SORPTION OF INORGANIC OXYANIONS BY ORGANO-ZEOLITE

by

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TABLE OF CONTENTS

LIST OF FIGURES IN CHAPTER 2

LIST OF TABLES IN CHAPTER 2

LIST OF APPENDICES FIGURES

LIST OF APPENDICES TABLES

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Finally, I'd like to dedicate this independent study to my parents Mary and John, and to my husband Marty. Their love, encouragement, and compassion have sustained me throughout the years.

CHAPTER 1

INTRODUCTION

This document is the culmination of an independent study and contains a journal article and supporting appendices. The independent study focused on a potential environmental application for natural geologic materials modified with organic cations - the removal of inorganic anions from aqueous solution. Inorganic anions such as chromate and selenate are often environmental contaminants in surface and ground waters. The objectives of the study were to quantify the sorption of anions by organo-zeolite and determine, if possible, the mechanism(s) of anion sorption.

This study was part of a joint study between New Mexico Institute of Mining and Technology (NMT) and New Mexico State University (NMSU) sponsered by the New Mexico Waste-management, Education, and Research Consortium (project WERC-91-41). NMSU has primarily studied the sorption of organic contaminants by organo-zeolite although some work is being done on sorption of inorganic anions as well.

The journal article is entitled "*Sorption of chromate and other inorganic anions by organo-zeolite*", and has been submitted to the journal Environment, Technology, and Science (ES&T). This article presents the results of batch isotherm experiments on the sorption of oxyanions by a clinoptilolite-dominated zeolite modified with the quaternary amine, hexadecyltrimethylammonium (HDTMA). Experiments were conducted with the oxyanions chromate, selenate, and sulfate in aqueous solution. An evaluation of the potential mechanisms for anion sorption is also presented in the article.

Appendix A contains information on the zeolite used in the study. This includes a summary of the mineralogical and physical characterization (Appendix A1) , scanning electron photomicrographs (Appendix A2), and a summary of cation exchange capacity (CEC) results (Appendix A3).

Appendix B contains a description of the experimental methods and materials, and tabulated and/or graphical results for the experiments conducted on the sorption of HDTMA by zeolite. Included are procedures used in the modification of the zeolite for batch isotherm studies (Appendix B1), sorption of radiolabeled HDTMA at varying percentages of the zeolite's external CEC (Appendix B2), and surface stability studies (Appendix B3).

Appendix C contains a description of the experimental methods and materials, and tabulated and/or graphical results, for the experiments quantifying sorption of oxyanions by natural zeolite and HDTMA-zeolite. The methods and materials are summarized in Appendix C1 for the batch isotherm studies. The tabulated and graphical results are included for batch sorption/desorption isotherms of chromate (Appendix C2), selenate (Appendix C3), sulfate (Appendix C4), and arsenate (Appendix C4).

Appendix D contains the results of a preliminary biodegradation study on HDTMA-zeolite.

Appendix E contains references used in the appendices. References for Chapter 2 are presented in that chapter. If references were used in both Chapter 2 and in the appendices then they are referenced in both Chapter 2 and Appendix E.

CHAPTER 2

PAPER ENTITLED "SORPTION OF CHROMATE AND OTHER INORGANIC ANIONS BY ORGANO-ZEOLITE

by G.M. Haggerty and R.S. Bowman

Sorption of Chromate and Other Inorganic Anions by Organo-Zeolite

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ABSTRACT

We performed batch sorption experiments which showed significantly enhanced removal of inorganic oxyanions from aqueous solution by clinoptilolite-dominated zeolite modified by the quaternary amine hexadecyltrimethylammonium (HDTMA). HDTMA was retained quantitatively by the zeolite up to the its external cation exchange capacity. The HDTMA-surface was stable when exposed to extremes in pH (3 - 10), ionic strength (up to 1.0 *M* CsCl) and to organic solvents. While the natural zeolite had no affinity for the oxyanions, the HDTMA-modified zeolite showed significant removal of chromate, selenate, and sulfate from 0.005 *M* $CaCl_2$ aqueous solution. Sorption data for each anion were well-described by the Langmuir isotherm equation. We found that sorption was highest when the zeolite was modified to its external cation exchange capacity. Our research indicates that the formation of an HDTMA-anion surface complex is the most likely mechanism for the sorption of anionic species.

INTRODUCTION

Zeolites are hydrated aluminosilicate minerals characterized by cage-like structures, internal and external surface areas of up to several hundred m^2/g, and cation exchange capacities (CECs) of up to several equivalents per kilogram (Ming and Mumpton, 1989). At least 41 naturally occurring zeolites exist and many others have been synthesized. Both natural and synthetic zeolites find use in industry as absorbants, soil amendments, ion exchangers, and molecular sieves (Barrer, 1978). Clinoptilolite is the most abundant naturally occurring zeolite. The unit-cell formula of clinoptilolite is $(Ca, Na_2, K_2)_3\ [Al_6Si_{30}O_{72}]\cdot 24\ H_2O$. It has a two-dimensional 8-ring and 10-ring channel structure with the largest cavity dimension measuring 4.4 by 7.2 Å (Newsam, 1986).

To some extent zeolite surface chemistry resembles that of smectite clays. In contrast to clays, however, natural zeolites can occur as mm- or greater-sized particles and are free of shrink-swell behavior. These properties result in superior hydraulic characteristics when zeolites are used as sorbents in filtration beds or in environmental applications such as permeable barriers.

Modification by ion exchange with cationic surfactants has been used to alter the surface properties of clays. Quaternary amines such as hexadecyltrimethylammonium (HDTMA) are tetrasubstituted ammonium salts with a permanently charged pentavalent nitrogen and at least one alkyl chain. HDTMA is strongly surface-active and contains a long straight alkyl chain (C16) which imparts a high degree of hydrophobicity. It is well-established that clays modified with quaternary amines such as HDTMA can substantially enhance removal of nonionic organic solutes from aqueous solution (Boyd et al., 1988; Lee et al., 1989; Cadena, 1989). Similarly, HDTMA-modified zeolites have been shown to remove chlorinated aliphatic compounds

(Huddleston, 1990) and benzene derivatives (Neel, 1992) from aqueous solution by means of a partitioning-like mechanism (Figure 1).

Like smectite clays, most zeolites possess a net negative structural charge resulting from isomorphic substitution of cations in the crystal lattice. Due to this negative charge, natural zeolites have little or no affinity for anionic species. Surface modification with quaternary amines at the external CEC of the zeolite may neutralize the negative charge but should not reverse it. Therefore, we would expect to see little or no sorption of anions by an organo-zeolite. On the contrary, however, we have found that HDTMA-zeolite shows strong sorption of inorganic oxyanions from aqueous solution.

We report here on the sorption of chromate, selenate, and sulfate by HDTMA-zeolite and discuss the potential mechanisms for this sorption. Chromate and selenate were chosen due to their importance as environmental contaminants. Sulfate was examined since it is also a divalent oxyanion, but one less subject to chemical reduction in natural waters.

MATERIALS AND METHODS

Characterization of Zeolite

A zeolite from the St. Cloud mine near Winston, New Mexico, was selected for this work due to its relatively high clinoptilolite content. The zeolite was obtained as crushed rock aggregate and was sieved to a size range of 0.15 to 2.0 mm. The mineralogical characterization of the zeolite was determined using scanning electron microscopy and x-ray diffraction.

The CEC of the zeolite was determined using several methods. The total CEC was measured using the method of Rhoades (1982). External and internal CECs were measured using a modification of the method of Ming and Dixon (1987). In this modification, HDTMA was used for surface exchange with sodium to measure external CEC. Preliminary studies showed that the same external CEC was measured whether HDTMA or tertbutylammonium, the exchanging cation suggested by Ming and Dixon (1987), was used. The external CEC is the most useful determination for organo-zeolites since large amines are excluded from the internal exchange sites of the zeolite.

Preparation of Organo-zeolite

Experiments were conducted to evaluate the sorption characteristics of HDTMA on the zeolite and to assess the stability of the bound amine. Exchange of HDTMA with externally bound cations of the zeolite to form an organo-zeolite was measured using $^{14}C-CH_3$-labeled HDTMA obtained from American Radiolabeled Chemicals, Inc., St. Louis, Missouri. Aqueous solutions, containing HDTMA at equivalent concentrations to satisfy percentages between 0 and 666% of the external CEC, were spiked with the ^{14}C-HDTMA. Five grams of natural zeolite and 20 mL of the radiolabeled HDTMA solution were placed in a 50-mL Oak Ridge polyallomer centrifuge tube. All initial conditions and appropriate blanks were prepared in duplicate. The tubes were mechanically shaken for 24 h at 25°C and centrifuged. Preliminary experiments proved that 24 h was sufficient to attain equilibrium. HDTMA retention by the zeolite was determined from the difference between ^{14}C-HDTMA in solution before and after equilibration.

Preparation of HDTMA-zeolite for batch sorption studies included sorption of the amine at a specified external CEC ratio followed by rinsing with distilled water to remove excess or loosely bound HDTMA. To estimate the amount of HDTMA which is 'permanently' sorbed following rinsing of the zeolite, a preliminary study was conducted using radiolabeled organo-zeolite modified at the varying external CECs described previously. Sorption of HDTMA at equilibrium conditions was determined as described above. After decanting the equilibrium solution, 10 milliliters of distilled water was added to the sample. The sample was mechanically shaken for 15 minutes at 25°C, centrifuged, and decanted. This process was repeated for a total of 5 rinses. An aliquot of the rinsate was then analyzed for ^{14}C-HDTMA and this mass accounted for when determining the total amount of HDTMA bound to the surface.

Stability studies were conducted over a 72-h period to determine how strongly the HDTMA molecules were bound to the zeolite's charged sites. For these experiments, HDTMA-zeolite was prepared as described above using an amount of ^{14}C-HDTMA equal to 100% of the zeolite external CEC. The organo-zeolite was rinsed several times with distilled water and air-dried. The rinsate was analyzed for ^{14}C-HDTMA to determine the mass of amine bound to zeolite. The radiolabeled organo-zeolite was subjected to solutions of extremes in buffered pH (3, 5, and 10) and in ionic strength (1.0 *M* $CaCl_2$ and 1.0 *M* CsCl), and to organic solvents (benzene, toluene, methanol). Twenty milliliters of each of these solutions was added to Teflon centrifuge tubes containing 2.5 g of the radiolabeled organo-zeolite and mechanically shaken at 25°C. Duplicate samples and appropriate blanks were prepared for each solution concentration. Aliquots of the solutions were extracted at intervals during the 72-h period and analyzed for ^{14}C-HDTMA.

For the batch sorption isotherm experiments described below, HDTMA was added in amounts equal to 50%, 100%, and 200% of the external CEC of the zeolite. To accomplish this, 40 g of zeolite and 120 mL of the appropriate HDTMA concentration in aqueous solution were placed in a 250-mL centrifuge container. The containers were mechanically shaken for 24 h at 25°C, centrifuged, and decanted. The organo-zeolite was then rinsed with distilled water several times before air-drying and storage.

Preparation of Anion Sorption Isotherms

Sorption isotherms were prepared using natural (unmodified) zeolite and organo-zeolite. Anion solutions were prepared using potassium chromate, sodium selenate, or sodium sulfate dissolved in a 0.005 *M* $CaCl_2$ aqueous solution. Initial concentrations of the anion solutions ranged from 5 mg/L to 200 mg/L. The pHs of the solutions were measured before and after equilibration. Two and one-half grams of zeolite and 10 mL of anion solution were placed in a 50-mL centrifuge tube. Duplicate samples and appropriate blanks were prepared for each solution concentration. The tubes were mechanically shaken for 24 h at 25°C, a period shown sufficient for attaining sorption equilibrium. Each sample was centrifuged and 5 mL of the supernatant was decanted for analysis. Total chromium and total selenium were determined using atomic absorption spectrometry. Sulfate was analyzed using ion chromatography.

Batch desorption isotherms were performed on the sorption samples which had initial anion concentrations of 25, 50, and 100 mg/L. After an initial 5 mL of equilibrium solution was decanted from a sorption isotherm sample, 5 mL of 0.005 *M* $CaCl_2$ solution was added to the sample. The sample was shaken for 24 h at 25°C, centrifuged, and 5 mL of the equilibrated solution was decanted for analysis. This process was repeated until a clear desorption trend was established.

RESULTS AND DISCUSSION

Characteristics of Zeolite

Photomicrographs of the natural zeolite revealed that individual grains consisted of aggregates with no defined crystalline structure. This is consistent with typical occurrences of clinoptilolite as microcrystalline masses (Gottardi et al., 1985). The aggregates were primarily clinoptilolite (60%) and quartz (20%) with minor constituents of lithic minerals and clays. The total CEC of the zeolite was 50 me/100 g (500 mmol/kg). This value is on the lower end of typical values for clinoptilolite. The measured external CEC was approximately 15 me/100 g (150 mmol/kg).

Organo-Zeolite Properties

HDTMA sorption to the zeolite was quantitative up to its external CEC (Figure 2). More than 94% of HDTMA was bound to the zeolite when the initial HDTMA concentration was below that required to satisfy the zeolite external CEC. A sorption plateau (no increase in HDTMA sorption) occurred between 140 mmol/kg and 400 mmol/kg. This probably indicates saturation of the negatively charged sites. At higher concentrations of HDTMA, sorption increased, most likely as a result of tail-tail interaction (admicelle formation) of the sorbed alkyl chain with those of the amine in solution.

Some HDTMA was desorbed after the organo-zeolite was rinsed with distilled water (data not shown). More than 80% of the amine remained bound to the zeolite when it was modified at or below its external CEC. However, most of the HDTMA sorbed above the external CEC was easily removed from the zeolite. This indicates that, during the surface modification process, most of the HDTMA molecules sorbed to the zeolite through tail-tail interaction alone would be removed from the organo-zeolite.

The surface stability study at the 100% external CEC coverage indicated that the HDTMA was essentially irreversibly bound to the zeolite. Over a 72-hour period, less than 1% of the amine was displaced under extremes in buffered pH (3, 5, and 10) and in ionic strength (1.0 *M* $CaCl_2$ and 1.0 *M* CsCl), or after exposure to organic solvents (benzene, toluene, methanol).

Anion Sorption and Desorption

The oxyanions CrO_4^{2-}, SeO_4^{2-}, and SO_4^{2-} predominated in the pH domains of the sorption equilibrium solutions which ranged from 6.5 to 7.5, 5.8 to 7.5, and 6.0 and 7.0, respectively. The effect of variable pH on anion sorption was not determined.

As shown on Figure 3, the natural zeolite had little affinity for chromate, selenate, and sulfate. In contrast, HDTMA-zeolite effectively removed all three oxyanions from aqueous solution. Chromate was the most strongly sorbed anion at the concentration range of the experiments.

The data for the sorption isotherms were fit to the linear form of the Langmuir equation:

$$\frac{C}{S} = \frac{1}{ab} + \frac{1}{b}C \tag{1}$$

where S is the sorbed mass (mmol/kg), C is the concentration remaining in solution (mmol/L), a is the "affinity" parameter or Langmuir constant (L/mg) and b is the "capacity" parameter (mmol/kg). The values of a and b are determined by linear regression when C is plotted versus C/S. Table 1 presents the fitted Langmuir parameters for all the batch sorption isotherm experiments. The isotherm data for initial concentrations of 5 and 10 mg/L selenate and sulfate were not included in the curve fittings due to poor analytical precision for the resultant low equilibrium concentrations.

Desorption isotherms showed some apparent variability in desorption behavior among the three anions and also among different concentrations of the same anion (Figure 4). In general, however, desorption did not appear to be completely reversible for any of the anions.

Batch sorption experiments using chromate and selenate solutions were conducted with organo-zeolite modified at 50%, 100%, and 200% of the external CEC to investigate potential sorption mechanisms and to determine an HDTMA:zeolite ratio that optimized anion sorption. Figures 5 and 6 clearly show that HDTMA loading at 100% of the zeolite external CEC resulted in the highest sorption capacity for both anions. Removal of chromate and selenate from aqueous solution was reduced at both the 50% and 200% external CEC loading. The sorption data for organo-zeolite modified at 50% and 100% of the external CEC were well-described by a Langmuir-type isotherm (Table 1). For organo-zeolite modified at 200% of the external CEC, the Langmuir equation did not describe the isotherm shape as well. As discussed previously, an organo-zeolite which has been modified to satisfy 200% of the external CEC actually only retains slightly more HDTMA than needed to satisfy 100% of the external CEC. The reduced sorption observed may be due to dissociation of excess, loosely-bound HDTMA from the organo-zeolite into the aqueous anion solution. This may result in competition for the oxyanions by HDTMA in solution and HDTMA on the surface of the zeolite.

Sorption experiments were also conducted using an initial concentration of 10 mg/L chromate and HDTMA-zeolite modified to satisfy different fractions of the external CEC as shown in Figure 2. Removal of chromate from solution increased with higher HDTMA coverage up to 100% external CEC (Figure 7). Above this, chromate sorption leveled off and even decreased slightly. These results are in agreement with the batch isotherms for chromate at 50%, 100%, and 200% of the external CEC (Figure 5).

Potential Sorption Mechanisms

The reasons for sorption of the oxyanions by HDTMA-zeolite are not immediately apparent. Three potential mechanisms are 1) sorption due to admicelle formation, 2) chemical reduction of anions to less soluble forms, and/or 3) precipitation of oxyanions with HDTMA as an organic salt.

The formation of surfactant admicelles on the external surfaces of the zeolite could create a positively charged interface which would attract anions (Figure 8). For anion adsorption to occur at HDTMA loadings at or below the external CEC, the HDTMA molecules would have to form clusters of admicelles before all the zeolite exchange sites were satisfied by HDTMA. This may occur to some extent due to heterogeneities in the substrate's surface charge density. Our experiments indicate, however, that significant admicelle formation probably does not occur until the zeolite has been modified above 100% of the external CEC (Figure 2). Most of the HDTMA sorbed in excess of the external CEC, forming admicelles, was easily removed by rinsing with distilled water. This weak bonding of the substituent chains indicates that admicelles probably do not cover significant surface area of an organo-zeolite, regardless of the amount of HDTMA initially sorbed. Additionally, chromate sorption did not continue to increase beyond a modification of 100% of the external CEC (Figures 5 and 7). If this mechanism is valid, sorption should continue to increase if admicelles are occuping an increasingly larger area of the interface. Both of these observations argue against sorption of anions by admicelles as a predominant mechanism.

Chemical reduction of the metals to strongly sorbed cationic forms can be invoked as another possible mechanism for removal of anions from aqueous solution. From the following observations, we conclude that chemical reduction did not occur during sorption. At the pH ranges of the aqueous solutions of our experiments, chromium, selenium, and sulfur exist as oxyanions. When chromate was sorbed, the initially white zeolite obtained a distinct yellow color as the yellow soluble chromate was removed from solution. Chemical reduction from Cr^{6+} to Cr^{3+} would produce a change in color from yellow to green. In addition, sulfate, which is not readily reduced, was also effectively removed from solution (Figure 3). Finally, we did not observe the strongly hysteretic desorption behavior characteristic of transition metal cation sorption (Bowman et al., 1981; Elrashidi and O'Connor, 1982).

Formation of a precipitate with the HDTMA molecule is a third potential mechanism. Oxyanions may associate with the cationic 'head' of the HDTMA on the zeolite surface to form an organic salt (Figure 9). In the hydrophobic environment created by the substituent chain, the dissociation energy of the HDTMA-anion salt would be extremely large. It is known that inorganic salts dissolved in organic solvents (analogous to the HDTMA-modified surface) have much higher energies of dissociation than the same salts dissolved in water. Evidence for this mechanism includes the formation of a precipitate when chromate solution is added to HDTMA-Cl solution in the absence of zeolite. The formation of an HDTMA-anion precipitate is also consistent with the Langmuir-type sorption behavior. As demonstrated by Veith and Sposito (1977), a precipitation mechanism will yield a "sorption" isotherm which follows the Langmuir model.

Preliminary results from IR spectroscopy of both the precipitate and the surface of the HDTMA-zeolite with sorbed chromate indicate very similar spectral patterns. This is compelling evidence that sorption is probably due to complexation of the HDTMA and anion.

The interaction between an organo-zeolite and anions is likely to be dependant on many factors which have not been fully explored during this study. For instance, there is some evidence that the long alkyl substituent chain on the HDTMA molecule must play a significant role in oxyanion sorption. Other experiments (data not presented) have shown that tetramethylammonium-zeolite does not display the same affinity for oxyanions.

CONCLUSIONS

We investigated the sorption of the inorganic anions chromate, selenate, and sulfate on clinoptilolite-dominated zeolite surface modified by HDTMA. HDTMA is bound to the zeolite quantitatively (hemimicelle formation) up to the zeolite's external CEC of about 15 me/100 g. The internal surfaces remain available for sorption of smaller cations. HDTMA is essentially 'irreversibly' bound to zeolite on its external surfaces. Sorption of HDTMA beyond the external CEC is probably due to admicelle formation.

No sorption of anions occurs on the unmodified zeolite. Sorption of chromate, selenate, and sulfate is significantly enhanced on HDTMA-zeolite. Sorption is maximized when the zeolite external CEC has been fully satisfied by HDTMA.

While more than one mechanism may influence removal of inorganic anions from solution, the most likely mechanism appears to be surface precipitation of an HDTMA-anion complex.

Organo-zeolites have excellent physical and chemical characteristics for treatment of a wide variety of organic and inorganic hazardous wastes. They may be an economical alternative to other adsorbants for uses such as filtration beds or in-situ permeable barriers. Permeable barriers using organo-zeolites would allow both containment and concentration of groundwater pollutants and simplify removal and remediation efforts.

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FIGURE CAPTIONS

Figure 1. Observed and predicted sorption of benzene, toluene, and p-xylene by HDTMA-zeolite (Fig. 4-13 of Neel(1992)). Dashed lines are those predicted from the K_{ow}s based on equation 6-20 of Dragun (1988).

Figure 2. HDTMA sorption onto external surface sites of the zeolite. Sorption follows ion exchange behavior up to the zeolite's external CEC of 15 me/100gm. Beyond the external CEC, HDTMA sorption is probably due to tail-tail interaction of the amine.

Figure 3. Sorption of oxyanions to natural zeolite and to HDTMA-zeolite modified at 100% of the external CEC. Fitted lines for the natural zeolite are based on simple linear regression. Fitted lines for the organo-zeolite are based on the Langmuir equation using the parameters in Table 1.

Figure 4. Desorption isotherms for chromate (A), selenate (B), and sulfate (C) on HDTMA-zeolite at 100% of the external CEC. Filled symbols are equilibrium sorption points prior to desorption. Open symbols are desorption points.

Figure 5. Chromate sorption by natural zeolite and organo-zeolite at 50%, 100%, and 200% of the external CEC. Fitted lines are based on the Langmuir equation using the parameters in Table 1.

Figure 6. Selenate sorption by natural zeolite and organo-zeolite modified at 50%, 100%, and

200% of the external CEC. Fitted lines are based on the Langmuir equation using the parameters in Table 1.

Figure 7. Chromate sorption on organo-zeolite modified with HDTMA at 0 to 666% of the external CEC. Initial chromate concentration was 10 mg/L.

Figure 8. Admicelle formation by HDTMA molecules on zeolite substrate. Anions could potentially be retained by interaction with the organic cationic "heads".

Figure 9. Hemimicelle formation of HDTMA molecules on zeolite with surface complexation of anions and HDTMA.

