilizers. Thus, toxic elements have the potential of being introduced into the food chain by the addition of phosphate fertilizers to the soil. Goodroad and Caldwell (1979) found no detectable increase in arsenic, chromium, lead, or vanadium concentrations following the application of 8888 kg ha\(^{-1}\) of concentrated superphosphate. If the content of these heavy metals are kept low, it is unlikely there is any danger of contamination from phosphate fertilizers. If the heavy metals are strongly adsorbed by soil along with phosphorus, then these contaminants may be transported with finer soil particles during rainfall and erosion.

The kinetics of phosphate retention and release has been widely studied by numerous investigators (Fried et al., 1956; Larsen et al., 1965; Griffin and Jurinak, 1973; Kuo and Lotse, 1972; Olsen, 1975; Barrow, 1978, 1983a, 1983b, 1984; Barrow et al., 1981; Bolan and Barrow, 1984; Chien and Clayton, 1980). In addition several models have been proposed to describe phosphate retention and release on soils and minerals.

The kinetic release of phosphate from a desert soil was studied by Evans and Jurinak (1976). An anion-exchange resin was utilized to simulate plant root uptake of phosphate and they equated the amount of resin-adsorbed phosphate to the amount of phosphate released by the soil. Experimental data could not be adequately described by either a single first order reaction or by two simultaneous first order reactions. The phosphate release data, however, was described successfully by three simultaneous first order reactions. The three reactions accounted for the fast, intermediate, and slow release of phosphate from the surface and the subsoil.
N. J. Barrow and his colleagues have conducted extensive research on phosphate adsorption and desorption by soils and minerals. Barrow (1978) evaluated several equations often used in describing phosphate adsorption on soil (i.e. Freundlich, Langmuir, and two-site Langmuir). Two main motivations cited by Barrow (1978) as reasons responsible for describing adsorption curves were: 1) to provide a shorthand method which allows for soil properties to be summarized using a few numbers rather than having to refer to a curve, and 2) to learn more about the nature of adsorption processes. Barrow (1978) compared the adsorption equations using the residual sum of squares as a criteria for goodness of fit. His approach was tested for phosphate adsorption on a Western Australian soil. Results showed the Freundlich equation to be superior in describing phosphate adsorption, however the two-site Langmuir equation produced curve shapes similar to the Freundlich. Barrow (1978) stresses the need for devoting more effort to deriving mechanistic adsorption equations to aid in understanding the mechanisms of phosphate adsorption.

Many investigators have concluded that when phosphate reacts with soil or soil constituents, the reaction involves two steps, an initial fast reaction and a subsequent slow reaction. Thus, Barrow et al. (1981) utilized a partial model developed by Bowden et al. (1980) to help explain the rapid adsorption and desorption of phosphate by goethite. The model was successful in describing phosphate adsorption for time periods up to one hour. Adsorption was observed (up to 24 h) to continue, however, at a much slower rate. The mechanism responsible for the slower adsorption is thought to be responsible for the slow desorption of phosphate from goethite (Madrid and Posner, 1979).
Chien and Clayton (1980) tested the applicability of the Elovich equation to describe kinetic phosphate retention and release on soils. A modified Elovich equation successfully described the retention and release of phosphate data that had previously failed to be described by a first order kinetic equation. The Elovich equation (when expressed in the linear form) provides a linear relationship between the amount of phosphate retained (or released) and the logarithm of reaction time. Chien and Clayton (1980) concluded the linearity of the Elovich equation does not negate the possibility that other forms of phosphorus which differ in dissolution rates may exist. The Elovich equation was also found to be useful in investigating changes of surface reactivity during a reaction, as these changes would be represented by changes in linearity. Moreover, the Elovich equation requires only a single rate constant, as compared to multiple constants for simultaneous first order kinetics. The constants obtained from the Elovich equation may be used for comparison of reaction rates of phosphate retention or release in different soils (Chien and Clayton, 1980).

Van Riemsdijk et al. (1984) developed a model to describe phosphate sorption by metal oxides in soil. The need for such a model was based upon studies of phosphate sorption on gibbsite and a sandy soil (Van Riemsdijk and Lyklema, 1980; Van Riemsdijk and de Haan, 1981) which have shown that a metal-phosphate coating can be formed on the surface of the metal oxide. Consequently, the diffusion of ions through this coating was considered as the rate-limiting step for the reaction. The diffusion-precipitation model of Van Riemsdijk et al. (1984) accounts for the slower phosphate reaction, following the initial rapid sorption, which is assumed to be a precipitation reaction. In reactions involving
phosphate concentrations greater than 1 mmol/L, precipitation was assumed to be the dominant reaction (Van Riemsdijk et al., 1984). The diffusion precipitation model was found to be valid for predicting phosphorus retention of varying concentrations on three acid sandy soils.

A considerable number of investigations on phosphate adsorption/desorption as well as other anions have been conducted by F. J. Hingston and his colleagues (i.e. Hingston et al., 1967, 1968, 1972, 1974). In the study conducted by Hingston et al. (1967) on anion adsorption, they established a relationship between the "apparent" Langmuir maximum and pH, and termed it the adsorption envelope. Hingston et al. (1972) attempted to relate the characteristics of the envelope to properties of the adsorbent and adsorbate. Good correlations were found between points of inflection in the adsorption envelopes and $pK_a$ values for conjugate acids of several adsorbates including tripolyphosphate, pyrophosphate, and orthophosphate. Hingston (1981) stresses that although anion reactions at solid-aqueous interfaces have been extensively studied, studies are still needed to help clarify reaction mechanisms especially those involving desorption of anions and competitive anion reactions. Moreover, there is a need to extend the work on anion reactions to systems containing a mixture of adsorbents.

Phosphorus desorption from soil material plays a major role in plant availability and water quality. Several investigators have reported the desorption of P to occur rapidly (Kunishi et al., 1972; Ryden and Syers, 1977; Oloya and Logan, 1980). Sharply et al. (1981) reported 75% of the P desorbed in 4 hours from several soils, occurred in the initial 30 minutes. Phosphorus movement is more likely to occur in sandy soils with a low P sorption capacity (Adriano et al., 1975;
Sawhney, 1977) and in waterlogged soils where a decrease in the Fe$^{3+}$ content has occurred (Gotoh and Patrick, 1974; Khalid et al., 1977).

Infrared spectroscopic techniques have been widely used to study the surface reactions between iron oxides and P ions. Atkinson et al. (1974) and Parfitt et al. (1975) were able to determine through infrared spectroscopy, that binuclear coordination of P ions to two Fe$^{3+}$ ions on goethite surface occurs. Thus, the exchange of adsorbed P with other anions in the solution phase is likely to be slow. Additionally, infrared studies have shown that when P is adsorbed onto a goethite surface, hydroxide ions which were singly coordinated to Fe$^{3+}$ are lost (Russell et al., 1974).

Borggaard (1982) studied the influence of iron oxides on the surface area of soils and reported that soil iron oxides may be treated as if they consist of only two fractions, an amorphous fraction and a crystalline fraction. Larsen (1967) and Parfitt (1978) reported soil P adsorption is related by a number of soil components, including the iron oxides (i.e. oxides, hydroxides, and oxyhydroxides). In studies comparing the P adsorption capacities of extractable soil iron oxides with various synthetic iron oxides, nearly equal amounts of P were adsorbed when expressed per unit of surface area (McLaughlin et al., 1981; Borggaard, 1983a). Furthermore, Borggaard (1983b) found the P adsorption capacity (using the Langmuir equation) of soils from Denmark and Tanzania, to be in good agreement with the capacity of various synthetic iron oxides. Juo and Fox (1977) found P adsorption on tropical and subtropical soils to be closely correlated with iron and aluminum in soils. Humic acid and fulvic acid have been shown to be strong competitors with P for adsorption sites on goethite at low pH values (Sibanda
and Young, 1986).

Of the iron oxide minerals, goethite has probably received the most attention due to its stability and ability to adsorb anions, particularly in iron rich soils. Research on the sorption of other anions on goethite found in the literature include, chloride, fluoride, selenite, silicate, and sulfate (Hingston et al., 1972, 1974; Hansmann and Anderson, 1985). This ability of goethite to adsorb anions is not only important from a plant nutrient viewpoint, but is also important in controlling the mobility of environmental contaminants.

In summary, batch kinetic studies can provide information on anion retention processes that cannot be obtained by thermodynamic considerations. Iron oxides, particularly goethite, play a major role in anion retention in soils. Although Cr reactions in soils are complex, the oxyanions species, like P, are retained by soil Fe oxides.
THEORETICAL CONSIDERATIONS

The term sorption is a collective term, often used to imply that either adsorption or precipitation of a solute species on some type of material is occurring. The types of sorption most commonly referred to in soil systems include adsorption, chemisorption, and ion exchange, of which adsorption appears to be the weakest form. Sorption reactions of solutes onto soil materials can occur as either a kinetic or equilibrium situation. Under equilibrium conditions the rate of sorption between the soil solution and the solid phase is much greater than the rate of change in concentration of solute in the soil solution because of any other cause, whereas with a kinetic reaction the relative amount of solute in the soil solution and in the soil matrix changes with time (Travis and Etnier, 1981). Adsorption isotherms are commonly used to model equilibrium reactions of solutes with the soil matrix. Two of the most commonly used equilibrium sorption isotherm equations used are the Langmuir and Freundlich. Although they were not originally derived to predict the sorption of solutes onto soil or mineral surfaces, the Langmuir and Freundlich equations have achieved partial success with these adsorbents. Sposito (1984) stated an important fact regarding the use of sorption isotherms, in that the adherence of experimental data to an adsorption isotherm equation provides no evidence as to the actual mechanism of a sorption process in a soil.

The nonlinear Freundlich equation, written in the form commonly used by soil scientists (Helfferich, 1962), is

\[ S = K C^N \]  \hspace{1cm} [1]

where \( S \) is the concentration of solute retained by the soil or mineral
material, \( C \) is the concentration of solute in solution, and \( K \) and \( n \) are constants. The equation does not express \( S \) as a linear function of \( C \) at low concentrations. In addition, it does not imply a maximum quantity of adsorption and the accuracy of extrapolation beyond the experimental data points is limited. The soil literature is abundant with studies of solute retention, in which the Freundlich equation is used to describe the data (see review by Travis and Etnier, 1981).

Like the Freundlich equation, originally developed to describe the sorption of gases by solids, the Langmuir equation has seen relative success in describing anion and cation sorption by soils and soil constituents. Numerous examples of solute sorption as described by the Langmuir equation can be found in the soils literature (see review by Travis and Etnier, 1981). Written in the form,

\[
S = \frac{K_b C}{1 + K C}
\]

\( S \) is the concentration of solute retained, \( C \) is the concentration of solute in solution, \( K \) is an affinity parameter, and \( b \) is the maximum retention capacity of the adsorbent. Veith and Sposito (1977) emphasize the equation is based on two major assumptions: (i) the adsorbed ions be bound in a monolayer on uniform localized sites and (ii) the energy of adsorption be the same for each ion regardless of the degree of completion of the monolayer (i.e. noninteracting ions). Extensive investigations have been conducted on using the Langmuir equation to describe phosphate reactions with soils (Cole et al., 1953; Fried and Shapiro, 1956; Olsen and Watanabe, 1957; Rennie and McKercher, 1959; Larsen, 1967; Kuo and Lotse, 1972; Syers et al., 1973).

To account for the possibility that more than one surface is responsible for adsorption, Langmuir (1918) proposed a two-surface (or
two-site) isotherm,

\[ S = \left( \frac{K_1 b_1 C}{1 + K_1 C} \right) + \left( \frac{K_2 b_2 C}{1 + K_2 C} \right) \]  \[3\]

where \( K_1 \) and \( K_2 \) are affinity parameters, \( b_1 \) and \( b_2 \) are the maximum quantities of solute that can be sorbed by the two sites, and \( S \) and \( C \) are as defined previously. The maximum sorption capacity, \( b \), is therefore \( b_1 + b_2 \). The two-site Langmuir takes into account two different bonding energies that can occur (i.e. a rapidly reacting high energy bond and a slower reacting low energy bond). Holford et al. (1974) compared the traditional Langmuir (Eqn. [2]) to the two-site Langmuir (Eqn. [3]) for their ability to describe P adsorption on numerous soils. They achieved an excellent fit with the two-site model and concluded that the suggestion of two-sites is much more than a convenient mathematical technique for improving the fit of the Langmuir equation. Other workers that have achieved success with the two-site Langmuir model, suggesting two different binding energies for P, include Shapiro and Fried (1959), Harter (1968), Syers et al. (1973), Helyar et al. (1976), and Munns and Fox (1976). In Sposito's (1982) evaluation of the two-site Langmuir equation, he determined that although the equation may provide a good fit to data, the chemical significance cannot be evaluated solely on the basis of goodness-of-fit.

Although models such as the Freundlich, Langmuir, two-site Langmuir, and their variations have seen relatively good success in describing sorption of solutes onto soil and soil constituents, there are situations in which a kinetic model would be more appropriate. A kinetic approach is more appropriate when the amount of solute in the soil solution and in the soil matrix are changing over time. Equilibrium-kinetic models such as the one proposed by Selim et al.
(1976) are being found as suitable alternatives for the two-site Langmuir model. The two-site equilibrium-kinetic model Selim, et al. (1976) proposed took into account the rapid initial retention (equilibrium) and the slow release (kinetic) of several solutes by soils via miscible displacement studies. Since two-site models appear to be more veracious in describing retention/release data with soils and soil constituents, Selim (1987) and Amacher et al. (1988) recently proposed a general-purpose non-linear multireaction model (Fig. 1) to describe the time-dependent retention of Cr(VI) and Cd by soils. A solute (C) is present in the soil solution and possibly retained in four phases (S₁, S₂, S₃, and S_{irr}) where C and S are expressed in mg L⁻¹ and mg kg⁻¹, respectively. The four phase (S₁, S₂, S₃, and S_{irr}) allow for the accountability for four types of reactions that the soil solute (C) may be undergoing. The solute (C) can react (i) rapidly and reversibly with S₁; (ii) slowly and reversibly with S₂; and (iii) irreversibly with S_{irr}. Inclusion of S₃ accounts for solute that is strongly retained by the soil that reacts slowly and reversibly with S₂, and the very slow release of solute from the soil. For the purpose of this research the S₃ retention phase was not needed, thus the reader is referred to Amacher et al. (1988) for further discussion of use of S₃ in the multireaction model.

Selim (1987) and Amacher et al. (1988) described the kinetic reactions between C and S by,

\[ \rho \frac{\partial S_1}{\partial t} = \Theta k_1 C^n - \rho k_2 S_1 \]  

where \( k_1 \) and \( k_2 \) (min⁻¹) are the forward and reverse rate coefficients, \( \rho \) is the bulk density (mg m⁻³), \( \Theta \) is the water content (m³ m⁻³) and \( t \) is time. The dimensionless parameter \( n \), is the reaction order, where for
Figure 1. Descriptive diagram of the multireaction model.
n ≠ 1, the reaction is nonlinear. The reaction assumes C and S react rapidly and reversibly, thus $k_1$ and $k_2$ are considered relatively large in magnitude. The ratio of $k_1$ over $k_2$ is the equilibrium constant for that reaction, where $K_1 = \frac{\Theta k_1}{\rho k_2}$, thus if equilibrium between C and $S_1$ is reached almost instantaneously then the reaction becomes

$$S_1 = K_1 C^n$$  \[5\]

as $t$ approaches infinity.

The kinetic reaction between C and $S_2$ is represented by,

$$\rho \frac{\partial S_2}{\partial t} = \Theta k_3 C^m - \rho k_4 S_2$$  \[6\]

where $k_3$ and $k_4$ (min$^{-1}$) are the forward and reverse rate coefficients respectively, and $m$ is the reaction order. Reaction [6] is considered to be more kinetic than reaction [4], thus the magnitude of the rate coefficients $k_3$ and $k_4$ are smaller than those in reaction [4]. Similar to equation [4], if upon reaction equilibrium between C and $S$ is attained almost immediately, then $K_2 = \Theta k_3/\rho k_4$ and

$$S_2 = K_2 C^m$$  \[7\]

The $S_{\text{irr}}$ represents an irreversible sink term. The reaction between C and $S_{\text{irr}}$ may be represented by,

$$\rho (\partial S_{\text{irr}}/\partial t) = \Theta k_{\text{irr}} C$$  \[8\]

where $k_{\text{irr}}$ is the rate coefficient for the irreversible retention reaction.

A second-order version of the multireaction model was developed by Selim and Amacher (1988). In this version the rate of formation of $S_1$ and $S_2$ (filled sorption sites) also depends on the concentrations of unfilled type 1 and type 2 reaction sites (designated $\varnothing_1$ and $\varnothing_2$). Equations [4] and [6] are replaced by the following equations in the second-order version,
\[
\rho(\partial S_1/\partial t) = \theta k_1 \theta_1 C - \rho k_2 S_1
\]
\[
\rho(\partial S_2/\partial t) = \theta k_3 \theta_2 C - \rho k_4 S_2
\]

The total concentrations of filled and unfilled type 1 and type 2 sites \( (S_{T1} \text{ and } S_{T2}) \) are given by,

\[
S_{T1} = \theta_1 + S_1 = fS_T
\]
\[
S_{T2} = \theta_2 + S_2 = (1-f)S_T
\]

The total concentration of all sites, \( S_T \), is therefore \( S_{T1} + S_{T2} \) and is equal to the maximum sorption capacity term, \( b \), of the Langmuir equation. The terms \( S_{T1} \) and \( S_{T2} \) are equal to \( b_1 \) and \( b_2 \) of the two-site Langmuir equation [3], which describes the equilibrium relationship between \( S \) and \( C \) for the second-order two-site model. The term, \( f \), is the fraction of type 1 sites. The irreversible sink term (equation [8]) remains the same.

