

AN ABSTRACT OF THE THESIS OF

Martin H. Schroth for the degree of Master of Science in Civil Engineering
presented on June 16, 1989.

Title: Chromium(VI) Sorption in Soils : Chemical Behavior and Solute Transport
Modeling

Abstract approved: Redacted for Privacy
Peter O. Nelson

Chromium spills on soils are causing severe groundwater contamination problems. To increase the performance of cleanup methods, the chemical behavior of chromium in soils and its transport through soils have to be understood. The objectives of this research were to investigate the sorption characteristics of chromium(VI) in soil and to develop a solute transport model that allows the prediction of chromium(VI) movement through soil columns. Of particular interest was the sorption behavior of chromium(VI) in the presence of phosphate, another adsorbing anion. Laboratory experiments were performed using soil samples taken from an area close to a chromium contamination site. Batch experiments were conducted for both chromium(VI) and phosphates to determine sorption parameters. Soil column breakthrough curves for chromium(VI) were determined with and without phosphate present. The batch studies indicated a strong kinetic sorption behavior for both chromium(VI) and phosphate, which was attributed to a physical

non-equilibrium transport process. The soil column experiments showed that the chromium(VI) removal rate from soil can be increased when phosphates are introduced into the soil solution during the desorption process. To interpret the results of these experiments, a physical non-equilibrium solute transport model was developed that incorporated competitive sorption. Numerical solutions of the transport equations were obtained by a partially implicit finite difference method. Computer simulations of experimental breakthrough and desorption curves had close agreement with experimental results. This study demonstrated that phosphate addition to the soil solution is a possible way of increasing desorption rates and, consequently, the effectiveness of chromium(VI) removal from contaminated soils.

**Chromium(VI) Sorption in Soils :
Chemical Behavior and
Solute Transport Modeling**

by

Martin H. Schroth

A THESIS

submitted to

Oregon State University

**in partial fulfillment of
the requirements for the
degree of**

Master of Science

Completed June 16, 1989

Commencement June 1990

APPROVED:

Redacted for Privacy

Professor of Civil Engineering in charge of major _____

Redacted for Privacy

Head of Department of Civil Engineering) _____

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Date thesis is presented _____ June 16, 1989 _____

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CHAPTER I: HEXAVALENT CHROMIUM CHEMISTRY IN SOILS: LABORATORY EXPERIMENTS

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- Schroth, M. H. : Model development, text

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my major advisor, Dr. Peter Nelson. Throughout this research, he provided me with scientific, moral and financial support which made the completion of this thesis possible. I would also like to thank Dr. Jack Istok for his help and encouragement during this research, in particular his great efforts of reviewing and editing chapter II and for letting me use his "fast machine". Thanks also to Dr. David Bella for inspiring ideas and great discussions during the model development.

Many thanks to Mohammad Azizian for his help in the lab, his contribution in the manuscript of Chapter I and for letting me use his experimental results. Thanks also to Greg Bean for letting me use his experimental data.

J I would also like to express my gratitude to the Fulbright Commission for providing me with a scholarship, which made it possible for me in the first place to take on this adventure in the wild, wild West.

Partial support for this research was obtained from:

1. NIH Biomedical Research Support Grant RR07079
2. U.S. Dept. of Interior, U.S. Geological Survey, program grant for Water Resources Research Institute, Oregon State University

Dedicated to Traudl
for her love and support

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CHROMIUM(VI) SORPTION IN SOILS: CHEMICAL BEHAVIOR AND SOLUTE TRANSPORT MODELING

INTRODUCTION

Groundwater is an important freshwater resource. Over the last decade, more and more cases of groundwater contamination by heavy metals, in particular chromium, have been discovered. These contaminations are of great concern due to the high toxicity exhibited by Cr(VI), posing a severe threat to human health as well as to the environment. Efficient cleanup methods are therefore required to preserve aquifers as a valuable freshwater source. To increase the cleanup efficiency it is necessary to be able to predict the movement of chromium through soils and aquifer systems and thus understand its transport mechanisms, its chemical behavior and its interactions with the soil matrix.

The objectives of this work were to investigate chromium(VI) behavior in a natural soil system, in particular to determine the effect of pH on Cr(VI) sorption onto the soil and to better understand the kinetic effects that accompany chromium(VI) sorption. Another important objective was to investigate the Cr(VI) removal effectiveness from contaminated soil when phosphate is used as a competitive anion during chromium(VI) desorption. As a step to improve the understanding of the chromium(VI) movement in aquifer systems, a solute transport model had to be developed to describe the movement of chromium(VI) through laboratory soil columns. This model had to be verified using experimentally determined breakthrough curves (BTC's).

LITERATURE REVIEW

Chromium(VI) adsorption studies have been conducted using a variety of solid media. Griffin et al.(9) conducted an adsorption study on kaolinite and montmorillonite clays. They found that Cr(VI) adsorption decreased as pH increased. Below pH 2, however, Cr(VI) adsorption also decreased gradually. These results were partially attributed to an increase of positive surface charges on clays and hydrous oxides as the pH was lowered. It was also believed that Cr(VI) speciation played an important role. At low pH, the fraction of HCrO_4^- present becomes smaller, favoring the uncharged H_2CrO_4 . This was believed to be the reason for less Cr(VI) adsorption below pH 2. At high pH, when Cr(VI) is present as CrO_4^{2-} , no sorption was observed. It was believed that the double charge on the CrO_4^{2-} anion caused it to be repelled by the negative clay surface charges. Davis and Leckie (5) conducted a Cr(VI) adsorption study on amorphous iron oxyhydroxide. In this study it was concluded that both CrO_4^{2-} and HCrO_4^- are sorbing species. The adsorption mechanism of Cr(VI) was also discussed by Stollenwerk and Grove (11). Here it was concluded that Cr(VI) adsorbed by nonspecific processes as well as by specific sorption site processes. The fraction of Cr(VI) that could be extracted easily from the solid phase was assumed to be adsorbed by nonspecific processes whereas the remainder of the Cr(VI) on the solid phase was assumed to be adsorbed by specific sorption site processes. The effect of other anions in solution on Cr(VI) adsorption was also investigated. It was found that the amount of chromium(VI) adsorbed is a function of the type

and concentration of the other anions in solution. A strong competitive effect observed for phosphate was explained by direct competition for specific surface sites. The smaller effect of Cl^- and NO_3^- on Cr(VI) adsorption was attributed to a decrease in electrostatic potential near the surface of a particle, leading to less anion adsorption by nonspecific processes. An earlier study by Bartlett and Kimble (2) showed similar results for phosphate, attributing its good extraction effect to specific site competition. A study of chromium(VI) adsorption on iron oxyhydroxides in the presence of paired solute systems and multiple ion mixtures was recently conducted by Zachara et al.(13). Their findings agreed with the previously conducted research, showing decreased Cr(VI) adsorption for each anion added to the solute mixture.

Another important mechanism for chromium(VI) behavior in natural soil systems, besides adsorption, is the transformation to Cr(III) by reduction. Bartlett and Kimble (2) found fast Cr(VI) reduction in soil in the presence of soil organic matter. An almost completely organic-free soil showed little Cr(VI) reduction potential. However, when manure was added and pH was adjusted below 3, most of the added Cr(VI) was reduced within 24 hours. In this study, no oxidation of Cr(III) to Cr(VI) was observed. In a later study, however, Bartlett and James (3) found Cr(III) oxidation in soil in the presence of oxidized manganese. A reduction process of Cr(VI) to Cr(III) followed by a precipitation of $\text{Cr}(\text{OH})_3$ was assumed to be at least partially the reason for a poor Cr(VI) recovery efficiency observed by Stollenwerk and Grove (11) for their soil column experiments. Extensive reduction of Cr(VI) in topsoil was also observed by Bloomfield and

Pruden (4). Experimental results also indicated a strong pH dependence for the reduction process leading to increased reduction rates with decreased pH.

A variety of solute transport models for both organic and inorganic species have been proposed. Most of these models incorporate the same dispersion-advection transport processes. They differ, however, in the way that sorption / desorption reactions are modeled. A review of sorption models for reactive solutes in soil was given by Travis and Etnier (24). Both equilibrium and first-order kinetic models were discussed. Equilibrium models were originally developed to describe sorption isotherms for gases and organic solutes. Bar-Yosef (14) derived a sorption model based on a competitive Langmuir isotherm for ionic species and applied it successfully to pH-dependent zinc adsorption by soils. This model did not include the effect of the electric potential (Ψ) and the electrolyte concentration on adsorption. Bar-Yosef believed that the effect of Ψ was to some extent accounted for by the binding constants of the different ions. A transport model based on ion exchange was presented by Valocchi et al. (25). Sorption processes for ionic species were modeled employing the well known principle of ion exchange selectivity. Although successful for the cases considered, the authors realized that the ion selectivity coefficients are typically not constant but instead are a function of the sorbed phase concentration. These coefficients are also highly variable in natural soil systems, thus hard to estimate. Cederberg et al. (15) presented a solute transport model that incorporated ion exchange and surface complexation coupled with a chemical equilibrium model. Good agreement was

found between predicted and measured concentrations of cadmium, chloride and bromide in laboratory soil columns.

For many transport problems, the assumption of equilibrium sorption is not valid (Van Genuchten (29)). Two classes of non-equilibrium models have been developed: chemical non-equilibrium and physical non-equilibrium.

Derivations of these models are in Van Genuchten and Cleary (28) and Van Genuchten (29).

The chemical non-equilibrium model assumes that there are two types of sorption sites. For one type of site the sorption reaction is assumed to be a slow, kinetically controlled process. For the other type of site sorption is assumed to be a kinetically faster or even an instantaneous equilibrium process. Such a two-site model was recently used by Selim and Amacher (23) to model chromium(VI) transport through three different soils. Kinetic Langmuir equations were used to describe the sorption reactions. This approach was partially successful in describing data from miscible displacement experiments. Grove and Stollenwerk (17) modeled chromium(VI) movement through alluvial materials coated with iron-oxide and hydroxide. They used a one-site chemical non-equilibrium model based on a kinetic Langmuir equation. This model agreed better with experimental data than when sorption was assumed to be at equilibrium.

Physical non-equilibrium models usually divide the total water content of a soil into a mobile and an immobile region and assume that the kinetic sorption behavior is caused by a physical mechanism, typically a diffusional process across the immobile water layer to the solid surface. Wu and Gschwend (30) recently

presented evidence that the sorption kinetics of hydrophobic organic compounds on natural sediments are controlled by such an intraparticle diffusion.

These two major groups of non-equilibrium solute transport models were compared by Nkedi-Kizza et al. (20). When a linear sorption reaction was used, the analytical solutions for the two models are equivalent. These authors concluded that the difference between the two models is of little practical importance and suggest that the occurrence of specific processes can only be verified with microscopic measurements.

CHAPTER I:
HEXAVALENT CHROMIUM CHEMISTRY IN SOILS:
LABORATORY EXPERIMENTS

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ABSTRACT

Knowledge of the fate of chromium(VI) in natural soil and aquifer systems is of great importance due to the high toxicity exhibited by Cr(VI) to both humans and the environment. The objectives of this work were to investigate Cr(VI) behavior in a Dayton series clay, in particular pH and kinetic effects on adsorption reactions. Another objective was to investigate the degree to which phosphate is able to increase the Cr(VI) extraction performance from contaminated soil.

Batch reactor experiments were conducted for chromium(VI) and phosphate. The results indicated that reduction of Cr(VI) to Cr(III) and subsequent removal, besides Cr(VI) adsorption, was a major process in soil suspensions. The total Cr(VI) removal increased with decreasing pH and increasing initial Cr(VI)

concentration. The adsorption process itself consisted of two steps, an initial fast uptake followed by a slower, kinetically controlled uptake. This behavior was attributed to a physical non-equilibrium process.

Soil column experiments were conducted for Cr(VI) using both distilled water and a phosphate solution as extraction agents. The phosphate solution improved the Cr(VI) removal effectiveness by increasing the chromium(VI) desorption rate significantly. This effect was attributed to specific anion competition. The amount of Cr(VI) recovered, however, did not increase significantly when phosphate was used compared to using distilled water for Cr(VI) desorption.

Additional Word Index : Chromium(VI) chemistry, adsorption, physical non-equilibrium, phosphate competition.

INTRODUCTION

Hexavalent chromium contaminations in aquifer systems are of great concern due to the high environmental toxicity exhibited by Cr(VI). Efficient cleanup methods are required to preserve aquifers as a valuable freshwater resource. To increase the cleanup efficiency it is necessary to better understand the behavior of chromium(VI) in natural soil systems. The objectives of this work were to investigate chromium(VI) behavior in a natural soil system, particularly to determine the effect of pH on Cr(VI) sorption onto the soil and to better understand the kinetic effects that accompany chromium(VI) sorption. Another important objective was to investigate the Cr(VI) removal effectiveness from contaminated soil when phosphate is used as a competitive anion during chromium(VI) desorption.

Chromium(VI) adsorption studies have been conducted using a variety of solid media. Griffin et al.(9) conducted an adsorption study on kaolinite and montmorillonite clays. They found that Cr(VI) adsorption decreased as pH increased. Below pH 2, however, Cr(VI) adsorption also decreased gradually. These results were partially attributed to an increase of positive surface charges on clays and hydrous oxides as the pH was lowered. It was also believed that Cr(VI) speciation played an important role. At low pH, the fraction of HCrO_4^- present becomes smaller, favoring the uncharged H_2CrO_4 . This was believed to be the reason for less Cr(VI) adsorption below pH 2. At high pH, when Cr(VI) is present as CrO_4^{2-} , no adsorption was observed. It was believed that the double

charge on the CrO_4^{2-} anion caused it to be repelled by the negative clay surface charges. Davis and Leckie (5) conducted a Cr(VI) adsorption study on amorphous iron oxyhydroxide. In this study it was concluded that both CrO_4^{2-} and HCrO_4^- are sorbing species. The adsorption mechanism of Cr(VI) was also discussed by Stollenwerk and Grove (11). Here it was concluded that Cr(VI) adsorbed by nonspecific processes as well as by specific sorption site processes. The fraction of Cr(VI) that could be extracted easily from the solid phase was assumed to be adsorbed by nonspecific processes whereas the remainder of the Cr(VI) on the solid phase was assumed to be adsorbed by specific sorption site processes. The effect of other anions in solution on Cr(VI) adsorption was also investigated. It was found that the amount of chromium(VI) adsorbed is a function of the type and concentration of the other anions in solution. A strong competitive effect observed for phosphate was explained by direct competition for specific surface sites. The smaller effect of Cl^- and NO_3^- on Cr(VI) adsorption was attributed to a decrease in electrostatic potential near the surface of a particle, leading to less anion adsorption by nonspecific processes. An earlier study by Bartlett and Kimble (2) showed similar results for phosphate, attributing its good extraction effect to specific site competition. A study of chromium(VI) adsorption on iron oxyhydroxides in the presence of paired solute systems and multiple ion mixtures was recently conducted by Zachara et al.(13). Their findings agreed with the previously conducted research, showing decreased Cr(VI) adsorption for each anion added to the solute mixture.

Another important mechanism for chromium(VI) behavior in natural soil

systems, besides adsorption, is the transformation to Cr(III) by reduction. Bartlett and Kimble (2) found fast Cr(VI) reduction in soil in the presence of soil organic matter. An almost completely organic-free soil showed little Cr(VI) reduction potential. However, when manure was added and pH was adjusted below 3, most of the added Cr(VI) was reduced within 24 hours. In this study, no oxidation of Cr(III) to Cr(VI) was observed. In a later study, however, Bartlett and James (3) found Cr(III) oxidation in soil in the presence of oxidized manganese. A reduction process of Cr(VI) to Cr(III) followed by a precipitation of Cr(OH)₃ was assumed to be at least partially the reason for a poor Cr(VI) recovery efficiency observed by Stollenwerk and Grove (11) for their soil column experiments. Extensive reduction of Cr(VI) in topsoil was also observed by Bloomfield and Pruden (4). Experimental results also indicated a strong pH dependence for the reduction process leading to increased reduction rates with decreased pH.

MATERIALS AND METHODS

Materials

The soil used in the experiments was a Dayton series silty clay collected from an uncontaminated field at the Corvallis Airport (7-15-87), near the United Chrome Products Superfund site (Ecology and Environment (6)). Previous investigations at that site showed that most of the chromium contamination is found in a zone of clayey silt extending from the surface to roughly six meters of depth; there was little variation between the soil in this zone and other surface soils in the area (Ecology and Environment (6)). The soils used in the present study should therefore be representative of much of the contaminated soil. The soil was taken from a zone of roughly 5 cm to 35 cm depth. Field conditions were such that no drying was required before further preparation. Large clumps were broken up and pebbles and large roots were removed by mechanical grinding in a "Dynacrush" soil grinder followed by passing the soil through a 2 mm mesh sieve. The ground, sieved soil was hand mixed and stored at field moisture and 4 °C until use.

All chemicals used in this study were ACS reagent grade. Glass and plasticware were soaked in 10% nitric acid and rinsed well with glass distilled water prior to all uses.

Experimental Procedures

The pH of the point-of-zero-charge (PZC) of the Dayton soil was determined by soil titrations performed in background electrolyte solutions. Soil-electrolyte suspensions were prepared with one gram of soil and 25 milliliters of solution. Solution ionic strengths were adjusted to 0.01 M and 0.10 M for two of the titrations by addition of KCl to glass distilled water; pH was adjusted by strong acid or base (HCl or KOH). In a third titration, no salt was added; ionic strength depended on acid or base strength only.

The organic matter content of the soil was determined by weight loss after ashing soil samples for 2 hours at 550 °C.

Batch reactor experiments were performed for both chromium(VI) and phosphate. Chromium(VI) and phosphate solutions were reacted with soil in 50 milliliter, screw-top plastic centrifuge tubes. Unless otherwise noted, 25 milliliters of solution were reacted with one gram of soil. All Cr(VI) and phosphate solutions were prepared with glass distilled water. Soil-suspensions were kept well mixed by continuous shaking in a 25 °C constant-temperature shaker bath. The headspace of the centrifuge tubes was air filled; no effort was made to control the O₂(g) or CO₂(g) content. Hexavalent chromium was added in solution as potassium dichromate; stock solutions were prepared at concentrations 1 gram per liter (0.192 M). Phosphate solutions were prepared from KH₂PO₄. Strong acid or base (HCl or KOH) was added to adjust pH between 2.5 and 9. After shaking for

the desired reaction time, the tubes were centrifuged at 10,000 rpm for 10 minutes and the supernatant solutions were passed through 0.45 μm Millipore filters. Samples were stored in plastic containers until analysis for pH, total Cr, and/or Cr(VI), or phosphate, respectively. Adsorbed chromium and phosphate were determined by difference from initial and final solution concentration.

Soil column experiments were conducted to more closely simulate field conditions of continuous hydraulic flow through a stationary porous medium. The soil columns utilized the same soil (uncontaminated) as those of the batch experiments described above, packed to approximate field density (about 1.1 g/cm^3). Columns employed were borosilicate glass with a fritted porous support plate. The 25 cm long by 3.2 cm inside diameter columns were typically packed with 50 g of soil to a porosity of 35-40 %, yielding a soil column of about 5.7 cm height. Hydraulic flow through the column was also set to approximate field conditions (about 11 ml/h).

For these column experiments chromium(VI) was first adsorbed on the soil columns in a distilled water solution until equilibrium (column effluent equals column influent chromium concentration) was approximately achieved between the soil and applied chromium solution. Then chromium(VI) was extracted from the soil columns by application of various extraction media. Initial Cr(VI) concentrations, pH, and different extractants that were used in the various column studies are presented in Table I.1.

Another soil column experiment was performed using a chloride (Cl^-)

solution. The soil column for this tracer experiment was prepared in the same manner as described above. The specific conditions of this experiment are also presented in Table I.1.

Table I.1 Soil column continuous flow experiments.

Cr(VI) soil column experiments:				
Experiment no	Pore volume ml	Initial Cr(VI) conc. mg/l	pH	Extractant
1	18.5	10	4.10	Distilled water
2	18.5	50	3.85	Distilled water
3	18.4	10	4.53	H ₂ PO ₄ ⁻ 0.02 M
Cl ⁻ tracer column experiment:				
Experiment no	Pore volume ml	Initial Cl ⁻ conc. mg/l	pH	Extractant
4	24.3	14.6	7.00	Distilled water

Analytical Methods

Chromium(VI) concentrations in solution were determined by the colorimetric method of Bartlett and Kimble (1). One milliliter of an s-diphenyl carbazide reagent solution was mixed with 1 ml of sample or standard plus 7 mls H₂O and measured for absorbance at 540 nm on a Bausch and Lomb Spectronic 88 spectrophotometer. The reagent solution was prepared by dissolving 200 mg s-diphenyl carbazide in 100 ml of 95% ethanol and adding 120 mls 85% H₃PO₄ in 280 mls distilled water. A small amount of KMnO₄ was added until a pink color developed: then the mixture was heated at 60 °C until the color disappeared. This solution was stored at 4 °C in a dark glass bottle. Standard solutions of 1, 3 and 5 mg/l were prepared from a 1000 mg/l K₂Cr₂O₇ stock solution. Concentrations of samples were calculated by using linear regression on the standard concentrations. The detection limit was determined to be 0.01 mg/l. Total chromium in solution was determined by flame atomic absorption spectroscopy using a Perkin Elmer Model 360 AAS. The detection limit was determined to be 1 μM (0.050 mg/l). The precision of this method was lower than for the colorimetric method; variations in results of up to 20% were sometimes observed in repeated analyses of individual samples in the optimum concentration range. Trivalent chromium (Cr(III)) concentrations were calculated by difference, subtracting the Cr(VI) from total chromium concentrations.