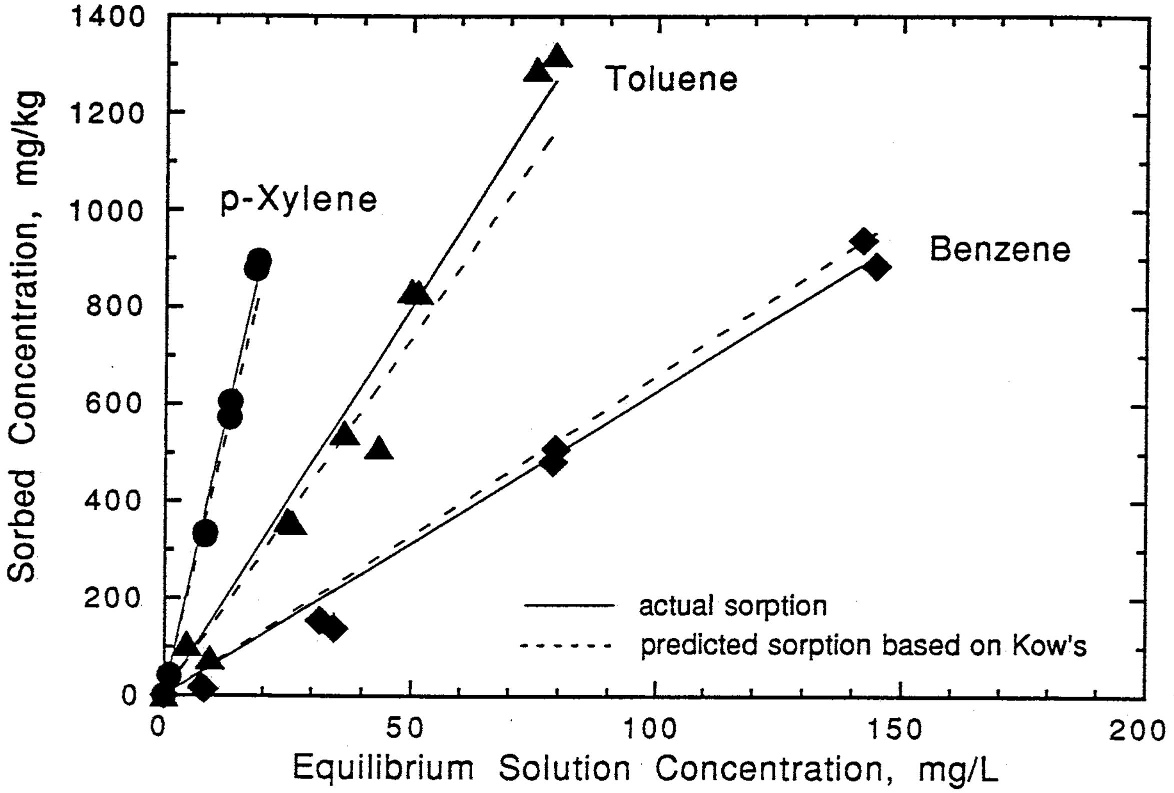

1400
1200
1000
800
600
400
200
0
0
50
100
150
200
Sorbed Concentration, mg/kg
Equilibrium Solution Concentration, mg/L
Toluene
p-Xylene
Benzene
actual sorption
predicted sorption based on Kow's

Figure 1

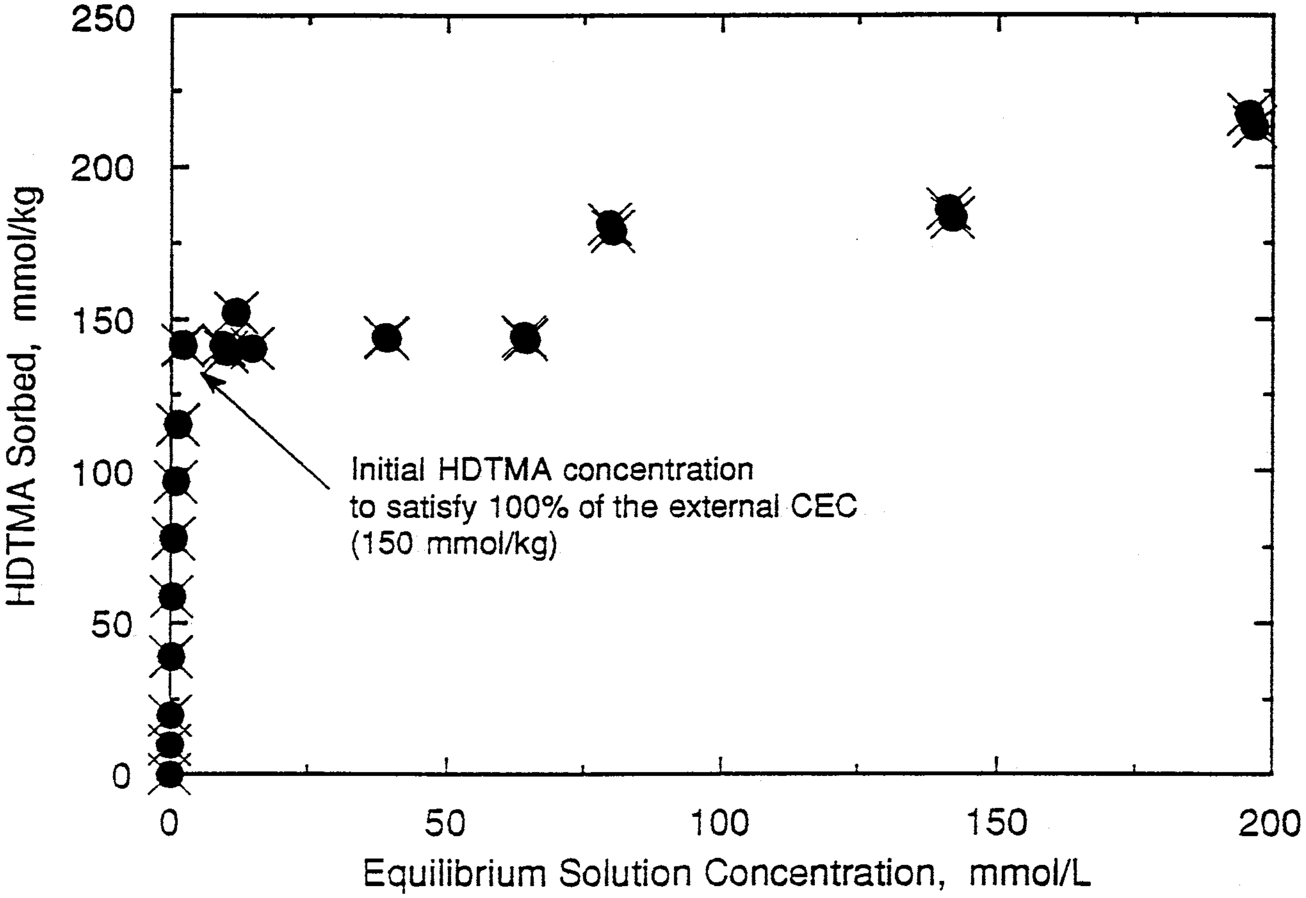

250
200
150
100
50
0
HDTMA Sorbed, mmol/kg
0
50
100
150
200
Equilibrium Solution Concentration, mmol/L
Initial HDTMA concentration
to satisfy 100% of the external CEC
(150 mmol/kg)

Figure 2

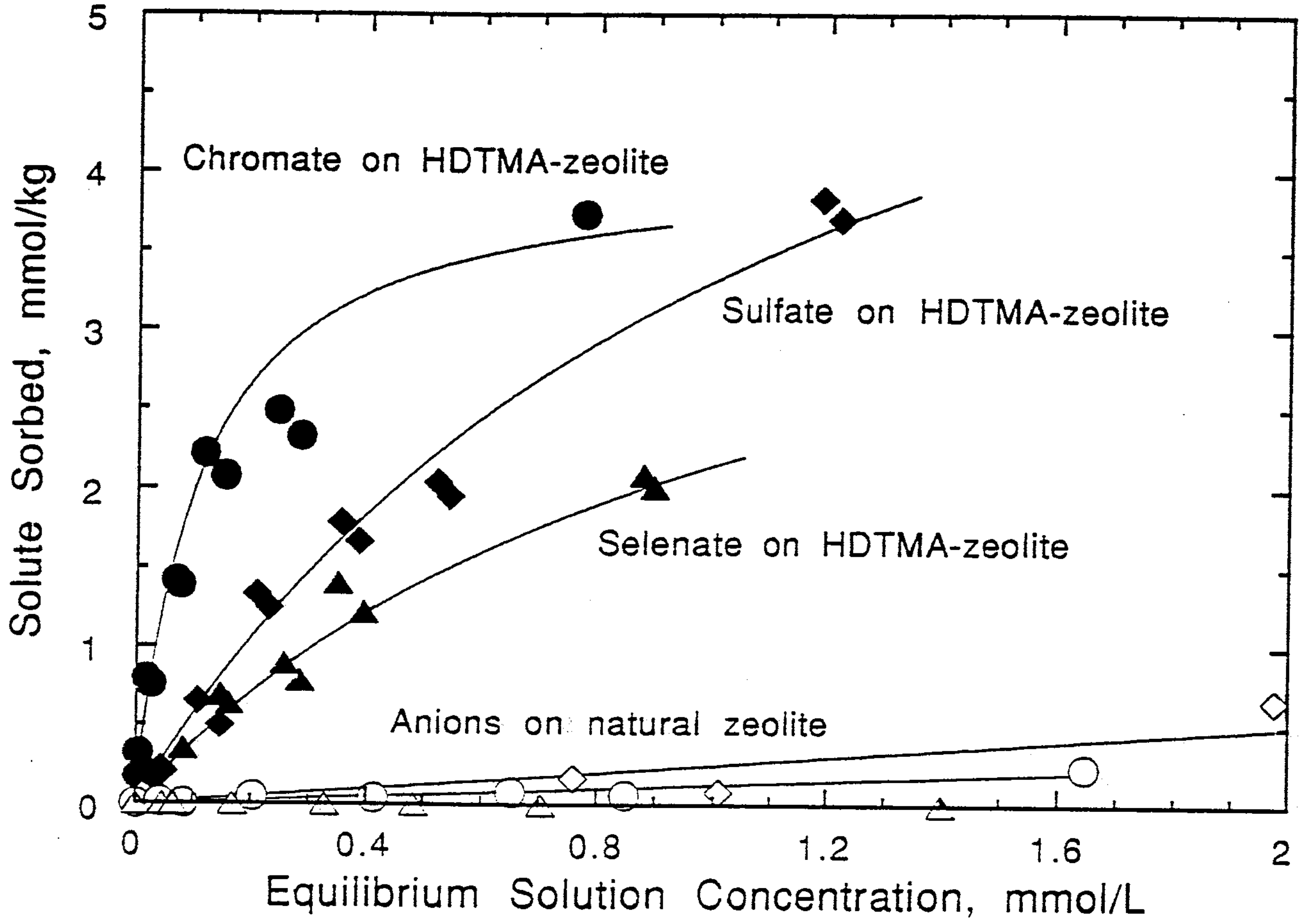

Chromate on HDTMA-zeolite
Sulfate on HDTMA-zeolite
Selenate on HDTMA-zeolite
Anions on natural zeolite
Solute Sorbed, mmol/kg
0
1
2
3
4
5
Equilibrium Solution Concentration, mmol/L
0
0.4
0.8
1.2
1.6
2

Figure 3

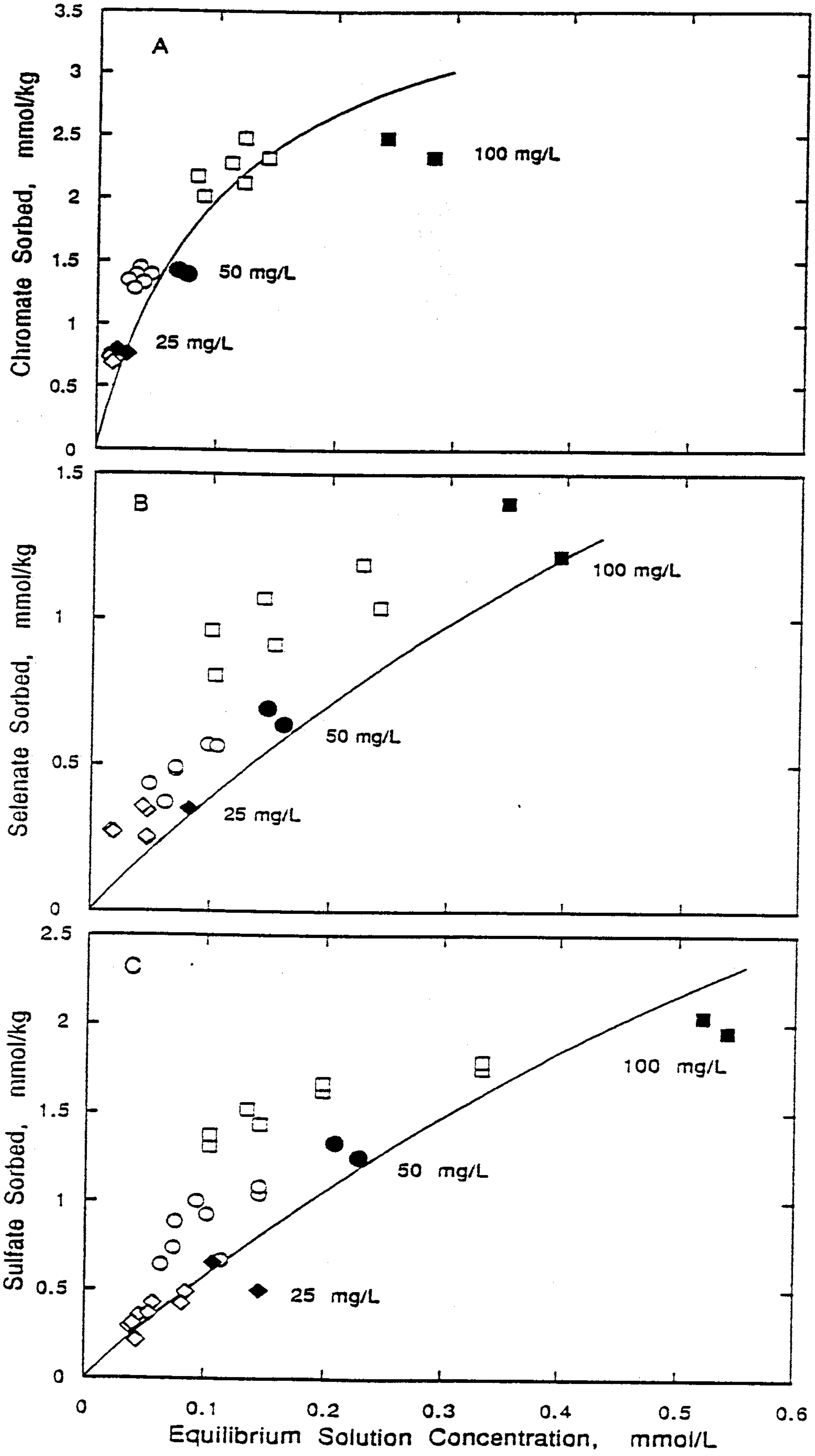
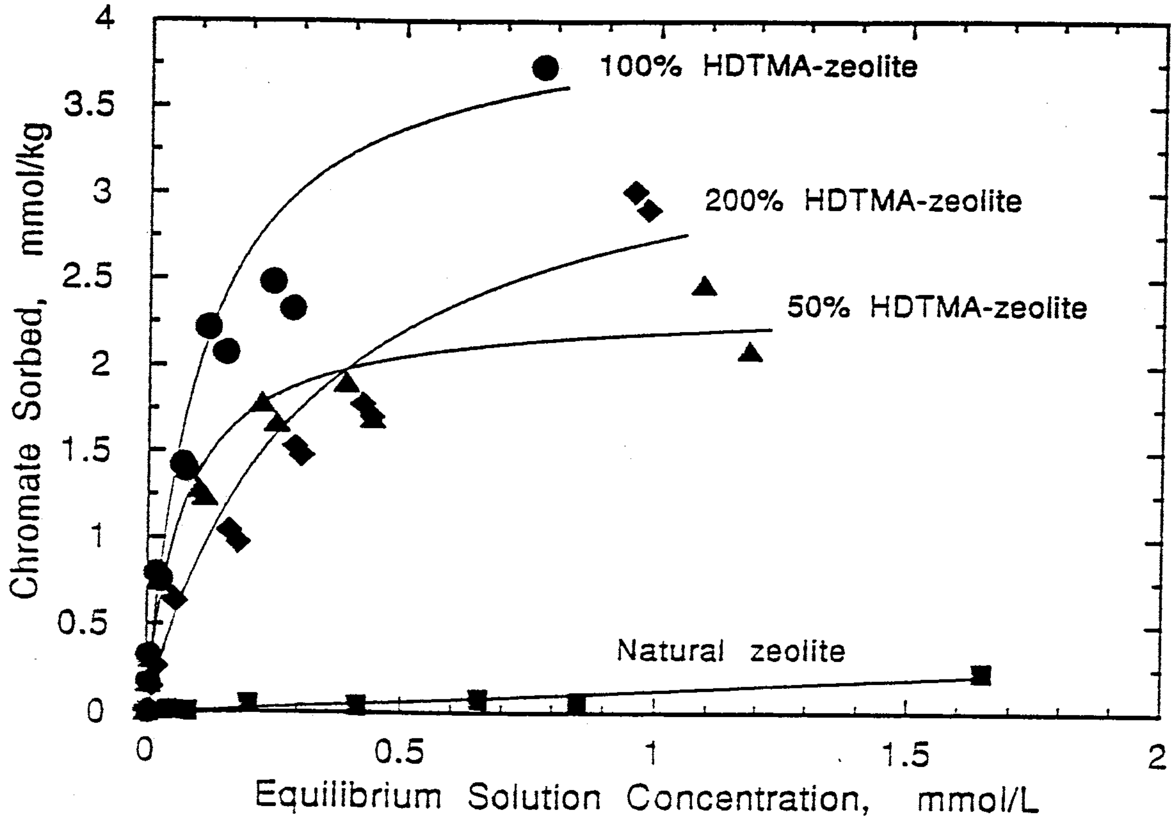

A
Chromate Sorbed, mmol/kg
3.5
3
2.5
2
1.5
1
0.5
0
100 mg/L
50 mg/L
25 mg/L
B
Selenate Sorbed, mmol/kg
1.5
1
0.5
0
100 mg/L
50 mg/L
25 mg/L
C
Sulfate Sorbed, mmol/kg
2.5
2
1.5
1
0.5
0
100 mg/L
50 mg/L
25 mg/L
0
0.1
0.2
0.3
0.4
0.5
0.6
Equilibrium Solution Concentration, mmol/L

Figure 4



4
3.5
3
2.5
2
1.5
1
0.5
0
Chromate Sorbed, mmol/kg
0
0.5
1
1.5
2
Equilibrium Solution Concentration, mmol/L
100% HDTMA-zeolite
200% HDTMA-zeolite
50% HDTMA-zeolite
Natural zeolite

Figure 5

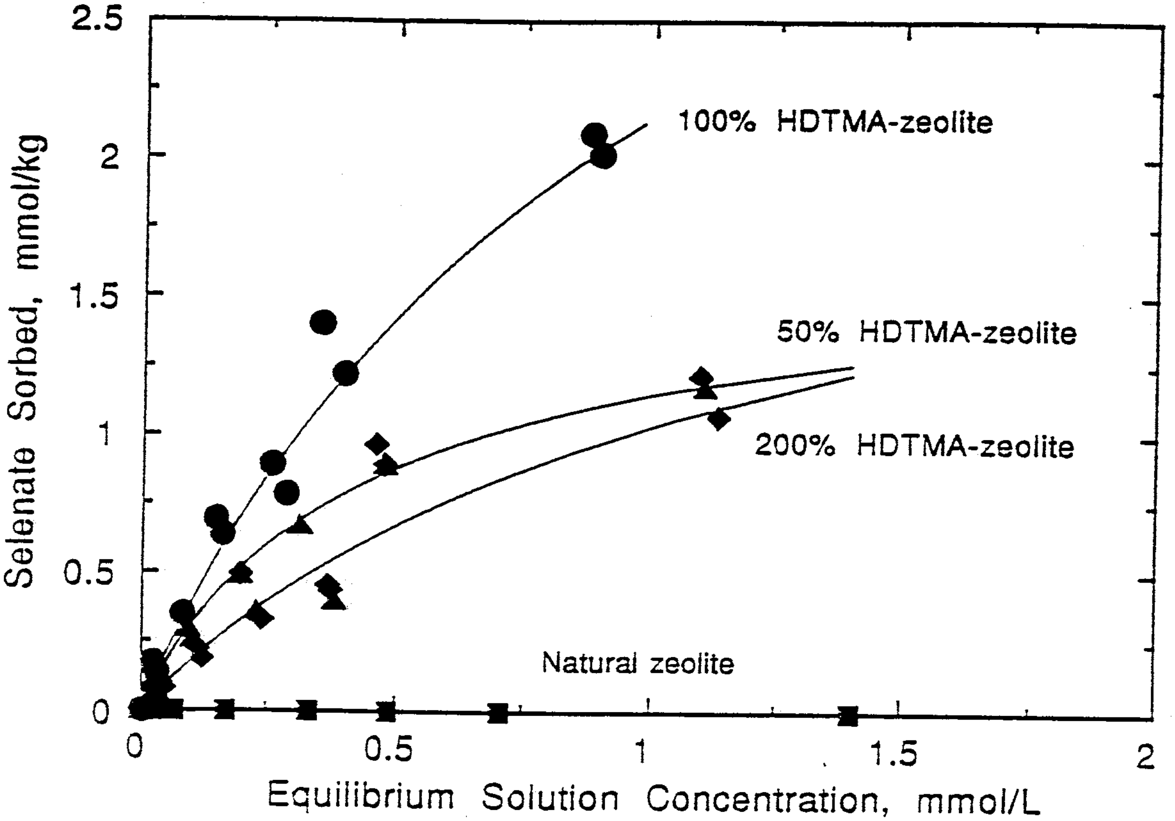
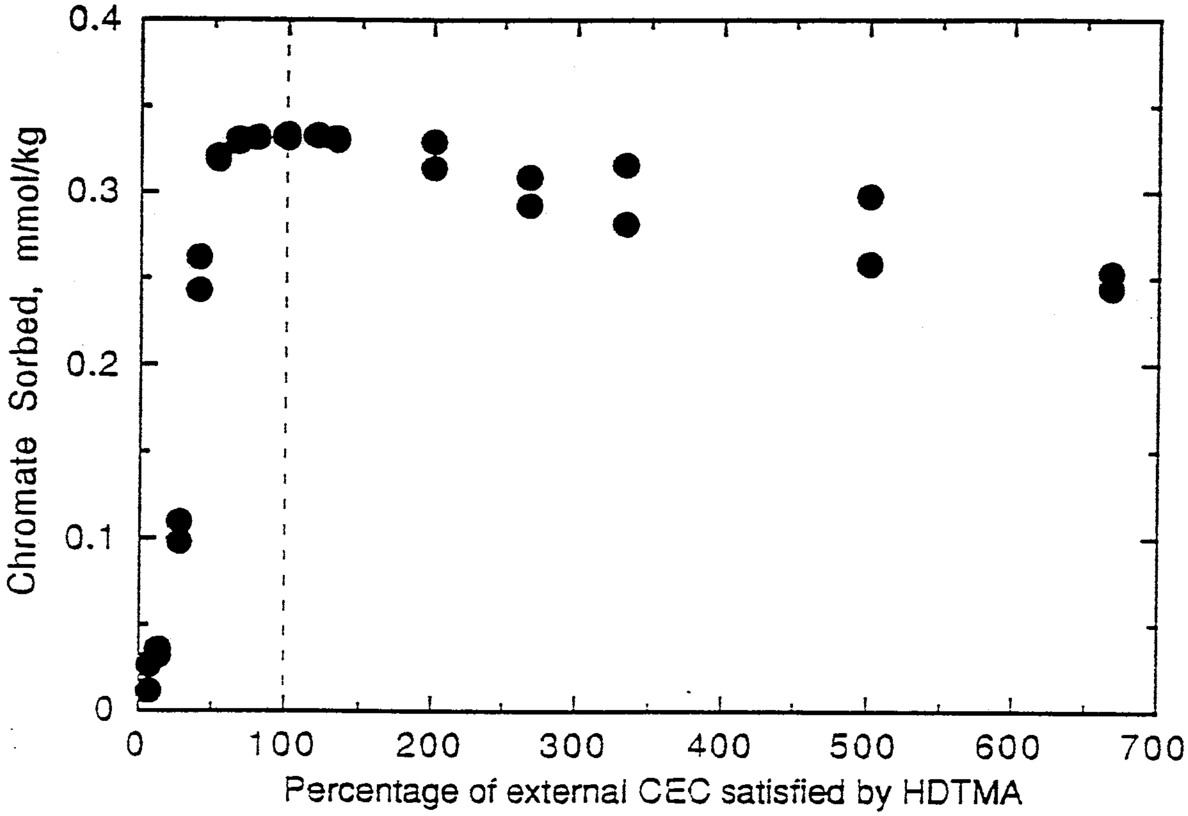

100% HDTMA-zeolite
50% HDTMA-zeolite
200% HDTMA-zeolite
Natural zeolite
Selenate Sorbed, mmol/kg
Equilibrium Solution Concentration, mmol/L
0
0.5
1
1.5
2
2.5
0
0.5
1
1.5
2

Figure 6



Chromate Sorbed, mmol/kg
0.4
0.3
0.2
0.1
0
0
100
200
300
400
500
600
700
Percentage of external CEC satisfied by HDTMA

Figure 7

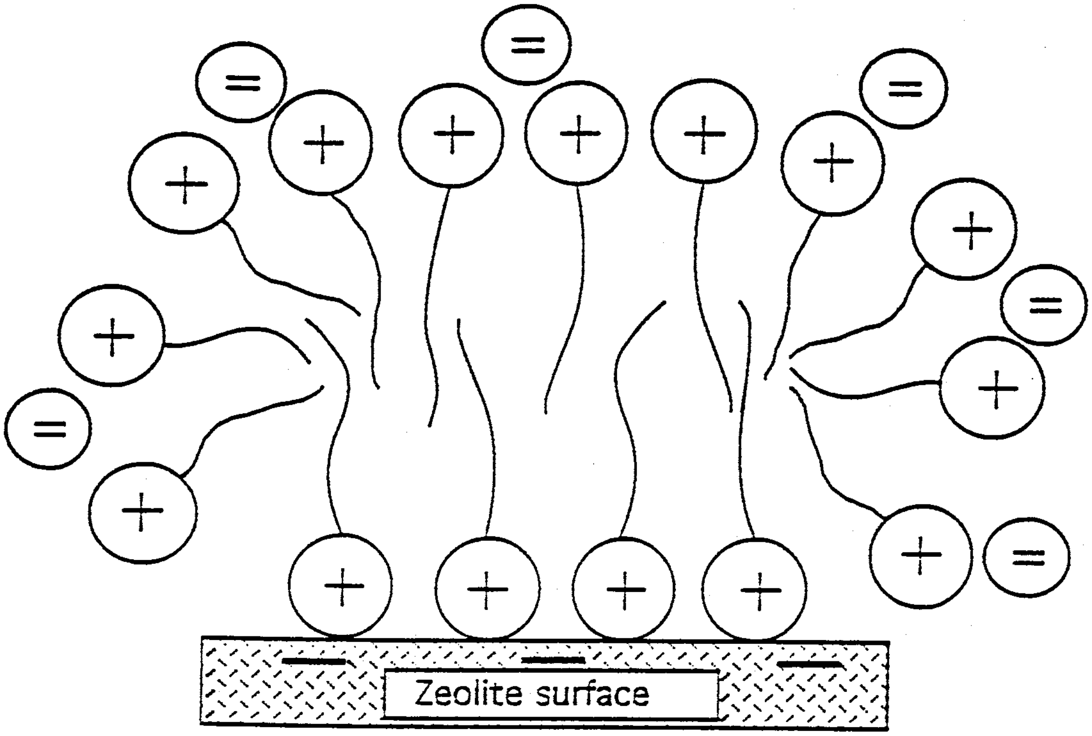


Figure 8

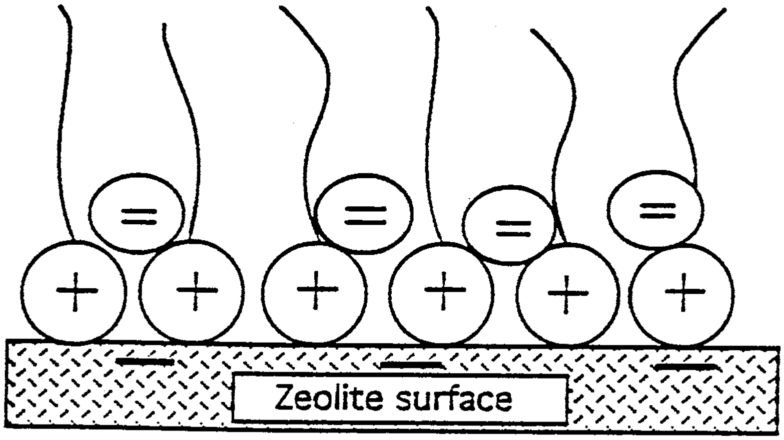


Figure 9

Table 1. Fitted Langmuir Parameters for Sorption of Chromate, Selenate, and Sulfate by HDTMA-zeolite

Anion	CrO_4^{2-}			SeO_4^{2-}			SO_4^{2-}
external CEC satisfied by HDTMA	50%	100%	200%	50%	100%	200%	100%
a, mmol/mg	2.35	4.09	3.60	1.65	4.40	2.25	7.12
b, L/mmol	13.83	9.44	3.15	2.29	0.96	0.85	0.87
R^2	0.991	0.985	0.947	0.998	0.935	0.553	0.921

APPENDIX A

ZEOLITE CHARACTERIZATION

The zeolite selected for this study was from a mine located near Winston, New Mexico. The mine is owned by the St. Cloud Mining Co. of Truth or Consequences, New Mexico. Previous studies by NMSU and NMT have used samples of this zeolite for experimentation. The zeolite was named the Winston in NMSU studies (Cazares-Rivera) and the St. Cloud in NMT studies (Flynn, 1993; Neel, 1992). It will be called the St. Cloud zeolite in this study as well.