The above reactions represent initial-value problems that were solved simultaneously using numerical (finite-difference) methods (Selim et al., 1976; Selim, 1978). The initial conditions were that of a given initial (or input) solute concentration in solution and assume no solute retention at time zero, as was the case for the batch kinetic experiments described below. Values for \( n \) and \( m \) are most conveniently found by applying the Freundlich equation to sorption isotherm data obtained at time, \( t \), when the reversible retention reactions are near equilibrium.

The above model is a general one in that "reactions" are distinguished solely on the basis of rate and no specific mechanisms or processes need to be invoked for the model to describe experimental data. An alternative approach is to postulate a specific mechanism for anion retention, develop the necessary kinetic equations, and compare
them to the general purpose model, which can describe experimental data. To account for the adsorption of inorganic oxyanions onto oxide surfaces a two-step ligand exchange reaction has been proposed (Sposito, 1984),

$$\text{SOH}(s) + H^+(aq) = \text{SOH}_2^+(s) \quad [13]$$

$$\text{SOH}_2^+(s) + L^-(aq) = \text{SL}^{1-}(s) + H_2O(l) \quad [14]$$

where S is a metal cation, SOH(s) is one mole of inorganic oxide surface hydroxyl groups, and L$^-$ is an inorganic oxyanion of valence 1. The species, SL$^{1-}$, is an inner-sphere complex between the oxide surface and the oxyanion ligand. The degree of anion adsorption is believed to be strongly controlled by the pH of the solution, thus the adsorption of anions is coupled with the release of OH$^-$ ions (i.e. low pH values favor anion adsorption). The proposed mechanistic model will establish the relationship between pH and oxyanion adsorption on inorganic oxide surface hydroxide groups.

Kinetic and equilibrium equations can be written for reactions [13] and [14]. The kinetic equation for reaction [13] is,

$$\frac{d[\text{SOH}_2^+]}{dt} = k_1[\text{SOH}][H^+] - k_2[\text{SOH}_2^+] \quad [15]$$

where $k_1$ and $k_2$ are the forward and reverse rate coefficients, respectively. At equilibrium reaction [13] becomes,

$$\frac{d[\text{SOH}_2^+]}{dt} = 0 \quad [16]$$

and

$$k_1[\text{SOH}][H^+] = k_2[\text{SOH}_2^+] \quad [17]$$

If equilibrium between $[\text{SOH}][H^+]$ and $[\text{SOH}_2^+]$ is reached, then the ratio of $k_1$ over $k_2$ is the equilibrium constant for the reaction, thus

$$[\text{SOH}_2^+] = \left[ \frac{k_1}{k_2} \right][\text{SOH}][H^+] = K_1[\text{SOH}][H^+] \quad [18]$$

where $K_1$ is the equilibrium constant for oxide surface protonation.

Similarly, the kinetic equation for reaction [14] in terms of the
ligand, L\textsuperscript{I-}, is expressed by

\[
d[L\textsuperscript{I-}]/dt = -k_3[SOH\textsuperscript{2+}][L\textsuperscript{I-}] + k_4[SL\textsuperscript{1-I}][H_2O] \tag{19}
\]

where \(k_3\) and \(k_4\) are the forward and reverse rate coefficients, respectively. Equation [19] can be expressed as,

\[
d[L\textsuperscript{I-}]/dt = -k_3[SOH\textsuperscript{2+}][L\textsuperscript{I-}] + k'_4[SL\textsuperscript{1-I}] \tag{20}
\]

and

\[
k'_4 = k_4[H_2O] \tag{21}
\]

where \(k'_4\) represents a pseudo rate coefficient. Equation [18] can then be substituted into equation [20] resulting in the following,

\[
d[L\textsuperscript{I-}]/dt = -k_3K_1[SOH][H^+][L\textsuperscript{I-}] + k'_4[SL\textsuperscript{1-I}] \tag{22}
\]

If a second pseudo rate coefficient is represented by

\[
k'_3 = k_3K_1[H^+] \tag{23}
\]

then equation [22] can be rewritten as,

\[
d[L\textsuperscript{I-}]/dt = -k'_3[SOH][L\textsuperscript{I-}] + k'_4[SL\textsuperscript{1-I}] \tag{24}
\]

Therefore, the change in inorganic oxyanion concentration over time is related to the concentration of the inorganic oxide surface hydroxyl groups and the concentration of the inorganic oxyanion adsorbed onto the metal cation. Moreover, equation [23] predicts the pseudo rate coefficient and equilibrium constant for ligand exchange would be pH dependent.

Equation [24] is identical in form to the kinetic Langmuir equation (Travis and Etnier, 1981). Selim and Amacher (1988) found that a two-site version of the kinetic Langmuir approach successfully described the kinetics of Cr(VI) retention by soils. Thus, equation [24] is fully consistent with the more general kinetic Langmuir model. If \([SOH] \gg [L\textsuperscript{I-}]\) so that its concentration changes little during the reaction, then a new pseudo rate coefficient \((k'_3')\) can be defined

\[
k'_3' = k'_3[SOH] \tag{25}
\]
If \([L''^-]\) reacts nonlinearly with the oxide surface, then equation [24] becomes

\[
\frac{d[L''^-]}{dt} = -k_3' [L''^-]^n + k_4' [SL''^-]
\]

Equation [26] is identical in form to equation [4] and [6] which have also been found to describe the kinetics of \([\text{Cr(VI)}]\) retention by several soils. Although equations [24] and [26] assume that there is only one type of oxide site, they can be readily extended for the two-site case considered in the multireaction model.

The ligand exchange mechanism shown in equation [13] and [14] is for an inner-sphere complex. If the oxyanion forms an outer-sphere complex with the oxide surface, then equation [14] becomes

\[
\text{SOH}_2^+(s) + L''^-(aq) = \text{SOH}_2^+L''^-(s)
\]

Equation [19], therefore, changes to

\[
\frac{d[L''^-]}{dt} = -k_5[SOH_2^+] [L''^-] + k_6[SOH_2^+L''^-]
\]

Substituting [18] into [28] produces

\[
\frac{d[L''^-]}{dt} = -k_5 K_1[SOH][H^+][L''^-] + k_6[SOH_2^+L''^-]
\]

and if

\[
k_5' = k_5 K_1[\text{H}^+]
\]

then

\[
\frac{d[L''^-]}{dt} = -k_5'[SOH][L''^-] + k_6[SOH_2^+L''^-]
\]

which is the second-order version. If

\[
k_5'' = k_5'[SOH]
\]

then

\[
\frac{d[L''^-]}{dt} = -k_5''[L''^-]^m + k_5[SOH_2^+L''^-]
\]

which is the nonlinear version.

If the outer- and inner-sphere complexes are both formed concurrently (i.e. reactions [14] and [27] occur together), then equations
[24] and [31], and [26] and [33] are equivalent to the two-site second-order and nonlinear models, respectively.

An additional possibility exists in that the reactions may occur consecutively. The outer-sphere complex is formed first and then the inner-sphere in a stepwise sequence:

\[ \text{SOH}_2^+(s) + L^{I^-}(aq) = \text{SOH}_2^+L^{I^-}(s) = SL^{1-I^-}(s) + H_2O(1) \]  

[34] This mechanism has no effect on the form of the kinetic equation for \( L^{I^-} \), however, because \( \text{SOH}_2^+L^{I^-} \) is a reactive intermediate. Equations [31] and [33] remain the same.
MATERIALS AND METHODS

Reagents

Batch kinetic experiments were conducted using chromate (CrO$_4^{2-}$), phosphate (PO$_4^{3-}$), arsenate (AsO$_4^{3-}$), borate (BO$_3^{3-}$), fluoride (F$^-$), molybdate (MoO$_4^{2-}$), selenite (SeO$_3^{2-}$), and silicate (H$_4$SiO$_4$). Potassium or sodium salts of the oxyanion elements were used in the study and their forms are listed in Table 1. The major background salt used in the kinetic reactions was 0.005 M Ca(NO$_3$)$_2$. Additional background salts used were 0.01, 0.05, and 0.10 M Ca(NO$_3$)$_2$, 0.005 M CaCl$_2$, 0.005 M NaCl, and 0.005 M NaClO$_4$. All salts were reagent grade.

Iron Oxide, Aluminum Oxide, and Humic Acid

A preparation of synthetic goethite served as the major adsorbent material for the kinetic studies. A 200 mM concentration of synthetic goethite was prepared by dissolving 27.03 g of FeCl$_3$·6H$_2$O in 100 mL of deionized water in each of two 250 mL plastic centrifuge bottles. The pH of each solution was adjusted to 7 by slowly adding 5 mM NaOH to the stirred solutions. The resulting suspensions were centrifuged for 20 minutes at 23,500 g (12,000 rpm) and the supernatant discarded at the completion of centrifugation. The precipitate was dispersed in deionized water, then centrifuged for another 20 minutes at 23,500 g. Again, at the completion of centrifugation the supernatant was discarded, while the precipitate was redispersed in deionized water. The process of centrifugation and dispersion was repeated until the precipitate ceased to centrifuge out, indicating all the electrolyte had been washed free. At this point the solutions were combined and made to 1.0 L. After six years of aging, x-ray diffraction analysis indicated
Table 1. Elements and their forms used in kinetic and sorption studies.

<table>
<thead>
<tr>
<th>Element</th>
<th>Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>$K_2Cr_2O_7$</td>
</tr>
<tr>
<td>P</td>
<td>$KH_2PO_4$</td>
</tr>
<tr>
<td>As</td>
<td>$Na_2HAsO_4\cdot 7H_2O$</td>
</tr>
<tr>
<td>B</td>
<td>$H_3BO_3$</td>
</tr>
<tr>
<td>Se</td>
<td>$Na_2SeO_3$</td>
</tr>
<tr>
<td>Si</td>
<td>$Na_2SiO_3$</td>
</tr>
<tr>
<td>F</td>
<td>$NaF$</td>
</tr>
<tr>
<td>Mo</td>
<td>$Na_2MoO_4\cdot 2H_2O$</td>
</tr>
</tbody>
</table>
that the iron oxide was goethite (FeOOH).

A preparation of gibbsite \((\text{Al(OH)}_3\)) was made by dissolving 24.14 g of \(\text{AlCl}_3\cdot6\text{H}_2\text{O}\) in 100 mL of deionized water in each of two 250 mL plastic centrifuge bottles. The procedure of pH adjustment, centrifugation, and dispersion was the same as that for the iron oxide material. After four months of aging, x-ray analysis indicated the \(\text{Al(OH)}_3\) material was not crystalline in nature.

A third adsorbent material investigated for its ability to adsorb oxyanions was humic acid. A Lafitte Muck soil from Louisiana was used as the source material from which the humic acid was extracted. The procedure followed for humic acid extraction can be found in Appendix 1.

**Soils**

In addition to the goethite serving as an absorbent material seven soils were also studied. This study was restricted to the kinetics of chromate retention in the soils selected. Their names, taxonomic classification, and selected properties are listed in Table 2. Soil characterization of the soils was conducted by the Soil Testing and Soil Characterization Laboratories at Louisiana State University. Details of procedures used in soil characterization can be found in Appendix 2. Prior to use, the soils were air-dried, ground, and passed through a 2-mm sieve.

**Experimental Procedure: Batch Kinetic Experiments**

Kinetic retention/release studies were carried out utilizing a batch stirred reaction vessel as shown in Figure 2. The apparatus design allowed for continuous monitoring of temperature and pH during kinetic runs. A constant temperature water bath was used for the
Table 2. Taxonomic classification and selected soil properties.

<table>
<thead>
<tr>
<th>Soil</th>
<th>Horizon</th>
<th>Taxonomic Classification</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alligator</td>
<td>Ap</td>
<td>very-fine, montmorillonitic, acid, thermic Vertic Haplaquept</td>
<td>4.8</td>
</tr>
<tr>
<td>Cecil</td>
<td>Ap</td>
<td>clayey, kaolinitic, thermic, Typic Hapludult</td>
<td>5.7</td>
</tr>
<tr>
<td>Cecil</td>
<td>B</td>
<td>clayey, kaolinitic, thermic, Typic Hapludult</td>
<td>5.4</td>
</tr>
<tr>
<td>Kula</td>
<td>Ap1</td>
<td>medial, isothermic, Typic Euthandept</td>
<td>5.9</td>
</tr>
<tr>
<td>Kula</td>
<td>Ap2</td>
<td>medial, isothermic, Typic Euthandept</td>
<td>6.2</td>
</tr>
<tr>
<td>Lafitte</td>
<td>Ap</td>
<td>euic, thermic, Typic Medisaprist</td>
<td>3.9</td>
</tr>
<tr>
<td>Molokai</td>
<td>Ap</td>
<td>clayey, kaolinitic, isohyper-thermic Typic Torrox</td>
<td>6.0</td>
</tr>
<tr>
<td>Webster</td>
<td>Ap</td>
<td>fine-loamy, mixed, mesic, Typic Haplaquoll</td>
<td>7.6</td>
</tr>
<tr>
<td>Windsor</td>
<td>Ap</td>
<td>mixed, mesic, Typic Udipsamment</td>
<td>5.3</td>
</tr>
<tr>
<td>Windsor</td>
<td>B</td>
<td>mixed, mesic, Typic Udipsamment</td>
<td>5.8</td>
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</table>
Table 2. (continued)

<table>
<thead>
<tr>
<th>Soil</th>
<th>Horizon</th>
<th>TOC %</th>
<th>Sum of cations</th>
<th>Exch. OH cmol/kg</th>
<th>Sand %</th>
<th>Silt %</th>
<th>Clay %</th>
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</thead>
<tbody>
<tr>
<td>Alligator</td>
<td>Ap</td>
<td>1.54</td>
<td>30.2</td>
<td>3.5</td>
<td>5.9</td>
<td>39.4</td>
<td>54.7</td>
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<tr>
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<td>2.0</td>
<td>78.8</td>
<td>12.9</td>
<td>8.3</td>
</tr>
<tr>
<td>Cecil</td>
<td>B</td>
<td>0.26</td>
<td>2.4</td>
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<td>30.0</td>
<td>18.8</td>
<td>51.2</td>
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<td>Ap1</td>
<td>6.62</td>
<td>22.5</td>
<td>82.4</td>
<td>73.7</td>
<td>25.4</td>
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<td>0.5</td>
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<tr>
<td>Lafitte</td>
<td>Ap</td>
<td>11.6</td>
<td>26.9</td>
<td>4.7</td>
<td>60.7</td>
<td>21.7</td>
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<tr>
<td>Molokai</td>
<td>Ap</td>
<td>1.67</td>
<td>11.0</td>
<td>7.2</td>
<td>25.7</td>
<td>46.2</td>
<td>28.2</td>
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<td>Webster</td>
<td>Ap</td>
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<td>48.1</td>
<td>14.1</td>
<td>27.5</td>
<td>48.6</td>
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<td>20.5</td>
<td>2.8</td>
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<tr>
<td>Windsor</td>
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<td>0.8</td>
<td>10.1</td>
<td>74.8</td>
<td>24.1</td>
<td>1.1</td>
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</table>
Table 2. (continued)

<table>
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<tr>
<th>Soil</th>
<th>Horizon</th>
<th>MnO₂</th>
<th>Fe₂O₃</th>
<th>amorph.</th>
<th>free</th>
<th>Al₂O₃</th>
<th>GaCO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alligator</td>
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<td>0.028</td>
<td>0.33</td>
<td>0.74</td>
<td>0.15</td>
<td></td>
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</tr>
<tr>
<td>Cecil</td>
<td>Ap</td>
<td>0.011</td>
<td>0.099</td>
<td>1.76</td>
<td>0.27</td>
<td></td>
<td>---</td>
</tr>
<tr>
<td>Cecil</td>
<td>B</td>
<td>0.002</td>
<td>0.082</td>
<td>7.48</td>
<td>0.94</td>
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</tr>
<tr>
<td>Kula</td>
<td>Ap1</td>
<td>0.093</td>
<td>1.68</td>
<td>5.85</td>
<td>3.51</td>
<td></td>
<td>---</td>
</tr>
<tr>
<td>Kula</td>
<td>Ap2</td>
<td>0.13</td>
<td>1.64</td>
<td>6.95</td>
<td>3.67</td>
<td></td>
<td>---</td>
</tr>
<tr>
<td>Lafitte</td>
<td>Ap</td>
<td>0.009</td>
<td>1.19</td>
<td>1.16</td>
<td>0.28</td>
<td></td>
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</tr>
<tr>
<td>Molokai</td>
<td>Ap</td>
<td>0.76</td>
<td>0.19</td>
<td>12.4</td>
<td>0.91</td>
<td></td>
<td>---</td>
</tr>
<tr>
<td>Webster</td>
<td>Ap</td>
<td>0.063</td>
<td>0.19</td>
<td>0.55</td>
<td>0.10</td>
<td>3.14</td>
<td></td>
</tr>
<tr>
<td>Windsor</td>
<td>Ap</td>
<td>0.041</td>
<td>0.42</td>
<td>1.23</td>
<td>0.56</td>
<td></td>
<td>---</td>
</tr>
<tr>
<td>Windsor</td>
<td>B</td>
<td>0.031</td>
<td>0.23</td>
<td>0.79</td>
<td>0.29</td>
<td></td>
<td>---</td>
</tr>
</tbody>
</table>
Figure 2. Diagram of reaction vessel used in kinetic studies.
different temperature experiments. After addition of the background electrolyte and adjustment of the pH of the goethite suspension (if required), a known volume and concentration of chromate was added at time zero to give an initial suspension volume of 2.0 L and yield the initial concentrations of reactant(s) desired. At pre-selected time intervals, the suspension was rapidly sampled with a 10 cc "Luer-Lok" syringe (Cat. # 9604, Becton Dickinson & Co., Rutherford, NJ) and immediately filtered through a 0.4 um polycarbonate membrane filter (Cat. # 110607, Nuclepore Corp., Pleasanton, CA) enclosed in a 25 mm "Swin-Lok" filter holder (Cat. # 420200, Nuclepore Corp., Pleasanton, CA). At the completion of a retention experiment (24 h), a known volume and concentration of phosphate was added to the suspension to give the desired initial reactant concentrations. The exchange of chromate by phosphate was followed by periodic sampling and filtering of the suspension as described above. Chromate and phosphate solution concentrations were determined colorimetrically (on a Hatachi 100-40 UV-VIS spectrophotometer) using the s-diphenylcarbohydrazide and ascorbic acid reduction methods, respectively (Reisenauer, 1982; Olsen and Sommers, 1982). For other anions studied using the batch experimental procedure, determinations were performed by ICP (inductively coupled plasma) emission spectrometry. A summary of the experimental variables (i.e. reactant concentrations, pH, temperature, background solution) is given in Table 3.