Phosphate and chloride concentrations were determined by anion chromatography using a DIONEX Series 4000i ion chromatograph (IC) equipped

with a conductivity detector. The columns used in the IC were a HPIC-AG4A guard column and a HPIC-AS4A separator column. The eluent solution injected was a 1.8 mM Na_2CO_3 + 1.7 mM NaHCO_3 at a flow rate of 2.0 ml/min. 3 ml/min of 25 mN H_2SO_4 solution were injected into the column as regenerant. Phosphate standards of 10, 20, 30 and 50 mg/l (as H_2PO_4^-) and chloride standards of 1, 5, 10 and 15 mg/l (as NaCl) were used to generate standard curves. Concentrations of unknowns were calculated by linear regression on the standard concentrations.

Solution pH was measured with an Orion research grade Ag/AgCl glass combination electrode (Model 91-02) with an Orion model 601a digital analyzer. Readings were made after five minute equilibration between electrode and sample solution. Before use, the system was calibrated to the appropriate pH range using buffer standard solutions prepared from METREPAK pHydrion buffer capsules.

RESULTS AND DISCUSSION

Soil Analyses

The pH of the point-of-zero-charge (PZC) of a soil is defined as the pH value at which the total net charge on the surface of a solid particle is zero (Sposito (10)). This value is commonly determined by soil titration experiments performed in background electrolyte solutions at two or more ionic strengths (Sposito (10); Stumm and Morgan (12)). When the net surface charge is zero, the activity of sorbed species is unaffected by ionic strength. Therefore, plots of proton or hydroxide surface densities versus pH intersect at the PZC. Figure I.1 shows the results for the soil used in this study. For each titration shown, some ions were dissolved from the soil into solution. However, no effort was made to quantify their contribution to the total ionic strength.

The determined PZC at pH 3.8 indicates that for a large pH range (pH>3.8) the soil contains more negative charges than positive charges and should electrostatically favor cation adsorption over anion adsorption. This could influence adsorption for anionic Cr(VI) as well as for cationic Cr(III). With a determined soil organic matter content of 4.4% and a relatively low soil pH, some Cr(VI) reduction to Cr(III) is likely to occur (Bartlett and Kimble (2)).

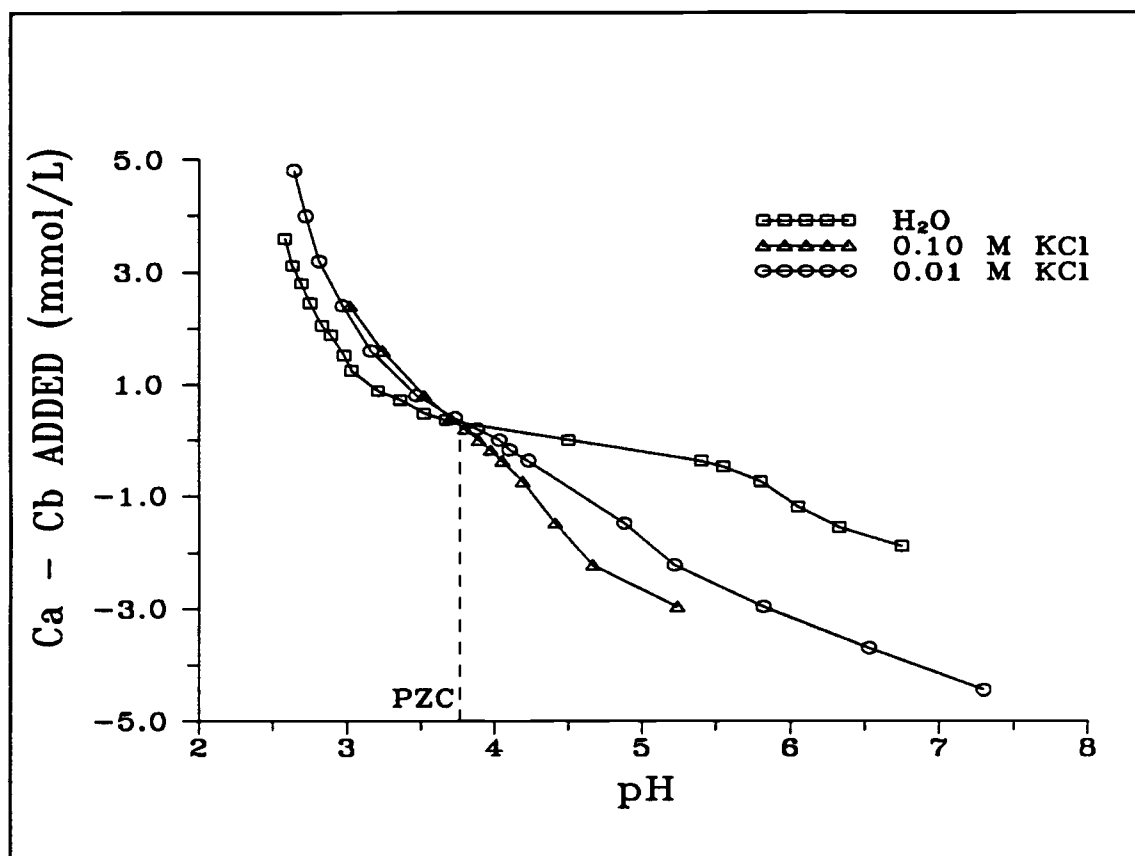


Figure I.1 Soil Point-of-Zero-Charge (PZC) determination using acid(Ca) - base(Cb) titrations in electrolytes with varying ionic strengths.

Cr(VI) Batch Reactor Experiments

A chromium(VI) adsorption batch reactor experiment was conducted to investigate the time dependence of the adsorption process for different pH values. Over the whole pH range considered, the adsorption reaction can be separated into two parts (Figure I.2). An initial, almost instantaneous uptake of chromium(VI) is followed by a much slower, kinetically controlled Cr(VI) uptake. The overall tendency is that the Cr(VI) uptake increases with decreasing pH. This agrees with the findings of Griffin et al.(9) and was explained by an increase in positive

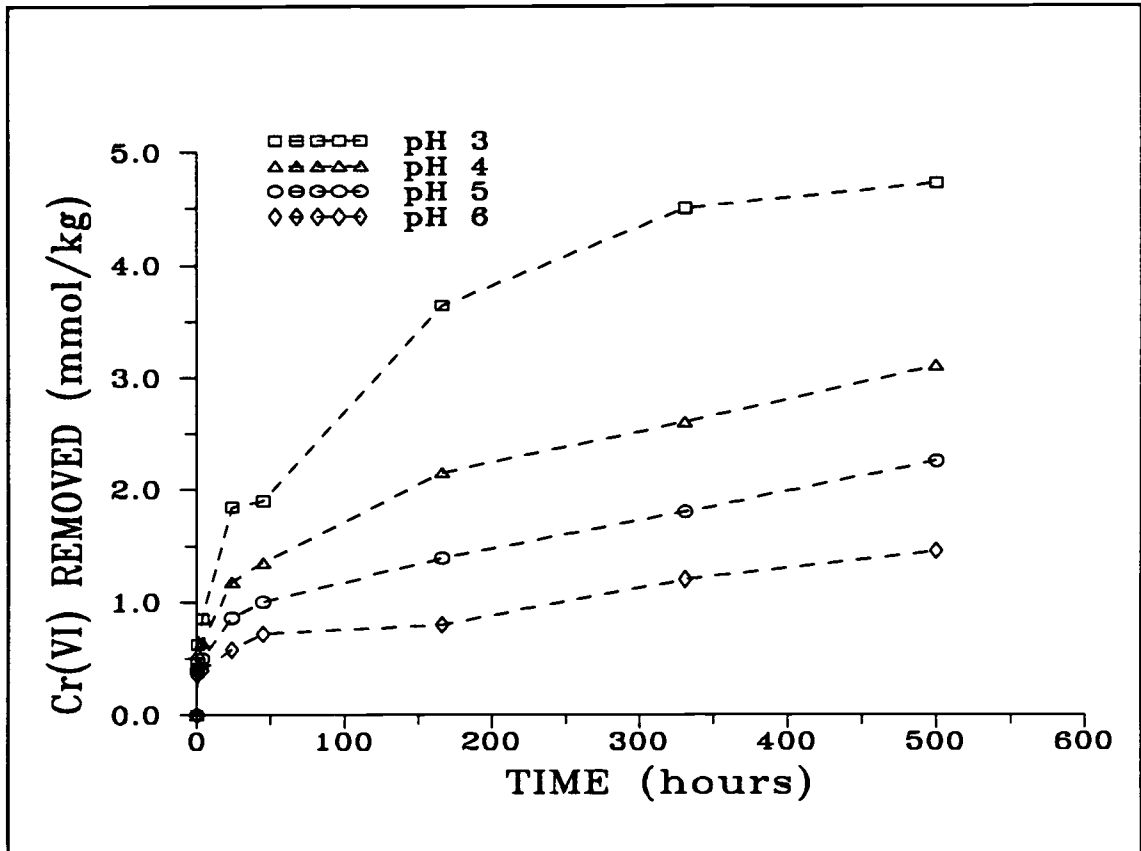


Figure I.2 Chromium(VI) removal from solution as a function of time and pH. The initial concentration for all samples was 10 mg/l (as Cr(VI)).

surface charges with decreasing pH, which results in more sorption sites that are available for anions.

After about three weeks reaction time, Cr(VI) equilibrium with the soil was still not achieved. Whether adsorption or a possible reduction of Cr(VI) to Cr(III) was responsible for this slow kinetic uptake behavior was not determined. Bartlett and Kimble (2) found Cr(VI) reduction for their experiments in the presence of soil organic matter and low pH. Both the organic matter content and pH conditions in the present study were such that a reduction reaction was likely to occur. Bloomfield and Pruden (4) showed the strong pH and time dependence

of the reduction process. Their graphical results looked quite similar to Figure I.2. Since the solid phase concentrations for Figure I.2 were calculated from the measured liquid phase concentrations, Cr(VI) uptake due to true adsorption could not be distinguished from the removal due to chromium(VI) reduction to Cr(III) and its subsequent removal.

A similarly strong kinetic behavior is shown in Figure I.3, where Cr(VI) removal is plotted as a function of time and different concentrations. The increased Cr(VI) removal for higher liquid phase concentrations could be explained by increased chromium(VI) reduction to Cr(III). Like in the experiment described

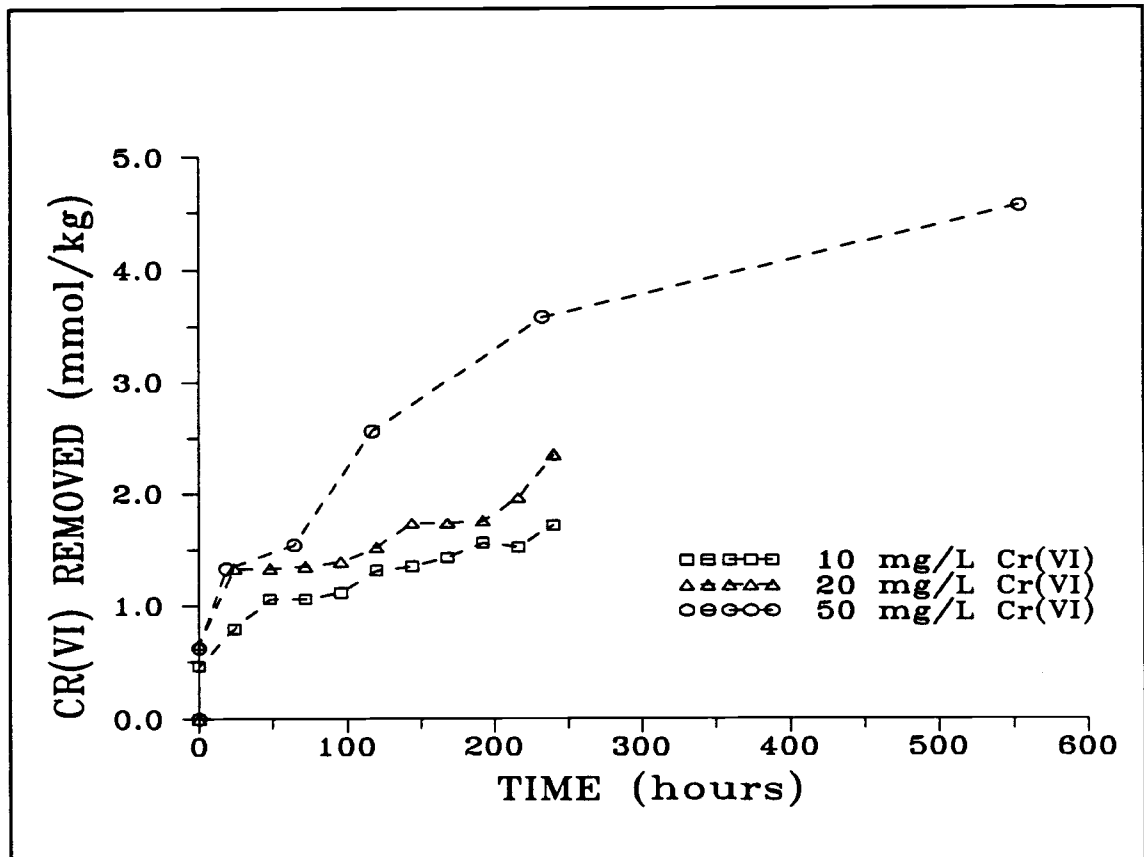


Figure I.3 Chromium(VI) removal from solution as a function of time and concentration at pH 4.5-4.8.

above, it could not be distinguished between Cr(VI) removal due to adsorption and Cr(VI) removal due to reduction.

To further investigate anion sorption kinetics on the test soil, a similar adsorption study for phosphate was conducted using the same soil as in the Cr(VI) experiments. Phosphate was selected because of its similar tetragonal shape to Cr(VI) and its direct competition with chromium(VI) for specific sorption sites (Stollenwerk and Grove (11), Bartlett and Kimble (2)). Additionally, phosphate does not undergo redox reactions and thus removal of phosphate from solution due to redox reactions, which was a suspected cause for kinetically slow Cr(VI) removal, could be excluded. Results of a phosphate adsorption experiment are presented in Figure I.4.

A pH of about 4 was chosen near the original soil pH. The graph indicates a somewhat similar adsorption behavior as observed for chromium(VI). A fast initial uptake was followed by a slower, kinetically controlled uptake. The phosphate removal process, however, in contrast to the Cr(VI) experiments, seemed to be closer to equilibrium after two weeks of reaction time. Under this assumption, about 56% of the phosphate removal occurred fast (within 4 hours), whereas 44% of the removal was kinetically controlled.

To verify that the observed phosphate removal was actually caused by adsorption and to exclude phosphate removal possibly caused by precipitation or complexation, a second set of phosphate batch experiments was conducted using a much lower initial phosphate concentration (0.001 M). For these experiments two sets of soil samples were prepared, one the originally prepared soil described in

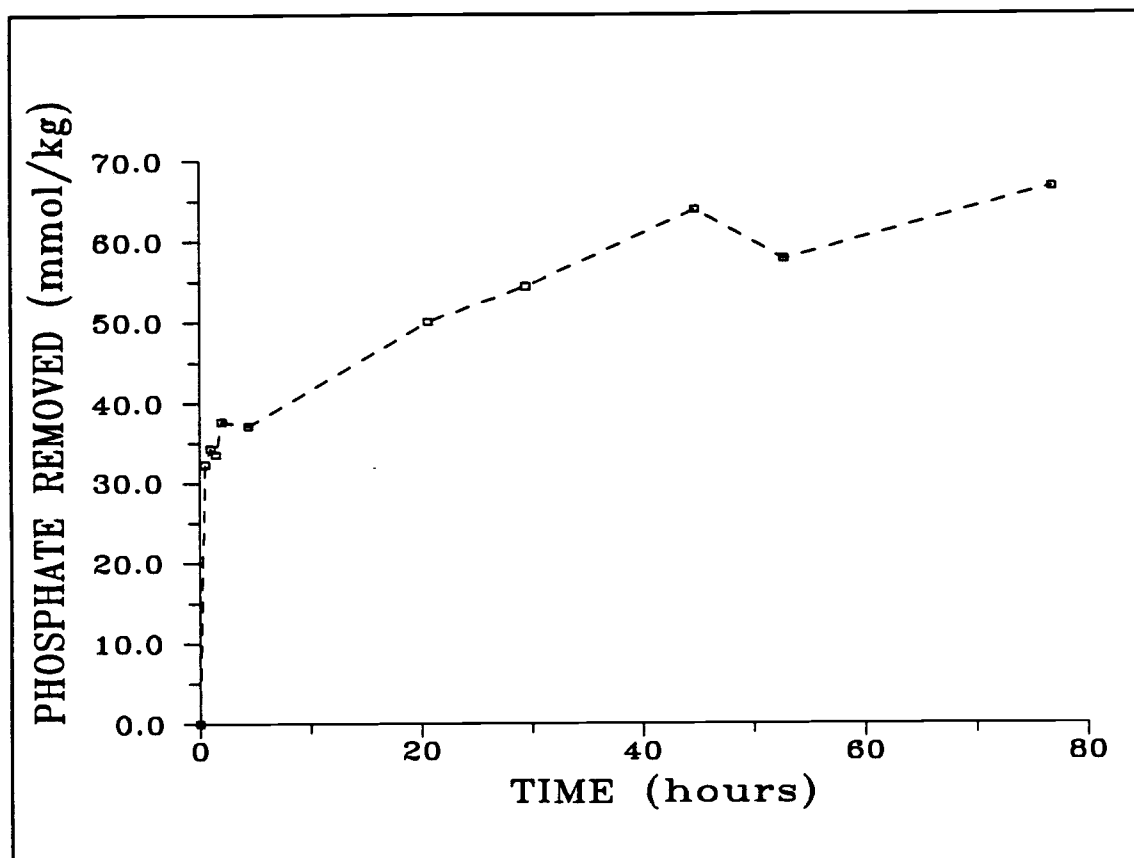


Figure I.4 Phosphate adsorption as a function of time. The initial phosphate concentration was 0.02 M and the pH range was 3.8-4.2.

the Materials section and a second for which the soil was additionally ground in a crucible for 15 minutes to create smaller soil particles. This latter experiment should indicate whether the kinetic behavior of the adsorption reaction was related to chemically controlled or physically controlled reaction kinetics.

A similar pattern of phosphate removal for the experiment utilizing the original soil (0.001 M phosphate) as for the 0.02 M phosphate solution experiment was observed (Figure I.5). The fraction of initial rapid uptake to total uptake was the same for both experiments (0.56). This indicates that no significant precipitation or complexation reactions occurred, since the fractions of initial rapid

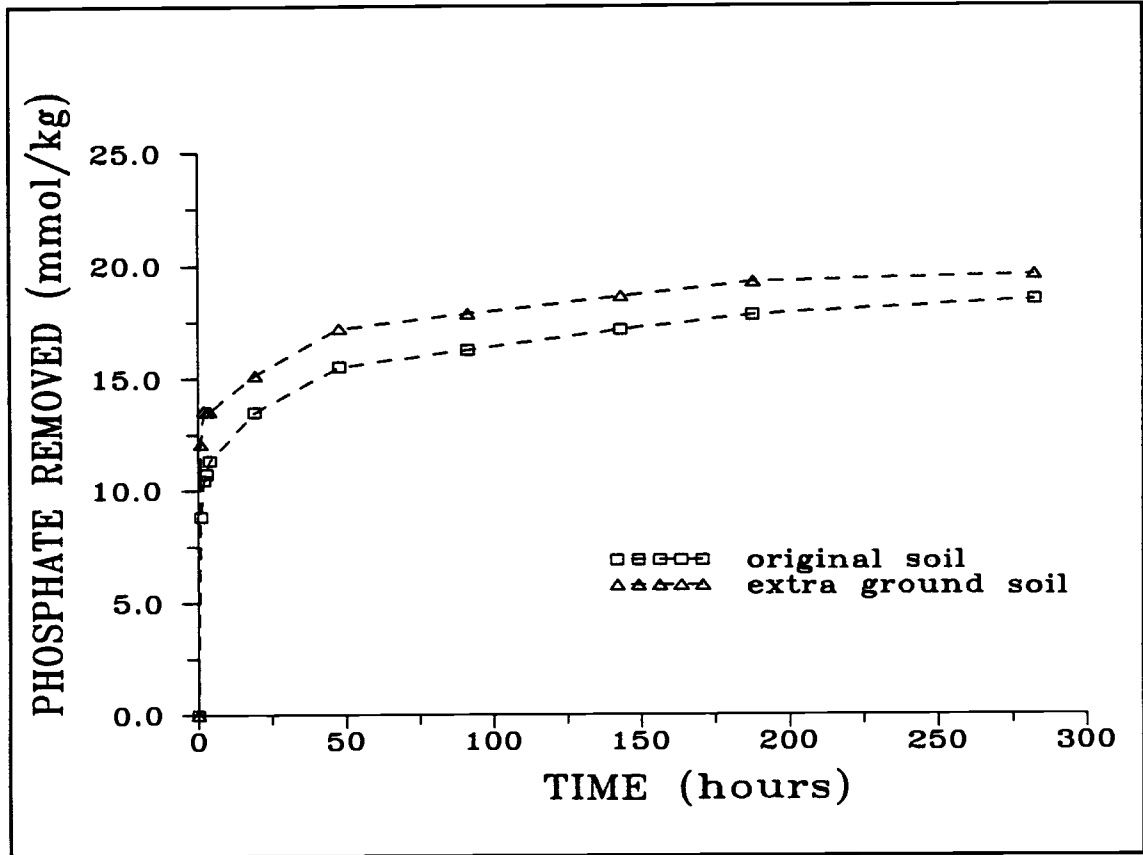


Figure I.5 Phosphate adsorption experiment conducted at pH 4 using a 0.001 M initial concentration. The experiment was performed for two different particle sizes.

uptake and kinetically controlled slow uptake would not remain constant for both experiments. It was concluded that the kinetic behavior in these phosphate experiments was due to adsorption.