This appendix compiles the results of the physical and mineralogical characterization which have been performed on the St. Cloud zeolite by NMT, NMSU, and the Gold Hill Research Co. The purpose of presenting results from this study as well as summarizing results from previous studies is to provide as complete a description of the zeolite to date as possible. It should then be easier to determine what, if any, further characterization is necessary for future work. X-ray diffraction results (Appendix. A1), scanning electron photomicrographs (Appendix A2) and cation exchange capacity determinations (Appendix A3) are the major sections in this appendix. Appendix A1 is further divided into results of analyzes by NMT (A1.1) and results obtained in other studies by NMSU and the St. Cloud Mining Co. (Appendix A1.2).

Appendix A1

Mineralogical Studies

A1.1 XRD analysis of NMT sample

The St. Cloud zeolite used for this study was supplied as a crushed rock aggregate commercially available as a food supplement for cattle ('cow chow'). The zeolite was sieved to a size range of 0.15 to 2.0 mm. A sample of sieved zeolite was analyzed by x-ray diffraction and microscopic examination by New Mexico Bureau of Mines and Mineral Resources. Their report is attached (Attachment A1.1). The sample consisted of clinoptilolite and quartz with some minor amounts of biotite, phlogopite or muscovite, and lithic fragments. Percentages of minerals were not provided. The zeolite composition provided in Chapter 2 is from Cazares-Rivera (1992). Results of their characterization are discussed briefly in Appendix A1.2.

Attachment A1.1 XRD Report

MEMO

DATE December 11, 1992
TO G. Haggerty
FROM C. McKee CJM
SUBJ. Analyses of Samples

The raw zeolite sample was ground in the WC grinding set of our Spex Mixer/Mill. X-ray diffraction analysis of the sample shows the presence of clinoptilolite and quartz.

J. Renault looked at the sample under a microscope and found biotite, a second mica (phlogopite,muscovite?), and what appeared to be lithic fragments probably volcanic.

Two splits of the raw zeolite was analyzed by x-ray spectrometry using a fundamental parameters method. The results are listed on the attached sheet.

I hope this helps you out.

	92K16A	92K16B
SiO_2	69.8	68.4
TiO_2	.17	.18
Al_2O_3	11.9	11.9
Fe_2O_3T	1.25	1.25
MgO	.72	.72
CaO	2.87	2.83
Na_2O	.47	.44
K_2O	2.05	2.04
MnO	.05	.05
P_2O_5	.02	.02
LOI	12.46	12.63
S	.007	.009
Total		
Ga		
Zn		
Cu		
Ni		
Ba		
V		
Cr		
Pb		
Th		
Rb		
U		
Sr		
Y		
Zr		
Nb		
Mo		

A1.2 Analyses of St. Cloud zeolite by others

Mineralogical characterization by x-ray diffraction was also performed by NMSU on a sample of the St. Cloud zeolite (Cazares-Rivera, 1992). The zeolite used in the NMSU studies was obtained at the same time NMT obtained their zeolite. NMSU also used 'cow chow' but the size range used is uncertain. To the best of my knowledge, no grain size separation was performed for their analyses. Their samples contained approximately 61% clinoptilolite, 20% quartz, 10% clay, and minor amounts of feldspar and cristobalite.

In his dissertation, Cazares-Rivera also reports the results of BET isotherm analyzes using N_2 performed by Sandia National Laboratories. They found the specific surface area to be 14.9 m^2/g. Cazares-Rivera noted that for the specific surface area obtained, the zeolite was heated to 100° C. According to Cazares-Rivera, at this temperature most of the water contained within the internal structure of the zeolite probably was not expelled. For the purposes of his calculations, he assumed that this surface area represents the external area only.

X-ray diffraction and thin section analyses were performed on several zeolite samples by a contractor for the St. Cloud Mining Company. Sections of their report are included as Attachment A1.2. They estimated the zeolite content to be approximately 84%. The zeolite type was identified as clinoptilolite. The remaining sample appeared to be volcanic glass, feldspar, and hematite.

Attachment A1.2 Gold Hill Geological Research report

FILE: ZEOLITES

GOLD HILL GEOLOGICAL RESEARCH

Post Office Box 3883
Albuquerque, New Mexico 87190 U.S.A.

Telephone
(505) 265-3716

November 21, 1990

Mr. Bernie Bockisch
St. Cloud Mining Company
P.O. Box 1570
Truth or Consequences, N.M. 87901

Dear Mr. Bockisch:

I labeled the one (1) thin section I prepared as Clino-1 because the sample was unnamed. The report about them is found below.

Thin Section Clino-1

Zeolite - 84% of rock (0.01 - 0.03mm)
Colorless, resemble fibrous flakes, very weak birefrigence and relief. Extinction angle: 8° to 11°. Probably Clinoptilolite.

Volcanic Glass - 12% of rock (0.1 - 0.3mm)
Reddish brown, some show banding.

Feldspar - 3% of rock (0.1 - 0.2mm)
Anhedral to subhedral laths and squares, found within volcanic glass. A few show Carlsbad twinning. The fine grain size made it impossible to determine composition of Feldspar, but high refractive index suggest it is Plagioclase Feldspar.

Hematite - 1% of rock (less than 0.03mm)
Red, as anhedral aggregates (0.1 - 0.3mm).

Clinoptilolite, according to Dana (1932) is a crystallized Mordenite which is a dimorphoris form of Ptilolite, Monoclinic, with a large extinction angle and he gave it the name Clinoptilolite. It would, therefore, have a chemical formula which is listed in Dana (1932) as: $[(Ca, Na_2) O.Al_2 O_3.9 SiO_2.6 H_2O]$.

The samples small grain size made identification difficult because no crystal outlines were observed. A larger grained sample or a rock sample for future thin section work may eliminate this problem.

The fine grain size of the sample minus 200 mesh (= 0.074mm = 0.0029 in.) created major problems with a sample preparation because the sample would not absorb Epoxy using standard vacuum impregnation techniques. The material had to be slowly stirred into the Epoxy before it was put under a vacuum. Stirring may have further reduced the grain size of any Zeolites present in the sample.

If you have any questions, please call me.

Sincerely,

Thomas A. Parkhill

Thomas A. Parkhill, M.S.
Geologist-Petrographer

Hazen Research, Inc.
4601 Indiana St. • Golden, Colo. 80403
Tel: (303) 279-4501 • Telex 45-860
FAX: (303) 278-1528

DATE	October 9 1990
HRI PROJECT	002-79-X
HRI SERIES NO.	I222/90
DATE RECD.	9/18/90
CUST P.O.#	None Recd

St. Cloud Mining Company
Mr. Bernard F. Bockisch
Post Office Box 1670
Truth or Consequences New Mexico 87901

REPORT OF ANALYSIS

SAMPLE NUMBER	SAMPLE IDENTIFICATION	Free Silica as SiO2 %
I222-1	Clinoptilolite	1.0

By:

Robert Rostad
Laboratory Manager

To: Bernie

What are these

1/5/90 PBV

SKYLINE LABS, INC.
SPECIALISTS IN EXPLORATION GEOCHEMISTRY
12090 WEST 50TH PLACE • WHEAT RIDGE, COLORADO 80033 • TEL.: (303) 424-7718

TO: PAT

REPORT OF SPECTROGRAPHIC ANALYSIS

FROM EAST OF STONE
HOUSE - WHITE CLI
BB

JOB NO. JYD 003
December 22, 1989

St. Cloud Mining Company
Attn: Bernard F. Bockisch
P.O. Box 1670
Truth or Consequences, N. M. 87901

cc/ Bernie - Please get
sample to Tech for
petrographic work
mineral/rock i.d.

Analysis of 2 Pulp Samples

PBV 1/15/90
File: Stone H.
Zeolites

The attached pages comprise this report of analysis. Values are reported in parts per million (ppm), except where otherwise noted, to the nearest number in the series 1, 1.5, 2, 3, 5, 7, 10, etc. within each order of magnitude. These numbers represent the approximate boundaries and midpoints of arbitrary ranges of concentration differing by the reciprocal of the cube root of ten. The 'accepted' value is considered to be within + or - 1 step of the range reported at the 68 % confidence level and within + or - 2 steps at the 95 % confidence level.

Gordon H. VanSickle
Manager

ITEM NO. SAMPLE NO.
1 = #4
2 = #5

ITEM	1	2
ELEMENT		
Fe	0.5%	1%
Ca	0.2%	0.3%
Mg	0.2%	0.3%
Ag	<1	<1
As	<200	<200
B	10	10
Ba	300	300
Be	3	3
Bi	<10	<10
Cd	<50	<50
Co	<5	<5
Cr	<10	<10
Cu	30	15
Ga	10	20
Ge	<20	<20
La	30	50
Mn	300	300
Mo	<2	<2
Nb	<20	<20
Ni	<5	<5
Pb	10	20
Sb	<100	<100
Sc	<10	<10
Sn	<10	<10
Sr	200	200
Ti	700	2000
V	20	30
W	<50	<50
Y	<10	20
Zn	<200	<200
Zr	50	150

4/3/90

New Mexico Tech
Socorro, NM 87801
Department of Mining, Environmental & Geological Engineering
(505) 835-5345

29 March, 1990

Mr. Bernie Bockisch
Project Geologist
St. Cloud Mining Company
P.O. Box 1670
Truth or Consequences, New Mexico 87901

Dear Bernie:

Enclosed please find x-ray diffraction results for two samples I prepared from suspected zeolitized tuff specimens you submitted in late January.

Sample preparation comprised crushing of homogeneous chips taken from several specimens; each of the two prepared samples contained chips from several tuff samples. Chip samples were crushed under acetone, then dropped by pipette onto a glass slide. Each sample was x-ray analysed (attached), and the x-ray pattern then examined. Because quartz and sanidine phases were suspected to be present in the tuffs, these peaks were identified initially; remaining peaks were then identified.

Clinoptilolite (zeolite) is the major phase in the samples; I also checked for other zeolites (chabazite, present at Bowie, Arizona; hormotome-group; and analcime); results were negative. It is concluded that clinoptilolite is the major zeolite phase in the St. Cloud samples, with minor quartz and sanidine. Note that a detailed analysis of samples for quantitative zeolite content and mineralogy would be complicated, and should be completed prior to contemlation of any potential uses for the zeolite. Your commentary regarding possible food supplement use for the zeolite is appropriate if the clinoptilolite occurs in sufficient quantities and can be extracted in such form as to be suitable for animal vitamin/antibiotic hosting.

I would like to recommend that you get in touch with a geologist who is familiar with zeolite uses and applications; Mr. Ted Eyde, Box 5
397-4530 GSA Resources, Cortaro, Arizona 85652. This man and his son, Daniel Eyde, are well-known in the industrial minerals field for their saavy of zeolite systems and may be able to help St. Cloud in assessment of the feasibility of using this clinoptilolite zeolite as an industrial mineral resource. If I can assist you in any other way, please let me know (or contact James Barker, Industrial Minerals Geologist, at the Bureau of Mines here in Socorro; 835-5114), as I would be happy to help.

Bernie, thanks for your consideration during the University of Cincinnati visit last week; we all had a great time and appreciate your time and efforts.

Best Regards,
Bill

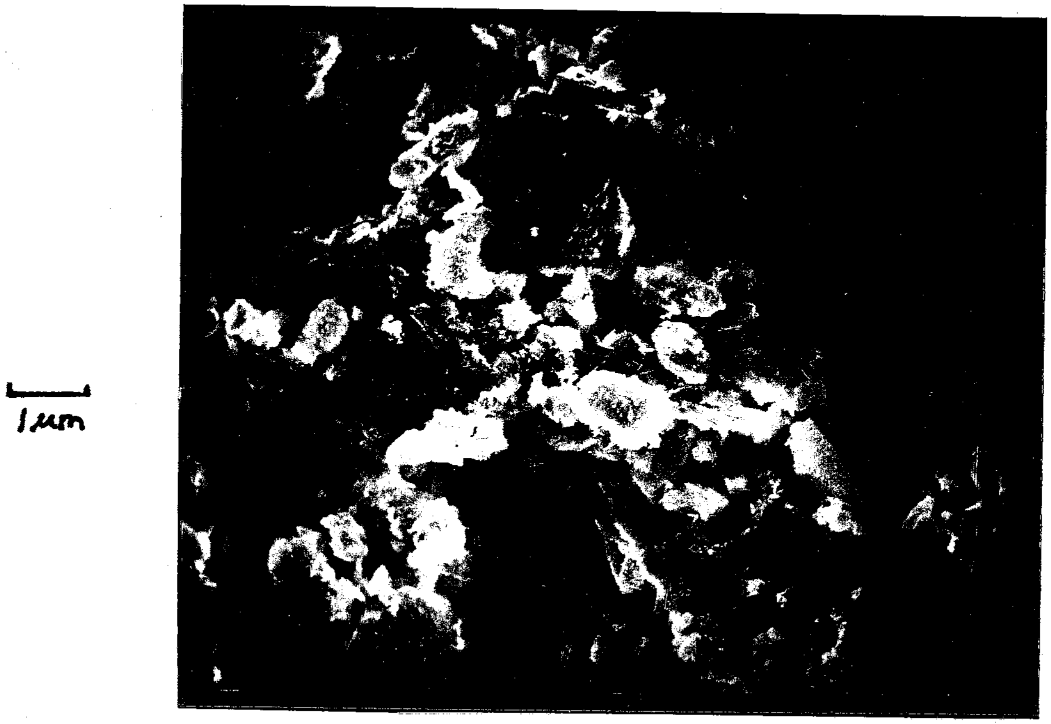
Appendix A2

Scanning Electron Microscopy

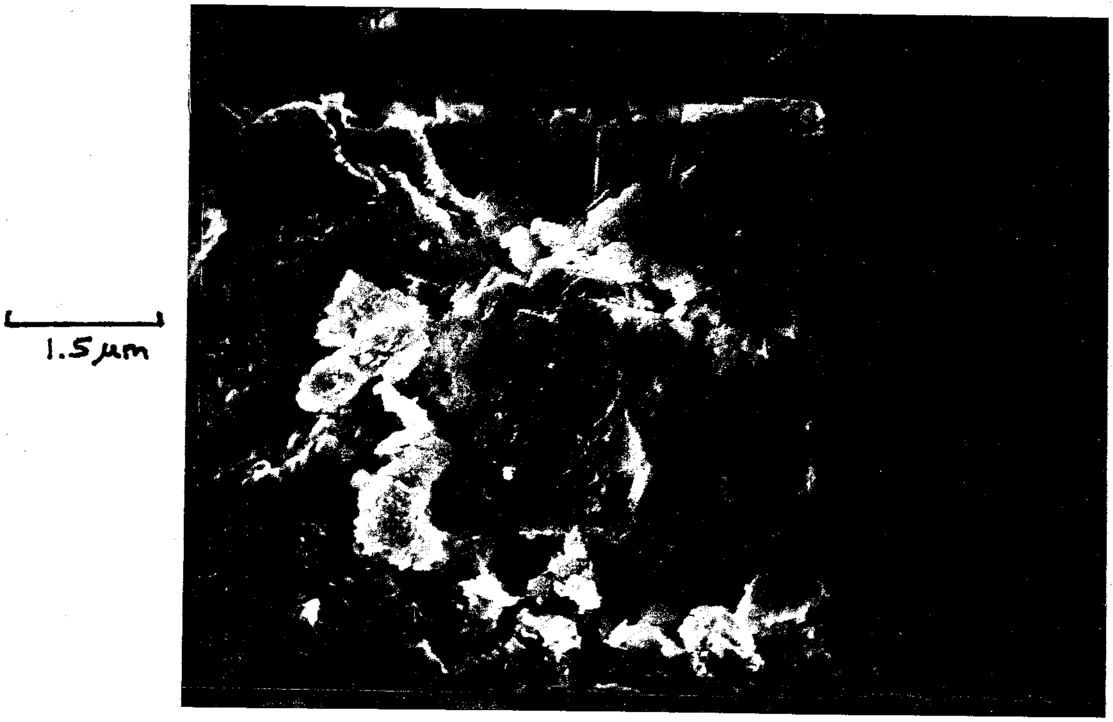
Photomicrographs of natural and organo-zeolite (size range of 0.15 mm and 2.0 mm) were prepared using the scanning electron microscope (SEM) at the NMT Metallurgy Department. These photomicrographs revealed that individual grains consisted of aggregates of particles with no defined crystalline structure. The aggregates appeared to be porous and particles were loosely cemented by amorphous materials.

In comparison to natural zeolite (Figures A2.1 and A2.2), the organo-zeolite appeared more amorphous and may have been either 'coated' (perhaps with HDTMA) or finer grained (Figure A2.3). Figure A2.4 shows an organo-zeolite with sorbed chromate.

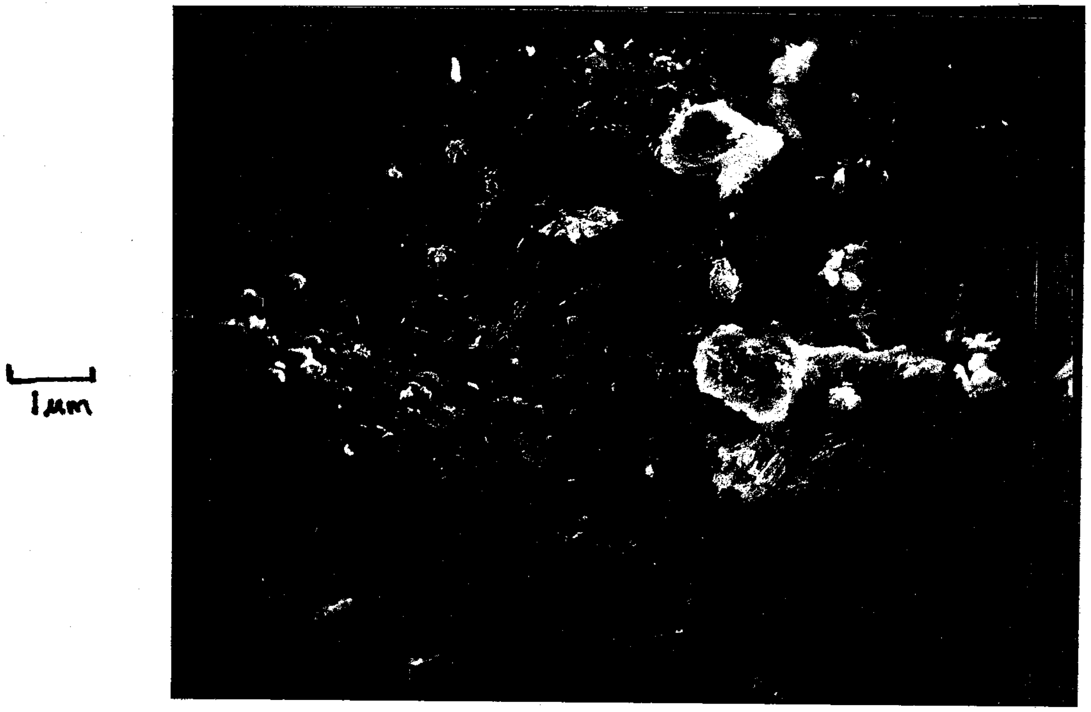
Figures A2.5 and A2.6 are enlargements of Figures A2.2 and A2.3, respectively. Huddleston (1990) noted that HDTMA tended to break the zeolite aggregates in his study into finer-grained particles. This was also observed during this study when the St. Cloud zeolite was surface-modified. It is reasonable to expect some physical change to occur with surface modification, however based on the samples examined with SEM, it was not clear if the differences noted between the natural and organo-zeolite were actually a result of a change in the physical character of the modified zeolite or natural heterogeneities of the zeolite aggregates.



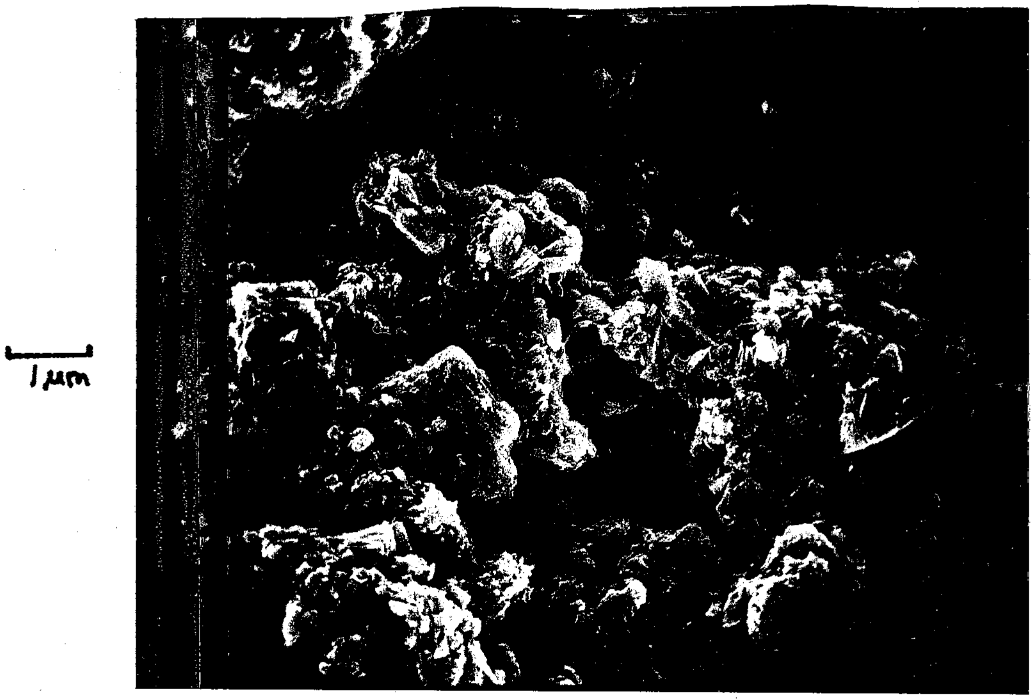
Appendix Figure A2.1. Scanning electron photomicrograph of unmodified St. Cloud zeolite.