Kinetic retention studies were conducted with the seven soils using only the chromate oxyanion. In these studies the background electrolyte used was 0.005 M Ca(NO₃)₂ and the total volume of the soil suspension was 2.0 L. Twenty grams of the respective soil were used in each
Table 3. Summary of experimental variables for the various kinetic experiments.

<table>
<thead>
<tr>
<th>[FeOOH] (mM)</th>
<th>[Cr(VI)]&lt;sub&gt;0&lt;/sub&gt; (uM)</th>
<th>[PO&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;2-&lt;/sup&gt;]&lt;sub&gt;0&lt;/sub&gt; (uM)</th>
<th>pH</th>
<th>Temp. (°C)</th>
<th>Background Solution</th>
<th>Ionic Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>------------—</td>
<td>----------------</td>
<td>----------------</td>
<td>---</td>
<td>-----------</td>
<td>----------------</td>
<td>---------------</td>
</tr>
<tr>
<td>0.1</td>
<td>19.2</td>
<td>32.2</td>
<td>5.31</td>
<td>23.0</td>
<td>0.005 M Ca(NO&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.015 M</td>
</tr>
<tr>
<td>0.2</td>
<td>19.2</td>
<td>32.2</td>
<td>5.31</td>
<td>23.0</td>
<td>0.005 M Ca(NO&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.015 M</td>
</tr>
<tr>
<td>0.5</td>
<td>19.2</td>
<td>32.2</td>
<td>5.30</td>
<td>23.0</td>
<td>0.005 M Ca(NO&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.015 M</td>
</tr>
<tr>
<td>1.0</td>
<td>19.2</td>
<td>32.2</td>
<td>5.08</td>
<td>23.0</td>
<td>0.005 M Ca(NO&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.015 M</td>
</tr>
</tbody>
</table>

---- FeOOH Experiments ----

| 0.5          | 9.6            | 16.1           | 5.05 | 23.0      | 0.005 M Ca(NO<sub>3</sub>)<sub>2</sub> | 0.015 M       |
| 0.5          | 19.2           | 32.2           | 5.25 | 24.0      | 0.005 M Ca(NO<sub>3</sub>)<sub>2</sub> | 0.015 M       |
| 0.5          | 38.4           | 64.6           | 5.26 | 23.5      | 0.005 M Ca(NO<sub>3</sub>)<sub>2</sub> | 0.015 M       |
| 0.5          | 96.2           | 161.4          | 4.84 | 23.0      | 0.005 M Ca(NO<sub>3</sub>)<sub>2</sub> | 0.015 M       |
| 0.5          | 192.3          | 322.9          | 4.57 | 23.0      | 0.005 M Ca(NO<sub>3</sub>)<sub>2</sub> | 0.015 M       |

---- Cr(VI) Experiments ----

| 0.5          | 19.2           | 32.2           | 5.11 | 2.0       | 0.005 M Ca(NO<sub>3</sub>)<sub>2</sub> | 0.015 M       |
| 0.5          | 19.2           | 32.2           | 5.20 | 11.0      | 0.005 M Ca(NO<sub>3</sub>)<sub>2</sub> | 0.015 M       |
| 0.5          | 19.2           | 32.2           | 5.30 | 23.0      | 0.005 M Ca(NO<sub>3</sub>)<sub>2</sub> | 0.015 M       |
| 0.5          | 19.2           | 32.2           | 5.16 | 31.0      | 0.005 M Ca(NO<sub>3</sub>)<sub>2</sub> | 0.015 M       |
| 0.5          | 19.2           | 32.2           | 5.16 | 40.0      | 0.005 M Ca(NO<sub>3</sub>)<sub>2</sub> | 0.015 M       |

---- Temperature Experiments ----

| 0.5          | 19.2           | 32.2           | 5.30 | 23.0      | 0.005 M Ca(NO<sub>3</sub>)<sub>2</sub> | 0.015 M       |
| 0.5          | 19.2           | 32.2           | 5.19 | 24.0      | 0.01 M Ca(NO<sub>3</sub>)<sub>2</sub> | 0.03 M       |
| 0.5          | 19.2           | 32.2           | 5.13 | 23.0      | 0.05 M Ca(NO<sub>3</sub>)<sub>2</sub> | 0.15 M       |
| 0.5          | 19.2           | 32.2           | 5.18 | 23.0      | 0.10 M Ca(NO<sub>3</sub>)<sub>2</sub> | 0.30 M       |

---- Ca(NO<sub>3</sub>)<sub>2</sub> Experiments ----

| 0.5          | 19.2           | 32.2           | 5.30 | 23.0      | 0.005 M Ca(NO<sub>3</sub>)<sub>2</sub> | 0.015 M       |
| 0.5          | 19.2           | 32.2           | 5.19 | 24.0      | 0.01 M Ca(NO<sub>3</sub>)<sub>2</sub> | 0.03 M       |
| 0.5          | 19.2           | 32.2           | 5.13 | 23.0      | 0.05 M Ca(NO<sub>3</sub>)<sub>2</sub> | 0.15 M       |
| 0.5          | 19.2           | 32.2           | 5.18 | 23.0      | 0.10 M Ca(NO<sub>3</sub>)<sub>2</sub> | 0.30 M       |
Table 3. (continued)

<table>
<thead>
<tr>
<th>[FeOOH] (mM)</th>
<th>[Cr(VI)]&lt;sub&gt;o&lt;/sub&gt; (uM)</th>
<th>[PO&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;2-&lt;/sup&gt;]&lt;sub&gt;o&lt;/sub&gt; (uM)</th>
<th>pH</th>
<th>Temp. (°C)</th>
<th>Background Solution</th>
<th>Ionic Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>----</td>
<td>0.5</td>
<td>19.2</td>
<td>----</td>
<td>5.30</td>
<td>23.0</td>
<td>0.005 M Ca(NO&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>----</td>
<td>0.5</td>
<td>19.2</td>
<td>----</td>
<td>5.24</td>
<td>22.5</td>
<td>0.005 M CaCl&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>----</td>
<td>0.5</td>
<td>19.2</td>
<td>----</td>
<td>5.02</td>
<td>24.5</td>
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<tr>
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<td>----</td>
<td>4.96</td>
<td>23.5</td>
<td>0.005 M NaClO&lt;sub&gt;4&lt;/sub&gt;</td>
</tr>
</tbody>
</table>

--- Background Salt Solution Experiments ---
reaction with no goethite suspension added. The experimental procedure of sampling and filtering was the same as described above.

**Experimental Procedure: Sorption Experiments**

Retention of five of the elements (Cr, P, As, Se, and Si) was studied using a batch equilibration method. Stock suspensions of goethite in 0.005 M Ca(NO$_3$)$_2$ were adjusted to pH 3, 4, 5, 6, 7, and 8. In addition, stock solutions of the oxyanion forms of Cr, P, As, Se, and Si were prepared at the concentrations of interest. Nine milliliters of each stock goethite suspension were mixed with 1.0 mL of the stock solution of the element and concentration of interest. This resulted in a total solution volume of 10.0 mL, yielding a goethite concentration of 2 mM and element concentrations ranging from 10 µM to 500 µM. The suspensions were allowed to shake for 24 h, filtered through 0.4 µm membrane filters, and analyzed by ICP emission spectrometry.

The amounts of each element retained by the goethite were calculated by

$$ S = \frac{C_\text{o} - C}{W} $$

where $S$ is the amount retained (µmol/mmol), $C_\text{o}$ is the initial concentration in solution (µmol/L), $C$ is the final concentration in solution (µmol/L), and $W$ is the concentration of goethite (mmol/L).

**Data Analysis**

A nonlinear, least squares, curve-fitting method of van Genuchten (1981) was used to obtained the rate coefficients of the nonlinear, multireaction model for the retention data. To determine the goodness-of-fit of the model to the data, the r-square and the root mean square (rms) statistics were used. The root mean square was calculated by the
following,
\[
\text{rms} = \left[ \frac{\text{rss}}{(m - p)} \right]^{0.5} \tag{36}
\]
where rss is the residual sum of squares, m is the number of data points, and p is the number of parameters.

To determine if there was any statistical significant improvement in the fit of the model to the data by the addition of more parameters to the model (i.e. the three parameter model versus the five parameter model) the extra sum of squares principle of Kinniburgh (1986) was employed. The F ratio needed for testing the statistical significance of the two model versions was calculated by,
\[
F(p_2 - p_1, m - p_2) = \frac{\left[ (\text{rss}_1 - \text{rss}_2) / (p_2 - p_1) \right]}{\left[ \text{rss}_2 / (m - p_2) \right]} \tag{37}
\]
where m, p, and rss are as previously defined above and the subscripts refer to the model variation. The extra sum of squares principle is only applicable if one model is a variation of another, as is the case in this study.
RESULTS AND DISCUSSION

Sorption Studies

Retention of several oxyanion species (Cr, P, As, Se, Si) on goethite were studied. Both the Freundlich equation (exponential form) and the two-site Langmuir were used to describe the retention isotherms. The Freundlich equation was used to determine the nonlinear exponent term in the nonlinear multireaction model. The two-site Langmuir equation was used to determine the quantities of type 1 and type 2 sites, which are used in the second-order model. The effect of pH on the Freundlich and Langmuir parameters was also determined so that the kinetic models could be used at different pH levels. For each oxyanion, fifteen concentrations were studied ranging from 10 to 500 μM. In most cases, there was complete retention of the oxyanion at low concentrations (< 50 μM) when the reaction was conducted at acid pH levels, however at alkaline pH levels, this was not always the case.

The retention isotherms for the two major oxyanions of interest, Cr and P, are shown in Figures 3 and 4. The Freundlich equation was found to adequately describe both Cr and P retention data at acid and alkaline pH values. Estimated values of K for Cr decreased as the pH increased. Conversely, n, the reaction order, increased as pH increased (Fig. 5). Estimated K values for P decreased linearly from pH 3 to 5, however at pH 6 and 7, K values increased slightly. Additionally, values of n followed a near linear trend with increasing pH, except for two deviations at pH 5 and 7 (Fig. 6). Overall, K values for P were of greater magnitude than those for Cr, however, estimated values for n were smaller for P than for Cr.
Figure 3. Chromate retention by goethite after 24 h - Freundlich model.

Figure 3 shows the retention of Cr by goethite at different pH levels (3, 4, 5, 6, 7, 8) after 24 hours. The graphs display the relationship between the concentration of Cr in solution and the concentration of Cr retained per mmol of FeOOH. The data points for each pH level are represented by different symbols and are fitted with straight lines. The concentration of FeOOH is fixed at 2 mM in the experiment. The Freundlich model is used to describe the retention process.
Figure 4. Phosphate retention by goethite after 24 h - Freundlich model.
Figure 5. Freundlich parameters $K$ and $n$ as a function of pH for Cr(VI) retention by goethite after 24 h.
Figure 6. Freundlich parameters $K$ and $n$ as a function of pH for P retention by goethite after 24 h.
Retention isotherms for As, Se, and Si by goethite are shown in Figures 7, 8, and 9, respectively. Similar to Cr and P, values of K as a whole decreased and n values generally increased as pH increased. The response of the Freundlich parameters to changes in pH for Si were the converse to Cr, P, As, and Se. With the exception of the pH 8 data, estimated K values increased and values of n decreased, as pH increased. Figures 10, 11, and 12 are graphical representations of the response of K and n to increasing pH for As, Se, and Si, respectively. A near linear relation was established between pH and K for As and Se, however for Si this was not the case. Alternatively, a least squares fit resulted in a second order regression providing an improved description of both K and n versus pH for the Si retention data (Fig. 13). Tables 4 and 5 summarize the Freundlich parameters for Cr, P, As, Se, and Si, and includes the $r^2$ values for the linear fit of the Freundlich model to the experimental data.

At pH 3 and at low concentrations, more P was retained by goethite than Se, Cr, As, or Si, however, as the concentration increased Se was more highly retained than the other ions. The K parameter is a good indication of the affinity an ion has for an adsorbent, with higher K values related to stronger retention. For all pH values studied, the order of the ions from the strongest retained to the weakest retained, was found to be As > P = Se > Cr > Si. Moreover, for Cr, P, As, and Se there was stronger retention of the ions at the acid pH levels as compared to the alkaline or neutral pH solutions. This is consistent with the mechanistic theory proposed earlier predicting greater anion adsorption on inorganic oxide surfaces at acid pH levels.
Figure 7. Arsenate retention by goethite after 24 h - Freundlich model.
Figure 8. Selenite retention by goethite after 24 h - Freundlich model.
Figure 9. Silicate retention by goethite after 24 h - Freundlich model.
Figure 10. Freundlich parameters $K$ and $n$ as a function of pH for As retention by goethite after 24 h.
Figure 11. Freundlich parameters $K$ and $n$ as a function of pH for Se retention by goethite after 24 h.
Figure 12. Freundlich parameters $K$ and $n$ as a function of pH for Si retention by goethite after 24 h.
Figure 13. Freundlich parameters $K$ and $n$ as a function of pH for Si retention by goethite as described by a second order regression.

Log $K = -9.74 + 3.24 \text{pH} - 0.250 \text{pH}^2$

$R^2 = 0.994$

Log $n = 1.44 - 0.517 \text{pH} + 0.039 \text{pH}^2$

$R^2 = 0.884$
Table 4. Freundlich model parameters for Cr and P after reaction with goethite for 24 h.

<table>
<thead>
<tr>
<th>pH</th>
<th>Cr(VI) K</th>
<th>Cr(VI) n</th>
<th>Cr(VI) r²</th>
<th>P K</th>
<th>P n</th>
<th>P r²</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
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<td>0.914</td>
<td>38.41</td>
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<td>0.955</td>
</tr>
<tr>
<td>4</td>
<td>12.59</td>
<td>0.177</td>
<td>0.990</td>
<td>26.76</td>
<td>0.105</td>
<td>0.998</td>
</tr>
<tr>
<td>5</td>
<td>9.22</td>
<td>0.241</td>
<td>0.988</td>
<td>17.24</td>
<td>0.210</td>
<td>0.998</td>
</tr>
<tr>
<td>6</td>
<td>5.76</td>
<td>0.309</td>
<td>0.988</td>
<td>20.20</td>
<td>0.157</td>
<td>0.886</td>
</tr>
<tr>
<td>7</td>
<td>2.13</td>
<td>0.458</td>
<td>0.989</td>
<td>23.17</td>
<td>0.126</td>
<td>0.994</td>
</tr>
<tr>
<td>8</td>
<td>0.08</td>
<td>0.725</td>
<td>0.998</td>
<td>16.50</td>
<td>0.201</td>
<td>0.992</td>
</tr>
</tbody>
</table>

Table 5. Freundlich model parameters for As, Se, and Si after reaction with goethite for 24 hours.