This kinetic adsorption behavior could be caused by either a chemical or physical non-equilibrium process (Enfield and Shew (7), Enfield et al. (8)).

From Figure I.5 it can be seen that the fraction of initial uptake increased (0.66) as the soil particle size was decreased. The kinetically controlled phase stayed essentially the same. If the kinetic adsorption behavior was caused by a chemical non-equilibrium, e.g. two different kinds of sorption sites, both parts of the

adsorption curve should have increased due to the larger surface area achieved by creating a smaller particle size. It was therefore concluded, that a physical process, likely intraparticle diffusion, was the major cause of the slow kinetic adsorption behavior.

Attempts to measure a chromium(VI) isotherm at true equilibrium failed, since even after 500 hours of reaction time equilibrium was not achieved (Fig. I.2 and Fig. I.3). It was concluded that besides adsorption, chromium(VI) reduction occurred and was the major cause of this non-equilibrium phenomenon. Since the two Cr(VI) removal phenomena could not be differentiated analytically, a Cr(VI) one-hour, non-equilibrium "isotherm" experiment was conducted (Figure I.6). For this experiment it was assumed that adsorption was the major chromium(VI) removal process, since the reduction reaction is a slower, time dependent process. Fitting the data to a Langmuir equation, adsorption maxima and Langmuir coefficients were determined for different pH values (Table I.2). The determined maximum adsorption capacities are most likely underestimated, since the slow kinetically controlled adsorption phase was neglected in the experiment. Using the phosphate batch experiments as a rough estimate, the maximum adsorption capacities for a true equilibrium isotherm for chromium(VI) can be expected to be almost twice the values determined in the one-hour experiments. This estimate would lead to adsorption capacities close to those determined by Griffin et al. (9) for montmorillonite clay.

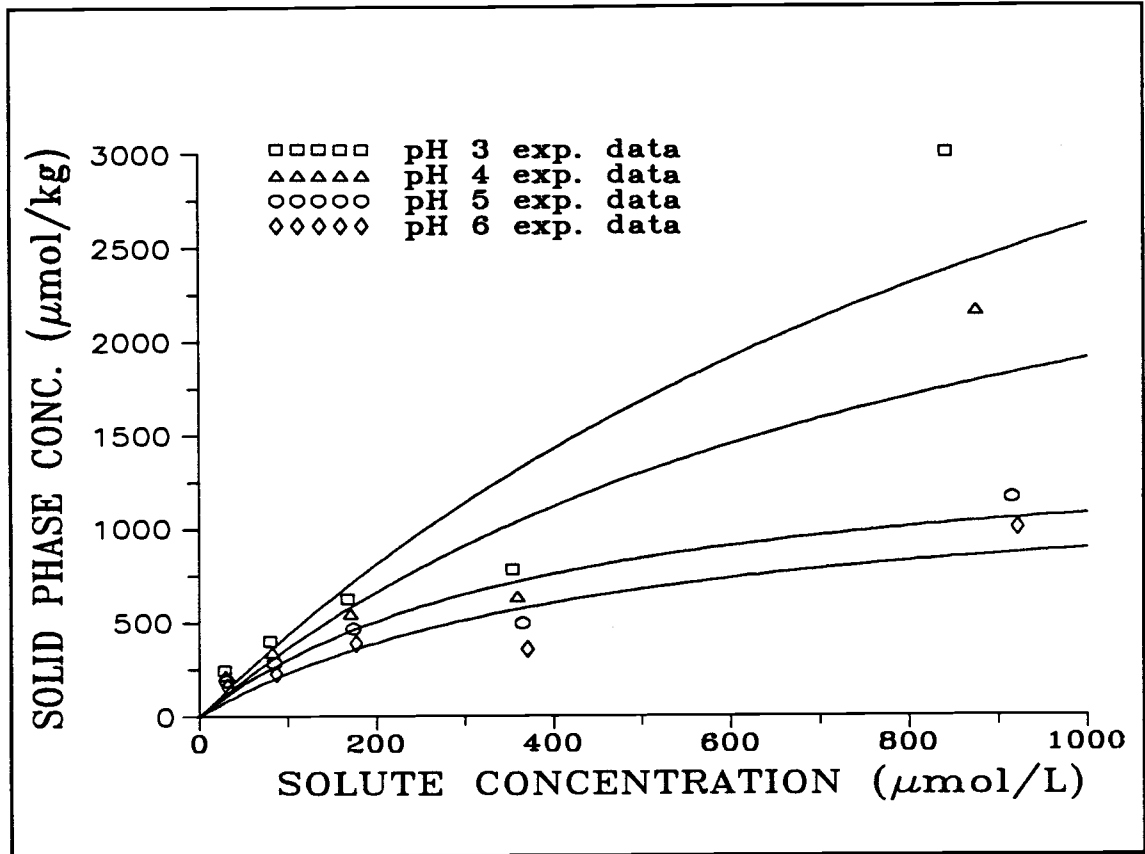


Figure I.6 Chromium(VI) one-hour isotherm. The solid lines represent the fitted Langmuir equations varying pH.

Table I.2 Cr(VI) one-hour Langmuir isotherm results for varying pH.

pH	3	4	5	6	7	8
Q_M (mmol/g)	5.94	3.58	1.49	1.30	1.17	0.84
b (L/mmol)	0.79	1.13	2.57	2.17	1.54	0.93
Q_M	=	maximum adsorption capacity				
b	=	Langmuir adsorption constant				

Soil Column Experiments

Soil column experiments were performed for Cr(VI) and Cl⁻. Figure I.7 presents the breakthrough and desorption curves for experiments no. 1, 2 and 4 (Table I.1). The time difference for breakthrough between the chromium(VI) and the Cl⁻ tracer experiments indicates the strong adsorption tendency exhibited by chromium(VI). The breakthrough for experiment no. 2 occurred earlier than the breakthrough for experiment no. 1, accompanied by steeper slopes of the breakthrough curve. These effects can be attributed to the higher initial

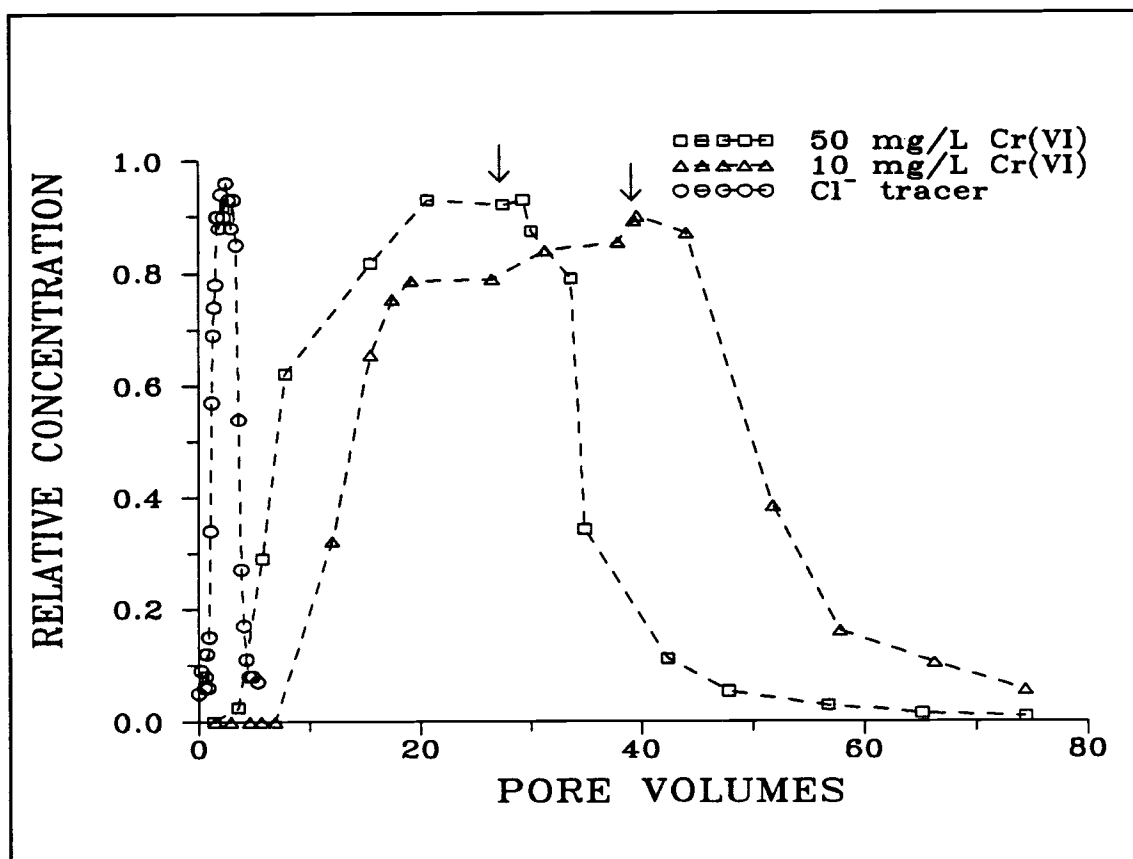


Figure I.7 Soil column breakthrough experiments. The Cr(VI) experiments were performed at pH 3.8-4.2. The desorption was conducted using distilled water. The arrows indicate the beginning of the desorption phases.

chromium(VI) concentration in experiment no. 2. Available sorption sites are more rapidly occupied, thus creating a higher mobility for the Cr(VI) remaining in solution. Noticeable in Figure I.7 is the asymmetry of the chromium(VI) breakthrough curves. The desorption limbs appear to be delayed. This can be attributed to non-equilibrium conditions during the experiment and is referred to as tailing. Similar breakthrough curves for Cr(VI) in alluvium were presented by Stollenwerk and Grove (11).

The breakthrough and desorption curve for experiment no. 3 is presented in Figure I.8. In this experiment, a 0.02 M H_2PO_4^- solution (at pH 4) was used

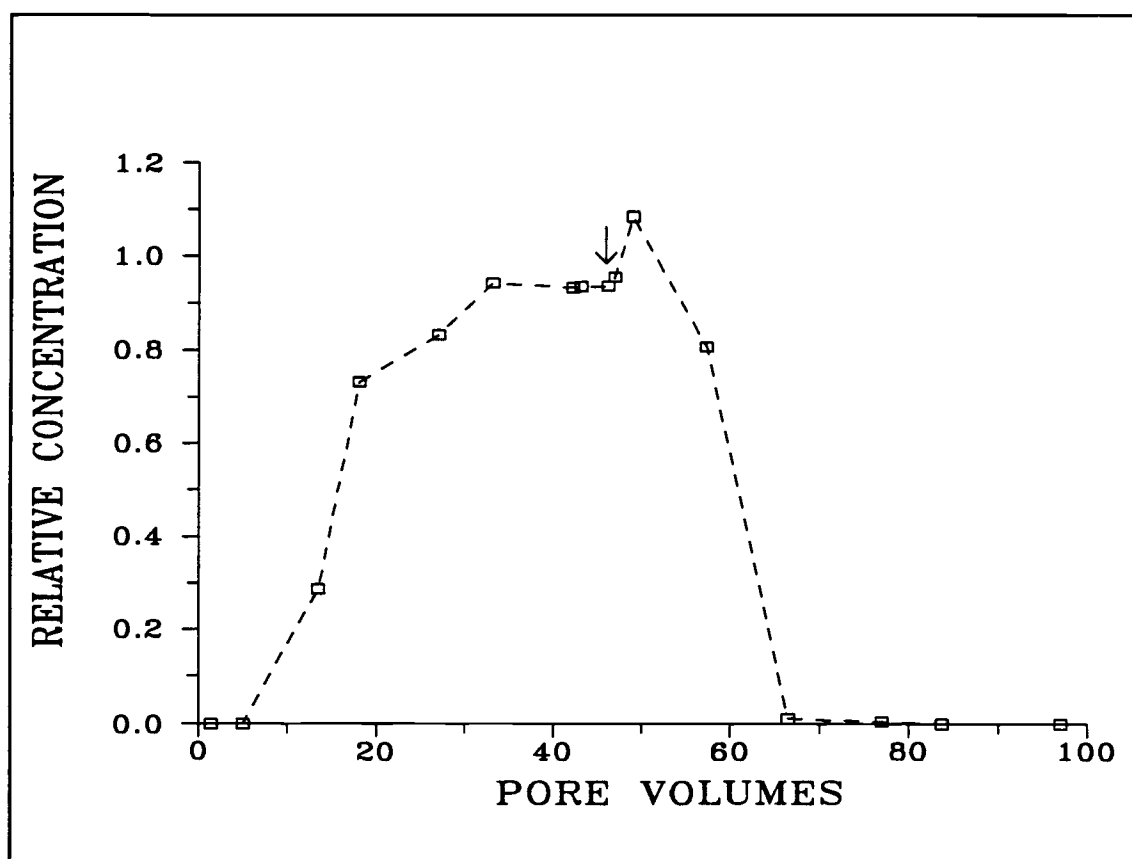


Figure I.8 Cr(VI) soil column experiment using a 0.02 M H_2PO_4^- solution as the extractant. The experiment was conducted at pH 3.8 - 4.2. The arrow indicates the beginning of the desorption phase.

for the chromium(VI) desorption phase instead of distilled water. The phosphate addition caused a Cr(VI) spike in the effluent, exceeding the initial influent Cr(VI) concentration. This spike was followed by a steep decline of Cr(VI) concentration to almost zero. No curve tailing was observed.

Phosphate, as observed in previous studies (Bartlett and Kimble (2), Stollenwerk and Grove (11)), showed a strong tendency to compete with Cr(VI) for adsorption sites. This competition caused Cr(VI) to be desorbed from the soil much more rapidly than observed for the distilled water desorption. The 0.02 M phosphate solution (Experiment no. 3) reduced the chromium(VI) concentration in the effluent to near zero in about 100 pore volumes less than for distilled water (Experiments no. 1 and 2, Table I.3). A mass balance performed on Cr(VI) for these soil column experiments (Table I.3) showed that only slightly more Cr(VI) could be recovered using the phosphate extraction method compared to the distilled water extraction. The amount of Cr(VI) residual in the soil was fairly constant. Relating these column results to the results of the Cr(VI) batch experiments, it seems likely that the unrecoverable amount of chromium(VI) is due to Cr(VI)

Table I.3 Cr(VI) extraction experiments - Mass balances.

Experiment no.	Pore volumes for extraction	Cr(VI) added (mol)	Cr(VI) recovered (mol)	Cr(VI) residual (mol)
1	155.8	$1.40 \cdot 10^{-4}$	$1.20 \cdot 10^{-4}$	$2.00 \cdot 10^{-5}$
2	158.3	$4.89 \cdot 10^{-4}$	$4.77 \cdot 10^{-4}$	$1.20 \cdot 10^{-5}$
3	50.8	$1.64 \cdot 10^{-4}$	$1.50 \cdot 10^{-4}$	$1.36 \cdot 10^{-5}$

reduction and is actually present in the soil as Cr(III). The phosphate extraction solution is ineffective for this fraction since Cr(III) at the experimental pH of 4 would be present (and adsorbed onto the soil) in the cationic form. The unrecoverable amount of Cr(VI) could also be due to very tight specific adsorption of Cr(VI). In this case, however, the addition of phosphate should have led to a more significant decrease in the amount of unrecoverable Cr(VI).

SUMMARY AND CONCLUSIONS

The behavior of Cr(VI) in a natural soil was studied utilizing batch reactor as well as soil column experiments.

Batch experiments were performed to investigate the effects of pH and initial concentration on chromium(VI) removal as a function of time. Difficulties were encountered distinguishing true adsorption from Cr(VI) reduction to Cr(III) and subsequent removal. For this reason, phosphate batch experiments were conducted under the assumption that phosphate exhibits an adsorption behavior comparable to that of Cr(VI). The similar shape of phosphate adsorption observed in previous studies and its competitive sorption effect on Cr(VI) seemed to justify such an assumption.

Soil column experiments were performed for Cr(VI) to more closely simulate field conditions of continuous hydraulic flow through a stationary porous medium. Breakthrough curves were determined for different influent concentrations of Cr(VI) using distilled water as the extracting agent. A chloride tracer breakthrough curve was determined and compared to the Cr(VI) breakthrough results. To investigate the effectiveness of phosphate on Cr(VI) removal from contaminated soil, another Cr(VI) soil column experiment was conducted in which a phosphate solution was used as the extraction agent.

From this study it was concluded that:

1. Cr(VI) removal in natural soil suspensions is most likely due to true adsorption as well as Cr(VI) reduction to Cr(III) and subsequent removal.
2. Cr(VI) removal increases strongly with decreasing pH and increasing initial Cr(VI) concentration.
3. The adsorption process for Cr(VI) likely consists of an initial fast uptake followed by a slower, more time dependent removal. Investigations indicated that this behavior can be attributed to a physical non-equilibrium process.
4. Phosphate strongly improved the Cr(VI) removal effectiveness by increasing the Cr(VI) desorption rate significantly, although it was not able to recover significantly more Cr(VI) from a contaminated soil during a soil column experiment.

REFERENCES

1. Bartlett, R. J., and Kimble, J. M., "Behavior of Chromium in Soils: I. Trivalent Forms," Journal of Environmental Quality, Vol. 5, No. 4, 1976, pp. 379-383.
2. Bartlett, R. J., and Kimble, J. M., "Behavior of Chromium in Soils: II. Hexavalent Forms," Journal of Environmental Quality, Vol. 5, No. 4, 1976, pp. 383-386.
3. Bartlett, R., and James, B., "Behavior of Chromium in Soils: III. Oxidation," Journal of Environmental Quality, Vol. 8, No. 1, 1979, pp. 31-35.
4. Bloomfield, C., and Pruden, G., "The Behaviour Of Cr(VI) In Soil Under Aerobic And Anaerobic Conditions," Environmental Pollution Series A, Vol. 23, 1980, pp. 103-114.
5. Davis, J. A., and Leckie, J. O., "Surface Ionization and Complexation at the Oxide/Water Interface 3. Adsorption of Anions," Journal of Colloid and Interface Science, Vol. 74, No. 1, March 1980, pp. 32-43.
6. Ecology and Environment, Inc., "Final Remedial Investigation Report,

Volume 2 of 2, United Chrome Products Site, Corvallis, Oregon,"
106.OL32.0, U.S. Environmental Protection Agency under Contract No.
68-01-6692, July 1985.

7. Enfield, C. G., and Shew, D. C., "Comparison of Two Predictive Nonequilibrium One-Dimensional Models for Phosphorus Sorption and Movement through Homogeneous Soils," Journal of Environmental Quality, Vol. 4, No. 2, 1975, pp. 198-202.
8. Enfield, C. G., Harlin, C. C., Jr., and Bledsoe, B. E., "Comparison of Five Kinetic Models for Orthophosphate Reactions in Mineral Soils," Journal of the Soil Science Society of America, Vol. 40, 1976, pp. 243-249.
9. Griffin, R. A., Au, A. K., and Frost, R. R., "Effect Of pH On Adsorption Of Chromium From Landfill-Leachate By Clay Minerals," Journal of Environmental Science and Health, A12(8), 1977, pp. 431-449.
10. Sposito, G., The Surface Chemistry of Soils, Oxford Press, New York, 1984.
11. Stollenwerk, K. G., and Grove, D. B., "Adsorption and Desorption of Hexavalent Chromium in an Alluvial Aquifer Near Telluride, Colorado,"

Journal of Environmental Quality, Vol. 14, No. 1, 1985, pp. 150-155.

12. Stumm, W., and Morgan, J. J., Aquatic Chemistry: An Introduction Emphasizing Equilibria in Natural Waters, 2nd Ed., Wiley-Interscience, New York, 1981.

13. Zachara, J. M., Girvin, D. C., Schmidt, R. L., and Resch, C. T., "Chromate Adsorption on Amorphous Iron Oxyhydroxide in the Presence of Major Groundwater Ions," Environmental Science and Technology, Vol. 21, No. 6, 1987, pp. 589-594.

CHAPTER II:
A Kinetic Solute Transport Model For
The Movement Of Chromium(VI) Through Soils

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ABSTRACT

To increase the performance of cleanup methods for chromium contaminated soils, the fate and transport of chromium through soils have to be investigated and better understood. The objective of this work was to develop and verify a solute transport model to predict chromium(VI) movement through soil columns. Of particular interest was the behavior of chromium(VI) in the presence of phosphate, another adsorbing anion. The model was developed under the assumption of one-dimensional, steady-state saturated groundwater flow through a homogeneous porous medium. Sorption of chromium(VI) and phosphate are described with a physical non-equilibrium model (mobile and immobile water phases) and a competitive Langmuir isotherm. Numerical solutions of the transport

equations were obtained by the partially implicit finite difference method. Computer simulations were fitted to experimental breakthrough curves using estimates for model parameters which could not be determined independently in experiments. Chromium(VI) breakthrough experiments were successfully modeled for varying chromium concentrations as well as for the case of phosphate competition. This study demonstrated that the use of phosphate as a desorption agent is a possible way of increasing chromium(VI) desorption rates and, consequently, the effectiveness of chromium removal from contaminated soils.