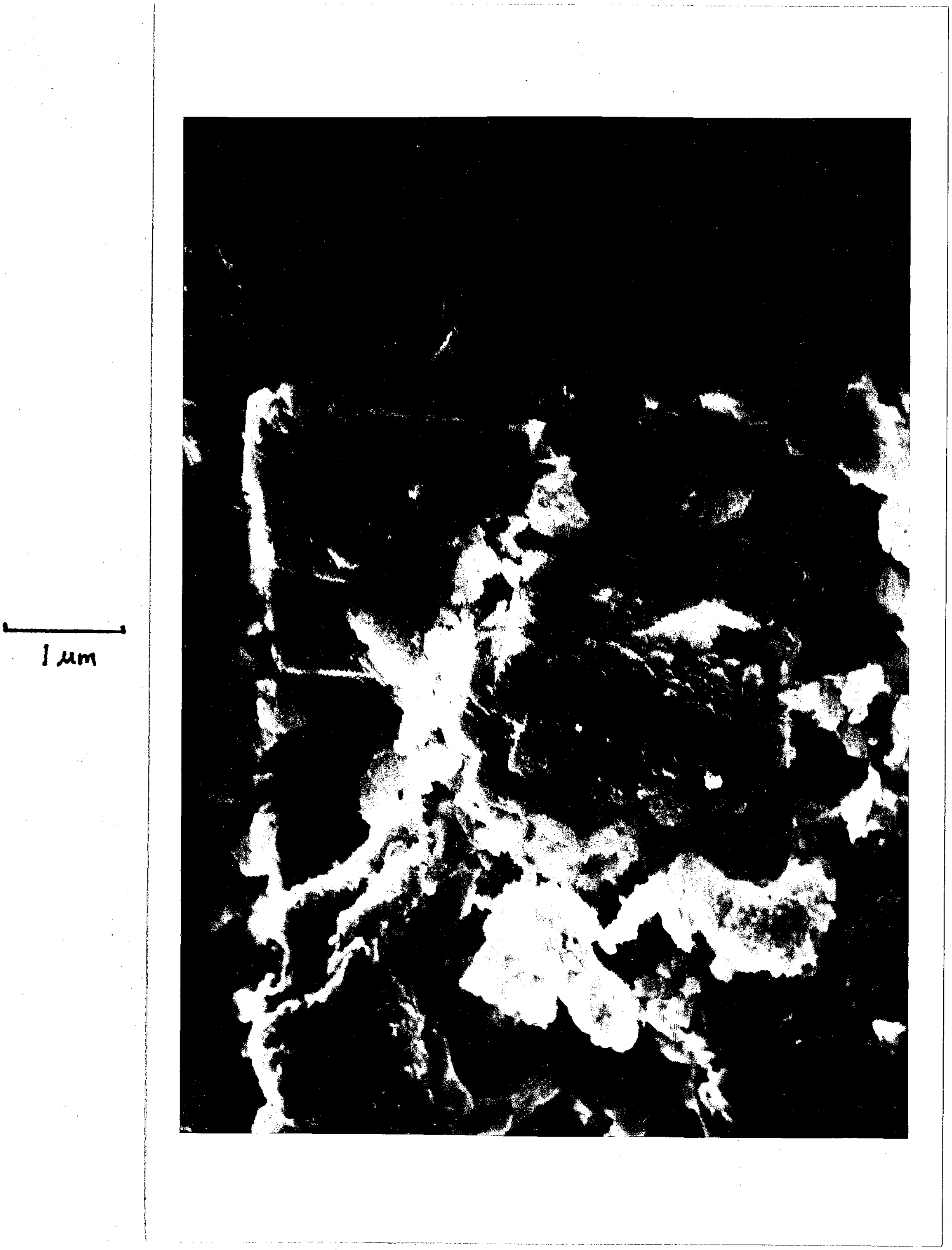
Appendix Figure A2.2. Enlargement of Appendix Figure A2.1. showing zeolite crystal.



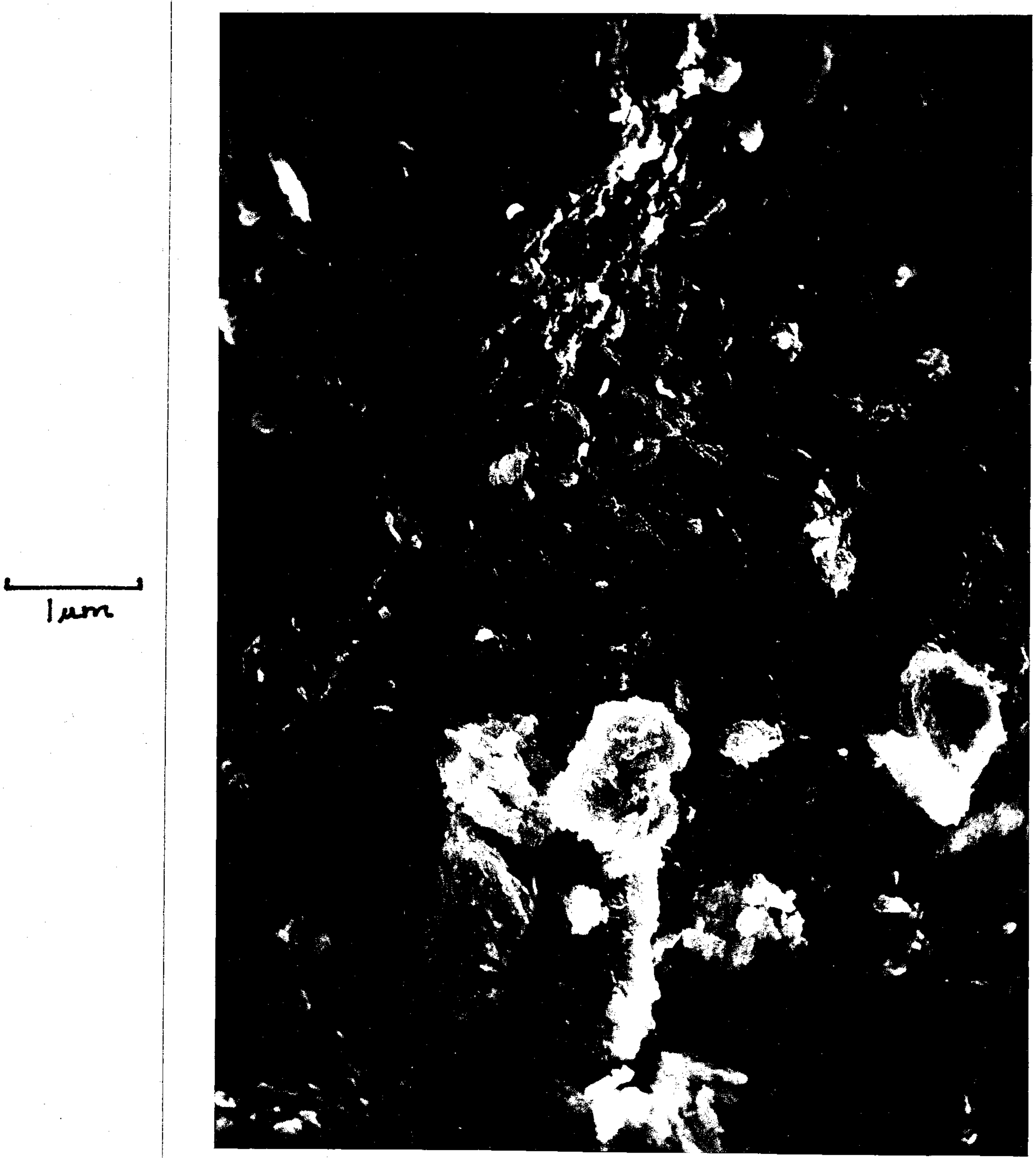
Appendix Figure 2.3. Photomicrograph of HDTMA-modified St. Cloud zeolite.



Appendix Figure A2.4. Photomicrograph of HDTMA-modified St. Cloud zeolite with sorbed chromate.



Appendix Figure A2.5. Enlargement of Figure A2.1.



Appendix Figure A2.6. Englargement of Figure A2.3.

Appendix A3

Cation Exchange Capacity Determinations

Two methods were used to determine the cation exchange capacity (CEC) of the St. Cloud zeolite. The method of Rhoades (1982) was used to estimate the total CEC of the zeolite. The method of Ming and Dixon (1987) was used to estimate a CEC for the external sites and a CEC for the internal sites of the zeolite. The Ming and Dixon (1987) method was modified by researchers at NMSU and NMT. At NMT, the quaternary amine HDTMA was used instead of the organic cation tertbutylammonium suggested by the Ming and Dixon (1987) method. NMSU used tetramethylammonium (TMA) as the exchanging cation. The procedures and modifications for the CEC determinations are described in greater detail in Huddleston (1990), Flynn (1993), and Cazares-Rivera (1992). Flynn performed a preliminary study to determine if tertbutylammonium and HDTMA were interchangeable for the external CEC determination. Additionally, the external CEC for the St. Cloud zeolite was determined in this study using HDTMA as the exchanging cation. The results of the various CEC determinations are listed in Table A3.1 *Summary of CEC values for St. Cloud zeolite*. The variations in CEC values obtained in the three studies may be due to differing mineralogical compositions of the zeolite samples used for the determinations or in differences in procedure or analytical precision.

A check on the external CEC of the zeolite is through comparison of the external CEC results with sorption results obtained using ^{14}C-HDTMA (Appendix B). Sorption of ^{14}C-HDTMA is quantitative to about 140 mmol/kg. Using the method of Ming and Dixon (1987), I determined the external CEC of the zeolite to be about 150 mmol/kg. These values compare fairly well. The external CEC used in this study for surface modification of the St. Cloud zeolite was 150 mmol/kg (15 me/100g).

Table A3. 1. Summary of CEC values for St. Cloud zeolite

CEC (me/100g)	Reference Flynn (1993)	 Cazares-Rivera (1992)	 This study
Total CEC*	84	50	-
Internal CEC**	52	-	-
External CEC**			
tertbutyl	20.5	-	-
TMA	-	15	8
HDTMA	21.6	-	15

* total CEC by the method of Rhoades, 1982

** internal and external CEC by the method of Ming and Dixon, 1987

The size and shape of the organic cation will affect its sorption capacity to a zeolite. Most of the organic cations are larger than the exchangeable cations they replace (Na, K). If the charge density of the zeolite is very high, as is reported by Cazares-Rivera (1992) for the St. Cloud zeolite, there may not be sufficient space on the surface of the zeolite to allow for a one to one exchange (i.e. 1 HDTMA: 1 Na). Therefore, the external CEC is actually a variable, depending on the specific organic cation. The maximum sorption capacity by ion exchange of a particular amine should be quantified before assuming that the amine sorbs at the external CEC determined using the method of Ming and Dixon. This can be done either by measuring sorption of a ^{14}C-spiked organic cation to the zeolite or by determining the external CEC by the method of Ming and Dixon using the specific organic cation of interest.

APPENDIX B

SORPTION OF HDTMA BY ST. CLOUD ZEOLITE

Appendix B1

Surface Modification Procedures

The procedure for surface modification of the zeolite used during this investigation has been modified from the method described by Huddleston (1990), and used by both Neel (1992) and Flynn (1993). One major difference in the procedure used for this study is the change in the stock solution. For all experiments prior to August 1992, an aqueous solution of 25% by weight HDTMA chloride (obtained from Aldrich Chemical Co., Milwaukee, WI) was used as the stock solution. This solution contains an unknown concentration of salts probably used to raise the aqueous solubility of HDTMA. The manufacturer was unable to provide information on the composition of aqueous phase. Therefore, solid HDTMA bromide (also obtained from Aldrich Chemical Co.) was chosen as the stock solution for all experiments performed in this study (unless otherwise noted). The aqueous solubility of the solid HDTMA bromide is lower (reportedly 100 g/L) than the concentration in the HDTMA chloride stock solution.

The following procedures were used to modify the St. Cloud zeolite for the experiments conducted during this investigation. Several modifications to these procedures are suggested following their description.

Initial Treatment of Zeolite

- Zeolite is sieved to a medium to fine grained size (0.15 to 2.0 mm).

- Zeolite is then treated with a 1.0 *M* sodium acetate-acetic acid pH 5 buffer to remove any $CaCO_3$ coating. Approximately 200 g of zeolite is placed in a glass container to which 500 mL of buffer solution is added. The mixture is replaced after approximately 24 hours with fresh buffer solution. After an additional 24 hours, the spent solution is decanted and the zeolite is rinsed by adding about 500 mL of distilled water to the zeolite, stirring the mixture, and decanting the rinsate. This process is repeated three to five times. The zeolite is then filtered, and air dried on a buchner funnel. After the zeolite is dried, it is placed in a plastic container for storage. (Note: The St. Cloud zeolite has very little $CaCO_3$ coating, therefore, this step may be skipped. All the zeolite used in experiments of this study were treated with the buffer solution.)

Treatment of Zeolite with Surfactant

The zeolite is treated to create a monolayer of HDTMA on the external surfaces of the zeolite. To accomplish this, HDTMA, as bromide salt in aqueous solution, is added to the zeolite so that the solution concentration, volume, and soil mass results in a number of organic cation equivalents equal to the zeolite's external CEC or the desired CEC loading (St. Cloud - 15 me/100 g). The basic procedure for surface modification follows that of Huddleston (1990). The procedures used in this study are as follows:

- 40 g of prepared zeolite is measured into 250-mL centrifuge bottle on a top-loading balance.
- 120 mL of the appropriate HDTMA concentration in distilled water aqueous solution is added to the bottle.
- Container is placed on shaker for 24 h at 25° C.
- Container is centrifuged for approximately 20 min to yield a clear supernatant.
- Supernatant is decanted and discarded.
- Organo-zeolite is then rinsed 3 times to remove excess HDTMA: 100 mL of distilled water is added to container, shaken for 15 min, centrifuged for 15 min, decanted and the process repeated.
- Organo-zeolite is then filtered and air-dried in a Buchner funnel and placed in a plastic storage container.

Suggestions

It is important to know how much HDTMA is actually sorbed to the zeolite so that direct comparison of sorption of different anions can be performed with better confidence. Large batches of zeolite should be modified so that the same product is used for a number of experiments. Radiolabeled HDTMA batches should be included for each batch, at least until confidence in the efficiency of modification is established. This was not done for the three batches of HDTMA-zeolite produced during this investigation. There seems to be enough variability in the anion sorption results to warrant such care in the modification of the zeolite.

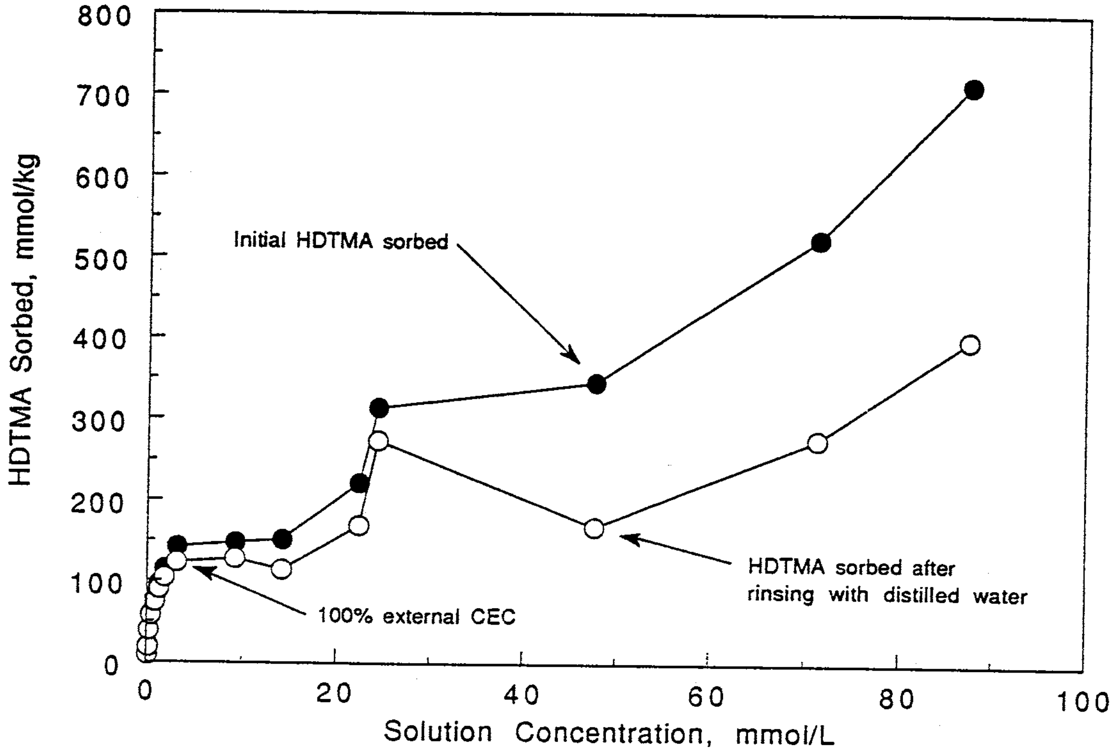
Further study may be necessary to determine whether the concentration of the HDTMA solution has an affect on the sorption of the amine to the zeolite. Review of the literature suggests that above the critical micelle concentration of the surfactant, sorption may be affected by the presence of surfactant micelles in solution. The concentrations of the HDTMA solutions used for modification of the zeolite in this study were well above the critical micelle concentration (CMC). Experimental CMC values for HDTMA bromide ranged from $8x10^{-4}$ to $1.5x10^{-3}$ *M* (Mukerjee and Mysels, 1971). Liquid crystals formed at ambient temperature after a solution of 0.05 *M* was prepared with HDTMA bromide. If practical, it would be preferable to modify the zeolite with an aqueous solution of HDTMA below its CMC.

Appendix B2

Quantification of HDTMA Sorption

Sorption isotherms for HDTMA on St. Cloud zeolite were generated using ^{14}C-labeled HDTMA supplied by American Radiolabeled Chemicals, Inc. (St. Louis, MO). A discussion of the methods and results are included in Chapter 2. Appendix Table B2.1 provides the data used to generate Figure 2 of Chapter 2. Appropriate blanks and duplicates ('a' and 'b' in table) were used for this study. Appendix Table B2.2 contains results from a second HDTMA sorption isotherm experiment ('c' samples). The results of this experiment are not discussed in Chapter 2 since no duplicates were used in this experiment. A preliminary rinse-off study followed the second sorption experiment using these samples. The methods and results are also described briefly in Chapter 2. Appendix Table B2.3 contains the results of the rinse-off study and Appendix Figure B2.1 shows the results graphically.

It should be noted that the results of the first and second HDTMA sorption isotherm experiment were consistent up to the external CEC of the zeolite. Sorption at concentrations above the external CEC appeared to be greater in the second experiment than in the first. Huddleston (1990) also observed a wide variation in sorption above the external CEC of the zeolite he was using. The stability of the bonds formed above the external CEC (admicelle formation) appears to be low as HDTMA sorbed at concentrations above the external CEC is easily removed by rinsing with distilled water (Figure B2.1). Formation of the admicelle bonds may be very sensitive to pH and temperature.



Appendix Figure B2.1. Rinse-off study of HDTMA bound to St. Cloud zeolite. Above the external CEC excess HDTMA is easily removed with distilled water.

Appendix Table B2.1. Results of First Experiment of Sorption of HDTMA by St. Cloud Zeolite

Data for Figure 2 of Chapter 2

Date of Analysis: 9/17/92
HDTMA-Br solution of varying molarity
Zeolite mass = 2.5 g
Solution volume added to each sample = 10 ml
C-14 solution concentration = 276.6 mg/l C-14 spike 10 ul added to 50 ml of HDTMA-Br aqueous solution for each concentration.
Average background activity = 40 cpm Background subtracted from cpms for all samples

Sample ID me/100g	Solution molarity M	Solution Concentration mg/l	% of CEC %	Solution Mass ug	Initial cpm conc. cpm / ml	Liq. Conc. cpm/ml	Ratio of equil: initial conc. dimensionless	Liquid Conc mg/L	Conc. Mass ug	Sorbed Conc. mg/kg	% remaining in solution %	Conversion mg/L to mmol/L	Conversion mg/Kg to mmol/kg
1 blank	0.0025	711.63	7%	7116.25	6901.30								
1a	0.0025	711.63	7%	7116.25		126.00	0.02	12.99	129.92	2794.53	1.83%	0.05	9.82
1b	0.0025	711.63	7%	7116.25		123.00	0.02	12.68	126.83	2795.77	1.78%	0.04	9.82
2 blank	0.005	1423.25	13%	14232.50	6479.10								
2a	0.005	1423.25	13%	14232.50		151.00	0.02	33.17	331.70	5560.32	2.33%	0.12	19.53
2b	0.005	1423.25	13%	14232.50		168.30	0.03	36.97	369.70	5545.12	2.60%	0.13	19.48
4 blank	0.01	2846.50	27%	28465.00	7176.20								
4a	0.01	2846.50	27%	28465.00		173.00	0.02	68.62	686.22	11111.51	2.41%	0.24	39.04
4b	0.01	2846.50	27%	28465.00		209.60	0.03	83.14	831.40	11053.44	2.92%	0.29	38.83
6 blank	0.015	4269.75	40%	42697.50	6909.30								
6a	0.015	4269.75	40%	42697.50		186.90	0.03	115.50	1154.99	16617.00	2.71%	0.41	58.38
6b	0.015	4269.75	40%	42697.50		188.30	0.03	116.36	1163.64	16613.54	2.73%	0.41	58.36
8 blank	0.02	5693.00	53%	56930.00	7068.80								
8a	0.02	5693.00	53%	56930.00		246.40	0.03	198.44	1984.43	21978.23	3.49%	0.70	77.21
8b	0.02	5693.00	53%	56930.00		228.30	0.03	183.87	1838.66	22036.54	3.23%	0.65	77.42
10 blank	0.025	7116.25	67%	71162.50	6793.50								
10a	0.025	7116.25	67%	71162.50		300.00	0.04	314.25	3142.53	27207.99	4.42%	1.10	95.58
10b	0.025	7116.25	67%	71162.50		285.10	0.04	298.64	2986.45	27270.42	4.20%	1.05	95.80
12 blank	0.03	8539.50	80%	85395.00	6657.20								
12a	0.03	8539.50	80%	85395.00		270.90	0.04	347.50	3474.96	32768.02	4.07%	1.22	115.12
12b	0.03	8539.50	80%	85395.00		329.60	0.05	422.79	4227.93	32466.83	4.95%	1.49	114.06

Sample ID me/100g	Solution molarity M	Solution Concentration mg/l	% of CEC %	Solution Mass ug	Initial cpm conc. cpm / ml	Liq. Conc. cpm/ml	Ratio of equil: initial conc. dimensionless	Liquid Conc mg/L	Conc. Mass ug	Sorbed Conc. mg/Kg	% remaining in solution %	Conversion mg/L to mmol/L	Conversion mg/Kg to mmol/Kg
15 blank	0.0375	10674.38	100%	106743.75	7063.50								
15a	0.0375	10674.38	100%	106743.75		418.90	0.06	633.04	6330.42	40165.33	5.93%	2.22	141.10
15b	0.0375	10674.38	100%	106743.75		389.40	0.06	588.46	5884.62	40343.65	5.51%	2.07	141.73
18 blank	0.045	12809.25	120%	128092.50	6608.90								
18a	0.045	12809.25	120%	128092.50		1495.20	0.23	2897.97	28979.69	39645.12	22.62%	10.18	139.28
18b	0.045	12809.25	120%	128092.50		1415.70	0.21	2743.88	27438.84	40261.46	21.42%	9.64	141.44
20 blank	0.05	14232.50	133%	142325.00	6970.60								
20a	0.05	14232.50	133%	142325.00		1660.60	0.24	3390.60	33905.96	43367.62	23.82%	11.91	152.35
20b	0.05	14232.50	133%	142325.00		2079.10	0.30	4245.09	42450.85	39949.66	29.83%	14.91	140.35
30 blank	0.075	21348.75	200%	213487.50	6850.00								
30a	0.075	21348.75	200%	213487.50		3568.50	0.52	11121.61	111216.08	40908.57	52.09%	39.07	143.72
30b	0.075	21348.75	200%	213487.50		3557.50	0.52	11087.33	110873.25	41045.70	51.93%	38.95	144.20
40 blank	0.1	28465.00	267%	284650.00	6815.70								
40a	0.1	28465.00	267%	284650.00		4354.30	0.64	18185.24	181852.41	41119.03	63.89%	63.89	144.45
40b	0.1	28465.00	267%	284650.00		4374.30	0.64	18268.77	182687.69	40784.92	64.18%	64.18	143.28
50 blank	0.125	35581.25	333%	355812.50	6876.70								
50a	0.125	35581.25	333%	355812.50		4415.60	0.64	22847.09	228470.88	50936.65	64.21%	80.26	178.94
50b	0.125	35581.25	333%	355812.50		4383.40	0.64	22680.48	226804.79	51603.08	63.74%	79.68	181.29
75 blank	0.1875	53371.88	500%	533718.75	6912.80								
75a	0.1875	53371.88	500%	533718.75		5223.30	0.76	40327.70	403276.99	52176.71	75.56%	141.67	183.30
75b	0.1875	53371.88	500%	533718.75		5197.40	0.75	40127.73	401277.32	52976.57	75.19%	140.97	186.11
100 blank	0.25	71162.50	667%	711625.00	6782.20								
100a	0.25	71162.50	667%	711625.00		5335.50	0.79	55982.94	559829.43	60718.23	78.67%	196.67	213.31
100b	0.25	71162.50	667%	711625.00		5308.60	0.78	55700.69	557006.94	61847.22	78.27%	195.68	217.27
200 blank	0.5	142325.00	1333%	1423250.00	4381.30								
200a	0.5	142325.00	1333%	1423250.00		3007.30	0.69	97691.09	976910.90	178535.64	68.64%	343.20	627.21
200b	0.5	142325.00	1333%	1423250.00		2675.90	0.61	86925.68	869256.77	221597.29	61.08%	305.38	778.49

Appendix Table B2.2. Results of Second Experiment for Sorption of HDTMA by St. Cloud Zeolite

Date of Analysis: 10/2/92
HDTMA-Br solution of varying molarity
Zeolite mass = 2.5 g
Solution volume added to each sample = 10 ml
C-14 solution concentration = 10 ul of C-14 spike added to 50 ml of HDTMA-Br solution of each concentration
Average background activity = 40 cpm. Background subtracted from cpms for all samples

Sample ID me/100g	Solution molarity *M*	Solution conc. mg/l	Percent external CEC %	Solution mass ug	Initial conc. cpm/ml	Liq. Conc. cpm/ml cpm/ml	Ratio of initial/ equilibrium conc. dimensionless	Liquid conc. mg/L	Conc. mass ug	Sorbed conc. mg/Kg	% remaining in solution %	Conversion mg/L to mmol/L	Conversion mg/kg to mmol/kg
1 blank	0.0025	711.63	7%	7116.25	6702.00								
1c	0.0025	711.63	7%	7116.25		176.00	0.03	18.69	186.88	2771.75	2.63%	0.066	9.737
2 blank	0.005	1423.25	13%	14232.50	7295.00								
2c	0.005	1423.25	13%	14232.50		180.00	0.02	35.12	351.18	5552.53	2.47%	0.123	19.507
4 blank	0.01	2846.50	27%	28465.00	7244.00								
4c	0.01	2846.50	27%	28465.00		161.00	0.02	63.26	632.64	11132.94	2.22%	0.222	39.111
6 blank	0.015	4269.75	40%	42697.50	7823.00								
6c	0.015	4269.75	40%	42697.50		198.00	0.03	108.07	1080.67	16646.73	2.53%	0.380	58.481
8 blank	0.02	5693.00	53%	56930.00	6999.00								
8c	0.02	5693.00	53%	56930.00		236.00	0.03	191.96	1919.63	22004.15	3.37%	0.674	77.302
10 blank	0.025	7116.25	67%	71162.50	6987.00								
10c	0.025	7116.25	67%	71162.50		278.00	0.04	283.14	2831.43	27332.43	3.98%	0.995	96.021
12 blank	0.03	8539.50	80%	85395.00	7056.00								
12c	0.03	8539.50	80%	85395.00		318.00	0.05	384.86	3848.58	32618.57	4.51%	1.352	114.592
15 blank	0.0375	10674.38	100%	106743.75	7645.00								
15c	0.0375	10674.38	100%	106743.75		442.00	0.06	617.15	6171.45	40228.92	5.78%	2.168	141.328