<table>
<thead>
<tr>
<th>pH</th>
<th>As K</th>
<th>As n</th>
<th>As r²</th>
<th>Se K</th>
<th>Se n</th>
<th>Se r²</th>
<th>Si K</th>
<th>Si n</th>
<th>Si r²</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>33.68</td>
<td>0.105</td>
<td>0.979</td>
<td>35.00</td>
<td>0.137</td>
<td>0.994</td>
<td>0.006</td>
<td>1.52</td>
<td>0.957</td>
</tr>
<tr>
<td>4</td>
<td>26.07</td>
<td>0.090</td>
<td>0.995</td>
<td>33.44</td>
<td>0.039</td>
<td>0.999</td>
<td>0.128</td>
<td>1.27</td>
<td>0.949</td>
</tr>
<tr>
<td>5</td>
<td>24.59</td>
<td>0.090</td>
<td>0.997</td>
<td>20.83</td>
<td>0.125</td>
<td>0.999</td>
<td>1.95</td>
<td>0.708</td>
<td>0.941</td>
</tr>
<tr>
<td>6</td>
<td>23.12</td>
<td>0.105</td>
<td>0.997</td>
<td>18.77</td>
<td>0.133</td>
<td>0.998</td>
<td>4.36</td>
<td>0.530</td>
<td>0.945</td>
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<td>7</td>
<td>23.04</td>
<td>0.107</td>
<td>0.998</td>
<td>18.43</td>
<td>0.122</td>
<td>0.997</td>
<td>6.31</td>
<td>0.465</td>
<td>0.959</td>
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<tr>
<td>8</td>
<td>20.78</td>
<td>0.118</td>
<td>0.998</td>
<td>12.25</td>
<td>0.203</td>
<td>0.997</td>
<td>1.42</td>
<td>0.743</td>
<td>0.969</td>
</tr>
</tbody>
</table>
Buchter et al. (1989) studied the retention of fifteen elements, including P, Cr, and As and found soils with large amounts of metal oxides to retain more of a given oxyanion species than soils with small percentages of metal oxides. In addition, in the eleven soils they studied, low pH soils retained more of a given oxyanion species than did high pH soils. In general, greater retention of P and As as compared to Cr was observed by Buchter et al. (1989), which is consistent with retention on goethite in this study. Amacher et al. (1986) investigated the ability of several equilibrium models to accurately describe the retention of Cr by ten soils varying in percentages of metal oxides. For reaction times ranging from 2 to 336 hours, the Freundlich equation was found to adequately describe the Cr retention data for all ten soils. Ainsworth et al. (1985) studied P adsorption on pure and aluminum substituted goethite samples. Adsorption of P was found to be pH dependent for both types of goethite materials, with adsorption increasing as the pH of the solution decreased from 7.6 to 2.6. More recently, Ainsworth et al. (1989) studied chromate adsorption on pure and aluminum substituted goethite and found chromate to be preferentially adsorbed by Fe sites as compared to Al-substituted sites. Moreover, they concluded that Al-substitution does reduce chromate adsorption due to the difference in the acid-base nature of Al and Fe sites and the consequent reactions of these sites with background electrolyte anions in solution.

In addition to the Freundlich equation, the equilibrium two-site Langmuir equation was tested for its ability to describe the goethite retention data for Cr, P, As, Se, and Si. The two-site Langmuir was successful in describing Cr retention data at acid solution pH levels,
but failed to describe the experimental data at pH 7 and 8 (Fig. 14). Figure 15 depicts the effect pH has upon the maximum retention capacity and the fraction of fast reacting type 1 sites. The quantity of type 1 sites decreases with increasing pH while the quantity of type 2 sites increases with increasing pH. At high pH levels, the quantity of type 1 sites may become vanishingly small and therefore the two-site Langmuir model will no longer work. The predicted values of the parameters in the two-site Langmuir are presented in Table 6 for Cr. For Cr retention at pH 3 and 4, Cr had a greater affinity for the slow reacting sites (type 2), as evident by the higher \( K_2 \) values, whereas at pH 5 and 6 Cr had a greater affinity for the fast reacting type 1 sites. In addition, the maximum adsorption capacity on the type 1 sites was greatest at pH 4, and at pH 6 for the type 2 sites. The study conducted by Amacher et al. (1986) on Cr retention by nine soils, resulted in the two-site Langmuir successfully describing the retention data. For all nine soils, \( K_1 >> K_2 \) and \( b_1 << b_2 \). The results found in this study on Cr retention on goethite were consistent with three of the soils (Cecil, Kula, and Molokai) Amacher, et al. (1986) studied, which contained high Fe\(_2\)O\(_3\) contents and in the pH range of 5 to 6.

For the P data, there was good agreement between predicted and experimental results at pH values of 4, 6, and 8 only (Fig. 16). Figure 17 shows the effect pH has on the maximum retention capacity and the fraction of type 1 sites for P adsorption by goethite. Holford et al. (1974) successfully used the two-site Langmuir equation to model phosphate adsorption on 41 soils. For Holford's et al. (1974) phosphate data, the maximum adsorption capacity (\( b_1 \)) for the rapidly reacting high energy site was found to be three times greater than the slow reacting
Figure 14. Chromate retention by goethite after 24 h - Two-site Langmuir model.
Figure 15. Effect of pH on maximum retention capacity (ST) and fraction of type 1 sites (f) for Cr(VI).
Table 6. Two-site Langmuir model parameters for Cr and P after reaction with goethite for 24 h.

<table>
<thead>
<tr>
<th>Element</th>
<th>pH</th>
<th>$K_1$</th>
<th>$K_2$</th>
<th>$b_1$</th>
<th>$b_2$</th>
<th>$r^2$</th>
</tr>
</thead>
<tbody>
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<td>Cr</td>
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<td>0.199</td>
<td>3.16</td>
<td>15.88</td>
<td>12.53</td>
<td>0.999</td>
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<tr>
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<td>4</td>
<td>2.67</td>
<td>0.003</td>
<td>19.86</td>
<td>36.40</td>
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</tr>
<tr>
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<td>5</td>
<td>5.82</td>
<td>0.001</td>
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<td>78.89</td>
<td>0.965</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>6.97</td>
<td>0.002</td>
<td>11.06</td>
<td>57.20</td>
<td>0.974</td>
</tr>
<tr>
<td>P</td>
<td>4</td>
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<td>1.17</td>
<td>14.97</td>
<td>35.28</td>
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</tr>
<tr>
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<td>10.44</td>
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<tr>
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<td>0.508</td>
<td>15.99</td>
<td>29.17</td>
<td>0.992</td>
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Figure 16. Phosphate retention by goethite after 24 h - Two-site Langmuir model.
Figure 17. Effect of pH on maximum retention capacity (ST) and fraction of type 1 sites (f) for P.
high energy site ($b_2$). Similarly, the affinity parameter $K_1$ was of greater magnitude (100 times) than the slower reacting affinity parameter $K_2$. On both alkaline and acid soils studied by Olsen and Watanabe (1957) using the Langmuir equation, the parameter K increased as the bonding energy of the soil for phosphate increased. Furthermore, acid soils were found to retain more phosphate per surface area unit and also held phosphate with a greater bonding energy than alkaline soils. In the study conducted by Olsen and Watanabe (1957), results showed a closer agreement with the Langmuir equation than with the Freundlich equation when describing phosphate adsorption by soils. They concluded that when phosphate adsorption data tends to follow both the Langmuir and Freundlich equations, it is preferable to use the Langmuir so that an adsorption maximum can be calculated. Goldberg and Sposito (1984) utilized the constant capacitance model to describe phosphate adsorption by goethite. Experimental data revealed the amount of phosphate adsorbed steadily decreased as the pH value increased. In addition, they concluded there was no direct relationship between solution speciation and surface speciation.

Figures 18 and 19 depict the two-site Langmuir model fitted to the As and Se experimental sorption data, respectively. The two-site Langmuir was successful in describing the data at pH 3, 4, 5, 6, 7, and 8 for both oxyanions. Additionally, for both As and Se, $K_2$ was greater than $K_1$ for all pH values studied. No significant correlations could be established between $K_1$, $K_2$, $b_1$, $b_2$ and pH. Table 7 summarizes the two-site Langmuir parameters for As and Se. Goldberg (1986) quantitatively described arsenate adsorption by goethite utilizing the constant capacitance model. The model was capable of describing arsenate adsorption
Figure 18. Arsenate retention by goethite after 24 h - Two-site Langmuir model.
Figure 19. Selenite retention by goethite after 24 h - Two-site Langmuir model.
Table 7. Two-site Langmuir model parameters for As, Se, and Si after reaction with goethite for 24 h.

<table>
<thead>
<tr>
<th>Element</th>
<th>pH</th>
<th>$K_1$</th>
<th>$K_2$</th>
<th>$b_1$</th>
<th>$b_2$</th>
<th>$r^2$</th>
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<tr>
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<tr>
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<tr>
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<td>12.42</td>
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</table>
behavior on goethite over the pH range of 4.5 to 10. Arsenate adsorption was greatest at acid pH values and decreased as pH increased. Goldberg (1986) points out that the constant capacitance model is capable of describing changes in adsorption as a function of solution pH using only one additional adjustable parameter than the Freundlich and Langmuir adsorption equations. Hingston et al. (1968) studied the adsorption of selenite by goethite and found that specific adsorption of selenite by goethite increases the pH of the suspension and the negative charge on the oxide surface. The Langmuir equation showed the amount of selenite taken up by goethite reaches a maximum value at a constant pH and cannot be exceeded by increasing the solution concentration. The maximum adsorption was found to vary with pH, with greater adsorption occurring at acid pH levels than alkaline pH levels. Moreover, a linear relationship was found between the log K (K being the affinity parameter) and pH at high pH values, while at low pH values the slope of log K versus pH approaches zero (i.e. K becomes constant with decreasing pH).

The two-site Langmuir was only capable of describing Si sorption data at pH 8 and the parameter estimates can also be found in Table 7. At the pH values studied, the major Si species that will be present is the neutral Si species, $\text{H}_4\text{SiO}_4$. McPhail et al. (1972) were able to describe the adsorption of Si by iron oxides using the Langmuir equation. An adsorption maxima of 2.67 mmoles Si/g of iron oxides at pH 7 was determined. McPhail et al. (1972) concluded that the soluble Si in soil solutions is related to complex adsorption reactions involving amorphous oxides of iron.
Cr(VI) and P Kinetics

Two model variations, a three-parameter version \((k_1, k_2, k_{irr})\) consisting of one nonlinear reversible and one first order irreversible reaction, and a five-parameter version \((k_1, k_2, k_3, k_4, k_{irr})\) consisting of two nonlinear reversible and one first order irreversible reactions were evaluated for their ability to predict retention of Cr and P by goethite. The reaction order used in nonlinear reversible reactions were those predicted by the Freundlich equilibrium isotherms in the sorption studies previously described. Five different experimental variables were studied (see Table 3) for their effect on the retention and release of Cr and P on goethite. Thus, the following is a discussion and presentation of the data collected from these studies.

The effect of Cr retention and Cr/P exchange on goethite, by varying the goethite suspension concentration was initially studied. This experimental series was also vital in establishing the most manageable goethite concentration with respect to filtration. The five-parameter model accurately described the experimental Cr retention data at each of the four goethite concentrations (Fig. 20). As expected, the amount of Cr retained increased as the goethite concentration increased, due to the increased availability of retention sites. The goodness-of-fit and the model parameter values for the goethite concentration studies are listed in Table 8. The irreversible first order site did not improve the prediction of Cr at goethite concentrations less than 1.0 mM. At the lowest goethite concentration there was no significant difference in the root mean squares (rms) of the three and five-parameter models. In addition, the low \(r^2\) values did not suggest a very good fit of the model to the data. Although the 1.0 mM goethite concentration gave the highest
Figure 20. Effect of varying FeOOH concentrations on the retention of Cr(VI).
Table 8. Nonlinear multireaction model parameters, goodness-of-fit, and parameter standard errors for describing Cr(VI) retention by different concentrations of FeOOH.

\[ [\text{Cr(VI)}]_0 = 19.2 \mu M \quad [\text{Ca(NO}_3)_2] = 5 \text{ mM} \]

<table>
<thead>
<tr>
<th>[FeOOH] (nM)</th>
<th>pH</th>
<th>T (°C)</th>
<th>No. of Parameters</th>
<th>( r^2 )</th>
<th>RMS</th>
<th>( k_1 )</th>
<th>SE</th>
<th>( k_2 )</th>
<th>SE</th>
<th>( k_3 )</th>
<th>SE</th>
<th>( k_4 )</th>
<th>SE</th>
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** and * indicate that the root mean squares (rms) are significantly different at the 0.01 and 0.05 levels of probability, respectively, according to the extra sum of squares criteria. NS = not significant.
r^2 value and one of the lowest root mean square values, the 0.5 mM goethite concentration was selected as the concentration to use in pending kinetic studies. This decision was based on the fact that at 1.0 mM the goethite suspension could not be filtered rapidly to investigate the short term kinetics (i.e. < 15 min.) of Cr and P.

With each of the Cr retention experiments, after a 24 hour reaction time, 32.2 µM of P were added to the stirred reaction to investigate the exchange of P for Cr under the same set of experimental conditions. Figure 21 shows the retention of P by varying concentrations of goethite and the resulting release of Cr back into solution. At goethite concentrations of 0.1 and 0.2 mM there was practically complete reversible release of the retained Cr back into solution, however, only small amounts of P were retained and the reaction was less kinetic in nature than the Cr retention reactions shown in Figure 20, resulting in the multireaction model failing to describe the experimental data. As the goethite concentration increased, the P retention reactions became more kinetic and the five-parameter model was significant in describing the data. The irreversible first order site of the model, for P retention, was unnecessary at 0.5 mM goethite and played only a minor role at 1.0 mM goethite, as evident by the small rate coefficient for K_{irr} (Table 9). The zero or near zero K_{irr} values for Cr retention give supporting evidence that at low Cr concentrations, Cr is not bound in irreversible sites and is capable of being released into solution if exchanged by P.

As mentioned in the theoretical presentation, the multireaction model allows for experimental rate coefficients (k_1, k_2, k_3, k_4, k_{irr}) for these reactions to be estimated. The magnitude of the rate coefficients are a reflection of the kinetics of the reaction and as the magnitudes
Figure 21. Effect of varying FeOOH concentrations on Cr/P exchange.
Table 9. Nonlinear multireaction model parameters, goodness-of-fit, and parameter standard errors for describing P retention by different concentrations of FeOOH.

\[
[p]_0 = 32.2 \mu M \quad [Ca(NO_3)_2] = 5 \text{ mM}
\]

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<tr>
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<th>( k_1 ) SE</th>
<th>( k_2 ) SE</th>
<th>( k_3 ) SE</th>
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** and * indicate that the root mean squares (rms) are significantly different at the 0.01 and 0.05 levels of probability, respectively, according to the extra sum of squares criteria. NS = not significant.
of the rate coefficients increase, so do the reactions rates. Moreover, the ratios of \( k_1 \) over \( k_2 \), and \( k_3 \) over \( k_4 \) provide an estimate of the equilibrium constants \( K_1 \) and \( K_2 \) for the two nonlinear reversible sites, respectively. For both the Cr and P retention data, at varying goethite concentrations, values of the two equilibrium constants, \( K_1 \) and \( K_2 \), increased with increasing goethite concentrations.

Retention of Cr and the exchange of Cr by P on goethite at several different Cr and P concentrations were also studied. Three Cr concentrations of 9.6, 19.2, and 38.4 \( \mu M \) were investigated for their ability to be retained by 0.5 \( mM \) suspension of goethite with a 5 \( mM \) concentration of \( Ca(NO_3)_2 \) serving as the background electrolyte (Fig. 22). The five parameter model was successful in describing the Cr retention data at all Cr concentrations studied, with the initial Cr concentration of 19.2 \( \mu M \) giving the best prediction as indicated by the \( r^2 \) and rms square values (Table 10). Rate coefficients for the nonlinear reversible \( S_1 \) site were of greater magnitude than those for the nonlinear reversible \( S_2 \) site, and were dependent on the initial Cr concentration. Moreover, the rate coefficients \( k_1 \) and \( k_2 \) and the equilibrium constants \( K_1 \) and \( K_2 \) were within one order of magnitude for the different initial applied Cr concentrations. The shapes of the experimental curves appeared to be similar, except between time 0 and the 1 min sample, where the data appears to be the most kinetic. As the initial Cr concentration increased from 9.6 to 38.4 \( \mu M \) the percentage of Cr retained decreased (i.e. from 78.4% for the lowest Cr concentration to 40% for the highest Cr concentration).

Three P concentrations, 16.1, 32.2, and 64.6 \( \mu M \), were used as exchangers for the three Cr concentrations of 9.6, 19.2, and 38.4 \( \mu M \),
Figure 22. Effect of varying the initial Cr(VI) concentration on the retention of Cr(VI) by goethite.
Table 10. Nonlinear multireaction model parameters, goodness-of-fit, and parameter standard errors for describing Cr(VI) retention by FeOOH at several initial concentrations.

\[ [\text{FeOOH}] = 0.5 \text{ mM} \quad [\text{Ca(NO}_3\text{)}_2] = 5 \text{ mM} \]

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<th>rms</th>
<th>( k_1 )</th>
<th>SE</th>
<th>( k_2 )</th>
<th>SE</th>
<th>( k_3 )</th>
<th>SE</th>
<th>( k_4 )</th>
<th>SE</th>
<th>( K_{irr} )</th>
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<th>( K_1 )</th>
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** and * Indicate that the root mean squares (rms) are significantly different at the 0.01 and 0.05 levels of probability, respectively, according to the extra sum of squares criteria. NS = not significant.
respectively. Figure 23 shows the exchange of P for Cr at the three concentrations, up to a reaction time of 60 min. These exchange reactions were conducted for 24 hours, after which analysis revealed 95, 90, and 95% of the initial Cr concentrations of 9.6, 19.2, and 38.4 μM respectively, was released back into solution through the exchange of P for Cr on the goethite. The five parameter model was capable of describing the P retention data at each of the concentrations, however at the lowest (9.6 μM) and highest (38.4 μM) P concentrations, there was no significant difference between the rms of the three parameter and five parameter models (Table 11). Rate coefficients, $k_1$ and $k_2$, for P retention increased with P concentration and were of greater magnitude than $k_3$ and $k_4$ which decreased as the P concentration increased. Equilibrium constants $K_1$ and $K_2$ for P retention were of similar magnitude. From these results on the retention of Cr at three concentrations, it appears the multireaction model is a good general model for describing Cr retention on goethite and is also equally successful in describing P retention for low concentrations. However, the systematic variation in rate coefficients with initial reactant concentrations indicates that the actual mechanism is more complex than that represented by the general multireaction model. If the general model were exactly correct, then no variation of rate coefficients with initial reactant concentrations would be expected.