Additional Word Index : chromium, solute transport, physical non-equilibrium, adsorption, competitive Langmuir equation.

INTRODUCTION

Groundwater is an important freshwater resource. Over the last decade, more and more cases of groundwater contamination by heavy metals, in particular chromium, have been discovered. Such contaminations pose a severe threat to human health as well as to the environment. To predict the movement of chromium through soils and aquifer systems, its transport mechanisms and particularly its interactions with the soil matrix have to be investigated and better understood. The objective of this work was to develop a solute transport model to describe the movement of chromium through laboratory soil columns, and to verify the model using experimentally determined breakthrough curves (BTC's). Of specific interest was the modeling of chromium(VI) solute transport in the presence of phosphate. Experimental results of an ongoing feasibility study on chromium extraction from a contaminated aquifer indicated that a higher Cr(VI) removal efficiency is possible if phosphate is added to the leaching water (Nelson (19)).

A variety of solute transport models for both organic and inorganic species have been proposed. Most of these models incorporate the same dispersion-advection transport processes. They differ, however, in the way that sorption / desorption reactions are modeled. A review of sorption models for reactive solutes in soil was given by Travis and Etnier (24). Both equilibrium and first-order kinetic models were discussed. Equilibrium models were originally developed to describe sorption isotherms for gases and organic solutes. Bar-Yosef

(14) derived a sorption model based on a competitive Langmuir isotherm for ionic species and applied it successfully to pH dependent zinc adsorption by soils. This model did not include the effect of the electric potential (Ψ) and the electrolyte concentration on adsorption. Bar-Yosef believed that the effect of Ψ was to some extent accounted for by the binding constants of the different ions. A transport model based on ion exchange was presented by Valocchi et al. (25). Sorption processes for ionic species were modeled employing the well known principle of ion exchange selectivity. Although successful for the cases considered, the authors realized that the ion selectivity coefficients are typically not constant but instead are a function of the sorbed phase concentration. These coefficients are also highly variable in natural soil systems, thus hard to estimate. Cederberg et al. (15) presented a solute transport model that incorporated ion exchange and surface complexation coupled with a chemical equilibrium model. Good agreement was found between predicted and measured concentrations of cadmium, chloride and bromide in laboratory soil columns.

For many transport problems, the assumption of equilibrium sorption is not valid (Van Genuchten (29)). Two classes of non-equilibrium models have been developed: chemical non-equilibrium and physical non-equilibrium. Derivations of these models are in Van Genuchten and Cleary (28) and Van Genuchten (29).

The chemical non-equilibrium model assumes that there are two types of sorption sites. For one type of site the sorption reaction is assumed to be a slow, kinetically controlled process. For the other type of site sorption is assumed to be

a kinetically faster or even an instantaneous equilibrium process. Such a two - site model was recently used by Selim and Amacher (23) to model chromium(VI) transport through three different soils. Kinetic Langmuir equations were used to describe the sorption reactions. This approach was partially successful in describing data from miscible displacement experiments. Grove and Stollenwerk (17) modeled chromium(VI) movement through alluvial materials coated with iron-oxide and hydroxide. They used a one-site chemical non-equilibrium model based on a kinetic Langmuir equation. This model agreed better with experimental data than when sorption was assumed to be at equilibrium.

Physical non-equilibrium models usually divide the total water content of a soil into a mobile and an immobile region and assume that the kinetic sorption behavior is caused by a physical mechanism, typically a diffusional process across the immobile water layer to the solid surface. Wu and Gschwend (30) recently presented evidence that the sorption kinetics of hydrophobic organic compounds on natural sediments are controlled by such an intraparticle diffusion.

These two major groups of non-equilibrium solute transport models were compared by Nkedi-Kizza et al. (20). When a linear sorption reaction was used, the analytical solutions for the two models are equivalent. These authors concluded that the difference between the two models is of little practical importance and suggest that the occurrence of specific processes can only be verified with microscopic measurements.

THEORY

Model Development

Based on the results of batch experiments (Schroth et al. (22)) it was believed that the kinetic sorption behavior of chromium(VI) is controlled by an intraparticle diffusional process. Therefore a physical non-equilibrium solute transport model was developed under the assumption of one-dimensional, steady-state saturated groundwater flow through homogeneous porous media. A derivation of a similar model is in Van Genuchten (29).

The model assumes that the total water content of the soil is divided into a mobile phase and an immobile phase, so that

$$\Theta = \Theta_m + \Theta_{im} \quad (1)$$

where Θ = total volumetric water content (cm^3/cm^3)

Θ_m = volumetric water content of the mobile phase (cm^3/cm^3)

Θ_{im} = volumetric water content of the immobile phase (cm^3/cm^3)

where the subscripts "m" and "im" identify the mobile and immobile phases, respectively. Conceptually, the mobile pore water content is understood to include the water in the pore space between soil particles, whereas the immobile water

content includes the water in the pore space within particles.

Solute transport due to advection and dispersion is limited to the mobile water phase. The following dispersive-advective transport equation is well documented in the literature (Van Genuchten and Wierenga (27), De Smedt and Wierenga (16), Rubin (21)) and has found wide application :

$$\frac{\partial c_m}{\partial t} = D \frac{\partial^2 c_m}{\partial x^2} - v \frac{\partial c_m}{\partial x} \quad (2)$$

where c_m = solute liquid phase concentration (mg/l)

t = time (h)

D = dispersion coefficient (cm²/h)

x = distance (cm)

v = average pore water velocity (cm/h)

The solute is transferred between the mobile and immobile water phases by an intraparticle diffusional process. In the mobile water phase this process is assumed to be controlled by the first-order expression :

$$\frac{\partial c_m}{\partial t} = - \frac{\alpha}{\Theta_m} (c_m - c_{im}) \quad (3)$$

and in the immobile water phase by :

$$\frac{\partial c_{im}}{\partial t} = \frac{\alpha}{\Theta_m} (c_m - c_{im}) \quad (4)$$

where α = rate coefficient for diffusion across the immobile water layer (h^{-1})

The rate coefficient is assumed to be the same for all solutes, thus neglecting the effect of molecular radius of solute species on the diffusional process.

Sorption occurs in both the mobile and immobile water phases. It is assumed that a certain mass fraction of the soil, f , is accessible in the mobile water phase and a fraction, $(1-f)$, is accessible in the immobile phase, so that

$$S = fS_m + (1-f)S_{im} \quad (5)$$

where S = total adsorbed concentration (mg solute/g soil)

S_m = adsorbed concentration for solid fraction which is in contact with mobile water phase (mg solute/g soil)

S_{im} = adsorbed concentration for solid fraction which is in contact with immobile water phase (mg solute/g soil)

The sorption reaction for both phases is assumed to be at equilibrium. This is referred to as the local equilibrium assumption (Jennings and Kirkner (18), Valocchi (26)). The change of solute concentration due to sorption is

$$\frac{\partial c_m}{\partial t} = -f \frac{\rho}{\Theta_m} \frac{\partial S_m}{\partial t} \quad (6)$$

in the mobile phase and

$$\frac{\partial c_{im}}{\partial t} = - (1-f) \frac{\rho}{\Theta_{im}} \frac{\partial S_{im}}{\partial t} \quad (7)$$

in the immobile phase,

where ρ = bulk density of soil (g soil/cm³)

The governing partial differential equation for the mobile phase can be obtained by combining Eq.(2), Eq.(3) and Eq.(6):

$$\frac{\partial c_m}{\partial t} = D \frac{\partial^2 c_m}{\partial x^2} - v \frac{\partial c_m}{\partial x} - f \frac{\rho}{\Theta_m} \frac{\partial S_m}{\partial t} - \frac{\alpha}{\Theta_m} (c_m - c_{im}) \quad (8)$$

and for the immobile water phase by combining Eq.(4) and Eq.(7):

$$\frac{\partial c_{im}}{\partial t} = - (1-f) \frac{\rho}{\Theta_{im}} \frac{\partial S_{im}}{\partial t} + \frac{\alpha}{\Theta_{im}} (c_m - c_{im}) \quad (9)$$

To solve Eq.(8) and Eq.(9), a sorption relationship has to be specified. For this solute transport model a competitive Langmuir equation, as presented by Bar-Yosef (14), was chosen to represent the sorption reaction. This type of equation, unlike the frequently chosen linear isotherm, allows for competition between different solutes for the available sorption sites. When applied to the mobile-immobile water phase model, the sorption equations become :

$$S_m(i) = \frac{Q_M b(i) c_m(i)^{1/z(i)}}{1 + \sum b(i) c_m(i)^{1/z(i)}} \quad (10)$$

and

$$S_{im(i)} = \frac{Q_M b(i) c_{im(i)}^{1/z(i)}}{1 + \sum b(i) c_{im(i)}^{1/z(i)}} \quad (11)$$

where Q_M = maximum adsorption capacity (μg solute/g soil)

b = Langmuir adsorption constant (l/mg)^z

z = valence of a species

i = solute species

The complete system is now defined by a set of four equations (8, 9, 10, 11) for each solute species considered.

Numerical Solution

Equations (8), (9), (10) and (11) form a system of coupled non-linear equations for each solute species. It is impossible to obtain exact analytical solutions for such a system (Van Genuchten and Cleary (28)). Therefore numerical methods have to be used.

A numerical solution approximation was developed using a partially implicit finite difference method, where the soil column is imagined to be divided into a certain number of adjacent cells. For each of these cells, dispersion,

advection and diffusional mass transfer between the mobile and immobile water phase is first computed explicitly, using equilibrium solution concentrations computed in the previous time step. Then the sorption reaction is accounted for by equilibrating the resulting solution concentrations with the solid phase using the Newton-Raphson method.

The finite difference approximation for the mobile water phase is given by:

$$\begin{aligned}
 c(i,n)_m^{t+\Delta t} = & c(i,n)_m^t + \frac{D\Delta t}{\Delta x^2} [c(i,n-1)_m^t - 2c(i,n)_m^t + c(i,n+1)_m^t] \\
 & + \frac{v\Delta t}{\Delta x} [c(i,n-1)_m^t - c(i,n)_m^t] - \frac{f\rho}{\Theta_m} [S(i,n)_m^{t+\Delta t} - S(i,n)_m^t] \\
 & - \frac{\alpha\Delta t}{\Theta_m} [c(i,n)_m^t - c(i,n)_{im}^t]
 \end{aligned} \tag{12}$$

and for the immobile water phase by:

$$\begin{aligned}
 c(i,n)_{im}^{t+\Delta t} = & c(i,n)_{im}^t - (1-f)\frac{\rho}{\Theta_{im}} [S(i,n)_{im}^{t+\Delta t} - S(i,n)_{im}^t] \\
 & + \frac{\alpha\Delta t}{\Theta_{im}} [c(i,n)_m^t - c(i,n)_{im}^t]
 \end{aligned} \tag{13}$$

where n = cell number

Δx = length of one cell (cm)

t = current calculation time (h)

Δt = length of time step (h)

The initial condition for both water phases is

$$c_m(x,t=0) = c_{im}(x,t=0) = c_i \quad (14)$$

where c_i = initial concentration inside the soil column (mg/l)

Boundary conditions apply only to equation (12), since only the mobile water phase is assumed to be in direct contact with the boundaries. A third-type, constant flux boundary condition was used to model the upper boundary:

$$\left(-D \frac{\partial c}{\partial x} + vc\right)_{x=0} = vc_0 \quad (15)$$

where c_0 = column influent concentration (mg/l)

The lower boundary was modeled using

$$\frac{\partial c}{\partial x}(L,t) = 0 \quad (16)$$

where L = column length (cm)

These boundary conditions and their influence on the solution of equations (12) and (13) were discussed by Van Genuchten and Wierenga (27) and Van Genuchten (29). These authors recommended the above described boundary conditions particularly for the size of soil columns used in this study.

EXPERIMENTAL APPROACH

Continuous flow soil column experiments and batch reactor experiments were performed using soil samples taken from an area close to a chromium contamination site to assure that the uncontaminated soil was similar to the contaminated soil of the site in terms of soil classification and soil properties. Column experiments were performed for chromium(VI) to investigate its transport behavior with and without phosphate present during the desorption. To determine the dispersivity in the soil columns, a tracer breakthrough experiment was conducted using chloride (Cl⁻) as the tracer ion. The specific conditions, under which these column experiments were conducted, are listed in Table II.1. Batch experiments were conducted for both chromium(VI) and phosphate to determine sorption parameters.

Experimental procedures and analytical methods for these experiments were discussed in detail elsewhere (Schroth et al. (22)).

Table II.1 Parameters for continuous flow soil column experiments

Cl ⁻ tracer column experiment :			
Experiment No.	Influent Cl ⁻ conc. (mg/l)	Loading time (mob. pore volumes)	Extraction with
1	14.6	2.58	H ₂ O
Cr(VI) column experiments :			
Experiment No.	Influent Cr(VI) conc. (mg/l)	Loading time (mob. pore volumes)	Extraction with
2	50	28.9	H ₂ O
3	10	41.4	H ₂ O
4	10	48.5	0.02 molar H ₂ PO ₄ ⁻

RESULTS AND DISCUSSION

Tracer Breakthrough Experiment

The experimental data of experiment no. 1 were imported into a computer program presented by Van Genuchten (29) to determine the dispersivity using a non-linear, least-square analysis. The transport equation to which the data was fitted contained a linear equilibrium sorption term. Since a tracer is assumed not to adsorb onto a solid phase, the retardation factor for the program input was set to one. The program output provided a dispersion coefficient from which a dispersivity of 0.30 cm was computed. The output also provided a retardation factor of 1.18, indicating that the tracer did not behave ideally, but showed a small tendency to adsorb to the soil. Such a retardation could be caused by a non-specific ion exchange process.

The shape of the experimental chloride breakthrough curve is of particular interest to the mobile-immobile water phases model (Figure II.1). The symmetric shape of the curve indicates little kinetic behavior for Cl^- movement. According to the mobile-immobile water phase model, the Cl^- anions are assumed to undergo the diffusional process between the mobile and immobile water phases. Since Cl^- exhibited only a small sorption tendency, equilibrium between the two phases is achieved more rapidly than for anions which adsorb more strongly onto the soil. However, if the water content of the immobile phase was large compared to the

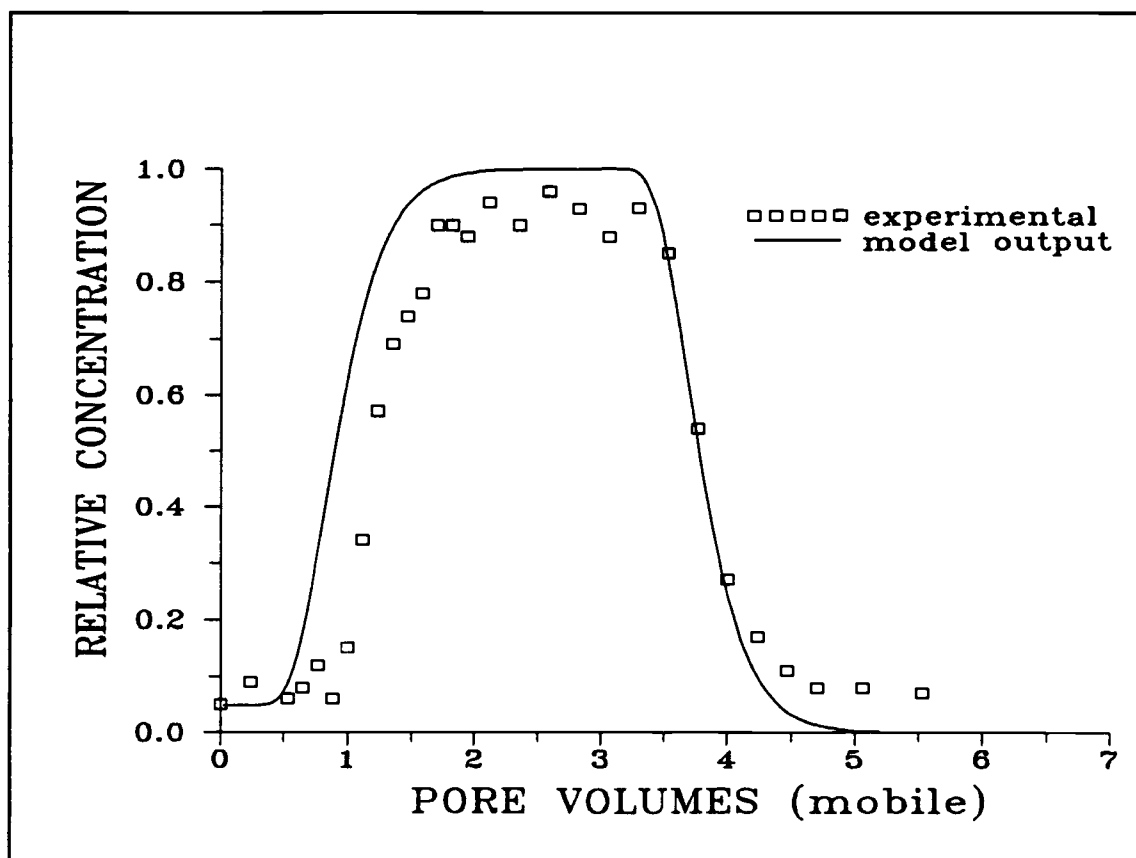


Figure II.1 Chloride tracer breakthrough curve.

water content of the mobile phase, the diffusional mass transfer into the immobile phase would require more time and therefore introduce more kinetics to the solute transport. This would create a larger asymmetry of the breakthrough curve, leading to more curve tailing. The little tailing observed therefore suggests a small water content of the immobile water phase compared to the water content of the mobile phase.

The output from the finite difference model is also shown in Figure II.1. During the computation, it was assumed that the tracer moving through the soil column would not interact with the solid phase. This caused the breakthrough to

appear earlier than experimentally observed. Experimental data and model output showed a better fit for the desorption part of the breakthrough curve. The discrepancy between observed and predicted concentration in the two parts of the breakthrough curve could be due to chemical hysteresis (Van Genuchten and Cleary (28)). Chemical hysteresis is caused by a difference between adsorption and desorption rates of a reacting solute. An experimentally observed background level of Cl^- is the cause for the deviation between model and experiment at the end of the desorption limb of the breakthrough curve. The Cl^- background level might be caused by mineral soil particles dissolving into solution during the solute transport process.

Chromium(VI) Breakthrough Curves

Chromium(VI) anions are known to adsorb strongly onto soil (Grove and Stollenwerk (17), Selim and Amacher (23)). Batch sorption experiments exhibited a strong kinetic behavior, showing fast initial Cr(VI) uptake from solution followed by a slower time dependent uptake (Schroth et al. (22)). This kinetic behavior is assumed to be controlled by a rate coefficient (α) for diffusional mass transfer across an immobile water phase. To demonstrate the effect of α on the solute transport of reactive solutes, chromate breakthrough curves were simulated for varying values of α using the numerical model. The breakthrough curve for $\alpha=0.0$ represents equilibrium conditions (Figure II.2). Although no kinetics are included,

the BTC is asymmetric. This is due to the non-linear sorption relationship used and was explained by Van Genuchten and Cleary (28). When kinetic behavior is

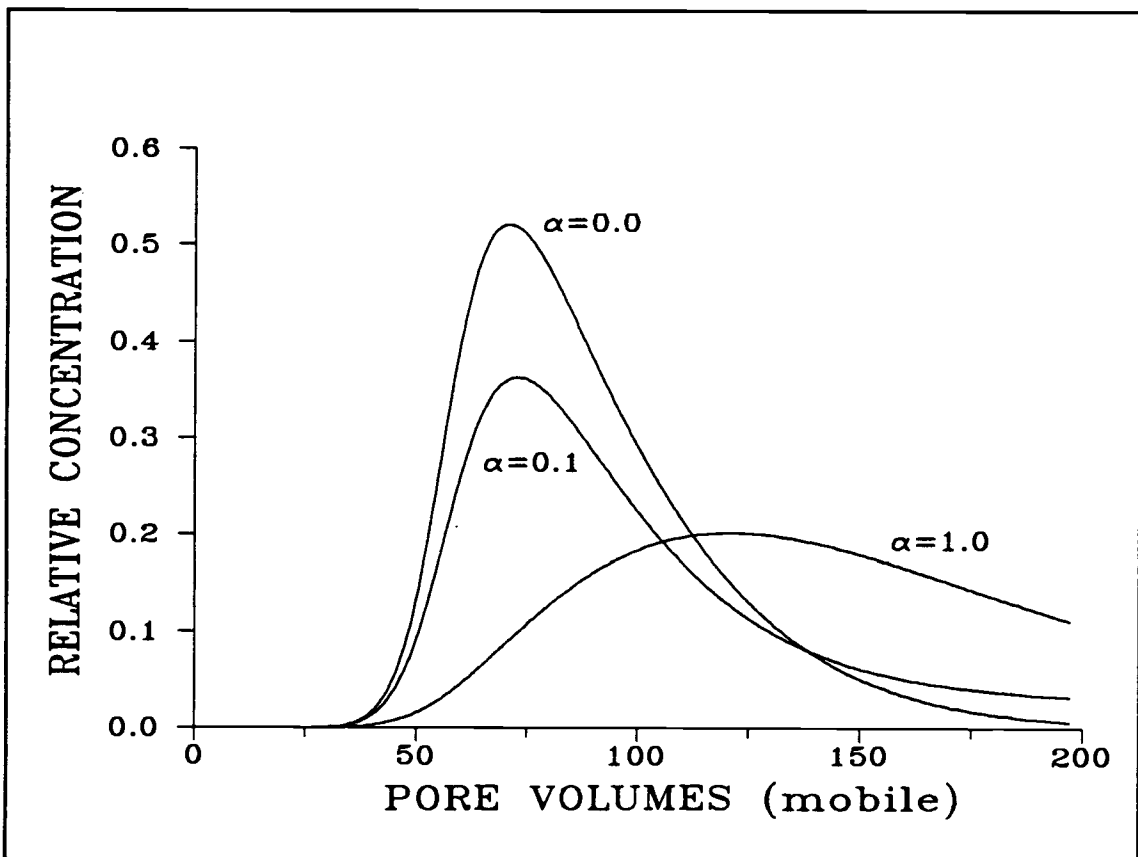


Figure II.2 Chromium(VI) breakthrough curve simulations for different values of the rate coefficient α .

included ($\alpha > 0$), the breakthrough curves show an increasingly asymmetric shape. Unfortunately, no laboratory experiment was found appropriate to measure this rate coefficient independently. In previously conducted studies, α was either estimated (Selim and Amacher (23)) or fitted (Wu and Gschwend (30), Van Genuchten (29)).