Sample ID me/100g	Solution molarity M	Solution conc. mg/l	Percent external CEC %	Solution mass ug	Initial conc. cpm/ml	Liq. Conc. cpm/ml cpm/ml	Ratio of initial/ equilibrium conc. dimensionless	Liquid conc. mg/L	Conc. mass ug	Sorbed conc. mg/Kg	% remaining in solution %	Conversion mg/L to mmol/L	Conversion mg/kg to mmol/kg
18 blank	0.045	12809.25	120%	128092.50	9579.00								
18c	0.045	12809.25	120%	128092.50		1758.00	0.18	2350.84	23508.36	41833.65	18.35%	8.259	146.965
20 blank	0.05	14232.50	133%	142325.00	6970.60								
20c	0.05	14232.50	133%	142325.00		1717.00	0.25	3505.75	35057.53	42906.99	24.63%	12.316	150.736
30 blank	0.075	21348.75	200%	213487.50	6975.00								
30c	0.075	21348.75	200%	213487.50		1834.00	0.26	5613.42	56134.20	62941.32	26.29%	19.720	221.118
40 blank	0.1	28465.00	267%	284650.00	6815.70								
40c	0.1	28465.00	267%	284650.00		1487.00	0.22	6210.29	62102.87	89018.85	21.82%	21.817	312.731
50 blank	0.125	35581.25	333%	355812.50	6792.00								
50c	0.125	35581.25	333%	355812.50		2108.00	0.31	11043.18	110431.79	98152.28	31.04%	38.796	344.817
75 blank	0.1875	53371.88	500%	533718.75	6803.00								
75c	0.1875	53371.88	500%	533718.75		2060.00	0.30	16161.41	161614.09	148841.87	30.28%	56.776	522.894
100 blank	0.25	71162.50	667%	711625.00	6998.00								
100c	0.25	71162.50	667%	711625.00		2012.00	0.29	20459.98	204599.81	202810.07	28.75%	71.878	712.489
200 blank	0.5	142325.00	1333%	1423250.00	4381.30								
200c	0.5	142325.00	1333%	1423250.00		3007.30	0.69	97691.09	976910.90	178535.64	68.64%	343.197	627.211

Appendix Table B2.3 Results of Rinse-off Study on Second Experiment of HDTMA Sorption

Approximately 50 mL of distilled water used to rinse samples (5 rinses - 10 mL each)
Date of Analysis: 10/2/92
HDTMA-Bromide Solution of varying molarity
Zeolite mass = 2.5 gm
Initial HDTMA solution volume = 10 ml
Average background activity = 40 cpm

Sample ID me/100g	Liquid Conc. mg/L	Sorbed Conc. mg/kg	Conversion mg/L to mmol/L	Conversion mg/kg to mmol/kg	HDTMA remaining on zeolite after rinses %
1c	18.69	2771.75	0.07	9.74	
1c after rinses	14.76	2471.84	0.12	8.68	89.18%
2c	35.12	5552.53	0.12	19.51	
2c after rinses	17.64	5198.80	0.19	18.26	93.63%
4c	63.26	11132.94	0.22	39.11	
4c after rinses	8.21	10970.33	0.25	38.54	98.54%
6c	108.07	16646.73	0.38	58.48	
6c after rinses	24.67	16151.95	0.47	56.74	97.03%
8c	191.96	22004.15	0.67	77.30	
8c after rinses	55.15	20897.65	0.87	73.42	94.97%
10c	283.14	27332.43	0.99	96.02	
10c after rinses	97.37	25380.00	1.34	89.16	92.86%
12c	384.86	32618.57	1.35	114.59	
12c after rinses	153.94	29491.67	1.89	103.61	90.41%
15c	617.15	40228.92	2.17	141.33	
15c after rinses	269.34	34955.29	3.11	122.80	86.89%
18c	2350.84	41833.65	8.26	146.97	
18c after rinses	276.54	36344.94	9.23	127.68	86.88%
20c	3505.75	42906.99	12.32	150.74	
20c after rinses	536.17	32348.65	14.20	113.64	75.39%

Appendix Table B2.3 continued

Sample ID me/100g	Liquid Conc. mg/L	Sorbed Conc. mg/kg	Conversion mg/L to mmol/L	Conversion mg/kg to mmol/kg	HDTMA remaining on zeolite after rinses %
30c	5613.42	62941.32	19.72	221.12	
30c after rinses		47915.72	22.36	168.33	76.13%
40c	6210.29	89018.85	21.82	312.73	
40c after rinses	720.84	77733.31	24.35	273.08	87.32%
50c	11043.18	98152.28	38.80	344.82	
50c after rinses	2537.63	47744.87	47.71	167.73	48.64%
75c	16161.41	148841.87	56.78	522.89	
75c after rinses	4162.74	78424.96	71.40	275.51	52.69%
100c	20459.98	202810.07	71.88	712.49	
100c after rinses	4426.56	113464.48	87.43	398.61	55.95%

Appendix B3

Surface Stability Experiments with HDTMA-zeolite

To confirm that the organo-zeolite would remain stable over a fairly wide range of aqueous solution conditions, a surface stability study was conducted using radiolabeled organo-zeolite. The methods and results (up to 72 h) of the study are described in Chapter 2. Buffered solutions were the same composition as used by Huddleston (1990) in a similar study conducted on the zeolite used in his study. The compositions of the three buffers used in this study were:

- 0.05 *M* Potassium hydrogen phthalate-0.02 M HCl pH 3.02 buffer
- 0.05 *M* KH_2PO_4-0.03 M NaOH pH 6.95 buffer
- 0.025 *M* $NaHCO_3$-0.01 M NaOH pH 9.85 buffer

Appendix Table B3.1 presents the average percent of HDTMA by mass remaining on the zeolite after being subjected to various solutions. Huddleston's (1990) results of a similar study conducted on a zeolite from Tilden, Texas, are also presented in this table for comparison. Appendix Table B3.2 contains the raw data from the study on the St. Cloud zeolite.

Appendix Table B3.1. Chemical Stability of HDTMA-zeolite

Solution Composition	% of remaining HDTMA St. Cloud*	Tilden**
Distilled water	99.33	99.51
0.005 m $CaCl_2$	99.08	99.56
pH 3	98.28	99.67
pH 5	98.28	-----
pH 10	98.99	99.56
0.1 *M* CsCl	98.55	99.59
1.0 *M* CsCl	97.21	99.14
Methanol	96.04	91.23
Toluene	99.61	-----
Benzene	99.55	99.83
50 mg/L CrO_4^{2-}	99.35	-----

* Study performed 6/1/92 on St. Cloud zeolite modified with HDTMA at 100% of the external CEC.

** Huddleston (1990) on zeolite from Tilden, Texas, modified with HDTMA at 100% of the external CEC.

Appendix Table B3.2 Results of Surface Stability Experiments

Date of Analysis: 6/1/92
Equilibrium desorption of HDTMA from zeolite in various solutions
Zeolite type: St. Cloud Clinoptilolite

Mass (g) of treated zeolite used for all experiments:			2.50	
Solution volume (ml) used in all experiments:			10.00	
Background cpm:	30	cpm/ml		
			Total C-14	
Initial C-14 cpm:	94136.35	cpm/ml	18821270.00	cpm
Rinsate concentrations:	1753	cpm/ml	344600.00	
	1137	cpm/ml	387450.00	
	659	cpm/ml	220150.00	
Total C-14 cpm on 80 gms of treated zeolites:			17869070.00	cpm
C-14 cpm/gm:			223363.38	
C-14 cpm/tube (of 2.5 gms each):			558408.44	cpm

Solution Composition	Time (hours)	Equil. Liquid cpm/ml	Bkgd corrected Total Liquid cpm * 10 ml	% cation removed	% cation remaining
Distilled Water	4	212.4	1824	0.33	99.67
Sample # 9, 10	4	217.4	1874	0.34	99.66
	8	243	2130	0.38	99.62
	8	367	3370	0.60	99.40
	24	300.8	2708	0.48	99.52
	24	328.9	2989	0.54	99.46
	48	486.8	4568	0.82	99.18
	48	1129.3	10993	1.97	98.03
	72	380.9	3509	0.63	99.37
	72	346.4	3164	0.57	99.43
	2 weeks	-	-	-	-
		998	9680	1.73	98.27

Appendix Table B3.2 continued

Solution Composition	Time (hours)	Equil. Liquid cpm/ml	Bkgd corrected Total Liquid cpm * 10 ml	% cation removed	% cation remaining
0.005 m CaCl2	4	506.5	4765	0.85	99.15
Sample # 11, 12	4	496.3	4663	0.84	99.16
	8	509	4790	0.86	99.14
	8	508	4780	0.86	99.14
	24	567.4	5374	0.96	99.04
	24	551.3	5213	0.93	99.07
	48	532.8	5028	0.90	99.10
	48	658.1	6281	1.12	98.88
	72	546.8	5168	0.93	99.07
	72	559	5290	0.95	99.05
	2 weeks	571.8	5418	0.97	99.03
		-	-	-	-
pH 3	4	245.5	2155	0.39	99.61
Sample # 13, 14	4	280.4	2504	0.45	99.55
	8	1277.9	12479	2.23	97.77
	8	369.7	3397	0.61	99.39
	8	402.8	3728	0.67	99.33
	24	602.3	5723	1.02	98.98
	24	612.5	5825	1.04	98.96
	24	307.1	2771	0.50	99.50
	48	852.1	8221	1.47	98.53
	48	502.9	4729	0.85	99.15
	48	399.3	3693	0.66	99.34
	72	531.4	5014	0.90	99.10
	72	2426.8	23968	4.29	95.71
	72	253.1			

Appendix Table B3.2 continued

Solution Composition	Time (hours)	Equil. Liquid cpm/ml	Bkgd corrected Total Liquid cpm * 10 ml	% cation removed	% cation remaining
pH 5	4	483.5	4535	0.81	99.19
Sample # 15, 16	4	737.4	7074	1.27	98.73
	8	726.3	6963	1.25	98.75
	8	581.4	5514	0.99	99.01
	24	745.8	7158	1.28	98.72
	24	714.1	6841	1.23	98.77
	48	811.7	7817	1.40	98.60
	48	3356.7	33267	5.96	94.04
	72	736.3	7063	1.26	98.74
	72	1032.1	10021	1.79	98.21
	2 weeks	1233.5	12035	2.16	97.84
		-	-	-	-
pH 10	4	467	4370	0.78	99.22
Sample # 17, 18	4	463.9	4339	0.78	99.22
	8	581.4	5514	0.99	99.01
	8	542.4	5124	0.92	99.08
	24	514.3	4843	0.87	99.13
	24	508.1	4781	0.86	99.14
	48	486.8	4568	0.82	99.18
	48	834.4	8044	1.44	98.56
	72	1032.1	10021	1.79	98.21
	72	484.6	4546	0.81	99.19
	2 weeks	689.2	6592	1.18	98.82
		-	-	-	-

Appendix Table B3.2 continued

Solution Composition	Time (hours)	Equil. Liquid cpm/ml	Bkgd corrected Total Liquid cpm * 10 ml	% cation removed	% cation remaining
0.1 m CsCl	4	980.7	9507	1.70	98.30
Sample # 19, 20	4	951.7	9217	1.65	98.35
	8	1011.4	9814	1.76	98.24
	8	1094.6	10646	1.91	98.09
	24	774.4	7444	1.33	98.67
	24	650.4	6204	1.11	98.89
	48	726.1	6961	1.25	98.75
	48	732.4	7024	1.26	98.74
	72	702.2	6722	1.20	98.80
	72	767	7370	1.32	98.68
	2 weeks	991.8	9618	1.72	98.28
		1037.1	10071	1.80	98.20
1.0 m CsCl	4	1361.8	13318	2.38	97.62
Sample # 21, 22	4	1377.8	13478	2.41	97.59
	8	1683.1	16531	2.96	97.04
	8	1744.6	17146	3.07	96.93
	24	1584.4	15544	2.78	97.22
	24	1554.2	15242	2.73	97.27
	48	1541.6	15116	2.71	97.29
	48	1632.1	16021	2.87	97.13
	72	1716.5	16865	3.02	96.98
	72	1681.7	16517	2.96	97.04

Appendix Table B3.2 continued

Solution Composition	Time (hours)	Equil. Liquid cpm/ml	Bkgd corrected Total Liquid cpm * 10 ml	% cation removed	% cation remaining
Methanol	4	2004.2	19742	3.54	96.46
Sample # 23, 24	4	2466.1	24361	4.36	95.64
	8	2435.8	24058	4.31	95.69
	8	2531.9	25019	4.48	95.52
	24	2112.6	20826	3.73	96.27
	24	2250	22200	3.98	96.02
	48	2091.8	20618	3.69	96.31
	48	2185.1	21551	3.86	96.14
	72	2081.7	20517	3.67	96.33
	72	2224.2	21942	3.93	96.07
Toluene	4	162	1320	0.24	99.76
Sample # 25, 26	4	158	1280	0.23	99.77
	8	234.4	2044	0.37	99.63
	8	222	1920	0.34	99.66
	24	223.5	1935	0.35	99.65
	24	256.9	2269	0.41	99.59
	48	294.9	2649	0.47	99.53
	48	305.2	2752	0.49	99.51
	72	313.9	2839	0.51	99.49
	72	308.7	2787	0.50	99.50
	2 weeks	509.8	4798	0.86	99.14

Appendix Table B3.2 continued

Solution Composition	Time (hours)	Equil. Liquid cpm/ml	Bkgd corrected Total Liquid cpm * 10 ml	% cation removed	% cation remaining
Benzene	4	153	1230	0.22	99.78
Sample # 27, 28	4	not recorded	-	-	-
	8	233.9	2039	0.37	99.63
	8	196.9	1669	0.30	99.70
	24	292.5	2625	0.47	99.53
	24	278.6	2486	0.45	99.55
	48	396.1	3661	0.66	99.34
	48	355.7	3257	0.58	99.42
	72	316.5	2865	0.51	99.49
	72	309.6	2796	0.50	99.50
	2 weeks	424.1	3941	0.71	99.29
50 ppm Chromate	4	291	2610	0.47	99.53
Sample #29, 30	4	322.7	2927	0.52	99.48
	8	327.7	2977	0.53	99.47
	8	317.4	2874	0.51	99.49
	24	368.4	3384	0.61	99.39
	24	394	3640	0.65	99.35
	48	520.7	4907	0.88	99.12
	48	455	4250	0.76	99.24
	72	455.2	4252	0.76	99.24
	72	475.8	4458	0.80	99.20

APPENDIX C

SORPTION OF OXYANIONS

Batch isotherms were performed for the oxyanions chromate, selenate, sulfate, and arsenate. The results of the batch isotherms are discussed in Chapter 2 of this document. This appendix contains the methodology for the isotherm experiments, tabulated isotherm results used to generate Figures 3, 4, 5, 6, and 7 of Chapter 2, curve fitting graphs; and additional pertinent data and figures not discussed explicitly in Chapter 2 (i.e. pH data, arsenate data). The appendix is divided into five sections. Appendix C1 contains the general batch isotherm procedures. Appendix C2 contains results for chromate experiments, Appendix C3 for selenate, Appendix C4 for sulfate, and Appendix C5 for arsenate. The arsenate data were not discussed in Chapter 2 because arsenate isotherm experiments were performed prior to the transition to organo-zeolite modified with HDTMA bromide. Additional problems with the arsenate results are discussed in Appendix C5.

Appendix C1

Batch Isotherm Procedures

C 1-1. Batch Isotherm Method

The following procedure was used for the batch isotherm experiments performed in this study:

<u>Sorption</u>

- 0.005 *M* $CaCl_2$ aqueous solution (unbuffered) is used to prepare the anion solutions to obtain the appropriate concentrations. The pH of the solution is measured.
- 2.5 g zeolite is weighed in 50-mL polyallomer centrifuge tube on a top-loading balance.
- 10 mL of solution containing varying concentrations of the anion of interest is pipetted into the centrifuge tube.
- Tube is mechanically shaken for 24 h at 25° C to obtain equilibrium.
- Tube is centrifuged to obtain a clear supernatant.
- 5 mL of supernatant is decanted into a polyethylene scintillation vial. The pH of the sample is measured and recorded. The sample is analyzed using the appropriate analytical method. (For these experiments, chromate, selenate, and arsenate were analyzed using atomic absorption spectrometry. Sulfate was analyzed using ion chromatography.)

<u>Desorption</u>

- 5 mL of 0.005 *M* $CaCl_2$ is added to the centrifuge tube.
- Tube is mechanically shaken for 24 h at 25° C.
- Tube is centrifuged to obtain a clear supernatant.
- 5 mL of supernatant is decanted and analyzed.
- Desorption process is repeated until a trend is established.

C1-2. General Comments

Results from isotherm experiments are plotted comparing the equilibrium solution concentration to solute mass sorbed.

Some of the experimental isotherms for the natural zeolite were not performed in duplicate. Previous experiments showed that natural zeolite essentially does not sorb oxyanions from aqueous solution.

Appendix C2

Chromate Results

C2-1. Chromate Isotherm Results

The results for chromate sorption isotherms with natural and HDTMA-zeolite modified at 50%, 100%, and 200% of the external CEC of the zeolite are in Appendix Tables C2.1, C2.2, and C2.3, respectively. These results were used to generate Figures 3 and 5 of Chapter 2.

Appendix Tables C2.4 and C2.5 contain the results for chromate sorption isotherms with natural and HDTMA-zeolite modified at varying percentages of the external CEC of the zeolite. The results in Table C2.4 were used to generate Figure 7 of Chapter 2.

The results for chromate desorption at initial concentrations of 25, 50, and 75 mg/L are summarized in Appendix Table C2.6. The results for desorption of chromate from HDTMA-zeolite at 100% of the external CEC were used to generate Figure 4A.

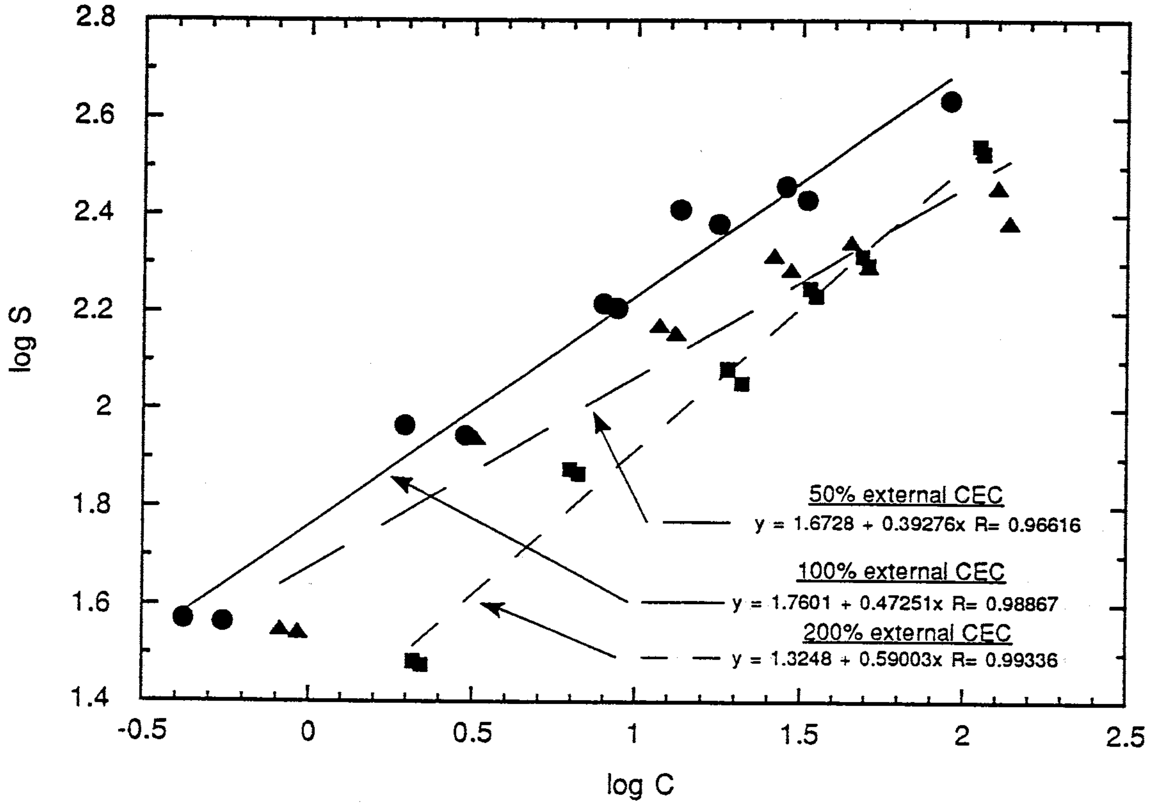
C2-2. Freundlich and Langmuir Fits for Chromate Sorption

The chromate data were fit to the Freundlich equation and the Langmuir equation. The Langmuir equation was found to fit the data best. Fitted curves on Figures 3, 4, and 5 in Chapter 2 are to the Langmuir equation. Table 1 of Chapter 2 contains the fitted parameters for chromate sorption results of the three HDTMA-zeolites. Appendix Figure C2.1 shows the chromate data linearized on a log-log scale for fitting to the Freundlich equation. Appendix Figure C2.2 shows the chromate data linearized to the Langmuir equation.

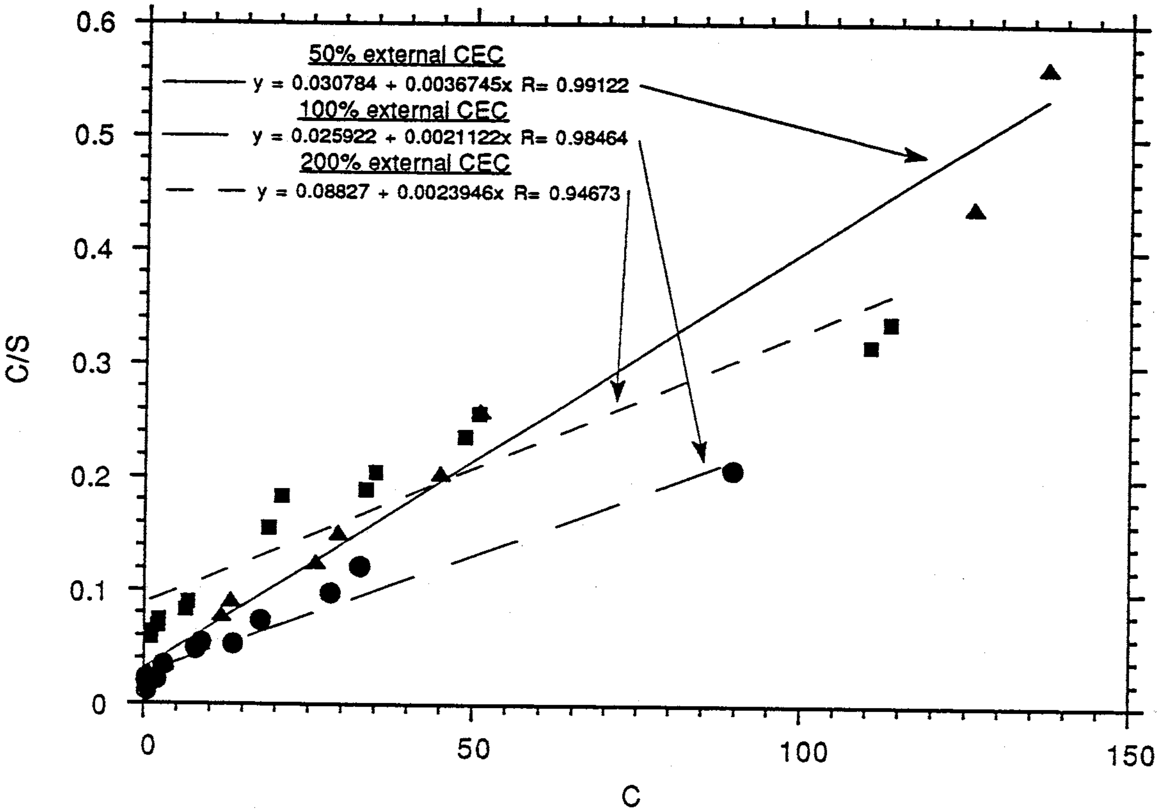
C2-3. pH Measurements

Anion solutions used in the isotherm experiments were unbuffered. The pHs of the equilibrated supernatant were measured either after decanting or metal analysis. Appendix Table C2.7 contains the pH results for chromate. Because the pHs were sometimes measured after chromate analysis was performed there may have been insufficient sample available for a pH measurement. No measurement was recorded in these cases. For future work, the pHs of the supernatants should be measured immediately after decanting. Appendix Figure C2.3 shows the pH distribution of the equilibrated solutions.