From the results of the goethite experimental series and the Cr concentration experimental series, a goethite solution concentration of 0.5 mM and a Cr concentration of 19.2 μM were selected as the reference concentrations to conduct further studies on the effects of temperature, pH, and background electrolyte on Cr retention and Cr/P exchange. Five
Figure 23. Exchange of P for Cr(VI) at three different initial concentrations of Cr(VI) and P. Open symbols indicate Cr(VI) released by exchange with P. Open circles, triangles, and squares represent [Cr(VI)]₀ of 9.6, 19.2, and 38.4 μM, respectively. Closed symbols indicate P retained by goethite. Closed circles, triangles, and squares represent [P]₀ of 16.1, 32.2, and 64.6 μM, respectively.
Table 11. Nonlinear multireaction model parameters, goodness-of-fit, and parameter standard errors for describing P retention by FeOOH at several initial concentrations.

$[\text{FeOOH}] = 0.5 \text{ mM}$  $[\text{Ca(NO}_3\text{)}_2] = 5 \text{ mM}$

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<th>$k_2$ SE</th>
<th>$k_3$ SE</th>
<th>$k_4$ SE</th>
<th>$K_{irr}$ SE</th>
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** and * Indicate that the root mean squares (rms) are significantly different at the 0.01 and 0.05 levels of probability, respectively, according to the extra sum of squares criteria. NS = not significant.
different temperature levels (2, 11, 23, 31, and 40 °C) were investigated for their effects on Cr retention and Cr/P exchange, with 23 °C being the room temperature value. For all temperatures, the five-parameter model was successful in describing the Cr retention data (Fig. 24). Moreover, the $r^2$ values of the five-parameter model were very high and in most cases twice as great as those of the three-parameter model. The 23 °C Cr retention data is the same as that shown in Figure 20 at 0.5 mM goethite. Goodness-of-fit and model parameter values for Cr retention are shown in Table 12. Rate coefficients for $k_1$ increased with temperature (except for the 23 °C data) and some dependence of $k_2$ values on temperature was observed where $k_2$ values were highest for 31 and 40 °C as opposed to 2 and 11 °C. However, values of $K_1$ and $K_2$ were within one order of magnitude for all five temperatures. Greater Cr retention was observed at 2 and 11 °C as compared to the 31 and 40 °C. The rate coefficients $k_1$ and $k_2$ in Table 12 suggest that Cr retention on the $S_1$ sites is most rapid at higher temperatures, and the reverse reactions are also faster than at the lower temperatures. Moreover, $K_{irr}$ values were nearly twice as great at 2 and 11 °C than at 31 and 40 °C which may account for the small differences in sorption percentages between high and low temperatures. An initial P concentration of 32.2 uM was used to exchange with Cr at each of the five solution temperatures studied. The five-parameter model was significantly better than the three-parameter model (according to the rms) in describing the retention of P. Model parameters and parameter values for the P retention at each of the five temperatures can be found in Table 13. Complete exchange of Cr for P occurred at the higher temperatures (31 and 40 °C), but this was not observed at the lower temperatures of 2 and
Figure 24. Effect of varying solution temperature on the retention of Cr(VI).
Table 12. Nonlinear multireaction model parameters, goodness-of-fit, and parameter standard errors for describing Cr(VI) retention by FeOOH at several reaction temperatures.

\[ \text{[Cr(VI)]}_0 = 19.2 \, \mu \text{M} \quad \text{[FeOOH]} = 0.5 \, \text{mM} \quad \text{[Ca(NO}_3)_2] = 5 \, \text{mM} \]

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** and * indicate that the root mean squares (rms) are significantly different at the 0.01 and 0.05 levels of probability, respectively, according to the extra sum of squares criteria. NS = not significant.
Table 13. Nonlinear multireaction model parameters, goodness-of-fit, and parameter standard errors for describing P retention by FeOOH at several reaction temperatures.

\[ [P]_0 = 32.2 \mu M \quad [\text{FeOOH}] = 0.5 \text{ mM} \quad [\text{Ca(NO}_3\text{)}_2] = 5 \text{ mM} \]

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<th>( k_3 ) SE</th>
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<th>( K_{irr} ) SE</th>
<th>SE</th>
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<td>0.00360</td>
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</tr>
</tbody>
</table>

** and * indicate that the root mean squares (rms) are significantly different at the 0.01 and 0.05 levels of probability, respectively, according to the extra sum of squares criteria. NS = not significant.
11 °C (Fig. 25). Conversely to the Cr retention data, there was a greater degree of P sorption at 31 and 40 °C as compared to 2 and 11 °C, thus more Cr was released back into solution at 31 and 40 °C than at 2 and 11 °C. From these kinetic studies it can be seen that solution temperatures do play a significant role in the amount of Cr retained or released, and may be instrumental in Cr retention and release in soil systems containing significant amounts of iron oxides. However, the magnitude of the temperature effect was too small to obtain reliable activation energies using the Arrhenius equation. The small temperature effect indicates that the kinetics of retention of the oxyanions were probably diffusion-controlled, even though the suspension was continuously stirred. Although concentration gradients within the bulk solution are eliminated by stirring, concentration gradients can still occur in the hydrodynamic film surrounding the particles and within the particles themselves (internal particle diffusion) (Sparks, 1989). The presence of a large temperature effect would have indicated chemical reaction controlled kinetics. If the kinetics of retention of oxyanions by goethite are indeed diffusion rather than reaction controlled, then the rate coefficients are actually mass transfer coefficients and not rate coefficients for elementary reactions. In such cases, the equilibrium constants calculated from the rate coefficients are not true equilibrium constants.

The effect of solution pH on the retention of Cr on goethite was studied at five levels ranging from pH 4.5 to 8.5. Both the three and the five-parameter model were evaluated for their ability to describe the kinetic data. Results from the testing of the multireaction model showed the five-parameter model to be significantly better in describing
Figure 25. Effect of varying solution temperature on Cr/P exchange.
the data at all pH levels, except pH 7.5. The experimental data and the fitted model are shown in Figure 26. While although the rate coefficients \( k_1, k_2, k_3, k_4, \) and \( k_{irr} \) varied as pH increased, the equilibrium constants \( K_1 \) and \( K_2 \) decreased with increasing pH (Table 14). This is consistent with the mechanistic model, in which equation [19] predicts the equilibrium constant for ligand exchange would be pH dependent. Moreover, Figure 26 shows the greatest sorption of Cr at pH 4.5 and 5.7, thus giving supporting evidence to the statement made earlier, in which it is believed the degree of anion adsorption to be strongly controlled by the pH of the solution.

Similar to the temperature exchange data, 32.2 uM P was used to exchange with the adsorbed Cr at each of the pH levels. The Cr/P exchange data is represented in Figure 27. The five-parameter model provided the best fit to the experimental data at all pH values studied. Retention of P at each of the five different pH levels were not as distinctly different as the Cr retention data. The amount of P retained and the kinetic curves were very similar for pH 5.7, 6.5, 7.5, and 8.5 (pH 6.5 not shown). Incomplete exchange of P for Cr occurred at pH 4.5, 5.7, and 6.5, with near complete exchange occurring at pH 7.5 and 8.5. Phosphorus ions, particularly \( \text{H}_2\text{PO}_4^- \), are known to react with soluble iron and insoluble iron oxides such as goethite. In acid mineral soils the amount of P fixed by hydrous oxides exceeds that due to chemical precipitation by soluble iron. However, in these kinetic studies, the least adsorption of P occurred at pH 4.5, when the Cr had been allowed to react prior to introducing the P. It is believed that even though P has a high affinity for iron oxides under acid conditions, the affinity Cr has for goethite is sufficiently high to result in incomplete
Figure 26. Effect of varying the solution pH on the retention of Cr(VI) by FeOOH.
Table 14. Nonlinear multireaction model parameters, goodness-of-fit, and parameter standard errors for describing Cr(VI) retention by goethite at several solution pH values.

\[ [\text{Cr(VI)}]_o = 19.2 \text{ M} \quad [\text{FeOOH}] = 0.5 \text{ M} \quad [\text{Ca(HCO}_3\text{)}_2] = 5 \text{ M} \]

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<th>SE</th>
<th>( k_2 )</th>
<th>SE</th>
<th>( k_3 )</th>
<th>SE</th>
<th>( k_4 )</th>
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** and * indicate that the root mean squares (rms) are significantly different at the 0.01 and 0.05 levels of probability, respectively, according to the extra sum of squares criteria. NS = not significant.
Figure 27. Effect of varying the solution pH on Cr/P exchange.
exchange. Table 15 gives the model parameters and their corresponding values for the nonlinear multireaction model.

To study the effect varying the background salt may have upon Cr retention, two sets of experiments were designed and performed. The first experimental series involved using Ca(NO₃)₂ as the background salt, but varying the concentration from 0.005 mM to 0.10 mM. The experimental retention data is exhibited in Figure 28. The five-parameter model provided the most significant description of the data at four concentrations of Ca(NO₃)₂. The amount of Cr adsorbed was found to increase as the Ca(NO₃)₂ concentration decreased. The equilibrium constant K₁ decreased with increasing Ca(NO₃)₂ concentration, and K₂ decreased and then increased slightly (Table 16). In addition to Ca(NO₃)₂, three other salts (0.005 mM) were studied as to their effect on Cr retention. These included, CaCl₂, NaCl, and NaClO₄. In each case the five-parameter model was significantly better in describing the Cr retention on goethite, however the shape of the curves and the amount retained were very similar (Fig. 29). The equilibrium constants calculated from the rate coefficients were also similar, particularly the K₁ values (Table 17).

Of the Cr kinetic studies presented, the data showed P was capable of exchanging with adsorbed Cr to varying degrees depending upon the experimental conditions. However, these studies did not involve exchanging equal molar concentrations of Cr and P. Therefore, an experiment was performed in which 20 μM of Cr were added to a 5 mM FeOOH suspension containing 0.005 mM Ca(NO₃)₂. This was allowed to react for 24 h, afterwhich 20 μM of P were added as an exchanger. Figure 30 shows the plotted data in which the five-parameter nonlinear multireaction
Table 15. Nonlinear multireaction model parameters, goodness-of-fit, and parameter standard errors for describing P retention by goethite at several solution pH values.

\[ [P]_0 = 32.2 \mu M \quad [FeOOH] = 0.5 \text{mM} \quad [Ca(NO_3)_2] = 5 \text{mM} \]

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<th>( \text{rms} )</th>
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<th>( k_4 ) SE</th>
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<tr>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5</td>
<td>0.963</td>
<td>0.459</td>
<td>** 16.7 &amp; 4.00 &amp; 2.61  &amp; 0.635 &amp; 0.0380 &amp; 0.00556 &amp; 0.0119 &amp; 0.00324 &amp; 0.000181 &amp; 0.000055 &amp; 6.40 &amp; 3.19</td>
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</tbody>
</table>

** and * indicate that the root mean squares (rms) are significantly different at the 0.01 and 0.05 levels of probability, respectively, according to the extra sum of squares criteria. NS = not significant.
Figure 28. Effect of different Ca(NO₃)₂ concentrations on Cr(VI) retention by FeOOH.
Table 16. Nonlinear multireaction model parameters, goodness-of-fit, and parameter standard errors for describing Cr(VI) retention by goethite using different concentrations of Ca(NO$_3$)$_2$.

\[
[\text{Cr(VI)}]_0 = 19.2 \ \mu\text{M} \quad [\text{FeOOH}] = 0.5 \ \text{mM}
\]

<table>
<thead>
<tr>
<th>[Ca(NO$_3$)$_2$] (mM)</th>
<th>pH</th>
<th>T (°C)</th>
<th>No. of Parameters</th>
<th>n$^2$</th>
<th>rms</th>
<th>k$_1$</th>
<th>SE</th>
<th>k$_2$</th>
<th>SE</th>
<th>k$_3$</th>
<th>SE</th>
<th>k$_4$</th>
<th>SE</th>
<th>K$_{irr}$</th>
<th>SE</th>
<th>K$_1$</th>
<th>K$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.005</td>
<td>5.2</td>
<td>25</td>
<td>3</td>
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<td>0.458</td>
<td>0.456</td>
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<td>2.73</td>
<td>3.16</td>
<td>0.693</td>
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<td>----</td>
<td>----</td>
<td>----</td>
<td>0.000113</td>
<td>0.000049</td>
<td>--</td>
</tr>
<tr>
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<td></td>
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<td>0.245</td>
<td>21.2</td>
<td>2.44</td>
<td>4.01</td>
<td>0.470</td>
<td>0.0258</td>
<td>0.00539</td>
<td>0.0251</td>
<td>0.00814</td>
<td>0.000000</td>
<td>0.000037</td>
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<td>3</td>
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<td>0.288</td>
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<td>----</td>
<td>----</td>
<td>----</td>
<td>0.000088</td>
<td>0.000028</td>
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<td></td>
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<td>0.0108</td>
<td>0.0974</td>
<td>0.0240</td>
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<td>6.03</td>
<td>0.840</td>
<td>1.52</td>
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<td></td>
<td></td>
<td>5</td>
<td>0.967</td>
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<td>0.00576</td>
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<td>----</td>
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<td>----</td>
<td>0.000092</td>
<td>0.000030</td>
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<td>0.135</td>
<td>17.3</td>
<td>3.69</td>
<td>6.14</td>
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<td>0.0104</td>
<td>0.000046</td>
<td>0.000011</td>
<td>2.82</td>
</tr>
</tbody>
</table>

** and * indicate that the root mean squares (rms) are significantly different at the 0.01 and 0.05 levels of probability, respectively, according to the extra sum of squares criteria. NS = not significant.
Figure 29. Effect of different background salts on Cr(VI) retention by FeOOH.

- $[\text{Cr}]_0 = 19.2 \mu\text{M}$
- $[\text{FeOOH}] = 0.5 \text{mM}$
- pH = 5.2

- $0.005 \text{M Ca(NO}_3\text{)}_2$
- $0.005 \text{M CaCl}_2$
- $0.005 \text{M NaCl}$
- $0.005 \text{M NaClO}_4$
Table 17. Nonlinear multireaction model parameters, goodness-of-fit, and parameter standard errors for describing Cr(VI) retention by goethite using different background salts.

\[ [\text{Cr(VI)}]_0 = 19.2 \, \mu M \quad [\text{FeOOH}]^+ = 0.5 \, \text{mM} \]

<table>
<thead>
<tr>
<th>Salt</th>
<th>pH</th>
<th>Temp (°C)</th>
<th>No. of Parameters</th>
<th>( r^2 )</th>
<th>rms</th>
<th>( k_1 )</th>
<th>SE</th>
<th>( k_2 )</th>
<th>SE</th>
<th>( k_3 )</th>
<th>SE</th>
<th>( k_4 )</th>
<th>SE</th>
<th>( K_{1RR} )</th>
<th>SE</th>
<th>( K_1 )</th>
<th>( K_2 )</th>
</tr>
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<td>Ca(NO_3)_2</td>
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<td>3</td>
<td>0.240</td>
<td>0.458</td>
<td>0.456</td>
<td>17.8</td>
<td>2.73</td>
<td>3.16</td>
<td>0.493</td>
<td>----</td>
<td>----</td>
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<td>----</td>
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<td>0.000113</td>
<td>0.000049</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td>0.844</td>
<td>0.245</td>
<td>**</td>
<td>21.2</td>
<td>2.44</td>
<td>4.01</td>
<td>0.470</td>
<td>0.0258</td>
<td>0.00539</td>
<td>0.0251</td>
<td>0.00814</td>
<td>0.000000</td>
<td>0.000037</td>
<td>5.29</td>
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<tr>
<td>CaCl_2</td>
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<td>3</td>
<td>0.240</td>
<td>0.559</td>
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<td>2.28</td>
<td>3.08</td>
<td>0.415</td>
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<td>0.000046</td>
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<tr>
<td>5</td>
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<td></td>
<td>0.933</td>
<td>0.163</td>
<td>**</td>
<td>21.6</td>
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<tr>
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<td>1.91</td>
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<td>0.000100</td>
<td>0.000030</td>
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<tr>
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<td></td>
<td></td>
<td>0.908</td>
<td>0.128</td>
<td>**</td>
<td>12.8</td>
<td>0.913</td>
<td>2.23</td>
<td>0.162</td>
<td>0.0142</td>
<td>0.00270</td>
<td>0.0224</td>
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<td>0.000021</td>
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<td>NaClO_4</td>
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<td>0.325</td>
<td>17.4</td>
<td>1.61</td>
<td>2.86</td>
<td>0.272</td>
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<td>----</td>
<td>----</td>
<td>----</td>
<td>0.000126</td>
<td>0.000039</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td>0.927</td>
<td>0.162</td>
<td>**</td>
<td>27.1</td>
<td>3.64</td>
<td>5.31</td>
<td>0.726</td>
<td>0.349</td>
<td>0.0514</td>
<td>0.306</td>
<td>0.0516</td>
<td>0.000101</td>
<td>0.000020</td>
<td>5.10</td>
</tr>
</tbody>
</table>

** and * indicate that the root mean squares (rms) are significantly different at the 0.01 and 0.05 levels of probability, respectively, according to the extra sum of squares criteria. NS = not significant.
Figure 30. Chromate retention and subsequent release with P acting as the exchanging anion.

$[\text{Cr(VI)}]_o = 20 \mu\text{M}$  
$[\text{P}]_o = 20 \mu\text{M}$  
$[\text{FeOOH}] = 0.5 \text{ mM}$
model successfully described. With equal molar concentrations of Cr and P there was near complete exchange occurring at sampling times ≥ 45 min. Conversely to this, it was also desired to know if P was added first, could Cr exchange for P causing P to be released back into solution. Thus, 20 µM of P were added to a suspension of goethite and Ca(NO₃)₂ containing the same concentrations as above. The P reacted with and was adsorbed onto the goethite for 24 h before 20 µM of Cr were added as the exchanger. Results showed Cr to be unable to exchange with P (Fig. 31). The P retention data was described by the five-parameter nonlinear multireaction model, however it was unable to predict the Cr retention due to the variability and nonkinetic nature of the data. Model parameters for Figures 30 and 31 are summarized in Table 18.