Chromium(VI) breakthrough curves were modeled using parameters previously determined in laboratory batch experiments (Schroth et al. (22)). Two chromate sorption parameters, the maximum sorption capacity and the Langmuir adsorption constant, were determined in an one-hour batch isotherm experiment. Efforts to measure these parameters using a long-term, true equilibrium isotherm failed because even after a reaction period of three weeks equilibrium could not be achieved. Therefore it had to be assumed that only a fraction of chromium was adsorbed during the one-hour experiment, and thus the maximum adsorption capacity was underestimated in this experiment. Comparable phosphate isotherm experiments showed that the maximum adsorption capacity was almost twice as high in a 14 day long-term experiment than in an one-hour experiment. For these phosphate experiments it could be assumed that sorption was the only major mechanism removing the phosphate from solution (Schroth et al. (22)).

Another important parameter for the model was the mass fraction of solids that is in contact with the mobile water phase (f). In a previous study Selim and Amacher (23) assumed this fraction to be the same as the fraction of pore water content in the mobile phase to the total water content of the soil. For this study the fraction, f , was estimated to be 0.56 using phosphate batch sorption experiments (Schroth et al. (22)). This value is smaller than the ones proposed by Selim and Amacher (23), meaning that a smaller portion of the soil is available for instantaneous equilibrium sorption. The fraction of the mobile water content to the total water content, (Θ_m/Θ), as a result of the tracer experiment, was set to 0.95, larger than the ones determined by Selim and Amacher (23).

The parameters which were determined in the laboratory experiments, in particular the sorption parameters, are conditional by nature and therefore have to be treated cautiously when applied to the solute transport model. The sorption parameters, as presented, are highly pH dependent. The solute transport model, however, does not account for a change in sorption parameters due to changing pH conditions. The model could therefore lead to errors in case of large pH changes during a soil column experiment. For all the experiments presented in this paper, pH changes were small enough to be neglected.

The parameters presented in Table II.2 were used to model a chromium(VI) breakthrough experiment previously conducted in laboratory experiment no.2 (Table II.1). Figure II.3 shows the strong sorption tendency of chromium(VI), requiring more than 20 mobile pore volumes to reach a relative effluent concentration close to 1. Also visible is the tailing of the breakthrough

Table II.2 Solute transport model parameters.

Parameter		Cr(VI) experiments	Cl ⁻ experiment
d	(cm)	0.30	0.30
ρ	(g/cm ³)	1.09	1.09
f	----	0.56	0.56
Θ_m/Θ	----	0.95	0.95
α	(hour ⁻¹)	0.20	0.20
Q_M	(μ mol/g)	5.00	0
b_{Cr}	(l/mmol)	1.13	----
b_{Ph}	(l/mmol)	1.24	----
z	----	1	1

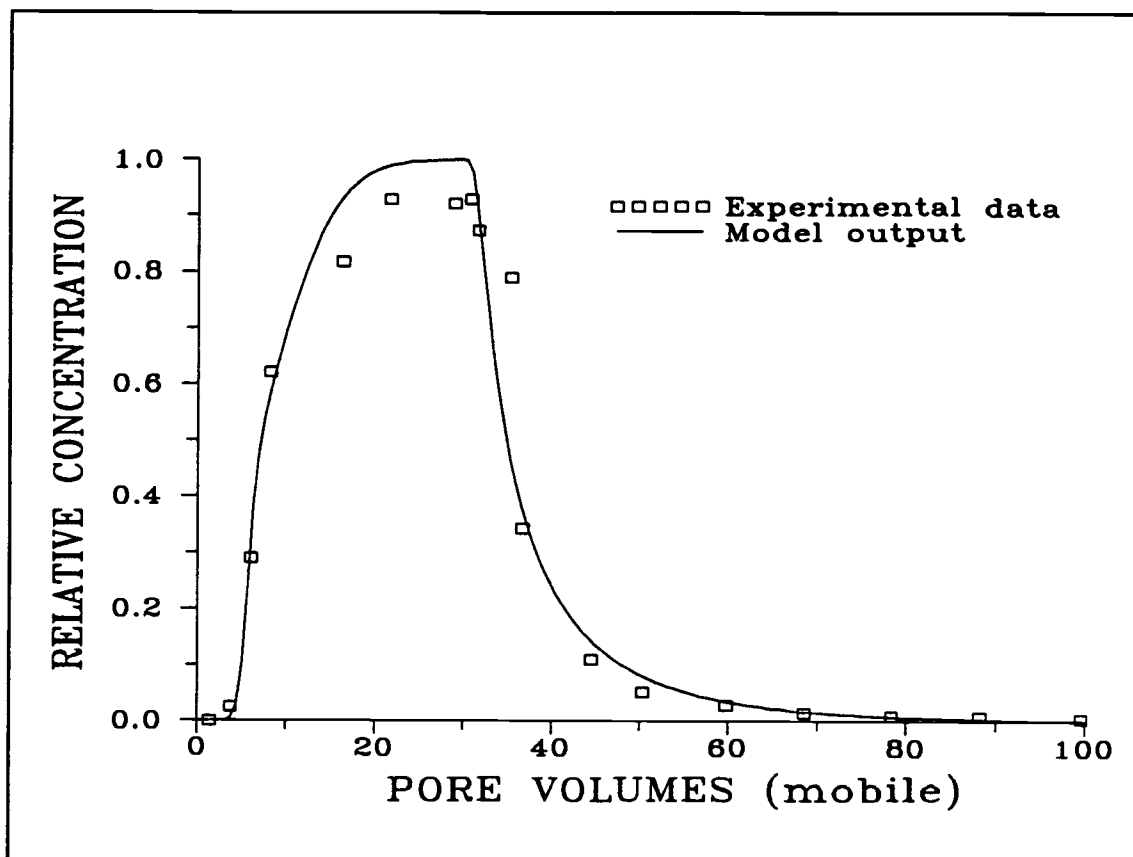


Figure II.3 Chromium(VI) breakthrough curve for an initial chromium concentration of 50 mg/l (as Cr) and desorption using distilled water.

curve, which to a large degree is due to the non-equilibrium condition inside the column and the strong sorption tendency of Cr(VI). Tailing occurs because the release of Cr(VI) adsorbed to surface sites which are in contact with the immobile water phase into the mobile water phase is slowed by the diffusional mass transfer process between the two phases, requiring more time for this Cr(VI) fraction to reach the mobile water phase. That causes the BTC not to decrease as fast as it would in an equilibrium process. This effect was described in detail by Van Genuchten and Cleary (28). The mass transfer coefficient α for the model was set to 0.2 hour^{-1} by adjusting the slope of the modeled breakthrough curve to the

experimental data. Using this α value, the model output agreed best with the experimental results. A deviation between model and experiment can be observed in the region where the relative concentration is close to 1. Here the model predicted a relative concentration of 1, whereas the experimental effluent chromium(VI) concentration never reached the influent concentration throughout the experiment. Assuming little experimental uncertainty, this could indicate that there is another chromium(VI) sink not accounted for in the model. Mass balances performed on the experimental data supported this suggestion. In all chromium(VI) experiments performed, a small percentage of chromate could never be recovered. This could be due to chromium(VI) reduction and is discussed elsewhere (Schroth et al. (22)).

Experiment no.3 (Table II.1) was modeled using the same parameters (Table II.2) as were used for experiment no.2. The model output agrees well with the experimental data (Figure II.4), although the breakthrough in the second experiment occurs later than in the first due to the different initial chromium(VI) concentration.

Chromium(VI) Breakthrough Experiment Including Anion Competition

To investigate the influence of a competitive anion on the desorption of chromium(VI) from soil, chromium(VI) breakthrough experiment no.4 (Table II.1) was conducted in which a 0.02 M phosphate solution, instead of distilled water,

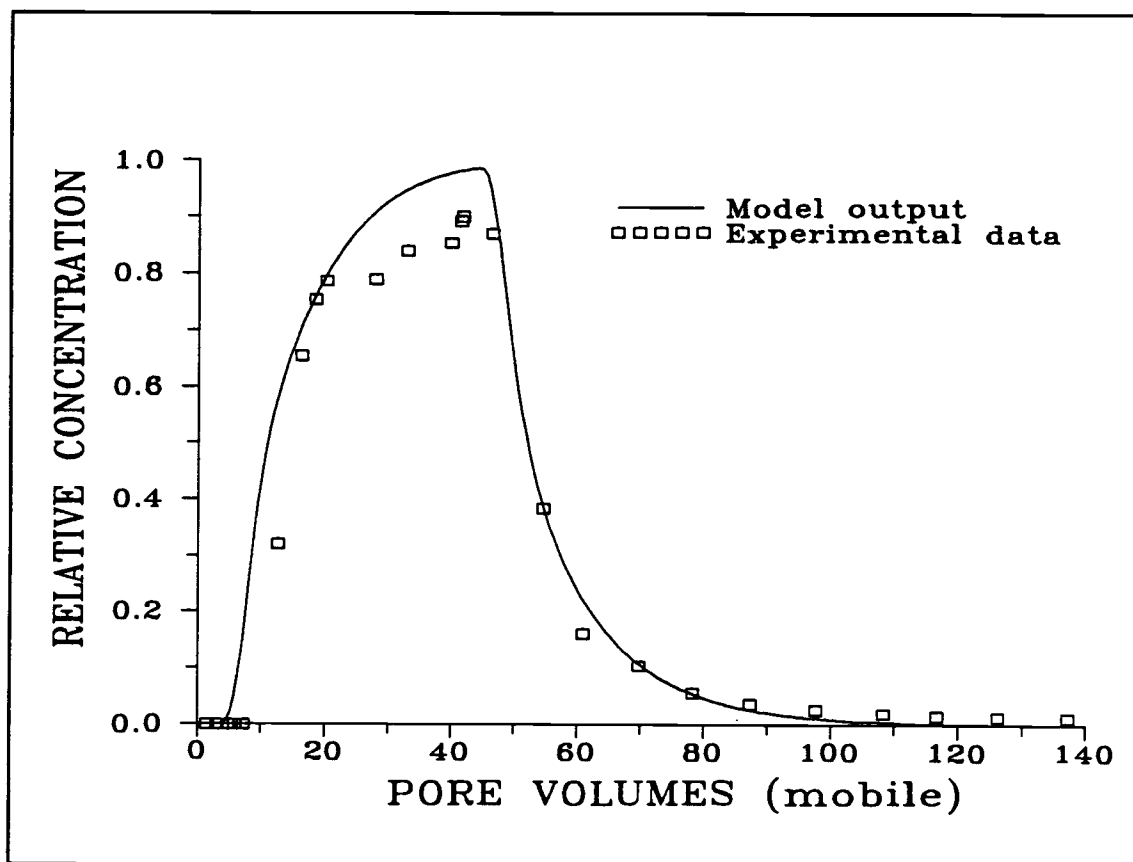


Figure II.4 Chromium(VI) breakthrough curve for an initial chromium concentration of 10 mg/l (as Cr) and desorption using distilled water.

was injected to desorb the chromate from the soil beginning at 48.5 mobile pore volumes. The results are presented in Figure II.5. The experimental data show a chromate concentration spike after 49 mobile pore volumes followed by a rapid decrease in concentration. This effect can be attributed to competitive sorption by the phosphate anion. The solid line in Figure II.5 shows the model prediction for the breakthrough using the phosphate solution for desorption. Similarly to the experiment, a chromate spike occurs at about 49 mobile pore volumes followed by a fast decline of chromate in the effluent to almost zero at 57 mobile pore volumes. The good fit between experiment and model demonstrated that the

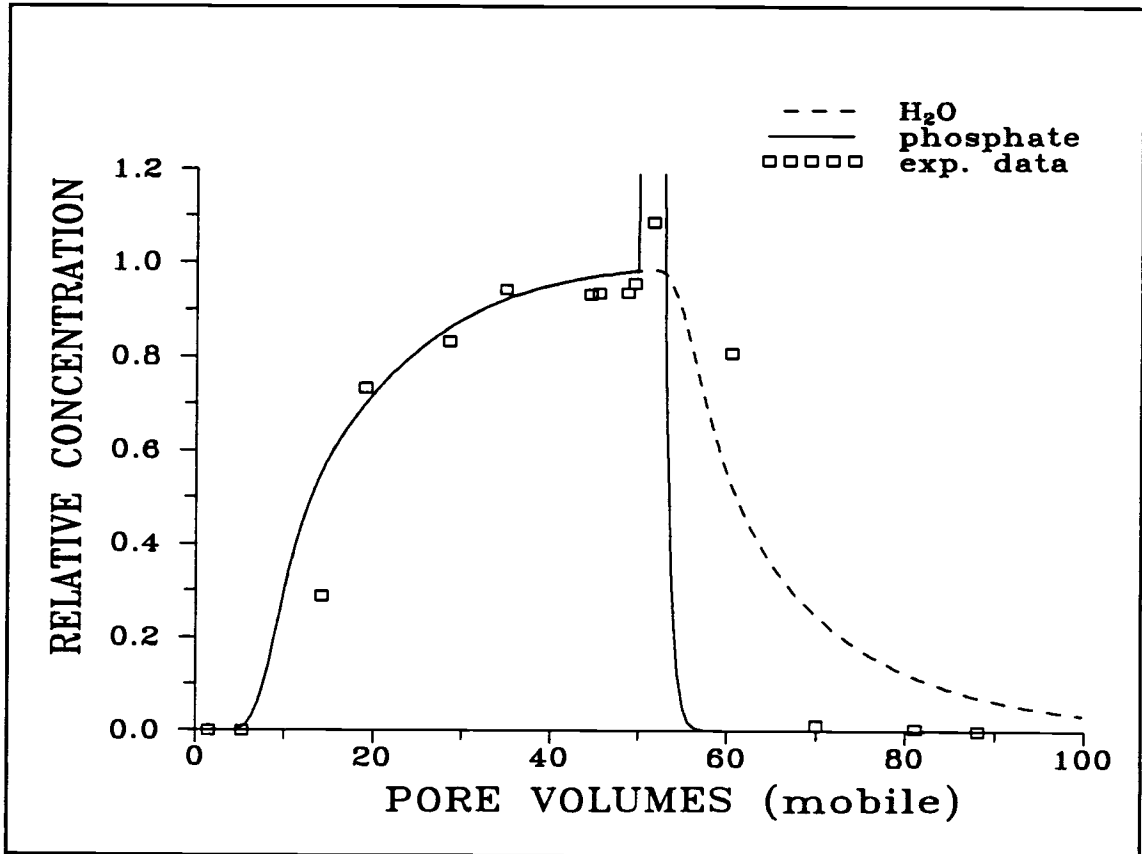


Figure II.5 Chromium(VI) breakthrough curve for an initial concentration of 10 mg/l (as Cr). In the experiment phosphate was injected for desorption. The solid/dashed lines show the model output for phosphate and H₂O desorption.

competitive Langmuir equation successfully modeled the anion competition for the available sorption sites. The dotted line shows the breakthrough prediction for chromate when distilled water is used for desorption (see also Fig. II.4) and indicates a much slower process compared to the one with phosphate competition.

The competitive Langmuir equation, although used successfully in the this case, has certain limitations. There is only one maximum sorption capacity Q_M used in the Langmuir term, thus neglecting soil selectivity effects for different anions. In the case above, the estimated maximum sorption capacity of Cr(VI) at pH 4 (Schroth et al. (22)) was used in the model equations for both Cr(VI) and

phosphate computations. Phosphate, however, adsorbs distinctively stronger onto the soil used in the experiments than Cr(VI). Therefore the phosphate liquid phase concentration was overestimated in the competitive model, causing an overestimation of the phosphate competition effect on chromium(VI) adsorption. Attempts to model the Cr(VI) breakthrough using the maximum sorption capacity determined for phosphate failed even after adjusting the valence z for Cr(VI) adsorption empirically to simulate a higher site coverage per anion adsorbed.

The successful use of the competitive Langmuir equation for the case above was due to the high phosphate influent concentration during the Cr(VI) extraction process. Although the true phosphate liquid phase concentration was smaller than assumed in the model calculations, it was still large compared to the Cr(VI) liquid phase concentration, therefore competing strongly for available adsorption sites.

SUMMARY AND CONCLUSIONS

A physical non-equilibrium solute transport model was developed to predict the movement of chromium(VI) through soil columns. The model incorporates mobile and immobile water phases to account for dispersion, advection, sorption and diffusional mass transfer between the two water phases. The sorption process was modeled under a local equilibrium assumption using a competitive Langmuir equation. To verify the model, a finite difference approximate solution to the nonlinear system of equations was developed to predict breakthrough curves. These BTC's were compared to experimentally determined soil column BTC's.

From this study the following was concluded :

1. A physical non-equilibrium solute transport model can be used to successfully model Cr(VI) soil column breakthrough experiments. The use of a non-equilibrium model for modeling Cr(VI) breakthrough experiments is essential.
2. A local equilibrium assumption can be used to model adsorption as an equilibrium process under the conditions present during the soil column experiments.

3. The competitive Langmuir equation was used successfully to model adsorption during pure chromium(VI) solute transport as well as competitive adsorption during Cr(VI) transport in the presence of phosphate.

4. The study demonstrated that the use of phosphate as a desorption agent is a possible way of increasing Cr(VI) desorption rates and, consequently, the effectiveness of chromium removal from contaminated soils.

REFERENCES

14. Bar-Yosef, B., "pH - Dependent Zinc Adsorption by Soils," Journal of the Soil Science Society of America, Vol. 43, 1979, pp. 1095-1099.
15. Cederberg, G. A., Street, R. L., and Leckie, J. O., "A Groundwater Mass Transport and Equilibrium Chemistry Model for Multicomponent Systems," Water Resources Research, Vol. 21, No. 8, Aug. 1985, pp. 1095-1104.
16. De Smedt, F., and Wierenga, P. J., "A Generalized Solution for Solute Flow in Soils With Mobile and Immobile Water," Water Resources Research, Vol. 15, No. 5, Oct. 1979, pp. 1137-1141.
17. Grove, D. B., and Stollenwerk, K. G., "Modeling the Rate-Controlled Sorption of Hexavalent Chromium," Water Resources Research, Vol. 21, No. 11, Nov. 1985, pp. 1703-1709.
18. Jennings, A. A., Kirkner, D. J., "Instantaneous Equilibrium Approximation Analysis," Journal of Hydraulic Engineering, Vol. 110, No. 12, Dec. 1984, pp. 1700-1717.
19. Nelson, P. O., "In-Situ Reclamation of Chromium-Contaminated Soil : Laboratory Study," WRRI, Oregon State University, July 1989 (in preparation).

20. Nkedi-Kizza, P., Biggar, J. W., Selim, H. M., Van Genuchten, M. Th., Wierenga, P. J., Davidson, J. M., and Nielsen, D. R., "On the Equivalence of Two Conceptual Models for Describing Ion Exchange During Transport Through an Aggregated Oxisol," Water Resources Research, Vol. 20, No. 8, Aug. 1984, pp. 1123-1130.
21. Rubin, J., "Transport of Reacting Solutes in Porous Media: Relation Between Mathematical Nature of Problem Formulation and Chemical Nature of Reactions," Water Resources Research, Vol. 19, No. 5, Oct. 1983, pp. 1231-1252.
22. Schroth, M. H., Azizian, M. F., Bean, G. R., Nelson, P. O., and Baham, J. E., "Hexavalent Chromium Chemistry In Soils: Laboratory Results," submitted for publication.
23. Selim, H. M., and Amacher, M. C., "A Second-Order Kinetic Approach for Modeling Solute Retention and Transport in Soils," Water Resources Research, Vol. 24, No. 12, Dec. 1988, pp. 2061-2075.
24. Travis, C. C., and Etnier, E. L., "A Survey of Sorption Relationships for Reactive Solutes in Soil," Journal of Environmental Quality, Vol. 10, No. 1, 1981, pp. 8-17.

25. Valocchi, A. J., Street, R. L., and Roberts, P. V., "Transport of Ion-Exchanging Solutes in Groundwater: Chromatographic Theory and Field Simulations," Water Resources Research, Vol. 17, No. 5, Oct. 1981, pp. 1517-1527.