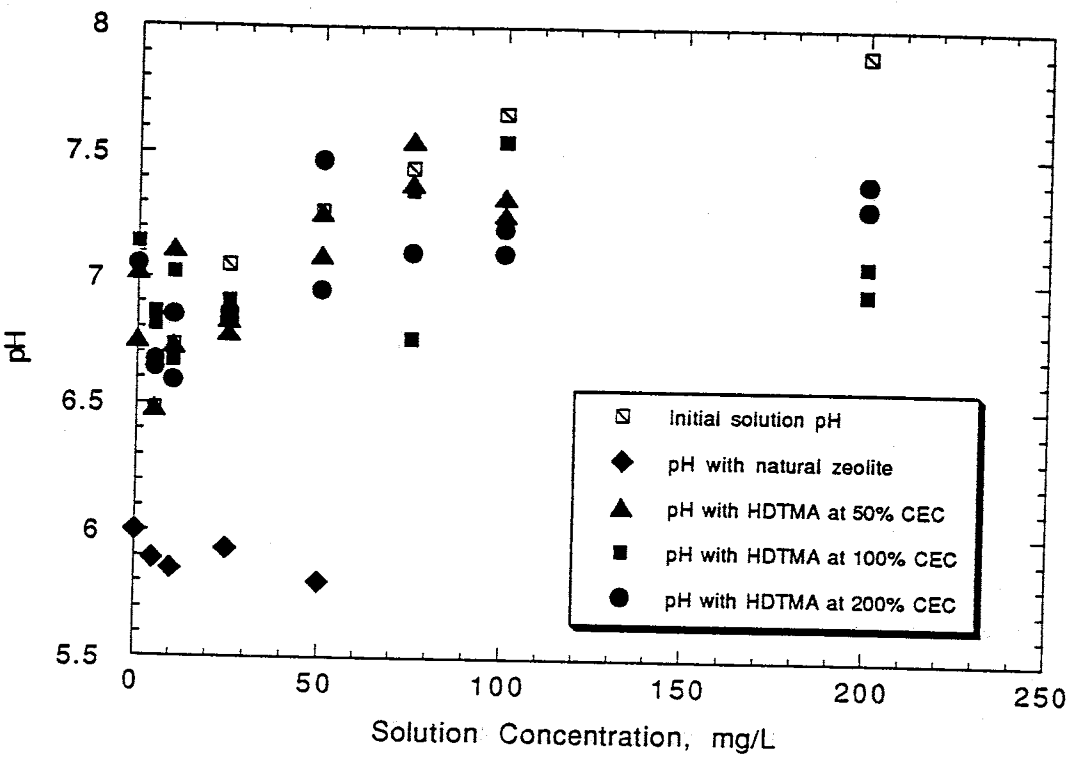
Attachment C2 contains diagrams on the stability of Cr species in aqueous solution at varying Eh and pH values from the *Atlas of Electrochemical Equilibria in Aqueous Solutions* (Marcel Pourbaix, 1974). The pH values for the equilibrated solutions ranged from about 6.5 to 7.5. According to Pourbaix (1974) chromate is the predominant species in a dilute aqueous solution at this pH range. The pHs of the initial solutions increased with increasing anion concentrations. No clear trend of either increasing or decreasing pHs in the equilibrated solutions was observed. More careful measurement of pHs may allow for a better evaluation of the nature of the interaction between the metals and the HDTMA-zeolite.



Appendix Figure C2.1. Fit of Freundlich equation to chromate sorption isotherms



Appendix Figure C2.2. Fit of Langmuir equation to chromate sorption isotherms



Appendix Figure C2.3. pH Values for 11/24/92 Chromate Sorption Isotherm Samples

Appendix Table C2.1. Chromate Sorption on Natural Zeolite and HDTMA-zeolite modified at 50% external CEC

Type of zeolite : St. Cloud
Mass of zeolite : 2.5 g
Date of analysis : 11/24/92
External CEC satisfied: 50% - 7.5 me/100g

Sample ID	Approx. Conc. mg/L	Dilute Equil. Concentration mg/L	Dilution Factor	Equilibrium Soln. Conc. mg/L	Solution Volume ml	Total Solute Mass µg	Equil. Solute Mass in Soln. µg	Equilibrium Mass Sorbed µg	Solute Mass Sorbed mg/kg
0TB	0	0	1	0	10	0.00			
0a	0	0	1	0	10		0.00	0.00	0.00
0b	0	0	1	0	10		0.00	0.00	0.00
0U	0	0	1	0	10		0.00	0.00	0.00
5TB	5	5.28	1	5.28	10	52.80			
5a	5	0.46	1	0.46	10		4.60	48.20	19.28
5b	5	0.39	1	0.39	10		3.90	48.90	19.56
5U	5	5	1	5	10		50.00	2.80	1.12
10TB	10	9.69	1	9.69	10	96.90			
10a	10	0.82	1	0.82	10		8.20	88.70	35.48
10b	10	0.93	1	0.93	10		9.30	87.60	35.04
10U	10	9.62	1	9.62	10		96.20	0.70	0.28
25TB	25	5	5	25	10	250.00			
25a	25	3.07	1	3.07	10		30.70	219.30	87.72
25b	25	3.22	1	3.22	10		32.20	217.80	87.12
25U	25	4.72	5	23.6	10		236.00	14.00	5.60

Appendix Table C2.1 continued

Sample ID	Approx. Conc. mg/L	Dilute Equil. Concentration mg/L	Dilution Factor	Equilibrium Soln. Conc. mg/L	Solution Volume ml	Total Solute Mass µg	Equil. Solute Mass in Soln. µg	Equilibrium Mass Sorbed µg	Solute Mass Sorbed mg/kg
50TB	50	9.81	5	49.05	10	490.50			
50a	50	2.35	5	11.75	10		117.50	373.00	149.20
50b	50	2.63	5	13.15	10		131.50	359.00	143.60
50U	50	9.59	5	47.95	10		479.50	11.00	4.40
75TB	75	7.78	10	77.8	10	778.00			
75a	75	5.2	5	26	10		260.00	518.00	207.20
75b	75	5.87	5	29.35	10		293.50	484.50	193.80
75U	75	7.56	10	75.6	10		756.00	22.00	8.80
100TB	100	10.02	10	100.2	10	1002.00			
100a	100	5.1	10	51	10		510.00	492.00	196.80
100b	100	4.5	10	45	10		450.00	552.00	220.80
100U	100	9.84	10	98.4	10		984.00	18.00	7.20
200TB	200	9.89	20	197.8	10	1978.00			
200a	200	2.52	50	126	10		1260.00	718.00	287.20
200b	200	2.74	50	137	10		1370.00	608.00	243.20
200U	200	3.82	50	191	10		1910.00	68.00	27.20

Sample ID explanation

Anion concentrations ranged from 0 to 200 mg/L (converted to mmol/L in Chapter 2 figures)

10TB - (test blank) no zeolite and 10 mg/L chromate solution

10a and 10b - duplicate HDTMA-zeolite samples and 10 mg/L chromate solution

10U - natural (unmodified) zeolite and 10 mg/L chromate solution

Appendix Table C2.2. Chromate Sorption on Natural Zeolite and HDTMA-zeolite modified at 100% external CEC

Type of zeolite : St. Cloud
Mass of zeolite : 2.5 g
Date of analysis : 11/24/92
External CEC satisfied: 100% - 15 me/100g

Sample ID	Approx. Conc. mg/L	Dilute Equil. Concentration mg/L	Dilution Factor	Equilibrium Soln. Conc. mg/L	Solution Volume ml	Total Solute Mass µg	Equil. Solute Mass in Soln. µg	Equilibrium Mass Sorbed µg	Solute Mass Sorbed mg/kg
0TB	0	0	1	0	10	0.00			
0a	0	0	1	0	10		0.00	0.00	0.00
0b	0	0	1	0	10		0.00	0.00	0.00
0U	0	0	1	0	10		0.00	0.00	0.00
5TB	5	5.28	1	5.28	10	52.80			
5a	5	0.39	1	0.39	10		3.90	48.90	19.56
5b	5	0.44	1	0.44	10		4.40	48.40	19.36
5U	5	5	1	5	10		50.00	2.80	1.12
10TB	10	9.69	1	9.69	10	96.90			
10a	10	0.42	1	0.42	10		4.20	92.70	37.08
10b	10	0.55	1	0.55	10		5.50	91.40	36.56
10U	10	9.62	1	9.62	10		96.20	0.70	0.28
25TB	25	5	5	25	10	250.00			
25a	25	1.96	1	1.96	10		19.60	230.40	92.16
25b	25	2.99	1	2.99	10		29.90	220.10	88.04
25U	25	4.72	5	23.6	10		236.00	14.00	5.60

Appendix Table C2.2 continued

Sample ID	Approx. Conc. mg/L	Dilute Equil. Concentration mg/L	Dilution Factor	Equilibrium Soln. Conc. mg/L	Solution Volume ml	Total Solute Mass µg	Equil. Solute Mass in Soln. µg	Equilibrium Mass Sorbed µg	Solute Mass Sorbed mg/kg
50TB	50	9.81	5	49.05	10	490.50			
50a	50	7.87	1	7.87	10		78.70	411.80	164.72
50b	50	8.71	1	8.71	10		87.10	403.40	161.36
50U	50	9.59	5	47.95	10		479.50	11.00	4.40
75TB	75	7.78	10	77.8	10	778.00			
75a	75	3.53	5	17.65	10		176.50	601.50	240.60
75b	75	2.7	5	13.5	10		135.00	643.00	257.20
75U	75	7.56	10	75.6	10		756.00	22.00	8.80
100TB	100	10.02	10	100.2	10	1002.00			
100a	100	6.55	5	32.75	10		327.50	674.50	269.80
100b	100	5.64	5	28.2	10		282.00	720.00	288.00
100U	100	9.84	10	98.4	10		984.00	18.00	7.20
200TB	200	9.89	20	197.8	10	1978.00			
200a	200	8.96	10	89.6	10		896.00	1082.00	432.80
200b	200	8.96	10	89.6	10		896.00	1082.00	432.80
200U	200	3.82	50	191	10		1910.00	68.00	27.20

Sample ID explanation

Anion concentrations ranged from 0 to 200 mg/L (converted to mmol/L in Chapter 2 figures)

10TB (test blank) - no zeolite and 10 mg/L chromate solution

10a and 10b - duplicate HDTMA-zeolite samples and 10 mg/L chromate solution

10U - natural (unmodified) zeolite and 10 mg/L chromate solution

Appendix Table C2.3. Chromate Sorption on Natural Zeolite and HDTMA-zeolite modified at 200% external CEC

Type of zeolite : St. Cloud
Mass of zeolite : 2.5 g
Date of analysis : 11/24/92
External CEC satisfied: 200% - 30 me/100g *

Sample ID	Approx. Conc. mg/L	Dilute Equil. Concentration mg/L	Dilution Factor	Equilibrium Soln. Conc. mg/L	Solution Volume ml	Total Solute Mass µg	Equil. Solute Mass in Soln. µg	Equilibrium Mass Sorbed µg	Solute Mass Sorbed mg/kg
0TB	0	0.00	1	0	10	0.00			
0a	0	0.00	1	0	10		0.00	0.00	0.00
0b	0	0.00	1	0	10		0.00	0.00	0.00
0U	0	0.00	1	0	10		0.00	0.00	0.00
5TB	5	5.28	1	5.28	10	52.80			
5a	5	1.07	1	1.07	10		10.70	42.10	16.84
5b	5	1.00	1	1	10		10.00	42.80	17.12
5U	5	5.00	1	5	10		50.00	2.80	1.12
10TB	10	9.69	1	9.69	10	96.90			
10a	10	2.09	1	2.09	10		20.90	76.00	30.40
10b	10	2.21	1	2.21	10		22.10	74.80	29.92
10U	10	9.62	1	9.62	10		96.20	0.70	0.28
25TB	25	5.00	5	25	10	250.00			
25a	25	6.61	1	6.61	10		66.10	183.90	73.56
25b	25	6.22	1	6.22	10		62.20	187.80	75.12
25U	25	4.72	5	23.6	10		236.00	14.00	5.60

Appendix Table C2.3 continued

Sample ID	Approx. Conc. mg/L	Dilute Equil. Concentration mg/L	Dilution Factor	Equilibrium Soln. Conc. mg/L	Solution Volume ml	Total Solute Mass µg	Equil. Solute Mass in Soln. µg	Equilibrium Mass Sorbed µg	Solute Mass Sorbed mg/kg
50TB	50	9.81	5	49.05	10	490.50			
50a	50	3.76	5	18.8	10		188.00	302.50	121.00
50b	50	4.15	5	20.75	10		207.50	283.00	113.20
50U	50	9.59	5	47.95	10		479.50	11.00	4.40
75TB	75	7.78	10	77.8	10	778.00			
75a	75	6.70	5	33.5	10		335.00	443.00	177.20
75b	75	7.00	5	35	10		350.00	428.00	171.20
75U	75	7.56	10	75.6	10		756.00	22.00	8.80
100TB	100	10.02	10	100.2	10	1002.00			
100a	100	9.73	5	48.65	10		486.50	515.50	206.20
100b	100	10.15	5	50.75	10		507.50	494.50	197.80
100U	100	9.84	10	98.4	10		984.00	18.00	7.20
200TB	200	9.89	20	197.8	10	1978.00			
200a	200	2.21	50	110.5	10		1105.00	873.00	349.20
200b	200	2.27	50	113.5	10		1135.00	843.00	337.20
200U	200	3.82	50	191	10		1910.00	68.00	27.20

Sample ID explanation

Anion concentrations ranged from 0 to 200 mg/L (converted to mmol/L in Chapter 2 figures)

10TB (test blank) - no zeolite and 10 mg/L chromate solution

10a and 10b - duplicate HDTMA-zeolite samples and 10 mg/L chromate solution

10U - natural (unmodified) zeolite and 10 mg/L chromate solution

* initial HDMTA concentration added, me of HDTMA remaining on zeolite after rinsing was not determined for this experiment

Appendix Table C2.4. Chromate Sorption on Natural Zeolite and HDTMA-zeolite modified at various percentages of the external CEC

Date of analysis : 09/28/92

Type of zeolite : St. Cloud

Mass of zeolite : 2.5 g

Anion solution concentration: 10 mg/L

Sample ID	Approx. Conc. mg/L	Dilute Equil. Concentration mg/L	Dilution Factor	Equilibrium Soln. Conc. mg/L	Solution Volume ml	Total Solute Mass µg	Equil. Solute Mass in Soln. µg	Equilibrium Mass Sorbed µg	Solute Mass Sorbed mg/kg
TB	10	9.78	1	9.78	10	97.80			
1a	10	9.45	1	9.45	10		94.50	3.30	1.32
1b	10	9.01	1	9.01	10		90.10	7.70	3.08
TB	10	9.78	1	9.78	10	97.80			
2a	10	8.74	1	8.74	10		87.40	10.40	4.16
2b	10	8.85	1	8.85	10		88.50	9.30	3.72
TB	10	9.78	1	9.78	10	97.80			
4a	10	6.61	1	6.61	10		66.10	31.70	12.68
4b	10	6.94	1	6.94	10		69.40	28.40	11.36
TB	10	9.78	1	9.78	10	97.80			
6a	10	2.74	1	2.74	10		27.40	70.40	28.16
6b	10	2.18	1	2.18	10		21.80	76.00	30.40
TB	10	9.78	1	9.78	10	97.80			
8a	10	0.47	1	0.47	10		4.70	93.10	37.24
8b	10	0.53	1	0.53	10		5.30	92.50	37.00

Appendix Table C2.4. continued

Sample ID	Approx. Conc. mg/L	Dilute Equil. Concentration mg/L	Dilution Factor	Equilibrium Soln. Conc. mg/L	Solution Volume ml	Total Solute Mass µg	Equil. Solute Mass in Soln. µg	Equilibrium Mass Sorbed µg	Solute Mass Sorbed mg/kg
TB	10	9.78	1	9.78	10	97.80			
10a	10	0.19	1	0.19	10		1.90	95.90	38.36
10b	10	0.23	1	0.23	10		2.30	95.50	38.20
TB	10	9.78	1	9.78	10	97.80			
12a	10	0.16	1	0.16	10		1.60	96.20	38.48
12b	10	0.16	1	0.16	10		1.60	96.20	38.48
TB	10	9.78	1	9.78	10	97.80			
15a	10	0.17	1	0.17	10		1.70	96.10	38.44
15b	10	0.11	1	0.11	10		1.10	96.70	38.68
TB	10	9.78	1	9.78	10	97.80			
18a	10	0.13	1	0.13	10		1.30	96.50	38.60
18b	10	0.13	1	0.13	10		1.30	96.50	38.60
TB	10	9.78	1	9.78	10	97.80			
20a	10	0.21	1	0.21	10		2.10	95.70	38.28
20b	10	0.18	1	0.18	10		1.80	96.00	38.40
TB	10	9.78	1	9.78	10	97.80			
30a	10	0.23	1	0.23	10		2.30	95.50	38.20
30b	10	0.68	1	0.68	10		6.80	91.00	36.40
TB	10	9.78	1	9.78	10	97.80			
40a	10	0.83	1	0.83	10		8.30	89.50	35.80
40b	10	1.3	1	1.3	10		13.00	84.80	33.92

Appendix Table C2.4. continued

Sample ID	Approx. Conc. mg/L	Dilute Equil. Concentration mg/L	Dilution Factor	Equilibrium Soln. Conc. mg/L	Solution Volume ml	Total Solute Mass µg	Equil. Solute Mass in Soln. µg	Equilibrium Mass Sorbed µg	Solute Mass Sorbed mg/kg
TB	10	9.78	1	9.78	10	97.80			
50a	10	0.62	1	0.62	10		6.20	91.60	36.64
50b	10	1.62	1	1.62	10		16.20	81.60	32.64
TB	10	9.78	1	9.78	10	97.80			
75a	10	1.15	1	1.15	10		11.50	86.30	34.52
75b	10	2.29	1	2.29	10		22.90	74.90	29.96
TB	10	9.78	1	9.78	10	97.80			
100a	10	2.45	1	2.45	10		24.50	73.30	29.32
100b	10	2.7	1	2.7	10		27.00	70.80	28.32
TB	10	9.78	1	9.78	10	97.80			
200a	10	3.23	1	3.23	10		32.30	65.50	26.20
200b	10	2.95	1	2.95	10		29.50	68.30	27.32

Sample ID explanation

Samples are identified according to the amount of HDTMA loading on the zeolite.

For example: Samples15a and 15b are duplicates of a zeolite sample modified with HDTMA at a concentration equivalent to 15 me/100g. This is a surface modification of 100% of the external CEC.

TB - (test blank) no zeolite

Appendix Table C2.5. Chromate Sorption on Natural Zeolite and HDTMA-zeolite modified at various percentages of the external CEC - second experiment

Date of analysis : 11/23/92
Type of zeolite : St. Cloud
Mass of zeolite : 2.5 g
Anion solution concentration: 10 mg/L

Sample ID	Approx. Conc. mg/L	Dilute Equil. Concentration mg/L	Dilution Factor	Equilibrium Soln. Conc. mg/L	Solution Volume ml	Total Solute Mass µg	Equil. Solute Mass in Soln. µg	Equilibrium Mass Sorbed µg	Solute Mass Sorbed mg/kg
TB	10	10.07	1	10.07	25	251.75			
1c	10	9.45	1	9.45	25		236.25	15.50	6.20
2c	10	8.99	1	8.99	25		224.75	27.00	10.80
4c	10	7.7	1	7.7	25		192.50	59.25	23.70
6c	10	6.24	1	6.24	25		156.00	95.75	38.30
8c	10	5.51	1	5.51	25		137.75	114.00	45.60
10c	10	2.85	1	2.85	25		71.25	180.50	72.20
12c	10	1.72	1	1.72	25		43.00	208.75	83.50
15c	10	1.38	1	1.38	25		34.50	217.25	86.90
18c	10	1.32	1	1.32	25		33.00	218.75	87.50

Appendix Table C2.5 continued

Sample ID	Approx. Conc. mg/L	Dilute Equil. Concentration mg/L	Dilution Factor	Equilibrium Soln. Conc. mg/L	Solution Volume ml	Total Solute Mass µg	Equil. Solute Mass in Soln. µg	Equilibrium Mass Sorbed µg	Solute Mass Sorbed mg/kg
20c	10	1.36	1	1.36	25		34.00	217.75	87.10
30c	10	1.21	1	1.21	25		30.25	221.50	88.60
40c	10	1.35	1	1.35	25		33.75	218.00	87.20
50c	10	1.49	1	1.49	25		37.25	214.50	85.80
75c	10	2.04	1	2.04	25		51.00	200.75	80.30
100c	10	2.23	1	2.23	25		55.75	196.00	78.40

Sample ID explanation

Samples are identified according to the amount of HDTMA loading on the zeolite. These are the same samples as in Appendix Table B2.2

For example: Sample15c is a zeolite sample modified with HDTMA at a concentration equivalent to 15 me/100g.

This is a surface modification of 100% of the external CEC.

Surface modification ranged from 0 to 666% of the external CEC.

TB - (test blank) no zeolite

Appendix Table C2.6. Summary of Chromate Desorption from HDTMA-zeolite

11/24/92 sorption isotherm samples

Zeolite: St. Cloud
Tailoring Agent: HDTMA
Analysis Date: 12/8/92

Solution volume: 10 mL
Zeolite Mass: 2.5 gms

% of external CEC satisfied

	50%	50%	100%	100%	200%	200%
Sample Number	Soln. Conc. (ppm)	Sorbed (mg/kg)	Soln. Conc. (ppm)	Sorbed (mg/kg)	Soln. Conc. (ppm)	Sorbed (mg/kg)
25 ppm						
25a	3.07	87.72	1.96	92.16	6.61	73.56
25a.1	2.57	83.58	1.56	89.84	2.9	75.18
25a.2	2.53	78.6	1.44	87.2	2.53	70.86
25a.3	2.52	73.58	1.36	84.64	2.52	65.84
25b	3.22	87.12	2.99	88.04	6.22	75.12
25b.1	2.68	82.84	2.18	85.3	2.76	76.52
25b.2	2.75	77.2	1.91	82.02	2.75	71.04
25b.3	2.59	72.34	1.59	79.48	2.59	66.18
50 ppm						
50a	10.75	157	7.87	168.52	18.8	124.8
50a.1	10.7	135.7	4.18	167.54	7.5	132.4
50a.2	6.86	129.66	3.83	160.58	4.83	128.08
50a.3	5.93	119.66	3.06	156	5.56	115.5
50b	13.15	147.4	8.71	165.16	20.75	117
50b.1	7.93	141.98	5.27	161.5	7.04	130.4
50b.2	7.6	127.44	4.54	153.88	4.78	128.08
50b.3	7.05	114.44	3.64	148.4	4.68	115.5
100 ppm						
100a	51	196	32.75	333.84	48.65	205.4
100a.1	22.15	209.4	16.54	333.18	16.64	236.14
100a.2	17.42	184.02	14.17	309.58	11.85	222.2
100a.3	14.76	159.82	10.22	297.04	13.93	190
100b	45	220	28.2	287.2	50.75	197
100b.1	19.93	230.28	14.22	286.72	16.23	233.58
100b.2	17.03	202.02	12.92	263.48	11.13	221.52
100b.3	14.45	178.28	9.61	250.88	14.12	187.3

Appendix Table C2.7. pH Values for Chromate Sorption Isotherm Experiment of November 24, 1992

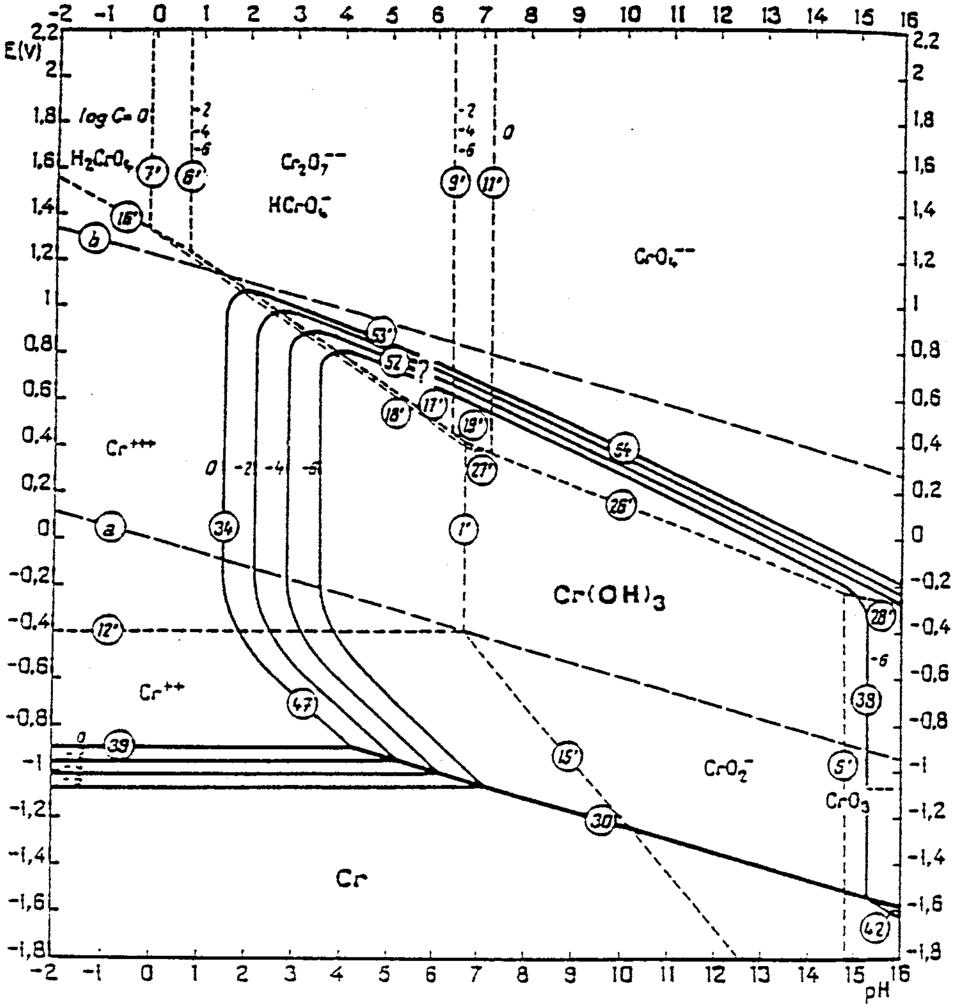
Initial Concentration mg/L	pH Values				
	Initial solution	Natural zeolite	50% modified HDTMA-zeolite	100% modified HDTMA-zeolite	200% modified HDTMA-zeolite
0	NA	6.00	6.75	7.02	7.05
0			7.02	7.14	NA
5	6.48	5.89	6.48	6.86	6.67
5			NA	6.81	6.64
10	6.73	5.85	6.73	6.67	6.85
10			7.11	7.02	6.59
25	7.05	5.93	6.78	6.85	6.83
25			6.83	6.91	6.86
50	7.27	5.80	7.09	NA	7.47
50			7.26	NA	6.95
75	7.44	NA	7.55	6.76	NA
75			7.38	7.35	7.10
100	7.66	NA	7.26	7.20	7.20
100			7.33	7.55	7.10
200	7.90	NA	NA	6.95	7.29
200			NA	7.06	7.39

NA - not available due to lack of solution for adequate pH measurement

Attachment C2

pH-eH Stability Diagrams for Chromate

Chromate



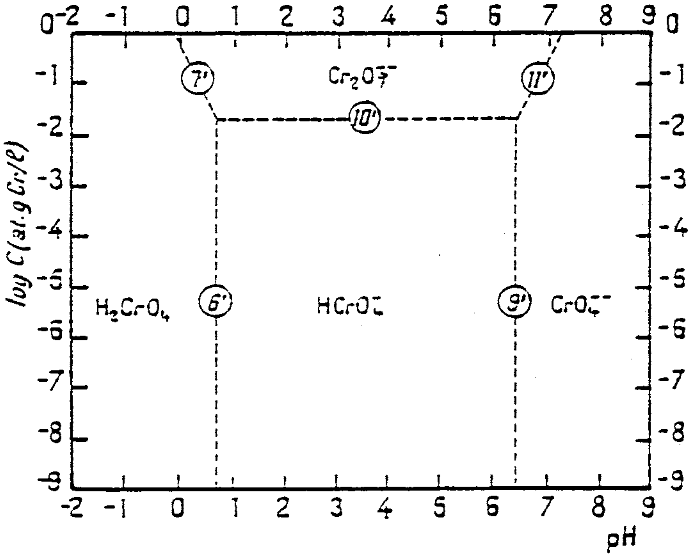


FIG. 1. Domains of relative predominance of the ions of hexavalent chromium, at 25°C.