In all of the kinetic studies presented thus far, the Cr retention reactions were conducted for a maximum time of 24 hours. However, at the completion of this time period the retention of Cr by goethite appeared to be still taking place as evident by the decreasing Cr solution concentration. Therefore, an experiment was designed and conducted to investigate the kinetics of Cr retention over an extended period of time. An initial Cr concentration of 19.2 µM was added to a 0.5 mM goethite suspension containing a 5 mM Ca(NO₃)₂ background salt solution. Temperature and pH were not adjusted and were the room temperature, (24 °C) and natural pH of the solution (5.3). The experiment was allowed to proceed for a total time of 360 hours (15 days). During the course of the reaction there was a gradual decrease in the solution Cr concentration even after 336 hours (14 days). The three-parameter and the five-parameter model versions of the nonlinear multireaction model were tested for their ability to describe the Cr retention data. The Cr
Figure 31. Phosphorus retention and subsequent release with Cr(VI) acting as the exchanging anion.

$[Cr]_0 = 20 \mu M \quad [P]_0 = 20 \mu M$

$[FeOOH] = 0.5 \text{ mM}$

- $\triangle$ P retained
- $\Delta$ P released
- $\bigcirc$ Cr retained

$[P]_0 = 20 \text{ uM} \quad [Cr(VI)]_0 = 20 \text{ uM}$
Table 18. Nonlinear multireaction model parameters, goodness-of-fit, and parameter standard errors for describing A) Cr(VI) retention and P retention/exchange on goethite and B) P retention on goethite.

\([\text{FeOOH}] = 0.5 \text{ mM} \quad [\text{Ca(NO}_3\text{)}_2] = 5 \text{ mM}\)

<table>
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<tr>
<th>Anion</th>
<th>pH</th>
<th>T (°C)</th>
<th>No. of parameters</th>
<th>(n)</th>
<th>(r^2)</th>
<th>rms</th>
<th>(k_1) SE</th>
<th>(k_2) SE</th>
<th>(k_3) SE</th>
<th>(k_4) SE</th>
<th>(k_{\text{irr}}) SE</th>
<th>(K_1)</th>
<th>(K_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A) Cr</td>
<td>5.2</td>
<td>24</td>
<td>3</td>
<td>0.300</td>
<td>0.501</td>
<td>0.327</td>
<td>18.9</td>
<td>2.55</td>
<td>3.64</td>
<td>0.501</td>
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</tr>
<tr>
<td></td>
<td>5</td>
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<td></td>
<td>0.954</td>
<td>0.088</td>
<td><strong>28.3</strong></td>
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<td>6.00</td>
<td>0.677</td>
<td>0.0772</td>
<td>0.006843</td>
<td>0.106</td>
<td>0.0121</td>
</tr>
<tr>
<td>B) P</td>
<td>5.1</td>
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<td>3</td>
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<td>0.807</td>
<td>0.772</td>
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<td>0.00385</td>
<td>0.00821</td>
<td>0.00351</td>
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</tbody>
</table>

** and * indicate that the root mean squares (rms) are significantly different at the 0.01 and 0.05 levels of probability, respectively, according to the extra sum of squares criteria. NS = not significant.
retention data after 360 h of reaction is shown in Figure 32. The five-parameter model provided the best fit to the data as evident by the rms value (Table 19) and thus was used in plotting the predicted values in Figure 32. With the exception for the amount of time the reaction was allowed to take place, the experimental conditions were the same as the FeOOH concentration experiment at 0.5 mM FeOOH (Table 8), and the Cr(VI) concentration experiment at 19.2 μM Cr(VI) (Table 10). The $k_1$ and $k_2$ values of the long-term kinetic experiment were of much greater magnitude than those of the 0.5 mM FeOOH experiment and the 19.2 μM Cr(VI) experiment, however the ratios of $k_1$ and $k_2$ ($K_1$), and $k_3$ and $k_4$ ($K_2$) were of similar magnitude. Therefore, as the Cr retention reaction is allowed to take place over extended time periods the rate coefficients increase in similar proportions, resulting in the equilibrium constants for both short-term and long-term types of reactions remaining nearly the same. Long-term detailed kinetic studies of anion sorption on goethite are not abundant in the literature. However, long-term studies of P adsorption on goethite were performed by Madrid and Posner (1979) and Anderson et al. (1985). Both studies reported a slow reaction occurred between goethite and P, and continued for several days.

Due to the nature of this research, the amount of time required to collect data for one kinetic run of Cr retention and P retention/exchange did not facilitate performing multiple runs or replications. One experiment series however, was conducted to show the reproducibility of the experimental method employed. Three separate kinetic runs of Cr retention were conducted under identical experimental conditions (i.e. $[\text{Cr}]_0 = 20.0$ μM; $[\text{FeOOH}] = 0.5$ mM, pH = 5.0, and Temp. = 24 °C). The data from these kinetic runs was plotted and is shown in Figure 33. In
Figure 32. Long term prediction of Cr(VI) retention by goethite. Model prediction is shown by the solid line and experimental data points are represented by the symbols. 

$[\text{Cr(VI)}]_0 = 20 \mu M$

$[\text{FeOOH}] = 0.5 \text{ mM}$

$pH = 5.3$
Table 19. Nonlinear multireaction model parameters, goodness-of-fit, and parameter standard errors for describing long term Cr(VI) retention by goethite.

\[ [\text{Cr(VI)}]_0 = 19.2 \mu\text{M} \quad [\text{FeOOH}] = 0.5 \text{ mM} \quad [\text{Ca(NO}_3)_2] = 5 \text{ mM} \]

<table>
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<tr>
<th>pH</th>
<th>T</th>
<th>No. of Parameters</th>
<th>n</th>
<th>( r^2 )</th>
<th>rms</th>
<th>( k_1 ) SE</th>
<th>( k_2 ) SE</th>
<th>( k_3 ) SE</th>
<th>( k_4 ) SE</th>
<th>( K_{1r} ) SE</th>
<th>( K_1 )</th>
<th>( K_2 )</th>
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<td>5.3</td>
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<td>12.7</td>
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<td>0.174</td>
<td>**</td>
<td>74.1</td>
<td>1.91</td>
<td>12.5</td>
<td>0.306</td>
<td>0.00862</td>
<td>0.00225</td>
<td>0.0104</td>
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</table>

** and * indicate that the root mean squares (rms) are significantly different at the 0.01 and 0.05 levels of probability, respectively, according to the extra sum of squares criteria. NS = not significant.
Figure 33. Three replications and prediction of Cr(VI) retention by goethite. Model prediction is shown by the solid line and experimental data points are represented by the symbols.

\[
\text{[Cr(VI)]}_0 = 20.0 \mu M \\
\text{[FeOOH]} = 0.5 \text{ mM} \\
\text{Temp.} = 24 ^\circ \text{C} \\
\text{pH} = 5.0
\]
each case the five-parameter model was significant in describing the retention of Cr. As can be seen from Figure 33 the three kinetic runs produced similar results with replications #2 and #3 producing more similar results at sampling times of < 10 minutes, and replications #1 and #3 producing similar results at sampling times > 10 minutes. Table 20 summarizes the model parameters for the nonlinear multireaction model for each of the three replications. The rate coefficients for the individual kinetic runs were similar, with a few exceptions (k_1, k_3, and k_{irr} for replication #3). Moreover, equilibrium constants were similar. Thus the experimental method was assumed to be a reliable and reproducible technique for studying the kinetics of oxyanions.

The loss of Cr from solution in the kinetic studies was assumed to be a direct result of adsorption onto the goethite, since Cr does not participate in precipitation reactions unless in the presence of barium. The other possible explanation for a decrease in the Cr solution concentration might be from adsorption of Cr onto the reaction vessel wall or impeller. The reaction vessel and impeller were constructed of polypropylene and polyethylene respectively, and are considered to be non-reactive. To confirm that Cr adsorption did not occur on the reaction vessel wall or impeller, a control study was conducted in which 20.0 μM of Cr was added to a 2 L solution of 5 mM Ca(NO_3)_2 with no goethite present. Sampling was conducted for selected time intervals up to a maximum time of 7 days. Analysis showed no appreciable amounts of Cr were adsorbed onto the reaction vessel wall (Fig. 34). Minor fluctuations in the data were assumed to be a result of analytical errors.
Table 20. Nonlinear multi-reaction model parameters, goodness-of-fit, and parameter standard errors for each replication of Cr(VI) retention by goethite.

\[ [\text{Cr(VI)}]_0 = 20 \text{ mM} \quad [\text{FeOOH}] = 0.5 \text{ mM} \quad [\text{Ca(NO}_3\text{)}_2] = 5 \text{ mM} \]

<table>
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<th>pH</th>
<th>T</th>
<th>No. of</th>
<th>n</th>
<th>( r^2 )</th>
<th>rms</th>
<th>( k_1 )</th>
<th>SE</th>
<th>( k_2 )</th>
<th>SE</th>
<th>( k_3 )</th>
<th>SE</th>
<th>( k_4 )</th>
<th>SE</th>
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<tr>
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<td>2.92</td>
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</table>

** and * indicate that the root mean squares (rms) are significantly different at the 0.01 and 0.05 levels of probability, respectively, according to the extra sum of squares criteria. NS = not significant.
Figure 34. Retention of Cr(VI) with no goethite present in solution.
$[Cr(VI)]_0 = 20.0 \mu M$

Temp. = 23 °C

$[FeOOH] = 0.5 \text{ mM}$

pH = 5.2

Mean = 20.01 μM

SE = 0.035
Effect of Competing Anions on Cr(VI) Adsorption

Since soil and mineral systems are never pure systems, with respect to containing only one anion, it was of interest to study the effect competing anions have upon Cr(VI) adsorption. The affinity an individual anion has for the available adsorption sites will be the determining factor as to which anion will be preferably adsorbed and to the degree of adsorption. Competitive adsorption between Cr and P, As, B, F, Mo, Se, and Si on a 0.5 mM goethite suspension containing 5 mM Ca(NO₃)₂ were studied. Prior to the competitive studies, kinetic retention experiments of each single anion were performed. Thus the figures being presented show not only the competitive adsorption, but also single anion adsorption on goethite.

In addition to studying the competitive nature of Cr adsorption, the nonlinear multireaction model was tested for its ability to describe the kinetic retention data. For the individual anions, the five-parameter model accurately described the retention data, except for B. Table 21 gives the nonlinear multireaction model parameters for each single anion studied and Tables 22 and 23 summarizes the model parameters for the competitive studies. Anion pairs not listed in Table 22 (i.e. Cr(+P), Cr(+As), F(+Cr), Mo(+Cr), and Cr(+Se)) indicates the nonlinear multireaction model was unsuccessful in describing the retention data. The reaction order (n) used in the multireaction model were those obtained from the previously discussed Freundlich isotherms with the exception of borate, fluoride, and molybdate. Twenty-four hour equilibrium sorption studies were not conducted on borate, fluoride, and molybdate due to a shortage of the aged goethite material, thus the reaction orders for B, and Mo were taken from literature values on soils.
Table 21. Nonlinear multireaction model parameters, goodness-of-fit, and parameter standard errors for describing Cr(VI), P, As, B, F, Ho, Se, and Si retention on goethite.

\[
[\text{FeOOH}] = 0.5 \text{ mM} \quad [\text{Ca(NO}_3)_2] = 5 \text{ mM}
\]

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<th>pH</th>
<th>T (°C)</th>
<th>No. of Parameters</th>
<th>( r^2 )</th>
<th>rms</th>
<th>( k_1 )</th>
<th>SE</th>
<th>( k_2 )</th>
<th>SE</th>
<th>( k_3 )</th>
<th>SE</th>
<th>( k_4 )</th>
<th>SE</th>
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** and * Indicate that the root mean squares (rms) are significantly different at the 0.01 and 0.05 levels of probability, respectively, according to the extra sum of squares criteria. NS = not significant.
Table 21. Continued

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</table>

** and * indicate that the root mean squares (rms) are significantly different at the 0.01 and 0.05 levels of probability, respectively, according to the extra sum of squares criteria. NS = not significant.
Table 22. Nonlinear multireaction model parameters, goodness-of-fit, and parameter standard errors for Cr(VI) retention by goethite with competitive anions B, F, Ho, and Si in solution.

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<th>rms</th>
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<th>k₂</th>
<th>SE</th>
<th>k₃</th>
<th>SE</th>
<th>k₄</th>
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<th>SE</th>
<th>K₁</th>
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** and * indicate that the root mean squares (rms) are significantly different at the 0.01 and 0.05 levels of probability, respectively, according to the extra sum of squares criteria. NS = not significant.
Table 23. Nonlinear multireaction model parameters, goodness-of-fit, and parameter standard errors for P, As, B, Se, and Si retention by goethite with Cr(VI) as the competitive anion in solution.

<table>
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<tr>
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<th>pH</th>
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<th>No. of Parameters</th>
<th>n</th>
<th>$r^2$</th>
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<td>5.96</td>
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<td>0.000065</td>
<td>8.90</td>
<td>3.34</td>
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<tr>
<td>B(+Cr)</td>
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<td>24</td>
<td></td>
<td>3</td>
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<td>0.941</td>
<td>0.367</td>
<td>0.287</td>
<td>0.0388</td>
<td>0.316</td>
<td>0.0504</td>
<td>---</td>
<td>---</td>
<td>---</td>
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<td>0.000022</td>
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</tr>
<tr>
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<td>0.151</td>
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<td>0.000020</td>
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<td>0.613</td>
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<td>Se(+Cr)</td>
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<td>0.820</td>
<td>0.501</td>
<td>41.1</td>
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<td>4.43</td>
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<td>---</td>
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<td>0.00531</td>
<td>0.00767</td>
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<td>0.000001</td>
<td>0.000179</td>
<td>9.03</td>
<td>2.90</td>
</tr>
<tr>
<td>Si(+Cr)</td>
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<td></td>
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<td>---</td>
<td>---</td>
<td>---</td>
<td>0.000031</td>
<td>0.000004</td>
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<tr>
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<td></td>
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<td>0.000028</td>
<td>0.000002</td>
<td>0.630</td>
<td>0.0788</td>
</tr>
</tbody>
</table>

** and * Indicate that the root mean squares (rms) are significantly different at the 0.01 and 0.05 levels of probability, respectively, according to the extra sum of squares criteria. NS = not significant.
data obtained by Buchter et al. (1989). The reaction order for F was obtained by curve fitting techniques.

Figure 35 shows the adsorption of Cr and P on 5 mM goethite and the competitive adsorption between Cr and P. In this, and each of the competitive adsorption plots to follow, the element in parenthesis is the secondary element in which the primary element is competing with for adsorption sites on goethite (i.e. Cr(+P) indicates that Cr is the anion for which the data is plotted, but P is in solution, also competing for adsorption sites). From the results of the previous study, in which P was attempted to be exchanged by Cr (Figure 31), it was expected that P would be adsorbed in preference over Cr, both individually and under competitive conditions. The five-parameter model was successful in describing P retention in the presence of Cr, however since Cr was not significantly adsorbed onto the goethite in the presence of P, the model could not describe the Cr retention reaction. Slightly smaller amounts of P were retained by goethite in the presence of Cr, due to small amounts of Cr occupying sorption sites.

Competitive and single adsorption of Cr and As are shown in Figure 36. Results were similar to those achieved with Cr and P competitive adsorption, in that As is preferentially adsorbed, with respect to Cr, both as a single anion and when competing with Cr in solution. The five-parameter model described the As data under both situations, but failed to describe the Cr(+As) data due to the non-kinetic nature of the Cr retention data. Arsenic can accumulate in agricultural soils and is considered to be toxic to both plants and animals. Arsenate (AsO$_4^{3-}$) ions can be readily fixed by clays, humus, and calcium, with Fe and Al oxides playing the most active role in As retention. Norrish (1975)
Figure 35. Competitive adsorption of Cr(VI) and P on 5 mM goethite.

$[\text{Cr(VI)}]_0 = 20 \, \mu\text{M} \quad [\text{P}]_0 = 20 \, \mu\text{M}$
Figure 36. Competitive adsorption of Cr(VI) and As on 5 mM goethite.
$[\text{Cr(VI)}]_o = 20 \ \mu\text{M}$  $[\text{As}]_o = 20 \ \mu\text{M}$
reported As to be strongly associated with goethite in soils under natural conditions and as added As. Harrison and Berkheiser (1982) and Lumsdon et al. (1984) concluded arsenate adsorption on iron oxides to be a result of ligand exchange with surface hydroxyls and/or surface aquo groups. Norrish (1975) and Woolson et al. (1973) both concluded that while little is known about As compounds in soil, research results support the idea that arsenate in soils behaves like phosphate, and in acid soils, Fe or Al arsenates are likely to be the most common. The results obtained in these Cr/P and Cr/As experiments support the above conclusions, in that rate coefficients for P and As (Table 21) were very similar and of equal magnitude. The constant capacitance model has also been used in describing anion adsorption in which ligand exchange mechanisms are considered to be involved. Goldberg (1986) successfully used the constant capacitance model to describe the sorption of arsenate on goethite.