26. Valocchi, A. J., "Validity of the Local Equilibrium Assumption for Modeling Sorbing Solute Transport Through Homogeneous Soils," Water Resources Research, Vol. 21, No. 6, June 1985, pp. 808-820.

27. Van Genuchten, M. Th., Wierenga, P. J., "Simulation of One-Dimensional Solute Transfer in Porous Media," Bulletin 628, New Mexico State University, Las Cruces, New Mexico, Nov. 1974.

28. Van Genuchten, M. Th., and Cleary, R. W., "Movement of Solutes in Soil: Computer-simulated and Laboratory Results," Developments in Soil Science 5B. Soil Chemistry B: Physico-Chemical Models, G.H. Bolt, ed., Elsevier Scientific Publishing Company, Amsterdam - Oxford - New York, 1979, pp. 349-383.

29. Van Genuchten, M. Th., "Non-Equilibrium Transport Parameters From Miscible Displacement Experiments," Research Report No. 119, United States Department of Agriculture Science and Education Administration, U.S. Salinity Laboratory Riverside, California, 1981.

30. Wu, S., and Gschwend, P. M., "Sorption Kinetics of Hydrophobic Organic Compounds to Natural Sediments and Soils," Environmental Science and Technology, Vol. 20, No. 7, 1986, pp. 717-725.

NOTATION

The following symbols are used in this paper:

- b = Langmuir adsorption constant
- c = solute liquid phase concentration
- c_i = initial concentration inside the soil column
- c_0 = column influent concentration
- d = soil column dispersivity
- D = dispersion coefficient
- f = mass fraction of soil which is accessible in the mobile water phase
- L = soil column length
- Q_M = maximum adsorption capacity
- S = adsorbed concentration
- t = time
- v = average pore water velocity
- x = distance in flow direction
- z = valence of a species
- α = rate coefficient for diffusion across the immobile water layer
- Δt = finite difference time increment
- Δx = finite difference distance increment
- Θ = volumetric water content
- ρ = bulk density of soil

Subscripts

i = solute species

n = finite difference cell number

m = symbol for the mobile water phase

im = symbol for the immobile water phase

Superscripts

t = time

Δt = finite difference time increment

BIBLIOGRAPHY

1. Bartlett, R. J., and Kimble, J. M., "Behavior of Chromium in Soils: I. Trivalent Forms," Journal of Environmental Quality, Vol. 5, No. 4, 1976, pp. 379-383.
2. Bartlett, R. J., and Kimble, J. M., "Behavior of Chromium in Soils: II. Hexavalent Forms," Journal of Environmental Quality, Vol. 5, No. 4, 1976, pp. 383-386.
3. Bartlett, R., and James, B., "Behavior of Chromium in Soils: III. Oxidation," Journal of Environmental Quality, Vol. 8, No. 1, 1979, pp. 31-35.
4. Bloomfield, C., and Pruden, G., "The Behaviour Of Cr(VI) In Soil Under Aerobic And Anaerobic Conditions," Environmental Pollution Series A, Vol. 23, 1980, pp. 103-114.
5. Davis, J. A., and Leckie, J. O., "Surface Ionization and Complexation at the Oxide/Water Interface 3. Adsorption of Anions," Journal of Colloid and Interface Science, Vol. 74, No. 1, March 1980, pp. 32-43.
6. Ecology and Environment, Inc., "Final Remedial Investigation Report,

Volume 2 of 2, United Chrome Products Site, Corvallis, Oregon,"
106.OL32.0, U.S. Environmental Protection Agency under Contract No.
68-01-6692, July 1985.

7. Enfield, C. G., and Shew, D. C., "Comparison of Two Predictive Nonequilibrium One-Dimensional Models for Phosphorus Sorption and Movement through Homogeneous Soils," Journal of Environmental Quality, Vol. 4, No. 2, 1975, pp. 198-202.
8. Enfield, C. G., Harlin, C. C., Jr., and Bledsoe, B. E., "Comparison of Five Kinetic Models for Orthophosphate Reactions in Mineral Soils," Journal of the Soil Science Society of America, Vol. 40, 1976, pp. 243-249.
9. Griffin, R. A., Au, A. K., and Frost, R. R., "Effect Of pH On Adsorption Of Chromium From Landfill-Leachate By Clay Minerals," Journal of Environmental Science and Health, A12(8), 1977, pp. 431-449.
10. Sposito, G., The Surface Chemistry of Soils, Oxford Press, New York, 1984.
11. Stollenwerk, K. G., and Grove, D. B., "Adsorption and Desorption of Hexavalent Chromium in an Alluvial Aquifer Near Telluride, Colorado,"

Journal of Environmental Quality, Vol. 14, No. 1, 1985, pp. 150-155.

12. Stumm, W., and Morgan, J. J., Aquatic Chemistry: An Introduction Emphasizing Equilibria in Natural Waters, 2nd Ed., Wiley-Interscience, New York, 1981.
13. Zachara, J. M., Girvin, D. C., Schmidt R. L., and Resch, C., T., "Chromate Adsorption on Amorphous Iron Oxyhydroxide in the Presence of Major Groundwater Ions," Environmental Science and Technology, Vol. 21, No. 6, 1987, pp. 589-594.
14. Bar-Yosef, B., "pH - Dependent Zinc Adsorption by Soils," Journal of the Soil Science Society of America, Vol. 43, 1979, pp. 1095-1099.
15. Cederberg, G. A., Street, R. L., and Leckie, J. O., "A Groundwater Mass Transport and Equilibrium Chemistry Model for Multicomponent Systems," Water Resources Research, Vol. 21, No. 8, Aug. 1985, pp. 1095-1104.
16. De Smedt, F., and Wierenga, P. J., "A Generalized Solution for Solute Flow in Soils With Mobile and Immobile Water," Water Resources Research, Vol. 15, No. 5, Oct. 1979, pp. 1137-1141.

17. Grove, D. B., and Stollenwerk, K. G., "Modeling the Rate-Controlled Sorption of Hexavalent Chromium," Water Resources Research, Vol. 21, No. 11, Nov. 1985, pp. 1703-1709.
18. Jennings, A. A., Kirkner, D. J., "Instantaneous Equilibrium Approximation Analysis," Journal of Hydraulic Engineering, Vol. 110, No. 12, Dec. 1984, pp. 1700-1717.
19. Nelson, P. O., "In-Situ Reclamation of Chromium-Contaminated Soil : Laboratory Study," WRRI, Oregon State University, July 1989 (in preparation).
20. Nkedi-Kizza, P., Biggar, J. W., Selim, H. M., Van Genuchten, M. Th., Wierenga, P. J., Davidson, J. M., and Nielsen, D. R., "On the Equivalence of Two Conceptual Models for Describing Ion Exchange During Transport Through an Aggregated Oxisol," Water Resources Research, Vol. 20, No. 8, Aug. 1984, pp. 1123-1130.
21. Rubin, J., "Transport of Reacting Solutes in Porous Media: Relation Between Mathematical Nature of Problem Formulation and Chemical Nature of Reactions," Water Resources Research, Vol. 19, No. 5, Oct. 1983, pp. 1231-1252.

22. Schroth, M. H., Azizian, M. F., Bean, G. R., Nelson, P. O., and Baham, J. E., "Hexavalent Chromium Chemistry In Soils: Laboratory Results," submitted for publication.
23. Selim, H. M., and Amacher, M. C., "A Second-Order Kinetic Approach for Modeling Solute Retention and Transport in Soils," Water Resources Research, Vol. 24, No. 12, Dec. 1988, pp. 2061-2075.
24. Travis, C. C., and Etnier, E. L., "A Survey of Sorption Relationships for Reactive Solutes in Soil," Journal of Environmental Quality, Vol. 10, No. 1, 1981, pp. 8-17.
25. Valocchi, A. J., Street, R. L., and Roberts, P. V., "Transport of Ion-Exchanging Solutes in Groundwater: Chromatographic Theory and Field Simulations," Water Resources Research, Vol. 17, No. 5, Oct. 1981, pp. 1517-1527.
26. Valocchi, A. J., "Validity of the Local Equilibrium Assumption for Modeling Sorbing Solute Transport Through Homogeneous Soils," Water Resources Research, Vol. 21, No. 6, June 1985, pp. 808-820.
27. Van Genuchten, M. Th., Wierenga, P. J., "Simulation of One-Dimensional Solute Transfer in Porous Media," Bulletin 628, New Mexico State

University, Las Cruces, New Mexico, Nov. 1974.

28. Van Genuchten, M. Th., and Cleary, R. W., "Movement of Solutes in Soil: Computer-simulated and Laboratory Results," Developments in Soil Science 5B, Soil Chemistry B: Physico-Chemical Models, G.H. Bolt, ed., Elsevier Scientific Publishing Company, Amsterdam - Oxford - New York, 1979, pp. 349-383.
29. Van Genuchten, M. Th., "Non-Equilibrium Transport Parameters From Miscible Displacement Experiments," Research Report No. 119, United States Department of Agriculture Science and Education Administration, U.S. Salinity Laboratory Riverside, California, 1981.
30. Wu, S., and Gschwend, P. M., "Sorption Kinetics of Hydrophobic Organic Compounds to Natural Sediments and Soils," Environmental Science and Technology, Vol. 20, No. 7, 1986, pp. 717-725.

APPENDICES

APPENDIX A

LABORATORY RESULTS

This appendix contains tables with the experimental data of the batch reactor and soil column experiments for Cr(VI), phosphate and chloride.

Table A.1 Chloride tracer experiment — Experimental data.

Chloride tracer test								
flowrate : 11 ml/h pore vol. : 24.6 ml column length : 5.5 cm diameter : 3.2 cm influent C = 14.6 mg/l (as NaCl)								
pV = 24.6 (100%) pV=23.37 (95%)								
sample no.	time (h)	time average	cum. pore volume	Conc mg/L	cum. pore volume	rel. conc.	cum. pore volume	rel. conc.
0	0.00	0.00	0.00	0.71	0.00	0.05	0.00	0.05
1	1.00	0.50	0.23	1.32	0.23	0.09	0.24	0.09
2	1.25	1.13	0.51	0.88	0.51	0.06	0.53	0.06
3	1.50	1.38	0.62	1.20	0.62	0.08	0.65	0.08
4	1.75	1.63	0.73	1.74	0.73	0.12	0.76	0.12
5	2.00	1.88	0.85	0.92	0.85	0.06	0.88	0.06
6	2.25	2.13	0.96	2.17	0.96	0.15	1.00	0.15
7	2.50	2.38	1.07	5.03	1.07	0.34	1.12	0.34
8	2.75	2.63	1.19	8.34	1.19	0.57	1.24	0.57
9	3.00	2.88	1.30	10.03	1.30	0.69	1.35	0.69
10	3.25	3.13	1.41	10.85	1.41	0.74	1.47	0.74
11	3.50	3.38	1.53	11.38	1.53	0.78	1.59	0.78
12	3.75	3.63	1.64	13.07	1.64	0.90	1.71	0.90
13	4.00	3.88	1.75	13.18	1.75	0.90	1.82	0.90
14	4.25	4.13	1.87	12.91	1.87	0.88	1.94	0.88
15	4.75	4.50	2.04	13.75	2.04	0.94	2.12	0.94
16	5.25	5.00	2.26	13.15	2.26	0.90	2.35	0.90
17	5.75	5.50	2.49	13.95	2.49	0.96	2.59	0.96
* 1	6.25	6.00	2.71	13.59	2.71	0.93	2.82	0.93
* 2	6.75	6.50	2.94	12.80	2.94	0.88	3.06	0.88
* 3	7.25	7.00	3.17	13.53	3.17	0.93	3.29	0.93
* 4	7.75	7.50	3.39	12.41	3.39	0.85	3.53	0.85
* 5	8.25	8.00	3.62	7.94	3.62	0.54	3.77	0.54
* 6	8.75	8.50	3.84	3.99	3.84	0.27	4.00	0.27
* 7	9.25	9.00	4.07	2.51	4.07	0.17	4.24	0.17

* desorption using distilled water

Table A.2 Phosphate batch experiment 1 — Experimental data.

Phosphate batch test no.1

add : 1 g soil
25 ml liquid at pH = 4
Initial Conc.: 1743 mg/L as H₂PO₄⁻
(about 0.02 M)

sample no.	time (h)	Phosphate Conc. (mg/l)	Solid Conc. (mg/g)	Solid Conc. (mmol/kg)
0	0	1743	0.0	0.00
1	0.50	1618	3.1	32.23
2	1.00	1610	3.3	34.29
3	1.50	1613	3.3	33.52
4	2.00	1597	3.7	37.64
5	4.42	1599	3.6	37.12
6	20.58	1549	4.9	50.02
7	29.42	1532	5.3	54.40
8	44.75	1496	6.2	63.81
9	52.75	1519	5.6	57.75
10	76.75	1485	6.5	66.64

Table A.3 Phosphate batch experiments 2 and 3 — Experimental data.

Phosphate batch tests II and III

add : 25 ml of solution w/ initial conc.: 100 mg/L as H₂PO₄⁻
1 g of soil (fine = Fi ; coarse = Co)

sample no.	time (h)	liquid conc. (Co) (mg/l)	liquid conc. (Fi) (mg/l)	solid conc. (Co) (mmol/kg)	solid conc. (Fi) (mmol/kg)
0	0	100	100	0	0
1	1.00	65.76	53.11	8.83	12.09
2	2.00	59.46	47.28	10.45	13.59
3	3.00	58.38	47.61	10.73	13.51
4	4.00	56.09	47.50	11.32	13.54
5	19.25	47.66	41.31	13.49	15.13
6	47.75	39.92	33.33	15.49	17.19
7	91.25	36.99	30.76	16.24	17.85
8	143.25	33.52	27.76	17.14	18.62
9	187.92	31.08	25.28	17.77	19.26
10	282.50	28.48	24.16	18.44	19.55

Table A.4 Chromium(VI) batch experiment 1 — Experimental data.

Sorption Rate at Various pH's:
 Compiled from q vs. pH curves at 6 rxn. times
 4 hrs-3 weeks rxn.
 All rxns. begin with 25 mls*10 ppm Cr(VI) in wellwater
 Maximum surface density= 4.81E-01 cmol/kg soil

pH	Rxn time, hours	Surface Density, cmol/kg	Surface Density, umol/kg	[Cr]eq ppm	[Cr]eq mol/l	[Cr], umol/l:
3	0.25	0.042	420	9.13	1.76E-04	175.5224
3	1	0.062	624	8.70	1.67E-04	167.3624
3	4	0.085	850	8.23	1.58E-04	158.3224
3	24	0.184	1840	6.17	1.19E-04	118.7224
3	45	0.190	1900	6.05	1.16E-04	116.3224
3	166	0.364	3640	2.43	4.67E-05	46.72248
3	331	0.450	4500	0.64	1.23E-05	12.32248
3	500	0.472	4720	0.18	3.52E-06	3.522486
4	0.25	0.0415	415	9.14	1.76E-04	175.7224
4	1	0.0545	545	8.87	1.71E-04	170.5224
4	4	0.064	640	8.67	1.67E-04	166.7224
4	24	0.118	1180	7.55	1.45E-04	145.1224
4	45	0.135	1350	7.19	1.38E-04	138.3224
4	166	0.215	2150	5.53	1.06E-04	106.3224
4	331	0.260	2600	4.59	8.83E-05	88.32248
4	500	0.310	3100	3.55	6.83E-05	68.32248
5	0.25	0.04	400	9.17	1.76E-04	176.3224
5	1	0.0466	466	9.03	1.74E-04	173.6824
5	4	0.050	500	8.96	1.72E-04	172.3224
5	24	0.086	860	8.21	1.58E-04	157.9224
5	45	0.100	1000	7.92	1.52E-04	152.3224
5	166	0.139	1390	7.11	1.37E-04	136.7224
5	331	0.180	1800	6.26	1.20E-04	120.3224
5	500	0.225	2250	5.32	1.02E-04	102.3224
6	0.25	0.035	350	9.27	1.78E-04	178.3224
6	1	0.0387	387	9.20	1.77E-04	176.8424
6	4	0.040	400	9.17	1.76E-04	176.3224
6	24	0.058	580	8.79	1.69E-04	169.1224
6	45	0.072	720	8.50	1.64E-04	163.5224
6	166	0.08	800	8.34	1.60E-04	160.3224
6	331	0.120	1200	7.50	1.44E-04	144.3224
6	500	0.145	1450	6.98	1.34E-04	134.3224

Table A.5 Chromium(VI) batch experiment 2 — Experimental data.

Chromium batch experiment :			
Reaction time/h.	Initial mass, ug/g	Final mass, ug/g	qe, mmol/g
0.00	250	250	0.000
0.02	250	226	0.462
24.00	250	209	0.789
48.00	250	195	1.058
72.00	250	195	1.058
96.00	250	192	1.115
120.00	250	182	1.308
144.00	250	180	1.346
168.00	250	176	1.423
192.00	250	169	1.558
216.00	250	171	1.519
240.00	250	161	1.712
0.00	500	500	0.000
0.02	500	466	0.654
24.00	500	431	1.327
48.00	500	431	1.327
72.00	500	430	1.346
96.00	500	428	1.385
120.00	500	421	1.519
144.00	500	410	1.731
168.00	500	410	1.731
192.00	500	409	1.750
216.00	500	398	1.962
240.00	500	378	2.346
0.00	1250	1250	0.000
0.02	1250	1215	0.673
18.50	1250	1181	1.327
64.50	1250	1170	1.539
117.00	1250	1117	2.558
232.50	1250	1064	3.577
554.00	1250	1013	4.558

Table A.6 Chromium(VI) column experiment 1 — Experimental data.

APPENDIX C. Adsorption and Desorption of 50 mg/l Cr(VI) in Distilled Water pore volume 18.5 ml										
Sample no	Cr(VI) mg/l	Cr (VI) mole	Volume mL	Pore vol. mL	Cum. pv mL	pH	Cr(VI) removed from soil			Cr(VI) ug/g
							point mol	cum mol	cum cmol/kg	
C 1	0.00	0.0E+00	25.0	1.35	1.35	3.85	0.0E+00	0.0E+00	0.000	0.00
C 2	1.23	2.4E-05	41.0	2.22	3.57	3.84	9.7E-07	9.7E-07	0.002	1.01
C 3	14.50	2.8E-04	40.5	2.19	5.76	3.82	1.1E-05	1.2E-05	0.025	11.75
C 4	31.10	6.0E-04	38.0	2.05	7.81	3.72	2.3E-05	3.5E-05	0.070	23.64
C 5	40.85	7.9E-04	142.5	7.70	15.51	3.72	1.1E-04	1.5E-04	0.294	116.42
C 6	46.44	8.9E-04	95.0	5.14	20.65	3.77	8.5E-05	2.3E-04	0.464	88.24
C 7	46.00	8.8E-04	126.0	6.81	27.46	3.83	1.1E-04	3.4E-04	0.687	115.92
CD8 *	46.44	8.9E-04	34.0	1.84	29.30	3.86	3.0E-05	3.7E-04	0.747	31.58
CD9 *	43.64	8.4E-04	14.0	0.76	30.05	3.76	1.2E-05	3.9E-04	0.771	12.22
CD10 *	39.45	7.6E-04	66.0	3.57	33.62	4.13	5.0E-05	4.4E-04	0.871	52.07
CD11 *	17.11	3.3E-04	23.0	1.24	34.86	4.40	7.6E-06	4.4E-04	0.886	7.87
CD12 *	5.57	1.1E-04	138.5	7.49	42.35	4.18	1.5E-05	4.6E-04	0.916	15.43
CD13 *	2.64	5.1E-05	101.0	5.46	47.81	4.55	5.1E-06	4.6E-04	0.926	5.33
CD14 *	1.41	2.7E-05	165.5	8.95	56.76	4.66	4.5E-06	4.7E-04	0.935	4.67
CD15 *	0.74	1.4E-05	155.0	8.38	65.14	4.83	2.2E-06	4.7E-04	0.939	2.29
CD16 *	0.47	9.0E-06	171.5	9.27	74.41	4.66	1.6E-06	4.7E-04	0.942	1.61
CD17 *	0.37	7.1E-06	174.0	9.41	83.81	5.16	1.2E-06	4.7E-04	0.945	1.29
CD18 *	0.24	4.6E-06	199.0	10.76	94.57	5.25	9.2E-07	4.7E-04	0.947	0.96
CD19 *	0.21	4.0E-06	133.0	7.19	101.76	4.80	5.4E-07	4.7E-04	0.948	0.56
CD20 *	0.17	3.3E-06	180.0	9.73	111.49	5.16	5.9E-07	4.7E-04	0.949	0.61
CD21 *	0.13	2.5E-06	204.0	11.03	122.51	5.18	5.1E-07	4.8E-04	0.950	0.53
CD22 *	0.11	2.1E-06	237.0	12.81	135.32	5.15	5.0E-07	4.8E-04	0.951	0.52
CD23 *	0.10	1.9E-06	141.0	7.62	142.95	5.20	2.7E-07	4.8E-04	0.952	0.28
CD24 *	0.09	1.7E-06	150.0	8.11	151.05	5.23	2.6E-07	4.8E-04	0.952	0.27
CD25 *	0.07	1.3E-06	204.0	11.03	162.08	5.26	2.7E-07	4.8E-04	0.953	0.29
CD26 *	0.07	1.3E-06	213.0	11.51	173.59	5.14	2.9E-07	4.8E-04	0.953	0.30
CD27 *	0.08	1.5E-06	115.0	6.22	179.81	5.54	1.8E-07	4.8E-04	0.954	0.18
CD28 *	0.07	1.3E-06	110.0	5.95	185.76	5.52	1.5E-07	4.8E-04	0.954	0.15

* Desorption with distilled water.