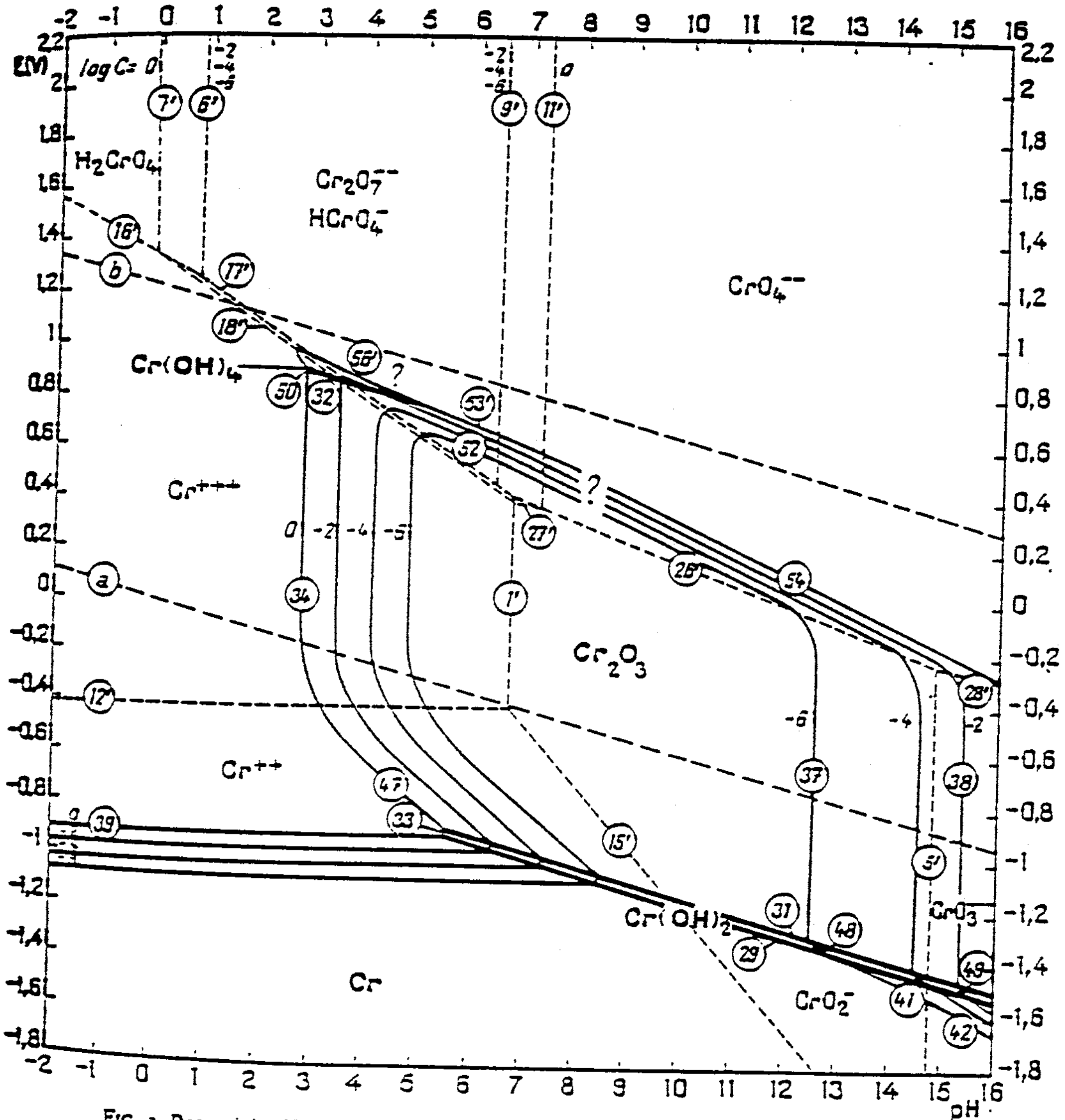


FIG. 3. Potential–pH equilibrium diagram for the system chromium–water, at 25°C.
In solutions not containing chloride.
(Figure established considering anhydrous Cr_2O_3.)

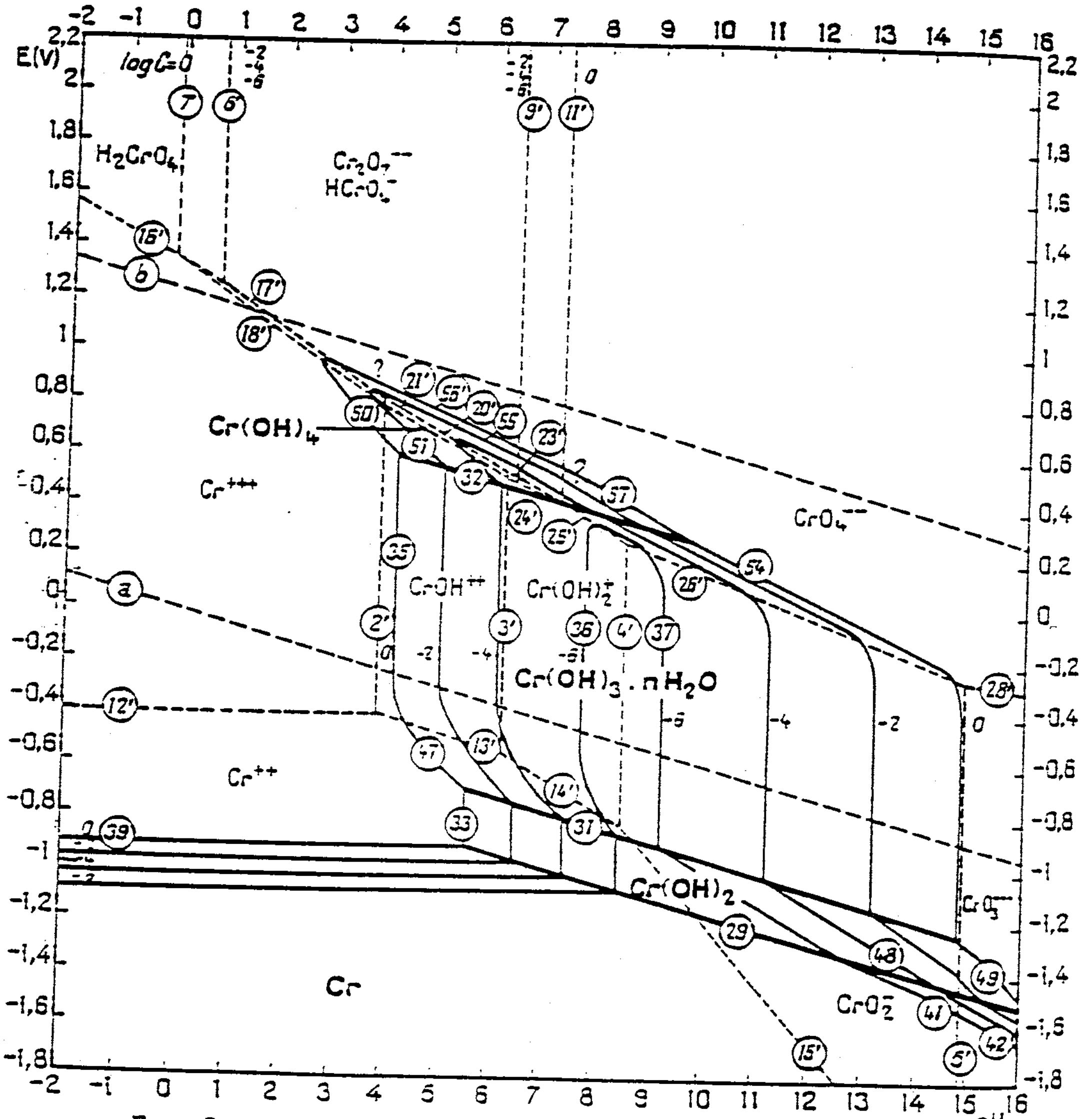


FIG. 4. Potential–pH equilibrium diagram for the system chromium–water, at 25°C. In solutions containing chloride.
[Approximate representation made by considering $Cr(OH)_3.nH_2O$.]

Appendix C3

Selenate Results

C3-1. Selenate Isotherm Results

Results for the selenate sorption isotherms with natural and HDTMA-zeolite modified at 50%, 100%, and 200% of the external CEC of the zeolite are contained in Appendix Tables C3.1, C3.2, and C3.3, respectively. These results were used to generate Figures 3 and 6 of Chapter 2.

The results for selenate desorption at initial concentrations of 25, 50, and 75 mg/L are summarized in Appendix Table C3.4. The results for desorption of selenate from HDTMA-zeolite at 100% of the external CEC were used to generate Figure 4B of Chapter 2.

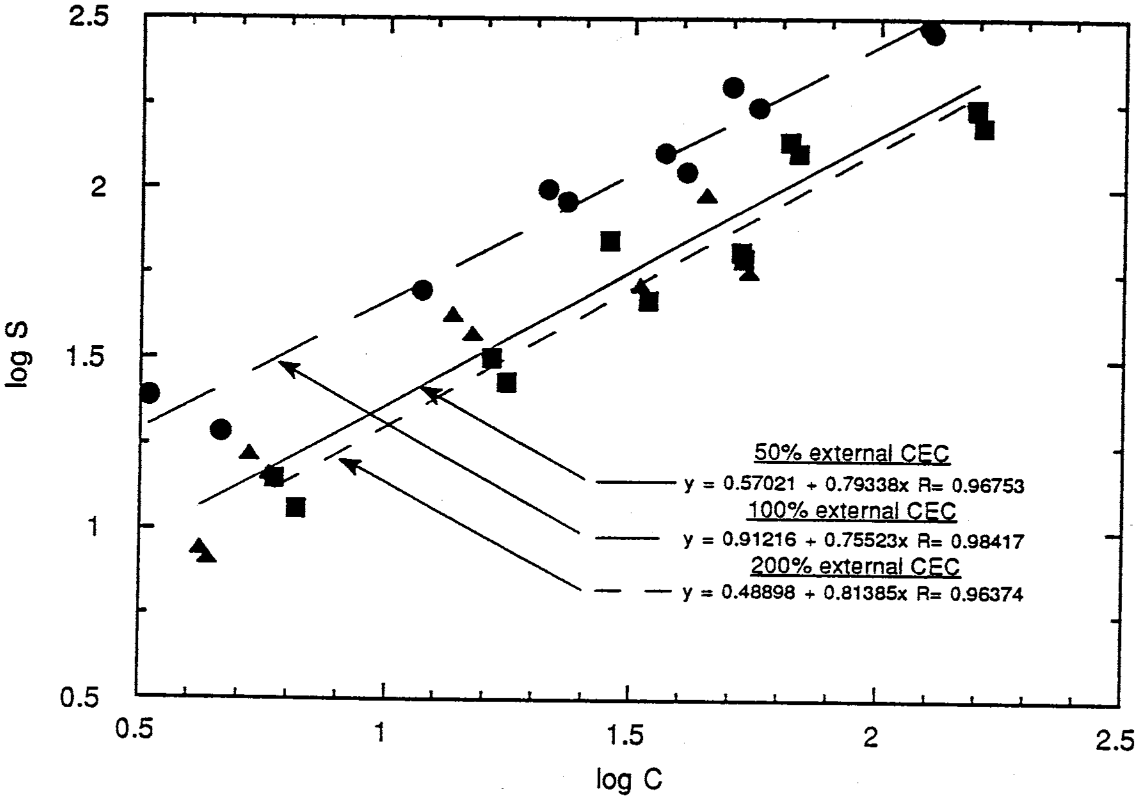
C3-2. Freundlich and Langmuir Fits for Selenate Sorption

The selenate data were fit to the Freundlich equation and the Langmuir equation. The Langmuir equation was found to fit the data best. Fitted curves for selenate on Figures 3, 4, and 6 in Chapter 2 are to the Langmuir equation. Table 1 of Chapter 2 contains the fitted parameters for selenate sorption results of the three HDTMA-zeolites. Appendix Figure C3.1 shows the selenate data linearized on a log-log scale for fitting to the Freundlich equation. Appendix Figure C3.2 shows the selenate data linearized to the Langmuir equation.

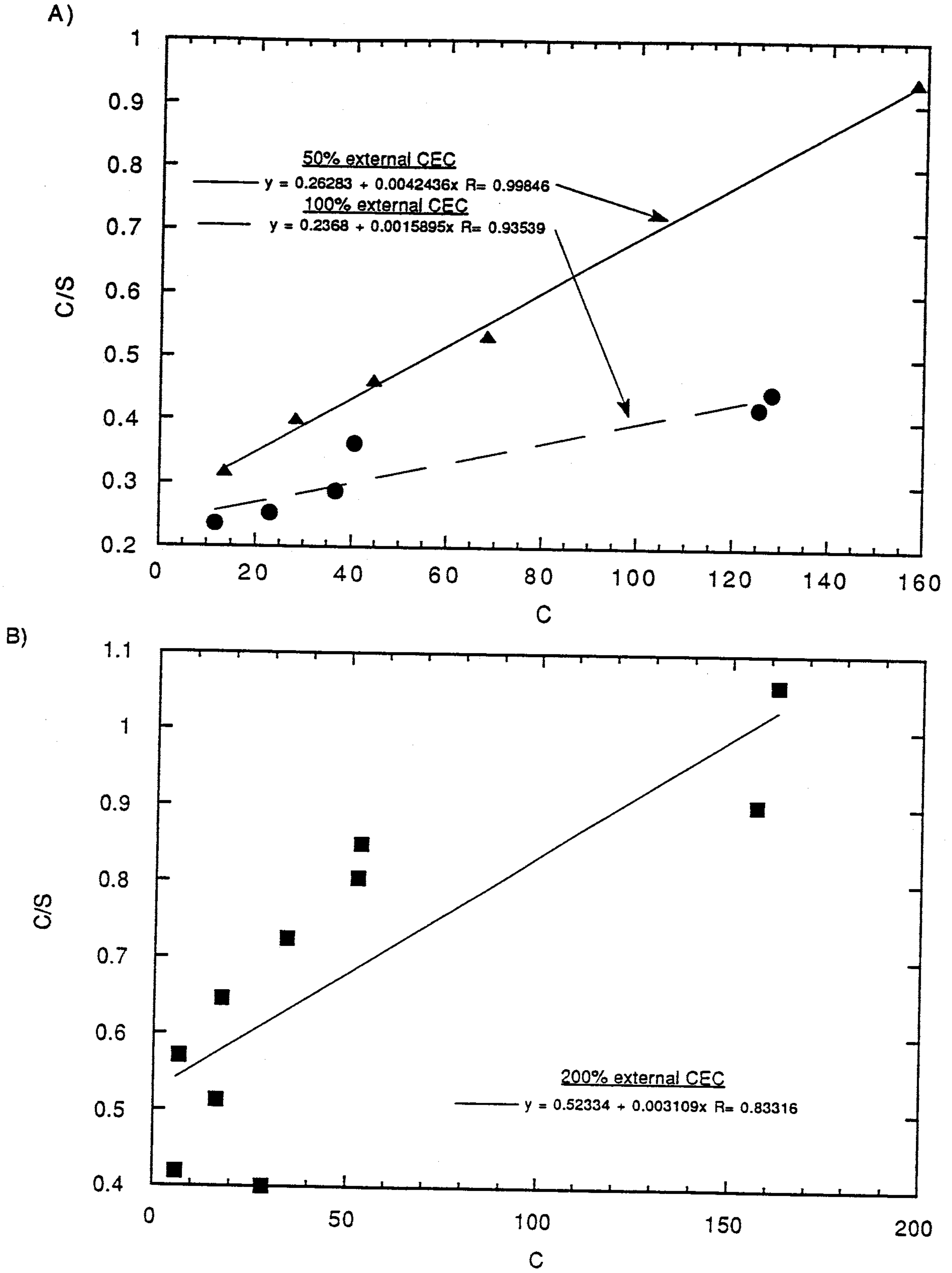
C3-3. pH Measurements

Anion solutions used in the isotherm experiments were unbuffered. The pHs of the equilibrated supernatant were measured after decanting. Appendix Table C3.5 contains the pH results for selenate. Appendix Figure C3.3 shows the pH distribution of the equilibrated solutions.

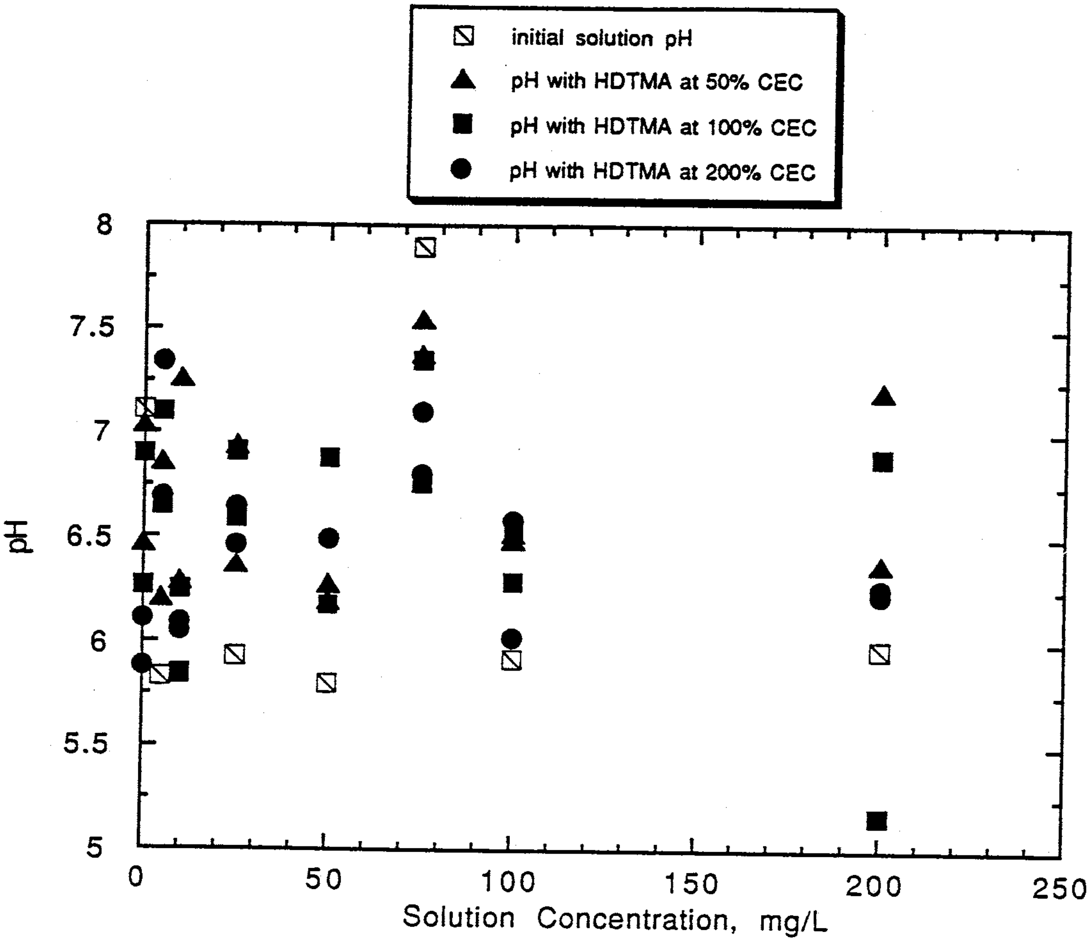
Attachment C3 contains diagrams on the stability of selenium species in aqueous solution from the *Atlas of Electrochemical Equilibria in Aqueous Solutions* by Marcel Pourbaix (1974). The pH values for the equilibrated solutions ranged from about 5.9 to 7.5. According to Pourbaix (1974), selenate (SeO_4^{2-})is the predominant species in a dilute aqueous solution at this pH range. The initial solutions for most concentrations were around pH 6, with the exception of 0 and 75 mg/L. Generally, an increase in pH occurred in the equilibrated supernatant with the exception, again, of 75 mg/L. This indicates that the initial pH measurement for this concentration was probably in error. No clear trend was noted as the percentage of surface modification of the zeolite increased.