From studies on competitive adsorption between Cr and B, Cr is preferably adsorbed onto goethite both as a single anion and under competitive conditions (Figure 37). There is a decrease in B adsorption when Cr is also in solution. For the individual adsorption of B and the competitive adsorption of B (in the presence of Cr) the five-parameter model was not significantly better than the three-parameter model in describing the retention data (see Tables 21 and 22). The sorption of B in soils has been shown to be correlated to the amount of Al and Fe oxides present. Scharrer et al. (1956) and Sims and Bingham (1968) studied the ability of crystalline and amorphous Fe oxide minerals to adsorb B and found sorption to increase with increasing pH. Sims and Bingham (1968) and McPhail et al. (1972) both concluded that anion
Figure 37. Competitive adsorption of Cr(VI) and B on 5 mM goethite. 
\[ [\text{Cr(VI)}]_0 = 20 \, \text{uM} \quad [B]_0 = 20 \, \text{uM} \]
exchange with hydroxyl ions may be the mechanism explaining B adsorption. Goldberg and Glaubig (1985) used the constant capacitance model to represent B adsorption behavior on Fe oxide minerals. In addition, Goldberg and Glaubig (1985) found B adsorption on goethite and amorphous iron oxide to increase at low pH, peak at pH 7-8 and decrease at high pH.

Competitive adsorption studies between Cr and F produced results resembling the Cr/B competitive study. With both anions in solution, Cr was found to be adsorbed to a greater degree than F (Fig. 38). Fluoride in the presence of Cr was capable of being adsorbed, however approximately 7.5 μM (or 38%) was absorbed within one minute after the initial 20 μM was added. After one minute, the F solution concentration changed only slightly. Because of the non-kinetic change in F solution concentration, the nonlinear multireaction model was unable to describe the retention data. Phosphate fertilizers, sewage sludge, and industrial by-products are known sources of F and may produce potentially toxic levels of F in the soil and/or groundwater. The adsorption behavior of F on iron oxide minerals and soils has been investigated (Hingston et al., 1974; Parfitt and Russell, 1977; Peek and Volk, 1985; Barrow and Ellis, 1986). Hingston et al., 1974 studied F sorption and desorption on goethite. They found F to be desorbed and to yield points which lie on the adsorption curve. Moreover, F is believed to form monodentate ligands at the oxide surface enabling the desorption reaction to occur. Parfitt and Russell (1977) also concluded F ions form monodentate ligands by replacing singly coordinated OH groups, but do not replace OH groups that are coordinated to two and three Fe$^{3+}$ ions. Barrow and Ellis (1986) found F retention to be greatest at pH 5.5 and decreased at
Figure 38. Competitive adsorption of Cr(VI) and F on 5 mM goethite. 
\[ [\text{Cr(VI)}]_0 = 20 \text{ uM} \quad [F]_0 = 20 \text{ uM} \]
both lower and higher pH. The preference Cr has for goethite over F may be related to the phenomenon that F is only capable of replacing singly coordinated OH groups. When both Cr and F are both in solution the more reversible F bonds are being replaced by stronger Cr ligands, thus creating a slight decrease in the Cr solution concentration and an increase in the F solution concentration.

Molybdenum adsorption by Fe and Al hydrous oxides accounts for a large percentage of the Mo retained by surface soils. These adsorption reactions are highly dependent on soil pH and Eh conditions and thus predicting Mo migration during weathering is often difficult. Norrish (1975) and Lindsay (1979) in their review on Mo behavior in soils, concluded that inorganic Mo forms are primarily associated with Fe oxides, probably as an adsorbed phase. Of the forms of Mo found in soils, Hodgson (1963) considered the anion adsorbed forms the most important. In addition, Jones (1956, 1957) found hydrous Fe oxides to adsorb Mo much more strongly than Al oxide. Acid soils (pH < 5.5) containing a low Mo content and a high Fe oxide level will render Mo unavailable to plants. In this study, when a goethite suspension containing both Cr and Mo were allowed to react with the goethite suspension, Mo was adsorbed in preference to Cr, however due to the fluctuation of the experimental Mo retention data, use of the nonlinear multireaction model was unsuccessful (Fig. 39). Moreover, of the initial 20 uM Mo added at time zero, 67% was adsorbed within one minute of reaction, when Mo was present as a single anion and as a competitive anion with Cr. The Cr retention data, in the presence of Mo, was capable of being described by the five-parameter version of the nonlinear multireaction model, however total absorption was less than when Cr was present alone in the goethite
Figure 39. Competitive adsorption of Cr(VI) and Mo on 5 mM goethite. 

[Cr(VI)]_0 = 20 uM  [Mo]_0 = 20 uM
suspension due to Mo occupying or blocking adsorption sites on goethite particles.

The multiple oxidation states of Se (Se^{2-}, Se^0, SeO_3^{2-}, and SeO_4^{2-}) make it an interesting element in which to study adsorption phenomena. In low concentrations Se is an essential element, however it is a toxic element at high concentrations. Figure 40 depicts single anion adsorption of Cr and Se on goethite, and competitive adsorption between Cr and Se. Selenium was adsorbed to a greater degree than Cr both as a single anion and as a competitive anion. Near equal amounts of Se were adsorbed under the two different conditions. A kinetic retention study using Se in the selenate form (SeO_4^{2-}) resulted in no adsorption taking place (figure not shown). Balistrieri and Chao (1987) found selenite to adsorb more strongly than selenate. In addition, Balistrieri and Chao (1987) found the influence of additional anions on selenite adsorption depends on the relative affinity of the anions for the surface, and the relative concentrations of the anions. Similar to Cr/Mo interactions on goethite, it is believed that when Cr is present in solution with equal initial concentrations of Se, the Se ions will occupy or block adsorption sites preventing large amounts of Cr from being adsorbed.

Finally, competitive studies between Cr and Si were conducted. Silica, whether present alone in solution or paired with Cr, adsorbs onto goethite in near equal amounts (Fig. 41). Silica, however, did depress Cr adsorption when both anions were present in solution. In all cases involving Cr and Si, the five-parameter nonlinear multireaction model was significant in describing the retention data. Zachara et al. (1987) reported a decrease in Cr adsorption when in the presence of Si, with the greatest reduction occurring at pH 6.3. Hingston et al. (1972)
Figure 40. Competitive adsorption of Cr(VI) and Se on 5 mM goethite. 

\[ [\text{Cr(VI)}]_o = 20 \text{ mM} \quad [\text{Se}]_o = 20 \text{ mM} \]
Figure 41. Competitive adsorption of Cr(VI) and Si on 5 mM goethite. 

\[ [\text{Cr(VI)}]_0 = 20 \ \mu\text{M} \quad [\text{Si}]_0 = 20 \ \mu\text{M} \]
and Zachara et al. (1987) have explained the depressed adsorption by changes in the surface charge. Specific adsorption of Si occupies surface sites on iron oxides and thus alter the surface charge and the zero point of charge of the adsorbent. Zachara et al. (1987) concluded silica consumes surface sites and forms a charged surface complex that reduces the positive charge, therefore decreasing the electrostatic attraction of \( \text{CrO}_4^{2-} \). Moreover, when iron oxyhydroxide was allowed to age for 168 h before being used, the result produced a systematic decrease in \( \text{CrO}_4^{2-} \) adsorption (Zachara et al., 1987).

The competitive anion experiments conducted in this study were effective in establishing the affinity Cr and other major oxyanions may have for goethite. Additionally, affinity sequences were capable of being determined for each of the oxyanions in the presence of Cr.

The data suggested the following affinity sequence for anion adsorption on goethite after 24 h: arsenate > selenite > phosphate > chromate - molybdate > fluoride > borate > silicate. When each of the anions was in solution with Cr a slightly different anion sequence was established: arsenate > selenite > molybdate = phosphate > fluoride > borate > silicate. Balistrieri and Chao (1987) studied selenium adsorption by goethite in the presence of competing anions and single anion adsorption. Results from their study of single anion adsorption produced the following affinity sequence: phosphate - silicate = arsenate > selenite > molybdate > fluoride = selenate. Hingston et al. (1968) studied anion adsorption on goethite and proposed an affinity sequence of: phosphate > silicate > selenite > fluoride. Infrared spectroscopy and surface area determination of crystalline structures are useful techniques in helping identify types of surface OH groups and estimating the maximum number of
surface sites. Hingston (1981) determined the mean areas occupied by anions on goethite at high solution concentrations and near optimum pH (Table 24). The data showed fluoride to occupy the smallest area (20 Å²) and silicate to occupy the greatest (62 Å²). The data reported in Table 24 is partially consistent to the affinity sequence determined in this study.

Many investigators have studied sorption reactions using oxides as the adsorbate material. Since natural oxides are difficult to extract from soil, most workers conduct studies with synthetic oxides. However, one should be aware of the fact that oxides, specifically iron oxides, can vary in their properties even when prepared from the same procedure. Atkinson et al. (1968) studied the conditions for the formation of goethite crystals and found different batches of prepared goethite to vary appreciably. Hingston (1970) prepared several batches of goethite using the same procedure and found the surface area to vary from 17 to 81 m² g⁻¹. Moreover, goethite samples can vary in their crystallinity due to differences in temperature (Schwertmann et al., 1985). At low temperatures, goethite crystals were found to be smaller, with each crystal containing numerous domains. Therefore, it is important to keep these concepts in mind when comparing sorption data conducted by different investigators.
Table 24. Mean areas occupied by anions at high solution concentrations and near optimum pH on goethite.

<table>
<thead>
<tr>
<th>Anion</th>
<th>pH</th>
<th>No. of samples</th>
<th>Area/Anion (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluoride</td>
<td>3.5</td>
<td>1</td>
<td>20</td>
</tr>
<tr>
<td>Molybdate</td>
<td>4.0</td>
<td>3</td>
<td>31, 32, 38</td>
</tr>
<tr>
<td>Selenite</td>
<td>4.0</td>
<td>3</td>
<td>50, 53, 58</td>
</tr>
<tr>
<td>Arsenate</td>
<td>3.0</td>
<td>1</td>
<td>61</td>
</tr>
<tr>
<td>Phosphate</td>
<td>4.0</td>
<td>3</td>
<td>61, 63, 68</td>
</tr>
<tr>
<td>Silicate</td>
<td>9.0</td>
<td>3</td>
<td>60, 61, 64</td>
</tr>
</tbody>
</table>

* Taken from Hingston (1981).
Kinetics of Cr(VI) Retention on Soils

Seven soils differing in taxonomic classification and properties (see Table 2) were evaluated for their ability to retain Cr under batch reaction conditions. The batch reaction procedure used was the same as that described in the materials and methods, with the exception of the use of the goethite. In place of the goethite, 20 g of the respective soil was used as the adsorbate. The nonlinear multireaction model was evaluated for its ability to describe the Cr retention data. With the exception of one soil, either the three or five-parameter version of the multireaction model was successful in describing the Cr retention data (Table 25).

The Webster soil failed to adsorb significant amounts of Cr under stirred batch reaction conditions, even after 24 h of reaction. Previously, Amacher et al. (1988) studied the kinetics of Cr(VI) retention on soils using a batch equilibration method. Using the same three and five-parameter multireaction model, Cr retention by the Webster soil could not be described by either the three or five-parameter model versions at initial solution concentrations of 1.0 mg L\(^{-1}\). At an initial Cr concentration of 10.0 mg L\(^{-1}\), model parameter standard errors for both the three and five-parameter model predictions were greatly inflated. Buchter et al. (1989) investigated the ability of Cr to be adsorbed onto soils using the batch equilibration method (Amacher et al., 1986) and also found the Webster soil unable to adsorb Cr in concentrations ranging from 0.01 to 100 mg L\(^{-1}\). Buchter et al. (1989) concluded the inability of the Webster soil to adsorb Cr was related to the pH of soil (i.e. soils high in pH are less likely to adsorb oxyanions). More recently, Selim et al. (1989) modeled the transport of
Table 25. Nonlinear multireaction model parameters, goodness-of-fit, and parameter standard errors for Cr(VI) retention by several soils. 

\([\text{Cr(VI)}]_0 = 20 \mu M\).

<table>
<thead>
<tr>
<th>Soil</th>
<th>pH</th>
<th>T (°C)</th>
<th>No. of Parameters</th>
<th>(n)</th>
<th>(r^2)</th>
<th>rms</th>
<th>(k_1) SE</th>
<th>(k_2) SE</th>
<th>(k_3) SE</th>
<th>(k_4) SE</th>
<th>(K_{irr}) SE</th>
<th>(K_1) SE</th>
<th>(K_2) SE</th>
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</thead>
<tbody>
<tr>
<td>AL</td>
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<td>0.813</td>
<td>0.197</td>
<td>0.164</td>
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<td>0.588</td>
<td>0.186</td>
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<td>---</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>5</td>
<td>0.906</td>
<td>0.139</td>
<td>**</td>
<td>0.367</td>
<td>0.244</td>
<td>2.15</td>
<td>1.47</td>
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<td>0.00392</td>
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<td></td>
<td>0.300</td>
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<td>0.837</td>
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<td>5</td>
<td>0.980</td>
<td>0.326</td>
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<td>12.0</td>
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<td>0.177</td>
<td>0.0352</td>
<td>0.121</td>
<td>0.0306</td>
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<tr>
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<td>5</td>
<td>0.990</td>
<td>0.311</td>
<td>**</td>
<td>0.708</td>
<td>0.129</td>
<td>1.22</td>
<td>0.236</td>
<td>0.0318</td>
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<tr>
<td>KU Ap2</td>
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<td>0.609</td>
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<tr>
<td></td>
<td></td>
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<td>5</td>
<td>0.986</td>
<td>0.329</td>
<td>**</td>
<td>0.229</td>
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<td>0.338</td>
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<td>0.00200</td>
</tr>
</tbody>
</table>

Soils: AL: Alligator, CE: Cecil, KU: Kula

** and * indicate that the root mean squares (rms) are significantly different at the 0.01 and 0.05 levels of probability, respectively, according to the extra sum of squares criteria. NS = not significant.
Table 25. Continued

<table>
<thead>
<tr>
<th>Soil</th>
<th>pH</th>
<th>T (°C)</th>
<th>No. of Parameters</th>
<th>n</th>
<th>( r^2 )</th>
<th>rms</th>
<th>( k_1 ) SE</th>
<th>( k_2 ) SE</th>
<th>( k_3 ) SE</th>
<th>( k_4 ) SE</th>
<th>( K_{IRR} ) SE</th>
<th>( K_1 )</th>
<th>( K_2 )</th>
</tr>
</thead>
<tbody>
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<td>0.114</td>
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<td>5</td>
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<td>0.667</td>
<td>0.644</td>
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<td>0.975</td>
<td>0.120</td>
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<td>0.350</td>
<td>0.00506</td>
<td>0.0149</td>
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<td>5</td>
<td>0.967</td>
<td>0.210</td>
<td>**</td>
<td>0.0001</td>
<td>0.121</td>
<td>0.823</td>
<td>138.2</td>
<td>0.0281</td>
<td>0.00504</td>
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<tr>
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<td>23</td>
<td>3</td>
<td>5</td>
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<td>0.804</td>
<td>0.249</td>
<td>0.730</td>
<td>0.146</td>
<td>1.32</td>
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<td>5</td>
<td>0.895</td>
<td>0.182</td>
<td>*</td>
<td>1.05</td>
<td>0.304</td>
<td>2.86</td>
<td>0.857</td>
<td>0.0452</td>
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</tbody>
</table>

Soils: LA: Lafitte, MO: Molokai, WI: Windsor

** and * indicate that the root mean squares (rms) are significantly different at the 0.01 and 0.05 levels of probability, respectively, according to the extra sum of squares criteria. NS = not significant.
Cr in soil columns of six different soils, including the Webster soil. Results of miscible displacement studies indicated the interaction of 10 mg L$^{-1}$ Cr with the Webster soil was similar to that of a nonreactive solute. The multireaction model (Amacher et al., 1988) was modified and incorporated into the convection - dispersion transport equation. This model was successful in predicting Cr breakthrough curves for the Webster soil. Thus, the inability of the Webster soil to adsorb Cr in this study is concluded to be a result of the higher pH and possibly due to low amorphous $\text{Fe}_2\text{O}_3$ content.

Figures 42 - 44 show the retention of Cr on the remaining soils studied. The five-parameter model was significantly better than the three-parameter in describing the data for each soil, except for the Windsor A soil where the five-parameter model overfit the experimental data, as observed by the inflated standard error values. In the cases where the five-parameter model was significantly better, the three-parameter model was considered to underfit the data. In four of the soils (Cecil Ap, Cecil B, Lafitte, and Molokai) the better fit of the five-parameter model was achieved without increasing the standard errors. The nonsignificant increase in the standard errors of the remaining soils (Alligator, Kula Ap1, Kula Ap2, and Windsor B) resulted in the five-parameter model accurately predicting Cr retention data. The reaction order ($n$) used in the model were taken from the study by Buchter et al. (1989) in which the Freundlich equation was used to determine $n$ values. From Table 25 it can be seen rate coefficients and equilibrium constants varied widely, however similar values were not expected since the soils vary with respect to their chemical and physical properties. Significant correlations between the amount of Cr
Figure 42. Prediction of Cr(VI) retention by Alligator, Cecil Ap, and Cecil B soils. Model predictions are shown as solid lines and data points as symbols.
Figure 43. Prediction of Cr(VI) retention by Kula Ap1, Kula Ap2, and Molokai soils. Model predictions are shown as solid lines and data points as symbols.
Figure 44. Prediction of Cr(VI) retention by Lafitte, Windsor A, and Windsor B soils. Model predictions are shown as solid lines and data points as symbols.
retained by the soil and percent amorphous Fe$_2$O$_3$, percent free Fe$_2$O$_3$,
percent Al$_2$O$_3$, soil pH, and exchangeable OH could not be established for
the soils studied. The combinations of all the soil properties is prob­
ably masking the correlations. The Cecil B, Kula Apl and Ap2, and Molokai soils had the largest amounts of retained Cr. These soils also are
high in Fe oxides, Al oxides, or amorphous material as measured by
exchangeable OH even though no significant correlations were obtained.
The relationship between the high percentages of Fe oxides and the
amount of Cr retained is consistent with the findings shown in Figure 20
in which Cr retention increased as goethite concentration increased.
The higher percentage of Al$_2$O$_3$ in the Kula Apl and Kula Ap2 soils may
also be contributing to the greater adsorption ability of these soils.
Chromate retention should be favored by low pH and high Fe oxide, Al
oxide, and amorphous material contents. Low Cr(VI) retention is favored
by high pH and low Fe oxide, Al oxide, and amorphous material content.