Table A.7 Chromium(VI) column experiment 2 — Experimental data.

APPENDIX B. Adsorption and Desorption of 10 mg/l Cr(VI) in Distilled Water pore volume 18.5 ml										
Sample no	Cr(VI) mg/l	Cr (VI) mole	Volume mL	Pore vol. mL	Cum. pv mL	pH	Cr(VI) removed from soil			Cr(VI) ug/g
							point mol	cum mol	cum cmol/kg	
AB 1	0.00	0.0E+00	27.0	1.46	1.46	4.20	0.0E+00	0.0E+00	0.00	0.00
AB 2	0.00	0.0E+00	27.0	1.46	2.92	3.63	0.0E+00	0.0E+00	0.00	0.00
AB 3	0.00	0.0E+00	30.5	1.65	4.57	3.68	0.0E+00	0.0E+00	0.00	0.00
AB 4	0.00	0.0E+00	20.0	1.08	5.65	3.71	0.0E+00	0.0E+00	0.00	0.00
AB 5	0.00	0.0E+00	23.0	1.24	6.89	3.82	0.0E+00	0.0E+00	0.00	0.00
AB 6	3.21	6.2E-05	95.0	5.14	12.03	3.85	5.9E-06	5.9E-06	0.01	6.10
AB 7	6.54	1.3E-04	64.0	3.46	15.49	3.90	8.0E-06	1.4E-05	0.03	8.37
AB 8	7.53	1.4E-04	37.0	2.00	17.49	3.85	5.4E-06	1.9E-05	0.04	5.57
AB 9	7.85	1.5E-04	31.0	1.68	19.16	3.88	4.7E-06	2.4E-05	0.05	4.87
AB10	7.88	1.5E-04	136.0	7.35	26.51	3.92	2.1E-05	4.5E-05	0.09	21.43
AB11	8.39	1.6E-04	88.5	4.78	31.30	3.68	1.4E-05	5.9E-05	0.12	14.85
AB12	8.53	1.6E-04	121.5	6.57	37.86	3.93	2.0E-05	7.9E-05	0.16	20.73
AB13	8.92	1.7E-04	27.0	1.46	39.32	3.93	4.6E-06	8.3E-05	0.17	4.82
ABD14*	9.00	1.7E-04	5.0	0.27	39.59	3.93	8.7E-07	8.4E-05	0.17	0.90
ABD15*	8.70	1.7E-04	82.5	4.46	44.05	4.30	1.4E-05	9.8E-05	0.20	14.35
ABD16*	3.84	7.4E-05	143.5	7.76	51.81	4.49	1.1E-05	1.1E-04	0.22	11.02
ABD17*	1.61	3.1E-05	111.0	6.00	57.81	4.51	3.4E-06	1.1E-04	0.22	3.57
ABD18*	1.04	2.0E-05	156.5	8.46	66.27	4.30	3.1E-06	1.2E-04	0.23	3.26
ABD19*	0.56	1.1E-05	150.0	8.11	74.38	4.49	1.6E-06	1.2E-04	0.23	1.68
ABD20*	0.37	7.1E-06	159.0	8.59	82.97	4.45	1.1E-06	1.2E-04	0.24	1.18
ABD21*	0.27	5.2E-06	181.5	9.81	92.78	4.47	9.4E-07	1.2E-04	0.24	0.98
ABD22*	0.20	3.8E-06	186.0	10.05	102.84	4.92	7.2E-07	1.2E-04	0.24	0.74
ABD23*	0.16	3.1E-06	148.0	8.00	110.84	4.74	4.6E-07	1.2E-04	0.24	0.47
ABD24*	0.13	2.5E-06	168.0	9.08	119.92	5.09	4.2E-07	1.2E-04	0.24	0.44
ABD25*	0.12	2.3E-06	193.0	10.43	130.35	4.96	4.5E-07	1.2E-04	0.24	0.46
ABD26*	0.11	2.1E-06	231.0	12.49	142.84	4.95	4.9E-07	1.2E-04	0.24	0.51
ABD27*	0.10	1.9E-06	165.0	8.92	151.76	5.06	3.1E-07	1.2E-04	0.24	0.32
ABD28*	0.06	1.2E-06	142.0	7.68	159.43	4.86	1.6E-07	1.2E-04	0.24	0.17
ABD29*	0.06	1.2E-06	200.0	10.81	170.24	5.05	2.3E-07	1.2E-04	0.24	0.24
ABD30*	0.05	9.6E-07	211.0	11.41	181.65	5.30	2.0E-07	1.2E-04	0.24	0.21
ABD31*	0.06	1.2E-06	115.0	6.22	187.86	5.32	1.3E-07	1.2E-04	0.24	0.14
ABD32*	0.05	9.6E-07	135.0	7.30	195.16	4.75	1.3E-07	1.2E-04	0.25	0.14

* Desorption with Distilled water

Table A.8 Chromium(VI) column experiment 3 — Experimental data.

APPENDIX G. Adsorption of 10 mg/l Cr(VI) in Distilled Water and Desorption with 0.02 M KH₂PO₄ at pH 4.53 and with pore volume of 18.4 ml.

Sample no	Cr(VI) mg/l	Cr (VI) mole	Volume mL	Pore vol. mL	Cum. pv mL	pH	Cr(VI) removed from soil			Cr(VI) ug/g
							point mol	cum mol	cum cmol/kg	
D 1	0.00	0.0E+00	26.5	1.43	1.43	3.89	0.0E+00	0.0E+00	0.000	0.00
D 2	0.00	0.0E+00	66.0	3.57	5.00	3.96	0.0E+00	0.0E+00	0.000	0.00
D 3	2.86	5.5E-05	157.0	8.49	13.49	3.96	8.6E-06	8.6E-06	0.017	8.98
D 4	7.32	1.4E-04	85.5	4.62	18.11	3.89	1.2E-05	2.1E-05	0.041	12.52
D 5	8.32	1.6E-04	166.0	8.97	27.08	4.30	2.7E-05	4.7E-05	0.094	27.62
D 6	9.42	1.8E-04	112.0	6.05	33.14	4.28	2.0E-05	6.8E-05	0.135	21.10
D 7	9.32	1.8E-04	168.5	9.11	42.24	4.04	3.0E-05	9.8E-05	0.195	31.41
D 8	9.34	1.8E-04	17.0	0.92	43.16	4.30	3.1E-06	1.0E-04	0.202	3.18
D 9	9.35	1.8E-04	56.5	3.05	46.22	4.24	1.0E-05	1.1E-04	0.222	10.57
DP10 *	9.55	1.8E-04	14.5	0.78	47.00	3.84	2.7E-06	1.1E-04	0.227	2.77
DP11 *	10.84	2.1E-04	37.0	2.00	49.00	4.14	7.7E-06	1.2E-04	0.243	8.02
DP12 *	8.06	1.6E-04	154.5	8.35	57.35	3.94	2.4E-05	1.5E-04	0.291	24.91
DP13 *	0.11	2.1E-06	168.5	9.11	66.46	3.98	3.6E-07	1.5E-04	0.291	0.37
DP14 *	0.04	7.7E-07	195.0	10.54	77.00	3.99	1.5E-07	1.5E-04	0.292	0.16
DP15 *	0.00	0.0E+00	124.0	6.70	83.70	3.97	0.0E+00	1.5E-04	0.292	0.00
DP16**	0.00	0.0E+00	246.0	13.30	97.00	3.67	0.0E+00	1.5E-04	0.292	0.00

* Desorption with 0.02 M KH₂PO₄ at pH 4.53.
 ** Desorption with 0.1 M KOH at pH 9.0.

Table A.9 Chromium(VI) one-hour isotherm — Experimental data.

One-Hour Rxn. "Isotherm" Data:						
Interpolated Results From q vs. C Graph:						
C _i , ppm:	C _i , umol/l:	pH:	S, cmol/kg:	S, umol/kg:	C, umol/l:	C/S, Kg/L:
2	38.46	3.00	0.0248	248.00	28.54	0.12
5	96.16	3.00	0.0403	403.00	80.04	0.20
10	192.32	3.00	0.0624	624.00	167.36	0.27
20	384.64	3.00	0.0778	778.00	353.52	0.45
50	961.61	3.00	0.3000	3000.00	841.61	0.28
C _i , ppm:	C _i , umol/l:	pH:	S, cmol/kg:	S, umol/kg:	C, umol/l:	C/S, Kg/L:
2	38.46	4.00	0.0219	219.00	29.70	0.14
5	96.16	4.00	0.0345	345.00	82.36	0.24
10	192.32	4.00	0.0545	545.00	170.52	0.31
20	384.64	4.00	0.0637	637.00	359.16	0.56
50	961.61	4.00	0.2160	2160.00	875.21	0.41
C _i , ppm:	C _i , umol/l:	pH:	S, cmol/kg:	S, umol/kg:	C, umol/l:	C/S, Kg/L:
2	38.46	5.00	0.0190	190.00	30.86	0.16
5	96.16	5.00	0.0287	287.00	84.68	0.30
10	192.32	5.00	0.0466	466.00	173.68	0.37
20	384.64	5.00	0.0496	496.00	364.80	0.74
50	961.61	5.00	0.1160	1160.00	915.21	0.79
C _i , ppm:	C _i , umol/l:	pH:	S, cmol/kg:	S, umol/kg:	C, umol/l:	C/S, Kg/L:
2	38.46	6.00	0.0160	160.00	32.06	0.20
5	96.16	6.00	0.0229	229.00	87.00	0.38
10	192.32	6.00	0.0387	387.00	176.84	0.46
20	384.64	6.00	0.0356	356.00	370.40	1.04
50	961.61	6.00	0.1000	1000.00	921.61	0.92

APPENDIX B

FINITE DIFFERENCE PROGRAM

The following is a complete listing of the finite difference program developed to generate soil column breakthrough curves. The program consists of the following subroutines:

- Main.Bas (main subroutine)
- Inp.Bas (input subroutine)
- Scont.Bas (screen control subroutine)
- Initial.Bas (initializing subroutine)
- Calc.Bas (calculation subroutine)
- Boundary.Bas (boundary subroutine)
- Estimate.Bas (estimation subroutine)
- Out.Bas (output subroutine)

Main.Bas Subroutine

```

*      Main.Bas
*      This is the Main program
*      It dimensions the 1-D arrays used in the program.
*      It calls up the subroutines.
*      It also links the subroutines at compile time.
*      IMPORTANT :
*      Before compiling the program, this subroutine has to be declared
*      "Main File" in the "File" options of the TURBO BASIC environment !!!

***** 1-D arrays are dimensioned *****

DIM Valence$(10), b$(10), Cinitial$(10), Cdesorb$(10), Csoil$(10), MW$(10)

DIM LastnewMOB$(10), LastnewIMMOB$(10), SoldMOB$(10), SoldIMMOB$(10),_
SnewMOB$(10), SnewIMMOB$(10), PrecalcMOB$(10), PrecalcIMMOB$(10),_
EfunctionMOB$(10), EfunctionIMMOB$(10), SlopeMOB$(10), SlopeIMMOB$(10),_
Effluent$(10)

***** Subroutines are linked together *****

$INCLUDE "Imp.Bas"
$INCLUDE "Scont.Bas"
$INCLUDE "Initial.Bas"
$INCLUDE "Calc.Bas"
$INCLUDE "Boundary.Bas"
$INCLUDE "Estimate.Bas"
$INCLUDE "Out.Bas"

***** Subroutines are called serially during program performance *****

CALL Inputsub
CALL Screencontrol
CALL Initialize
CALL Calculation
CALL Outputfile

CLS
PRINT
PRINT "Program terminated"

END

```

Inp.Bas Subroutine

```

*      INP.BAS
*      This is the Input subroutine. It allows to create a new input
*      file as well as to use and/or modify an already existing file.
*      Finally one can also save the created input file.
*      The sub also dimensions the 2-D arrays

```

SUB Inputsub

```

***** Variable declarations *****

SHARED SpeciesNo%, I%, CellNo%, Stepchoice%
SHARED Dispersivity#, Diameter#, Density#, WatercontMOB#, WatercontIMMOB#, _
      Alpha#, DX#, Totaltime#, Timestep#, Tdesorb#, Convergence#, F#, Q#,_
      Flowrate#
SHARED Valence#(), b#(), Cinitial#(), Cdesorb#(), Csoil#, MW#(), ColdMOB#(),_
      ColdIMMOB#(), CnewMOB#(), CnewIMMOB#(), Cellarray#()
SHARED Outputfilename$

LOCAL Previous%, Ok%, Savefile%, Locpos%, Sstop%, Choice%, SStep%
LOCAL Oldinputfilename$, Newinputfilename$

CLS
PRINT "Would you like to use and/or modify an already existing input file ?"
PRINT
PRINT "Yes --> hit <1> <enter> , No --> hit <0> <enter> ";
INPUT Previous%
***** the following edits/modifies an already existing file *****
IF Previous% = 1 THEN
  PRINT
  PRINT "Specify the drive and the filename ."
  PRINT "Make sure the disk is in your specified drive and ready to go !"
  PRINT
  INPUT "Input filename ";Oldinputfilename$
  ***** here the data file is read into memory *****
  OPEN Oldinputfilename$ FOR INPUT AS #1
  INPUT #1, SpeciesNo%
  FOR I% = 1 TO SpeciesNo%
    INPUT #1, MW#(I%), Valence#(I%), b#(I%), Cinitial#(I%), Cdesorb#(I%), Csoil(I%)
  NEXT I%
  INPUT #1, Dispersivity#, Diameter#, Density#, Q#, F#, WatercontMOB#,_
    WatercontIMMOB#, Alpha#, CellNo%, Dx#, Totaltime#, Timestep#,_
    Tdesorb#, Convergence#, Stepchoice#, Flowrate#
  CLOSE #1
  Ok% = 0
  Choice% = 0
  DO
    ***** here the data file is displayed on screen *****
    CLS
    LOCATE 1,15
    PRINT "D A T A S H E E T of ";Oldinputfilename$
    PRINT
    PRINT "Spec-No. MW Valence Langmuir coeff. Cinput(L) Cdesorb(L) Cinit(SL)"
    PRINT " (g/mol) (L/mmol) (mg/L) (mg/L) (mg/L)"
    PRINT
    FOR I% = 1 TO SpeciesNo%
      Locpos% = 5 + I%
      LOCATE Locpos%,3
      PRINT USING "##";I%
      LOCATE Locpos%,10
      PRINT USING "##";MW#(I%)
      LOCATE Locpos%,21
      PRINT USING "##";Valence#(I%)
      LOCATE Locpos%,31

```

```

PRINT USING "####.##";b#(I%)
LOCATE Locpos%,48
PRINT USING "####.##";Cinitial#(I%)
LOCATE Locpos%,60
PRINT USING "####.##";Cdesorb#(I%)
LOCATE Locpos%,72
PRINT USING "####.##";Csoil#(I%)
NEXT I%
LOCATE 11,1
PRINT "Aquifer / Soil parameters :           General parameters :"
```

PRINT	
PRINT "Dispersivity	(cm)";
PRINT USING "###.##";	Dispersivity#
PRINT "Bulk density	(g/cm ³)";
PRINT USING "###.##";	Density#
PRINT "Max. adsorp. cap.	(umol/g)";
PRINT USING "###.##";	Q#
PRINT "Soil-Frac.(f) ->	mobile H2O";
PRINT USING "###.##";	F#
PRINT "Water content (mob)	";
PRINT USING "###.##";	WatercontMOB#
PRINT "Water content (immob)	";
PRINT USING "###.##";	WatercontIMMOB#
PRINT "Transfer coeff. Alpha	(1/h)";
PRINT USING "###.##";	Alpha#
PRINT "Flowrate	(cm ³ /h)";
PRINT USING "###.##";	Flowrate#
PRINT "Column diameter	(cm)";
PRINT USING "###.##";	Diameter#
LOCATE 15,40	
PRINT "Number of cells	";CellNo%
LOCATE 16,40	
PRINT "Length of one cell	(cm)";
PRINT USING "###.###";	Dx#
LOCATE 17,40	
PRINT "Total calculation time	(h)";
PRINT USING "###.###";	Totaltime#
LOCATE 18,40	
PRINT "Length of time step	(h)";
PRINT USING "###.###";	Timestep#
LOCATE 19,40	
PRINT "Desorption start time	(h)";
PRINT USING "###.###";	Tdesorb#
LOCATE 20,40	
PRINT "Convergence criteria	(mmol)";
PRINT USING "#####";	Convergence#
LOCATE 21,40	
PRINT "Output interval :	each ";Stepchoice%,"steps"
LOCATE 25,1	
INPUT "To continue, hit <enter>	";Sstop%
***** display of data change option menu *****	
CLS	
PRINT "	*****
PRINT "	* OPTION MENU *
PRINT "	*****
PRINT	
PRINT "	Change the following parameters :"
PRINT	
PRINT " 1. Number of species (max. 10)	13. Number of cells"
PRINT " 2. Valence / MW of a species	14. Length of one cell"
PRINT " 3. Langmuir coeff. of a species	15. Total calculation time"
PRINT " 4. Initial concentrations of a species	16. Length of time step"
PRINT "	17. Desorption time"
PRINT " 5. Dispersivity	18. Convergence criteria"
PRINT " 6. Column diameter	19. Output Interval"
PRINT " 7. Bulk density	20. Flowrate"
PRINT " 8. Adsorption capacity"	
PRINT " 9. Fraction in contact w mobile H2O"	
PRINT "10. Water content (mobile)"	
PRINT "11. Water content (immobile)"	

```

PRINT "12. Transfer coefficient Alpha"
PRINT
PRINT "Choose by hitting <number> <enter>. To exit Option Menu, hit <enter>"
INPUT "Your choice ";Choice%
CLS
***** select case carries out the chosen change option *****
SELECT CASE Choice%
CASE 0
  Ok% = 1
CASE 1
  PRINT "Number of species :";SpeciesNo%
  INPUT "New value (max. 10) ";SpeciesNo%
  PRINT
CASE 2
  INPUT "For which species do you want to change the valence / mol. weight ";I%
  PRINT "Species No : ";I%;" Valence : ";Valence#(I%);" Mol. weight : ";MW#(I%)
  INPUT "New Valence ";Valence#(I%)
  INPUT "New Molecular Weight ";MW#(I%)
CASE 3
  INPUT "For which species do you want to change the Langmuir coeff. ";I%
  PRINT "Species No : ";I%;" Langmuir coeff. : ";b#(I%)
  INPUT "New Langmuir coeff. ";b#(I%)
CASE 4
  INPUT "For which species do you want to change init. concentrations ";I%
  PRINT "Species No : ";I%
  PRINT "Initial liquid concentr. ";Cinitial#(I%)
  PRINT "Desorption concentr. ";Cdesorb#(I%)
  PRINT "Init. soil-Liquid conc. ";Csoil#(I%)
  PRINT
  INPUT "New init. liquid conc. ";Cinitial#(I%)
  INPUT "New desorption conc. ";Cdesorb#(I%)
  INPUT "New init. soil-liquid conc. ";Csoil#(I%)
CASE 5
  PRINT "Dispersivity : ";Dispersivity#
  INPUT "New value ";Dispersivity#
CASE 6
  PRINT "Column diameter : ";Diameter#
  INPUT "New value ";Diameter#
CASE 7
  PRINT "Bulk density : ";Density#
  INPUT "New value ";Density#
CASE 8
  PRINT "Max. adsorption capacity : ";Q#
  INPUT "New value ";Q#
CASE 9
  PRINT "Soil fraction (f) in contact with mobile water : ";F#
  INPUT "New value ";F#
CASE 10
  PRINT "Water content (mobile) : ";WatercontMOB#
  INPUT "New value ";WatercontMOB#
CASE 11
  PRINT "Water content (immobile) : ";WatercontIMMOB#
  INPUT "New value ";WatercontIMMOB#
CASE 12
  PRINT "Transfer coefficient Alpha : ";Alpha#
  INPUT "New value ";Alpha#
CASE 13
  PRINT " Number of cells : ";CellNo%
  INPUT " New value ";CellNo%
CASE 14
  PRINT "Length of one cell : ";Dx#
  INPUT "New value ";Dx#
CASE 15
  PRINT "Total calculation time : ";Totaltime#
  INPUT "New value ";Totaltime#
CASE 16
  PRINT "Length of time step : ";Timestep#
  INPUT "New value ";Timestep#
CASE 17
  PRINT "Desorption time : ";Tdesorb#