The Cecil B soil retained the greatest amount of Cr (87.4%) after
24 hours of reaction, while the Alligator soil retained the least
(11.8%). Cecil Ap, Molokai, Windsor A, and Windsor B soils retained Cr
in quantities similar to the Alligator soil. In studies conducted by
Amacher et al. (1988) the three and five-parameter models could not pre­
dict Cr retention on the Kula, Lafitte, Molokai, and Webster soils with­
out containing inflated values for the standard errors. The poor fit of
the data was explained by the fact the first data point for these soils
was taken at 24 h, therefore it was thought the reaction reached equili­
brium by the time the first data point was taken. The data in Figures
42 - 44 shows the data to be very time dependent the first 60 min and
the most kinetic the first 10 min of reaction. Since the kinetics were
studied over the first 60 min only, sorption rather than reduction of chromate by organic matter was undoubtedly being studied. The reduction of chromate in soils is very slow except at very acid pH levels.

The heterogeneous nature of soils with respect to the wide variability of anions and other minerals present, increases the challenge in predicting the fate of anions versus studying anion retention/release reactions on pure systems. However, many times the results from studies on pure systems such as goethite, can provide insight into reactions involving heterogeneous systems.

**Kinetics of Cr(VI) Retention by Al Oxide and Humic Acid**

Two additional adsorbent materials investigated for their ability to retain Cr under batch kinetic conditions included a synthetic aluminum oxide mineral and humic acid extracted from a Lafitte Muck soil. Analysis of the aluminum oxide material by x-ray diffraction techniques indicated the material was non-crystalline and of amorphous nature. For this study, only the retention of Cr at an initial concentration of 20.0 \( \mu \text{M} \) was studied, however two concentrations of aluminum oxide (0.5 and 1.0 mM) and two quantities of humic acid were examined.

Results from the aluminum oxide studies can be seen in Figure 45. The aluminum oxide material did retain small amounts of Cr at oxide concentrations of 0.5 and 1.0 mM. Moreover, because of the capricious nature of the data, the three- and five-parameter versions of the multireaction model were unable to describe the retention data. Numerous investigators including Reisenauer et al. (1962); McPhail et al. (1972); Van Riemsdijk and Lyklema (1980b); Bolan and Barrow (1984); Goldberg and Glaubig (1985); and Goldberg (1986) have studied the
Figure 45. Retention of Cr(VI) by two concentrations of aluminum oxide.
sorption of various anions by aluminum oxide minerals. The Freundlich, Langmuir, and Constant Capacitance models have been successful in describing the sorption of anions by aluminum oxide minerals. The lack of significant amounts of Cr being adsorbed by the aluminum oxide in this study is believed to be a result of the amorphous nature of the material. However, in studies previously mentioned by other researchers, crystalline and amorphous aluminum oxide minerals have shown a capability to adsorb anions.

Similar to the aluminum oxide material, two quantities of humic acid (0.1 and 1.0 g) also failed to retain significant amounts of Cr (figure not shown). The retention data exhibited an erratic nature, thus the multireaction model was unsuccessful in describing the retention of Cr. Various researchers have previously investigated the ability of humic acid to sorb metals from an aqueous solution (Schnitzer and Skinner, 1965; Van Dijk, 1971; Stevenson, 1977; Kerndorff and Schnitzer, 1980). The functional groups of humic acid generally agreed upon as the ones responsible for the binding of metals are the carboxyl, hydroxyl, and carbonyl groups, which are effective in binding metal cations rather than anions. Szalay and Szilagyi (1967) concluded anions cannot be directly fixed by humic acids even in trace amounts. They stated metal ions which can exist as both anionic and cationic complexes, would have to be converted to a cationic complex before being sorbed by humic acid. The findings of Szalay and Szilagyi (1967) is consistent with the findings in this study on Cr sorption by humic acid. Moreover, since the initial time frame in which this study was conducted was short, significant reduction of chromate into cationic forms is believed not to have taken place.
SUMMARY AND CONCLUSIONS

A general purpose nonlinear multireaction model was examined for its capability to describe batch kinetic retention reactions of chromate and phosphate by synthetic goethite under varying experimental conditions. Other adsorbent materials studied for their ability to adsorbed chromate included several soils of different pH values, amorphous aluminum oxide, and humic acid contents. The Freundlich and two-site Langmuir equilibrium models were also utilized to describe the sorption of chromate, phosphate, arsenate, selenite, and silicate by goethite and to obtain descriptive parameters to be used in the nonlinear multireaction model. In addition, a pH dependent mechanistic model was proposed to account for the adsorption of inorganic oxyanions onto oxide surfaces.

The Freundlich equation adequately described the sorption (after 24 h of reaction) of Cr, P, As, Se, and Si at pH values of 3, 4, 5, 6, 7, and 8. The affinity parameter, K, of the Freundlich equation generally decreased as pH increased for chromate, phosphate, arsenate, and selenite, while the reaction order, n, increased with increasing pH. Conversely, for Si, K increased and n decreased as pH increased. The relationships established between pH and the Freundlich equilibrium model parameters (K and n) allow for the calculation of these parameters at other pH values for which no data exists. In addition, the reaction orders (n) determined by the Freundlich equilibrium model were successfully used in the multireaction model to describe the kinetic retention data. The two-site Langmuir equilibrium model was partially successful in describing Cr, P, and Si sorption by goethite and well described As and Se sorption at all pH values investigated. Only at acid pH values
was the two-site Langmuir equilibrium model successful in describing Cr sorption. The maximum retention capacity for chromate was greatest at pH 5 and decreased at pH values greater and less than 5. The quantity of type 1 sites decreased as pH increased for both Cr and P and may become so small at high pH levels that the two-site Langmuir equilibrium model is not capable of describing the data. The quantities of type 1 and type 2 sites determined from the two-site Langmuir equilibrium model were used in the second-order version of the multireaction model.

The ability to predict chromate retention by goethite as a function of goethite concentration, Cr concentration, temperature, pH, and background salt solution was also investigated using the nonlinear multireaction model. Chromate retention and experimental rate coefficients (determined by the nonlinear multireaction model) increased with increasing goethite concentrations, however, experimental rate coefficients decreased with increasing initial chromate concentrations. The effect of different reaction temperatures upon rate coefficients for chromate retention did not produce strong dependencies. Equilibrium constants calculated from the rate coefficients decreased only slightly but were of equal magnitude. The dependence of rate coefficients on initial reactant concentrations and the lack of a strong temperature dependence of rate coefficients indicates that the rate coefficients from the multireaction model are not those for elementary reactions at the molecular level. Thus, these rate coefficients can best be defined as pseudo or descriptive type rate coefficients for overall reactions. Moreover, the actual mechanism is more complex than that represented by the general multireaction model. In addition, because of the small temperature effect, diffusion-controlled kinetics (physical nonequili-
brium) may be dominant rather than reaction-controlled kinetics (chemical nonequilibrium).

The retention of chromate by goethite as a function of pH showed equilibrium constants to decrease with increasing pH. The rate equations derived from the mechanistic model predicted that the pseudo rate coefficients for ligand exchange to be pH dependent, which was found to be supported in this study. Thus, the proposed mechanistic model for the adsorption of inorganic oxyanions onto oxide surfaces was found to be consistent with the general purpose nonlinear multireaction model. However, the second-order version of the multireaction model failed to adequately describe the kinetic data.

The effect of background salts upon the retention of chromate by goethite was such that retention decreased as the ionic strength of Ca(NO$_3$)$_2$ increased. Moreover, the equilibrium constants decreased with increasing ionic strength. Major differences in the amount of chromate retained by goethite by varying the type of background salt were not observed. Results of kinetic exchange reactions between Cr and P on goethite showed P to be retained in preference to Cr. Phosphate readily replaced Cr on goethite surface sites, but exchange was incomplete at high reactant concentrations, low temperatures (2 and 11 °C), and acid pH levels.

The effect of competing anions on Cr adsorption was also investigated. The relative affinity an anion has for an adsorption site was found to be a determining factor as to which anion was preferentially adsorbed. Both single and paired kinetic retention studies were performed for Cr, P, As, B, F, Mo, Se, and Si. Individual kinetic anion studies revealed the following affinity sequence on goethite: As > Se >
P > Mo > Cr > F > B > Si. A similar affinity sequence was established by examination of the sorption data as described by the Freundlich equilibrium model. Of the anions studied the following affinity sequence was determined by the Freundlich equilibrium model at pH 5: As > Se > P > Cr > Si. Thus both the multireaction kinetic model and the Freundlich equilibrium model are consistent with each other in establishing anion affinities on goethite.

Since the affinity parameters of the Freundlich and two-site Langmuir are often considered comparable to equilibrium constants, they can be compared to the equilibrium constants calculated from the pseudo rate coefficients of the nonlinear multireaction kinetic model. The equilibrium constants determined from the Freundlich equilibrium model were consistently greater in magnitude than those of the two-site Langmuir and the multireaction model for the anions studied. Additionally, the two-site Langmuir equilibrium constants were consistently much smaller in magnitude than those of the Freundlich and multireaction models. The equilibrium constants calculated from the multireaction model were in closer agreement to the Freundlich than the two-site Langmuir equilibrium model.

Seven soils differing in chemical and physical properties were studied to evaluate the retention behavior of chromate under batch kinetic reaction conditions. The five parameter version of the multireaction model adequately described the experimental retention data for five of the seven soils. The Cecil B, Kula Apl, Kula Ap2, and Molokai soils retained the largest amounts of chromate. The percentage of free Fe$_2$O$_3$ content in the soils includes goethite, hematite, ferrihydrite, and other iron oxides, thus iron oxides are believed to be the soil
component responsible for chromate retention. Although Cr(VI) is capable of undergoing reduction in soils, the initial time frame studied (24 h) was too short for significant reduction to occur. Therefore, Cr(VI) reduction in the batch solution can be discounted as a possible explanation for the decrease in chromate solution concentration. In addition, in separate experiments, it was found that amorphous aluminum oxide and humic acid did not adsorbed significant amounts of chromate. Consequently, the multireaction model was not capable of describing these reactions.


APPENDIX
Appendix 1. Procedure for extraction and purification of humic acid from soil, peat, sludge, and other materials.

1. Add 200 mL of 0.5 M NaOH to a 250 mL centrifuge bottle.
2. Bubble N\textsubscript{2} gas through the NaOH solution for a few minutes to remove O\textsubscript{2}.
3. Add 40 g of soil (10 g of peat, sludge, etc.) to the bottle.
4. Fill the airspace above the liquid with N\textsubscript{2} and cap the bottle tightly.
5. Shake for 18 hr. at 120 osc/min.
6. Centrifuge for 20 min. at 15,380 g (10,000 rpm).
7. Decant the supernatant into a 500 mL Erlenmeyer flask.
8. Adjust the pH of the supernatant to 1.0 using 6 M HCl.
9. Add 200 mL of 0.5 M NaOH to the residue in the bottle.
10. Bubble N\textsubscript{2} gas through the NaOH solution, fill the airspace with N\textsubscript{2}, and cap the bottle tightly.
11. Shake for 1 hr. at 120 osc/min.
12. Centrifuge for 20 min. at 15,380 g (10,000 rpm).
13. Decant the supernatant into the Erlenmeyer flask and discard the residue.
14. Readjust the combined supernatant pH to 1.0 using 6 M HCl.
15. Allow the precipitated humic acid to settle out overnight.
16. Siphon or decant as much of the fulvic acid supernatant as possible into a 1 L Erlenmeyer flask.
17. Transfer the remaining suspension to a 250 mL plastic centrifuge bottle.
18. Centrifuge for 20 min. at 15,380 g (10,000 rpm).
19. Decant the supernatant into the 1 L Erlenmeyer flask.
20. Add 50 mL of 0.5 M NaOH to the humic acid residue in the bottle and shake to disperse the residue.
21. Adjust the pH to 1.0 using 6 M HCl.
22. Allow the humic acid to settle out for 1 hr.

23. Centrifuge for 20 min. at 15,380 g (10,000 rpm).

24. Decant the supernatant into the 1 L Erlenmeyer flask.

25. Repeat steps (20) through (24) one more time.

26. Wash the humic acid in deionized water by adding 100 mL of deionized water to the bottle, shaking to disperse the humic acid, centrifuging for 20 min. at 15,380 g, and discarding the wash water. Repeat twice more.

27. If it is necessary to further purify the humic acid, shake the humic acid for 48 hr. at 120 osc/min. with 100 mL of 0.5% HCl-0.5% HF solution, centrifuge the suspension for 20 min. at 15,380 g, discard the supernatant, wash the residue three times with deionized water and freeze-dry the humic acid (or dry in an oven at 105 °C).

28. If necessary filter the fulvic acid solution through a 0.45 um membrane filter under suction and adjust the pH of the fulvic acid solution to 2.5 using 5 M and 0.5 M NaOH.

29. Allow the B-humus to settle out for 1 hr.

30. Transfer the suspension to 250 mL plastic centrifuge bottle, centrifuge for 20 min. at 15,380 g, combine the supernatants in a 1 L Erlenmeyer flask, and discard the residue.

31. Repeat steps (29) through (31) raising the pH 1.0 unit interval each time until a pH of 7.5 is reached.

32. Remove the salt from the fulvic acid solution by passing the solution at a rate of 20-40 mL/min through a cation exchange column containing about 1 L of Dowex 50W-X8 resin, 20-50 mesh, in H-form. Collect the effluent when the pH sharply drops indicating fulvic acid is in the effluent, add deionized water to the top of the column to maintain a constant head on the column, and cease collecting the effluent when the pH sharply rises.

33. Regenerate the column by passing 0.6 M HCl through the column until no Na⁺ can be detected in the effluent using atomic emission spectrometry (AES) followed by passing deionized water through the column until the influent and effluent pH values are the same.

34. Analyze the fulvic acid for Na⁺ and if any is detected pass the solution through the column again.

35. Freeze dry the fulvic acid, weigh to obtain the yield, and store in a dessicator.
Appendix 2. Procedures followed for characterizing the soils used in this study.

1. Soil pH was measured using a 1:1 soil/water suspension (McLean, 1982).

2. Total organic carbon (TOC) and carbonates were determined by wet combustion methods with gravimetric determination of CO$_2$ (Nelson, 1982; Nelson and Sommers, 1982).

3. Cation exchange capacity (CEC) was determined by summing the exchangeable bases plus aluminum as determined by replacement with 0.1 M BaCl$_2$ - 0.1 M NH$_4$Cl (Thomas, 1982).

4. Exchangeable OH was determined by replacement with F ions (Perrott et al., 1976).

5. MnO$_2$ and amorphous Fe$_2$O$_3$ were determined by extraction with 0.25 M NH$_4$OH - 0.25 M HCl at 50 °C (Chao and Zhou, 1983).

6. Free Fe$_2$O$_3$ and Al$_2$O$_3$ were determined by extraction with dithionite-citrate-bicarbonate (Mehra and Jackson, 1960) following destruction of inorganic matter using pH 9.5, 5.25% NaOCl (Anderson, 1963).

7. The sand content was determined by wet and dry sieving, the clay content was determined by the pipette method (Gee and Bauder, 1986), and the silt content by difference.
VITA


He attended Harding University in Searcy, Arkansas from 1976 - 1980 and graduated with a B.S. in Biology in May 1980. From January 1981 to December 1981 he was employed by the Agronomy Research Support Laboratory, IFAS, University of Florida, Gainesville as a Laboratory Technologist and Field Supervisor. From January 1982 to December 1982 he was a graduate research assistant in the Department of Civil Engineering, Louisiana State University and served as the chief aerial photographer for the Remote Sensing and Image Processing Laboratory, Louisiana State University, College of Engineering, Baton Rouge.

From January 1983 to December 1985 he was a graduate research assistant in the Department of Agronomy, Louisiana State University, Baton Rouge. In December 1985 he received a M.S. in Agronomy specializing in Soil Physics. In January 1986 he began pursuing a Ph.D. in Agronomy with emphasis in Soil Chemistry while serving as a graduate teaching assistant for introductory crop science and soil science laboratories. Currently he is a candidate for the Ph.D. degree in the Department of Agronomy at Louisiana State University, Baton Rouge.

The author is married to Deborah Joy Davidson of Gainesville, Florida. While a graduate student at Louisiana State University, two daughters, Melissa and Natalie, have become additions to the family.

He is member of the American Society of Agronomy, Soil Science
Society of America, the Soil and Water Conservation Society, and the Louisiana Association of Agronomists.
Candidate: David S. Burden

Major Field: Agronomy

Title of Dissertation: Kinetics of Chromate and Phosphate Sorption By Oxide Minerals and Soils

Approved:

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

Robert P. Zambello

Sam E. Feagley

Mark Hattan

Harry J. Brand

RayBrand

Date of Examination:

November 3, 1989