```

```

        INPUT "New value ";Tdesorb#
    CASE 18
        PRINT "Convergence criteria : ";Convergence#
        INPUT "New value ";Convergence#
    CASE 19
        PRINT "Output intervall : ";Stepchoice%;" timesteps"
        INPUT "New value ";Stepchoice%
    CASE 20
        PRINT "Flowrate (cm^3/h) ";Flowrate#
        INPUT "New value ";Flowrate#
    END SELECT
LOOP UNTIL Ok% = 1
PRINT
CLS
INPUT "Specify drive and name of OUTPUT data file : ";Outputfilename$
ELSE
***** here a whole new data file can be entered *****
Ok% = 0
DO
    CLS
    INPUT "Number of species to include into model (max. 10) ";SpeciesNo%
    PRINT
    PRINT
    CLS
    FOR I% = 1 TO SpeciesNo%
        PRINT "Species No. : ";I%
        INPUT "Valence ";Valence#(I%)
        INPUT "Molecular Weight (g/mol) ";MW#(I%)
        INPUT "Langmuir coefficient b ( (L/mmol)^Valence ) ";b#(I%)
        INPUT "Input liquid concentration (mg/L) ";Cinitial#(I%)
        INPUT "Desorption - Input liquid conc. (mg/L) ";Cdesorb#(I%)
        INPUT "Initial liquid conc. in soil column (mg/L) ";Csoil#(I%)
        PRINT
    NEXT I%
    PRINT
    PRINT "Is the input correct ? If yes, hit <1> <enter>";
    INPUT Ok%
LOOP UNTIL Ok% = 1
Ok% = 0
DO
    CLS
    PRINT "Enter the following AQUIFER/SOIL parameters : "
    PRINT
    INPUT "Dispersivity (cm) ";Dispersivity#
    INPUT "Bulk density (g/cm^3) ";Density#
    INPUT "Max. adsorption capacity (umol/g) ";Q#
    INPUT "Fraction of solids in contact w/ mobile water (0-1) ";F#
    INPUT "Water content (mobile) (cm^3/cm^3) ";WatercontMOB#
    INPUT "Water content (immobile) (cm^3/cm^3) ";WatercontIMMOB#
    INPUT "Transfer coeff. ALPHA (1/h) ";Alpha#
    INPUT "Flowrate (cm^3/h) ";Flowrate#
    PRINT
    PRINT "Is the input correct ? If yes, hit <1> <enter>";
    INPUT Ok%
LOOP UNTIL Ok% = 1
Ok% = 0
DO
    CLS
    PRINT "Enter the following general parameters : "
    PRINT
    INPUT "Number of cells ";CellNo%
    INPUT "Length of one cell (cm) ";Dx#
    INPUT "Column diameter (cm) ";Diameter#
    INPUT "Total Calculation Time (h) ";Totaltime#
    INPUT "Length of time step (h) ";Timestep#
    INPUT "Time when DESORPTION begins (h) ";Tdesorb#
    INPUT "Convergence criteria (mmol) ";Convergence#
    INPUT "Frequency of output (timesteps) ";Stepchoice%
    PRINT
    INPUT "Specify drive and name for OUTPUT data file : ";Outputfilename$

```

```

PRINT
PRINT "Is the input correct ? If yes, hit <1> <enter>";
INPUT Ok%
LOOP UNTIL Ok% = 1
***** end of data input or modification *****
END IF
***** 2-D arrays are dimensioned here *****
DIM ColdMOB#(SpeciesNo%+1,CellNo%+1), ColdIMMOB#(SpeciesNo%,CellNo%),_
  CnewMOB#(SpeciesNo%,CellNo%), CnewIMMOB#(SpeciesNo%,CellNo%)
SStep% = INT(Totaltime# / (Timestep# * Stepchoice%)) + 1
DIM Cellarray#(SStep%,SpeciesNo%+1)
CLS
***** the following contains the option to save the current data file *****
Savefile% = 0
PRINT "Now you have entered all necessary input data !"
PRINT
PRINT "You have now the option to save all this data in a file ..."
INPUT "If you wish to do this, hit <1> <enter>";Savefile%
IF Savefile% = 1 Then
  CLS
  PRINT
  PRINT "Please prepare your disk and make sure everything is ready to go !"
  PRINT
  PRINT "Please specify the drive and the filename ."
  PRINT
  PRINT "*****"
  PRINT "** DANGER !!! If a file with the same name already exists, the new **"
  PRINT "**           file will OVERWRITE the old one !           **"
  PRINT "*****"
  PRINT
  INPUT "Input Filename      ";Newinputfilename$
  ***** here the data is saved in a file *****
  ***** the format has to be consistent with the data read section above *****
  OPEN Newinputfilename$ FOR OUTPUT AS #1
  WRITE #1, SpeciesNo%
  FOR I% = 1 TO SpeciesNo%
  WRITE #1, MW#(I%), Valence#(I%), b#(I%), Cinitial#(I%), Cdesorb#(I%), Csoil#(I%)
  NEXT I%
  WRITE #1, Dispersivity#, Diameter#, Density#, Q#, F#, WatercontMOB#,_
    WatercontIMMOB#, Alpha#, CellNo%, Dx#, Totaltime#, Timestep#,_
    Tdesorb#, Convergence#, Stepchoice%, Flowrate#
  CLOSE #1
END IF
END SUB

```


Scont.Bas Suroutine

```
' Scont.Bas  
' This is the Sreen control sub. It allows the user to tell, which  
' part of the program is being processed currently.  
' The sub gets its input from "locate" and "print" statements within  
' each sub.
```

```
SUB Screencontrol  
CLS  
PRINT "          PROGRAM CONTROL "  
PRINT  
PRINT "Program is currently processing : "  
PRINT  
PRINT  
PRINT "Current stepnumber :"  
PRINT  
END SUB
```

Initial.Bas Subroutine

```

'      Initial.Bas
'      This sub initializes the cells (using Csoil(I%))
'      It also performs the precalculation of constant parameters
'      used in the calculation sub.

```

Sub Initialize

```

'***** variable declarations *****
      SHARED SpeciesNo%, I%, CellNo%, N%
      SHARED ColdMOB#0, ColdIMMOB#0, Cinitial#0, Cdesorb#0, Csoil#0, MW#0,
      Valence#0
      SHARED Dispersivity#, Porevelocity#, Dx#, Timestep#, F#, Alpha#, Density#,_
      WatercontMOB#, WatercontIMMOB#, Value1#, Value2#, Value3#, Value4#,_
      Value5#, Value6#, Totalvolume#, Flowrate#, Diameter#,
      LOCAL Disp#, Dispersion#, Pi#

'***** statement for screen control sub *****
LOCATE 3,36
PRINT "Initialize Subroutine"
'***** mass conc. are converted to molar conc. ; if the initial conc. of a species
'      is zero, it gets the conc.1E-100 assigned to allow for division later to
'      convert to relative concentrations *****
FOR I% = 1 TO SpeciesNo%
  Cinitial#(I%) = Cinitial#(I%) / MW#(I%)
  Cdesorb#(I%) = Cdesorb#(I%) / MW#(I%)
  Csoil#(I%) = Csoil#(I%) / MW#(I%)
  IF Csoil#(I%) = 0 THEN Csoil#(I%) = 1E-100
NEXT I%
'***** cell conc. are initialized *****
FOR N% = 1 TO CellNo%
  FOR I% = 1 TO SpeciesNo%
    ColdMOB#(I%,N%) = Csoil#(I%)
    ColdIMMOB#(I%,N%) = Csoil#(I%)
  NEXT I%
NEXT N%
'***** calculation of average pore velocity, column vol. and dispersion coeff.;
'      dispersion coeff. is corrected for numerical disp. error and
'      is not allowed to be smaller than zero *****
Pi# = 4 * ATN(1)
Porevelocity# = Flowrate# / ((Diameter#/2)^2 * Pi# * WatercontMOB#)
Totalvolume# = (Diameter#/2)^2 * Pi# * CellNo% * Dx#
Dispersion# = Porevelocity# * Dispersivity#
Disp# = Dispersion# - Porevelocity# * (Dx# - Porevelocity# * Timestep#) / 2
IF Disp# < 0 THEN Disp# = 0
'***** constant fractions for FD equations are computed and
'      displayed on screen *****
Value1# = Disp# * Timestep# / (Dx# * Dx#)
Value2# = Porevelocity# * Timestep# / Dx#
Value3# = F# * Density# / WatercontMOB#
Value4# = Alpha# * Timestep# / WatercontMOB#
Value5# = (1 - F#) * Density# / WatercontIMMOB#
Value6# = Alpha# * Timestep# / WatercontIMMOB#
LOCATE 10,1
PRINT "Dispersion factor      : ";
PRINT USING "#####.#####";Value1#
PRINT "Advection factor      : ";
PRINT USING "#####.#####";Value2#
PRINT "Sorption factor (mob) : ";
PRINT USING "#####.#####";Value3#
PRINT "Transfer factor (mob) : ";
PRINT USING "#####.#####";Value4#
PRINT "Sorption factor (im) : ";
PRINT USING "#####.#####";Value5#

```

```
PRINT "Transfer factor (im) : ";
PRINT USING "#####.#####";Value6#
***** absolute of valence in case of negative input value *****
FOR I% = 1 TO SpeciesNo%
  Valence#(I%) = ABS(Valence#(I%))
NEXT I%
END SUB
```

Calc.Bas Subroutine

```

'      Calc.Bas
'
'      This sub performs the finite difference calculations.
'      It contains a convergence loop for each cell within a time
'      loop.
'      The results of the calculations are written to a 2-D array

SUB Calculation
***** variable declarations *****
SHARED I%, SpeciesNo%, N%, CellNo%, Flag1%
SHARED ColdMOB#(), ColdIMMOB#(), CnewMOB#(), CnewIMMOB#(),_
Cellarray#(), LastnewMOB#(), LastnewIMMOB#(), b#(), Valence#(),_
SoldMOB#(), SoldIMMOB#(), SnewMOB#(), SnewIMMOB#(), Cinitial#(),_
Cdesorb#(), PrecalcMOB#(), PrecalcIMMOB#(), EfunctionMOB#(),_
EfunctionIMMOB#(), SlopeMOB#(), SlopeIMMOB#(), Effluent#()
SHARED T#, Timestep#, Totaltime#, Q#, Convergence#, Value1#, _
Value2#, Value3#, Value4#, Value5#, Value6#, Stepchoice%, Stepcheck#
LOCAL StepNo&
LOCAL SumoldMOB#, SumoldIMMOB#, SumnewMOB#, SumnewIMMOB#,_
Check#, Check1#, Check2#

***** statement for screen control sub *****
LOCATE 3,36
PRINT "Calculation Subroutine"
***** begin time loop *****
StepNo& = 0
FOR T# = Timestep# TO Totaltime# STEP Timestep#
  INCR StepNo& , 1
  ***** statement for screen control *****
  LOCATE 6,22
  PRINT StepNo&
  ***** calling up boundary conditions *****
  Call Boundaries
  ***** begin cell loop *****
  FOR N% = 1 TO CellNo%
    ***** computing the sum of b*C(I) for old time *****
    SumoldMOB# = 0
    SumoldIMMOB# = 0
    FOR I% = 1 TO SpeciesNo%
      SumoldMOB# = SumoldMOB# + b#(I%) * ColdMOB#(I%,N%)^_
      (1/Valence#(I%))
      SumoldIMMOB# = SumoldIMMOB# + b#(I%) * ColdIMMOB#(I%,N%)^_
      (1/Valence#(I%))
    NEXT I%
    ***** computing solid phase conc. for all species at the old time using
    '      competitive Langmuir equation
    '      computing the explicit part of FD equations and saving the results
    '      in Precalc arrays *****
    '      in select case the upper boundary is applied (for cell 1) *****
    FOR I% = 1 TO SpeciesNo%
      SoldMOB#(I%) = (Q# * b#(I%) * ColdMOB#(I%,N%)^(1/Valence#(I%))) /_
      (1 + SumoldMOB#)
      SoldIMMOB#(I%) = (Q# * b#(I%) * ColdIMMOB#(I%,N%)^(1/Valence#(I%))) /_
      (1 + SumoldIMMOB#)
      SELECT CASE N%
        CASE >1
          PrecalcMOB#(I%) = ColdMOB#(I%,N%) + Value1# * (ColdMOB#(I%,N%-1)_
          - 2 * ColdMOB#(I%,N%) + ColdMOB#(I%,N%+1)) + Value2# * _
          (ColdMOB#(I%,N%-1)-ColdMOB#(I%,N%)) - Value4# * (ColdMOB#(I%,N%)_
          - ColdIMMOB#(I%,N%))
          CASE 1
            PrecalcMOB#(I%) = ColdMOB#(I%,N%) + Value1# * (- ColdMOB#(I%,N%)_
            + ColdMOB#(I%,N%+1)) + Value2# * (ColdMOB#(I%,N%-1)_
            - ColdMOB#(I%,N%)) - Value4#*(ColdMOB#(I%,N%) - ColdIMMOB#(I%,N%))
      END SELECT
      PrecalcIMMOB#(I%) = ColdIMMOB#(I%,N%) + Value6# * (ColdMOB#(I%,N%) -

```

```

ColdIMMOB#(I%,N%)
NEXT I%
Flag1% = 0
***** begin iteration loop within each cell *****
DO
***** calling estimation sub, allowing for relaxation *****
CALL Estimates
***** computing sum of b*C(I) at new time *****
SumnewMOB# = 0
SumnewIMMOB# = 0
FOR I% = 1 TO SpeciesNo%
SumnewMOB# = SumnewMOB# + b#(I%) * CnewMOB#(I%,N%)^_
(1/Valence#(I%))
SumnewIMMOB# = SumnewIMMOB# + b#(I%) * CnewIMMOB#(I%,N%)^_
(1/Valence#(I%))
NEXT I%
***** computing solid phase conc. at new time using competitive
Langmuir equation *****
FOR I% = 1 TO SpeciesNo%
SnewMOB#(I%) = (Q# * b#(I%) * CnewMOB#(I%,N%)^(1/Valence#(I%))) /_
(1 + SumnewMOB#)
SnewIMMOB#(I%) = (Q# * b#(I%) * CnewIMMOB#(I%,N%)^(1/Valence#(I%))) /_
(1 + SumnewIMMOB#)
NEXT I%
***** FD equations rewritten as zero functions (Efunction has to become zero)
for both water phases; slope defines the derivative of the Efunctions
with respect to the new conc. of a species (Cnew(I%,N%). Cnew
of other species are treated as constants. *****
FOR I% = 1 TO SpeciesNo%
EfunctionMOB#(I%) = PrecalcMOB#(I%) - Value3# * (SnewMOB#(I%) -_
SoldMOB#(I%)) - CnewMOB#(I%,N%)
EfunctionIMMOB#(I%) = PrecalcIMMOB#(I%) - Value5# * (SnewIMMOB#(I%) -_
SoldIMMOB#(I%)) - CnewIMMOB#(I%,N%)
SlopeMOB#(I%) = - Value3#*((1+SumnewMOB#)*Q#*b#(I%)*CnewMOB#(I%,N%)^_
(1/Valence#(I%)-1)/Valence#(I%) - Q#*b#(I%)^2*CnewMOB#(I%,N%)^_
(2/Valence#(I%)-1)/Valence#(I%))/(1+SumnewMOB#)^2 -1
SlopeIMMOB#(I%) = - Value5#*((1+SumnewIMMOB#)*Q#*b#(I%)*CnewIMMOB#(I%,N%)^_
(1/Valence#(I%)-1)/Valence#(I%) - Q#*b#(I%)^2*CnewIMMOB#(I%,N%)^_
(2/Valence#(I%)-1)/Valence#(I%))/(1+SumnewIMMOB#)^2 -1
NEXT I%
***** Newton-Raphson approximation *****
FOR I% = 1 TO SpeciesNo%
CnewMOB#(I%,N%) = LastnewMOB#(I%) - EfunctionMOB#(I%) / SlopeMOB#(I%)
CnewIMMOB#(I%,N%) = LastnewIMMOB#(I%) - EfunctionIMMOB#(I%) / SlopeIMMOB#(I%)
Next I%
***** checking the convergence criterium for all species *****
Check# = 0
FOR I% = 1 TO SpeciesNo%
Check1# = ABS(EfunctionMOB#(I%))
Check2# = ABS(EfunctionIMMOB#(I%))
IF Check1# > Check# THEN
Check# = Check1#
ELSEIF Check2# > Check# THEN
Check# = Check2#
END IF
NEXT I%
LOOP UNTIL Check# <= Convergence#
***** end of iteration loop within a cell *****
NEXT N%
***** end of cell loop *****
***** check for very small conc.; to prevent values from running out of
range they are set to zero; new conc. are assigned to old conc. *****
FOR N% = 1 TO CellNo%
FOR I% = 1 TO SpeciesNo%
IF CnewMOB#(I%,N%) < 1*10^-300 THEN CnewMOB#(I%,N%) = 0
IF CnewIMMOB#(I%,N%) < 1*10^-300 THEN CnewIMMOB#(I%,N%) = 0
ColdMOB#(I%,N%) = CnewMOB#(I%,N%)
ColdIMMOB#(I%,N%) = CnewIMMOB#(I%,N%)
Next I%
NEXT N%

```

```
'***** check for sampling time, if yes, conc. and time is written  
' to Cellarray *****  
Stepcheck# = StepNo& / Stepchoice%  
IF Stepcheck# = INT(Stepcheck#) THEN  
  FOR I% = 1 TO SpeciesNo%  
    Cellarray#(Stepcheck#,I%) = Effluent#(I%)  
  NEXT I%  
  Cellarray#(Stepcheck#,SpeciesNo%+1) = T#  
END IF  
NEXT T#  
'***** end of time loop *****  
END SUB
```

Boundary.Bas Subroutine

```

'      Boundary.Bas
'
'      This sub sets the boundary conditions before a next time step
'      is performed. The "FOR..NEXT" loop sets the lower boundary,
'      whereas the "IF" loop sets the upper boundary initial conc.. This upper
'      boundary is controlled by the time counter "T" and by the
'      event "Tdesorb".
SUB Boundaries
  ***** variable declarations *****
  SHARED I%, SpeciesNo%, CellNo%
  SHARED ColdMOB#(), Cinitial#(), Cdesorb#(), Effluent#()
  SHARED T#, Tdesorb#
  LOCAL First%

  ***** set lower boundary for all species *****
  FOR I% = 1 TO SpeciesNo%
    ColdMOB#(I%,CellNo%+1) = ColdMOB#(I%,CellNo%)
    Effluent#(I%) = ColdMOB#(I%,CellNo%+1)
  NEXT I%
  ***** set initial conc. for upper boundary
  '      the actual boundary restriction is in the Calculation sub *****
  First% = 0
  IF T# < Tdesorb# THEN
    FOR I% = 1 TO SpeciesNo%
      ColdMOB#(I%,First%) = Cinitial#(I%)
    NEXT I%
  ELSE
    FOR I% = 1 TO SpeciesNo%
      ColdMOB#(I%,First%) = Cdesorb#(I%)
    NEXT I%
  END IF
END SUB

```

Estimate.Bas Subroutine

```

' Estimate.Bas
'
' This sub calculates estimates for the new cell concentrations
' of all species in both the mobile and immobile layer. It also
' saves the previous (T-DT) concentrations in an array.
' "CASE 0" is used for the initial(first) estimate of the cell
' concentrations."CASE 1" is used for estimates during the
' convergence procedure. This sub is being called by the
' "CALCULATION" sub.
' STATUS : use old conc. as estimates

SUB Estimates
***** variable declarations *****
  SHARED I%, SpeciesNo%, Flag1%, N%
  SHARED ColdMOB#(), ColdIMMOB#(), CnewMOB#(), CnewIMMOB#(),
  LastnewMOB#(), LastnewIMMOB#()

  SELECT CASE Flag1%
CASE 0
  FOR I% = 1 TO SpeciesNo%
    CnewMOB#(I%,N%) = ColdMOB#(I%,N%)
    CnewIMMOB#(I%,N%) = ColdIMMOB#(I%,N%)
    LastnewMOB#(I%) = ColdMOB#(I%,N%)
    LastnewIMMOB#(I%) = ColdIMMOB#(I%,N%)
  NEXT I%
CASE 1
***** save Cnew in Lastnew *****
  FOR I% = 1 TO SpeciesNo%
    LastnewMOB#(I%) = CnewMOB#(I%,N%)
    LastnewIMMOB#(I%) = CnewIMMOB#(I%,N%)
  NEXT I%
  END SELECT
  Flag1% = 1
END SUB

```


Out.Bas Subroutine

```

'      Out.Bas
'      First the concentrations are converted to relative conc..
'      Then the sub creates an output file (ASCII), which has
'      been named previously (in the Input sub)

SUB Outputfile

      ***** variable declarations *****
      SHARED Cellarray#(), MW#(), Cinitial#()
      SHARED I%, SpeciesNo%
      SHARED Outputfilename$
      SHARED Stepcheck#, Flowrate#, WatercontMOB#, Totalvolume#
      LOCAL Number%

      ***** statement for Screen control sub *****
      LOCATE 3,36
      PRINT "      Output Subroutine"
      ***** set cinitial to allow for deviation *****
      FOR I% = 1 TO SpeciesNo%
        IF Cinitial#(I%) = 0 THEN Cinitial#(I%) = 1E-100
      NEXT I%
      Stepcheck# = INT(Stepcheck#)
      FOR Number% = 1 TO Stepcheck#
        ***** compute relative concentrations
        '      convert real time to mobile pore volumes *****
        FOR I% = 1 TO SpeciesNo%
          Cellarray#(Number%,I%) = Cellarray#(Number%,I%) / Cinitial#(I%)
        NEXT I%
        Cellarray#(Number%,SpeciesNo%+1) = Cellarray#(Number%,SpeciesNo%+1) * _
          Flowrate# / (Totalvolume# * WatercontMOB#)
      NEXT Number%
      ***** write to output data file *****
      OPEN Outputfilename$ FOR APPEND AS #1
      FOR Number% = 1 TO Stepcheck#
        PRINT #1, USING "###.###"; Cellarray#(Number%,SpeciesNo%+1);
        FOR I% = 1 TO SpeciesNo%
          PRINT #1, USING "###.###"; Cellarray#(Number%,I%);
        NEXT I%
        PRINT #1, ""
      NEXT Number%
      CLOSE #1

END SUB

```