Appendix Figure C3.1. Fit of Freundlich equation to selenate sorption isotherms



Appendix Figure C3.2. Fit of Freundlich equation to selenate sorption isotherms



Appendix Figure C3.3. pH Values for 11/24/93 Selenate Sorption Isotherm Samples

Appendix Table C3.1. Selenate Sorption on Natural Zeolite and HDTMA-zeolite modified at 50% external CEC

Type of zeolite : St. Cloud clinoptilolite
Mass of zeolite : 2.5 g
Date of analysis : 11/24/92
External CEC satisfied: 50% - 7.5 me/100g

Sample ID	Approx. Conc. mg/L	Dilute Equil. Concentration mg/L	Dilution Factor	Equilibrium Soln. Conc. mg/L	Solution Volume ml	Total Solute Mass µg	Equil. Solute Mass in Soln. µg	Equilibrium Mass Sorbed µg	Solute Mass Sorbed mg/kg
0TB	0	0	1	0	10	0			
0a	0	0	1	0	10		0	0	0
0b	0	0	1	0	10		0	0	0
0U	0	0	1	0	10		0	0	0
5TB	5	6.4	1	6.4	10	64			
5a	5	4.2	1	4.2	10		42	22	8.8
5b	5	4.34	1	4.34	10		43.4	20.6	8.24
5U	5	6.7	1	6.7	10		67	-3	-1.2
10TB	10	9.42	1	9.42	10	94.2			
10a	10	5.25	1	5.25	10		52.5	41.7	16.68
10b	10	5.77	1	5.77	10		57.7	36.5	14.6
10U	10	9.55	1	9.55	10		95.5	-1.3	-0.52
25TB	25	24.25	1	24.25	10	242.5			
25a	25	13.58	1	13.58	10		135.8	106.7	42.68
25b	25	14.88	1	14.88	10		148.8	93.7	37.48
25U	25	24.25	1	24.25	10		242.5	0	0

Appendix Table C3.1 continued

Sample ID	Approx. Conc. mg/L	Dilute Equil. Concentration mg/L	Dilution Factor	Equilibrium Soln. Conc. mg/L	Solution Volume ml	Total Solute Mass µg	Equil. Solute Mass in Soln. µg	Equilibrium Mass Sorbed µg	Solute Mass Sorbed mg/kg
50TB	50	9.16	5	45.8	10	458			
50a	50	6.55	5	32.75	10		327.5	130.5	52.2
50b	50	5.64	5	28.2	10		282	176	70.4
50U	50	9.42	5	47.1	10		471	-13	-5.2
75TB	75	13.71	5	68.55	10	685.5			
75a	75	8.9	5	44.5	10		445	240.5	96.2
75b	75	10.85	5	54.25	10		542.5	143	57.2
75U	75	13.84	5	69.2	10		692	-6.5	-2.6
100TB	100	10	10	100	10	1000			
100a	100	6.81	10	68.1	10		681	319	127.6
100b	100	6.81	10	68.1	10		681	319	127.6
100U	100	10.07	10	100.7	10		1007	-7	-2.8
200TB	200	20	10	200	10	2000			
200a	200	15.79	10	157.9	10		1579	421	168.4
200b	200	15.79	10	157.9	10		1579	421	168.4
200U	200	20	10	200	10		2000	0	0

Sample ID explanation

10TB (test blank) - no zeolite and 10 mg/L selenate solution

10a and 10b - duplicate HDTMA-zeolite samples and 10 mg/L selenate solution

10U - natural (unmodified) zeolite and 10 mg/L selenate solution

Appendix Table C3.2. Selenate Sorption on Natural Zeolite and HDTMA-zeolite modified at 100% external CEC

Type of zeolite : St. Cloud clinoptilolite
Mass of zeolite : 2.5 g
Date of analysis : 11/24/92
External CEC satisfied: 100% - 15 me/100g

Sample ID	Approx. Conc. mg/L	Dilute Equil. Concentration mg/L	Dilution Factor	Equilibrium Soln. Conc. mg/L	Solution Volume ml	Total Solute Mass µg	Equil. Solute Mass in Soln. µg	Equilibrium Mass Sorbed µg	Solute Mass Sorbed mg/kg
0TB	0	0	1	0	10	0			
0a	0	0	1	0	10		0	0	0
0b	0	0	1	0	10		0	0	0
0U	0	0	1	0	10		0	0	0
5TB	5	6.4	1	6.4	10	64			
5a	5	4.34	1	4.34	10		43.4	20.6	8.24
5b	5	3.95	1	3.95	10		39.5	24.5	9.8
5U	5	6.7	1	6.7	10		67	-3	-1.2
10TB	10	9.42	1	9.42	10	94.2			
10a	10	3.3	1	3.3	10		33	61.2	24.48
10b	10	4.6	1	4.6	10		46	48.2	19.28
10U	10	9.55	1	9.55	10		95.5	-1.3	-0.52
25TB	25	24.25	1	24.25	10	242.5			
25a	25	11.76	1	11.76	10		117.6	124.9	49.96
25b	25	11.76	1	11.76	10		117.6	124.9	49.96
25U	25	24.25	1	24.25	10		242.5	0	0

Appendix Table C3.2. continued

Sample ID	Approx. Conc. mg/L	Dilute Equil. Concentration mg/L	Dilution Factor	Equilibrium Soln. Conc. mg/L	Solution Volume ml	Total Solute Mass µg	Equil. Solute Mass in Soln. µg	Equilibrium Mass Sorbed µg	Solute Mass Sorbed mg/kg
50TB	50	9.16	5	45.8	10	458			
50a	50	4.6	5	23	10		230	228	91.2
50b	50	4.21	5	21.05	10		210.5	247.5	99
50U	50	9.42	5	47.1	10		471	-13	-5.2
75TB	75	13.71	5	68.55	10	685.5			
75a	75	7.33	5	36.65	10		366.5	319	127.6
75b	75	8.11	5	40.55	10		405.5	280	112
75U	75	13.84	5	69.2	10		692	-6.5	-2.6
100TB	100	10	10	100	10	1000			
100a	100	4.99	10	49.9	10		499	501	200.4
100b	100	5.64	10	56.4	10		564	436	174.4
100U	100	10.07	10	100.7	10		1007	-7	-2.8
200TB	200	20	10	200	10	2000			
200a	200	12.8	10	128	10		1280	720	288
200b	200	12.54	10	125.4	10		1254	746	298.4
200U	200	20	10	200	10		2000	0	0

Sample ID explanation

10TB (test blank) - no zeolite and 10 mg/L selenate solution

10a and 10b - duplicate HDTMA-zeolite samples and 10 mg/L selenate solution

10U - natural (unmodified) zeolite and 10 mg/L selenate solution

Appendix Table C3.3. Selenate Sorption on Natural Zeolite and HDTMA-zeolite modified at 200% external CEC

Type of zeolite : St. Cloud clinoptilolite
Mass of zeolite : 2.5 g
Date of analysis : 11/24/92
External CEC satisfied: 200% - 30 me/100g *

Sample ID	Approx. Conc. mg/L	Dilute Equil. Concentration mg/L	Dilution Factor	Equilibrium Soln. Conc. mg/L	Solution Volume ml	Total Solute Mass µg	Equil. Solute Mass in Soln. µg	Equilibrium Mass Sorbed µg	Solute Mass Sorbed mg/kg
0TB	0	0	1	0	10	0			
0a	0	0	1	0	10		0	0	0
0b	0	0	1	0	10		0	0	0
0U	0	0	1	0	10		0	0	0
5TB	5	6.4	1	6.4	10	64			
5a	5	5.25	1	5.25	10		52.5	11.5	4.6
5b	5	6.16	1	6.16	10		61.6	2.4	0.96
5U	5	6.7	1	6.7	10		67	-3	-1.2
10TB	10	9.42	1	9.42	10	94.2			
10a	10	5.9	1	5.9	10		59	35.2	14.08
10b	10	6.55	1	6.55	10		65.5	28.7	11.48
10U	10	9.55	1	9.55	10		95.5	-1.3	-0.52
25TB	25	24.25	1	24.25	10	242.5			
25a	25	17.48	1	17.48	10		174.8	67.7	27.08
25b	25	16.31	1	16.31	10		163.1	79.4	31.76
25U	25	24.25	1	24.25	10		242.5	0	0

Appendix Table C3.3 continued

ID	Conc. mg/L	Concentration mg/L	Factor	Soln. Conc. mg/L	Volume ml	Mass µg	Mass in Soln. µg	Mass Sorbed µg	Sorbed mg/kg
50TB	50	9.16	5	45.8	10	458			
50a	50	5.64	5	28.2	10		282	176	70.4
50b	50	6.81	5	34.05	10		340.5	117.5	47
50U	50	9.42	5	47.1	10		471	-13	-5.2
75TB	75	13.71	5	68.55	10	685.5			
75a	75	10.46	5	52.3	10		523	162.5	65
75b	75	10.59	5	52.95	10		529.5	156	62.4
75U	75	13.84	5	69.2	10		692	-6.5	-2.6
100TB	100	10	10	100	10	1000			
100a	100	6.55	10	65.5	10		655	345	138
100b	100	6.81	10	68.1	10		681	319	127.6
100U	100	10.07	10	100.7	10		1007	-7	-2.8
200TB	200	20	10	200	10	2000			
200a	200	16.18	10	161.8	10		1618	382	152.8
200b	200	15.66	10	156.6	10		1566	434	173.6
200U	200	20	10	200	10		2000	0	0

Sample ID explanation

10TB (test blank) - no zeolite and 10 mg/L selenate solution

10a and 10b - duplicate HDTMA-zeolite samples and 10 mg/L selenate solution

10U - natural (unmodified) zeolite and 10 mg/L selenate solution

* initial HDMTA concentration added, me of HDTMA remaining on zeolite after rinsing was not determined for this experiment

Appendix Table C3.4. Summary of Selenate Desorption from HDTMA-zeolite

11/24/92 sorption isotherm samples

Zeolite: St. Cloud
Tailoring Agent: HDTMA
Analysis Date: 12/8/92

	% of external CEC satisfied					
	50%	50%	100%	100%	200%	200%
Sample Number	Soln. Conc. (ppm)	Sorbed (mg/kg)	Soln. Conc. (ppm)	Sorbed (mg/kg)	Soln. Conc. (ppm)	Sorbed (mg/kg)
25 ppm						
25a	13.58	0.00	11.76	0.00	17.48	0.00
25a.1	10.38	5.43	6.88	4.70	8.75	6.99
25a.2	7.50	4.15	6.88	2.75	8.00	3.50
25a.3	3.13	3.00	2.51	2.75	3.88	3.20
25b	14.88	0.00	11.76	0.00	16.31	0.00
25b.1	8.50	5.95	6.38	4.70	9.00	6.52
25b.2	8.63	3.40	6.88	2.55	7.75	3.60
25b.3	2.38	3.45	2.88	2.75	2.88	3.10
50 ppm						
50a	32.75	0.00	23.00	0.00	28.20	0.00
50a.1	19.74	13.10	14.00	9.20	18.49	11.28
50a.2	12.87	7.90	10.13	5.60	11.00	7.40
50a.3	6.26	5.15	9.00	4.05	7.13	4.40
50b	28.20	0.00	21.05	0.00	34.05	0.00
50b.1	19.74	11.28	15.12	8.42	18.62	13.62
50b.2	13.75	7.90	10.25	6.05	11.25	7.45
50b.3	8.63	5.50	7.13	4.10	7.38	4.50
100 ppm						
100a	68.10	0.00	49.90	0.00	65.50	0.00
100a.1	39.71	27.24	32.47	19.96	38.72	26.20
100a.2	24.36	15.88	20.49	12.99	22.36	15.49
100a.3	14.62	9.74	14.25	8.20	14.74	8.94
100b	68.10	0.00	56.40	0.00	68.10	0.00
100b.1	41.09	27.24	34.60	22.56	40.84	27.24
100b.2	23.11	16.44	21.86	13.84	22.74	16.34
100b.3	15.12	9.24	14.74	8.74	14.37	9.10

Appendix Table C3.5. pH Values for Selenate Sorption Isotherm for November 24, 1992 data

Initial Concentration mg/L	pH Values Initial solution	50% modified HDTMA-zeolite	100% modified HDTMA-zeolite	200% modified HDTMA-zeolite
0	7.11	7.04	6.27	5.88
0		6.47	6.90	6.11
5	5.83	6.21	7.10	6.69
5		6.86	6.65	7.34
10	5.85	7.26	6.25	6.09
10		6.29	5.84	6.05
25	5.93	6.94	6.59	6.46
25		6.37	6.91	6.64
50	5.8	6.28	6.18	6.49
50		6.20	6.88	6.49
75	7.9	7.55	6.76	6.80
75		7.38	7.35	7.10
100	5.92	6.52	6.29	6.58
100		6.49	6.53	6.02
200	5.97	7.21	5.17	6.26
200		6.38	6.89	6.23

Attachment C3

pH-eH Stability Diagrams for Selenate

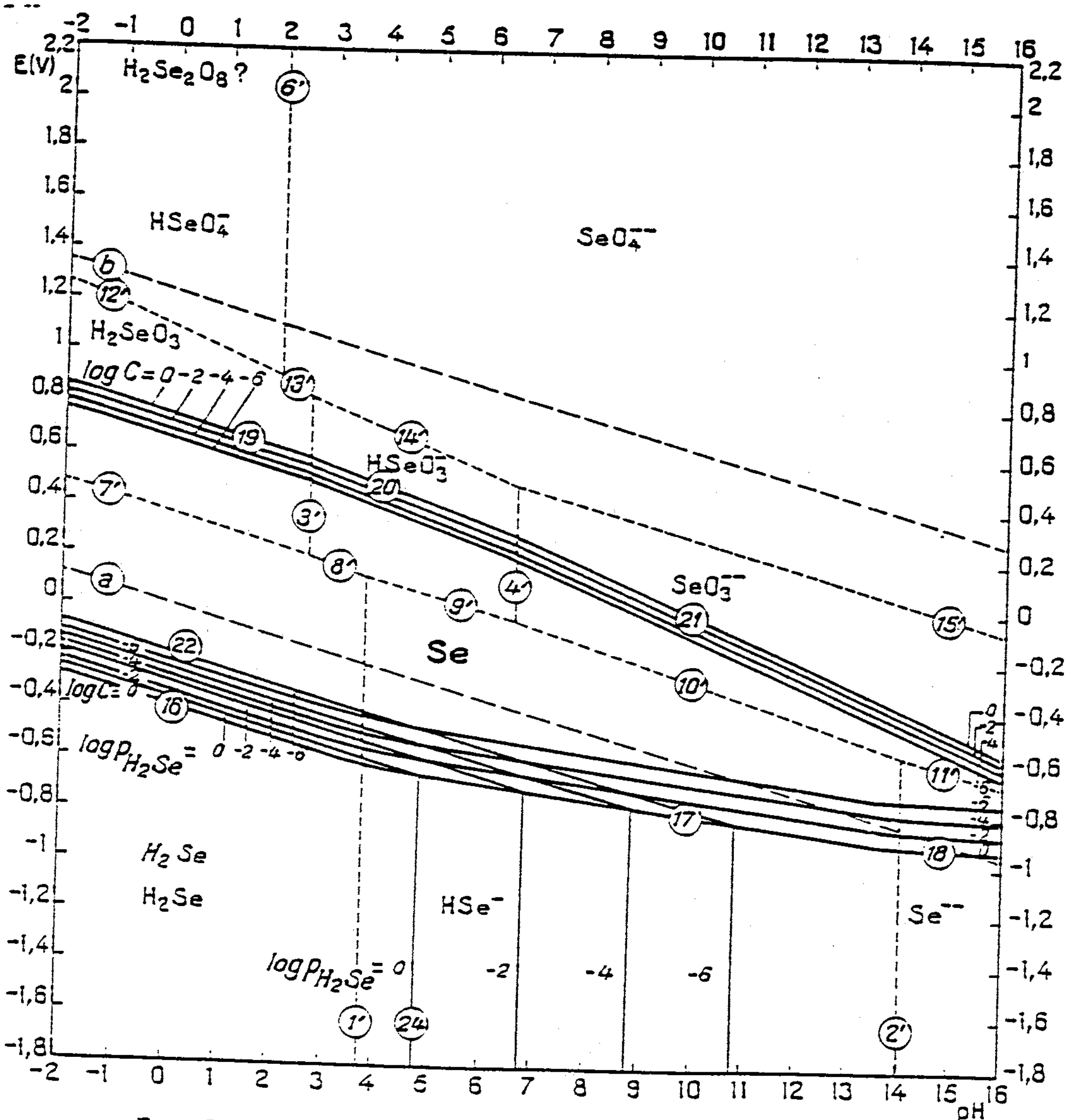


FIG. 1. Potential–pH equilibrium diagram for the system selenium–water, at 25°C.

The part of the diagram outside the line log C = 0 refers to solutions which are not saturated with solid selenium but contain 1 g-at/l (79 g/l) of selenium, dissolved in the forms

$$H_2Se + HSe^- + Se^{--} + H_2SeO_3 + HSeO_3^- + SeO_3^{--} + HSeO_4^- + SeO_4^{--}$$

The part of the diagram inside this line refers to solutions saturated with solid selenium.

Appendix C4

Sulfate Results

C4-1. Sulfate Isotherm Results

Results for the sulfate sorption isotherms with natural and HDTMA-zeolite modified at 100% of the external CEC of the zeolite are contained in Appendix Table C4.1. These results were used to generate Figure 3 of Chapter 2.

The results for sulfate desorption at initial concentrations of 10, 25, and 50, and 100 mg/L are summarized in Appendix Table C4.2. The results for desorption of sulfate from HDTMA-zeolite at 100% of the external CEC were used to generate Figure 4C of Chapter 2.

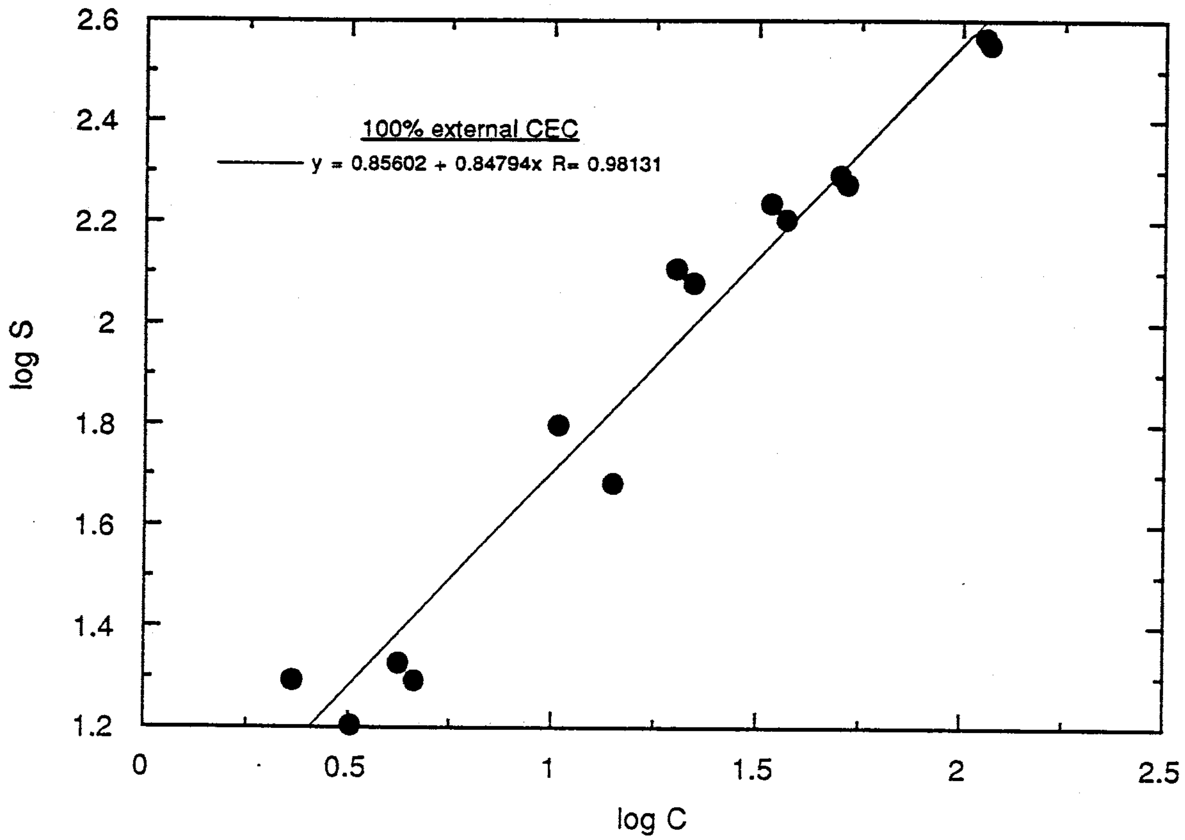
C4-2. Freundlich and Langmuir Fits for Sulfate Sorption

The sulfate data were fit to the Freundlich equation and the Langmuir equation. The Langmuir equation was found to fit the data best. Fitted curves for sulfate on Figures 3, and 4C in Chapter 2 are to the Langmuir equation. Table 1 of Chapter 2 contains the fitted parameters for sulfate sorption results. Appendix Figure C4.1 shows the sulfate data linearized on a log-log scale for fitting to the Freundlich equation. Appendix Figure C4.2 shows the sulfate data linearized to the Langmuir equation.

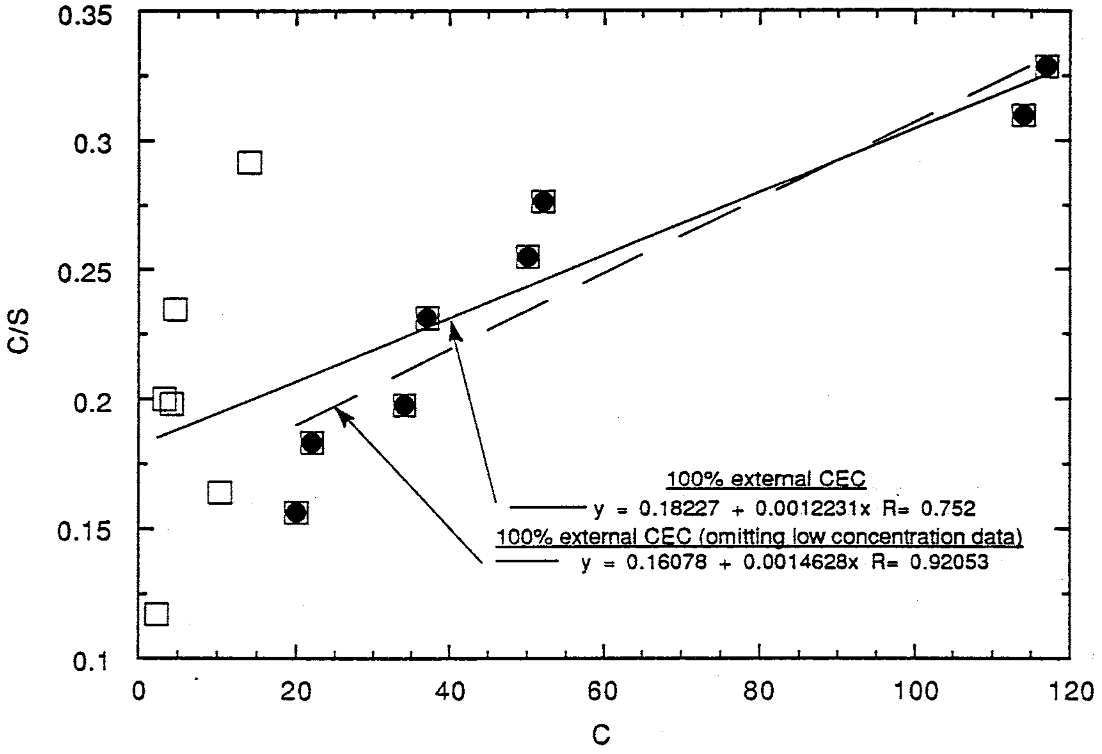
C4-3. pH Measurements

Anion solutions used in the isotherm experiments were unbuffered. The pHs of the equilibrated supernatant were measured after decanting. Appendix Table C4.3 contains the pH results for sulfate. Appendix Figure C4.3 shows the pH distribution of the equilibrated solutions.

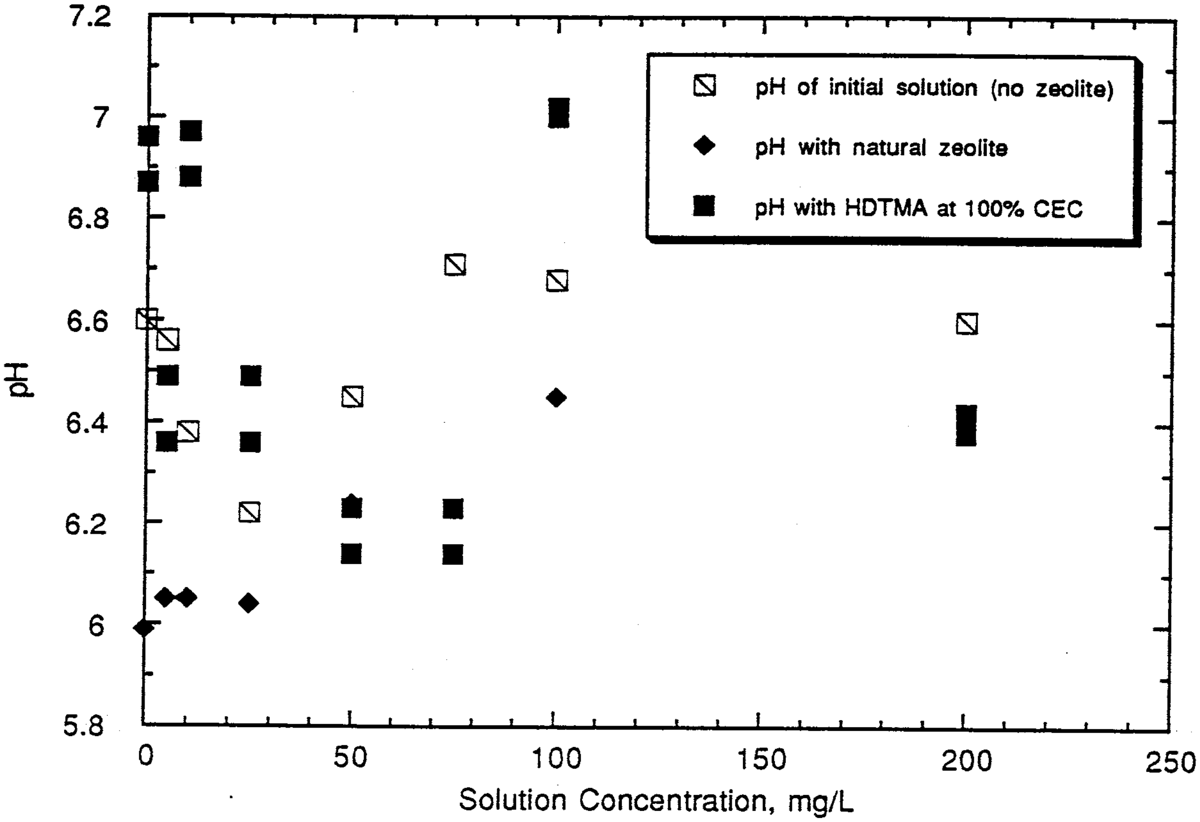
Attachment C4 contains a diagram on the stability of sulfate species in aqueous solution from the *Atlas of Electrochemical Equilibria in Aqueous Solutions* by Marcel Pourbaix (1974). The pH values for the equilibrated solutions ranged from about 6.1 to 7.0. According to Pourbaix (1974), sulfate (SO_4^{2-}) is the predominant species in a dilute aqueous solution at this pH range. The initial solutions for most concentrations were around pH 6.5. No clear trend was observed in pH changes with changes in the substrate or anion concentration.



Appendix Figure C4.1. Fit of Freundlich equation to sulfate sorption isotherm



Appendix Figure C4.2. Fit of Langmuir equation to sulfate sorption isotherm



Appendix Figure C4.3. pH Values for 2/17/93 Sulfate Sorption Isotherm Samples

Appendix Table C4.1. Sulfate Sorption on Natural Zeolite and HDTMA-zeolite modified at 100% external CEC

Type of zeolite : St. Cloud
Mass of zeolite : 2.5 grams
Date of analysis : 2/17/93

Sample ID	Approx. Conc. mg/L	Dilute Equil. Concentration mg/L	Dilution Factor	Equilibrium Soln. Conc. mg/L	Solution Volume ml	Total Solute Mass µg	Equil. Solute Mass in Soln. µg	Equil. Sorbed µg	Solute Mass Sorbed mg/kg
0TB	0	2.5	1	2.5	10	25			
0U	0	1.3	1	1.3	10		13.00	12.00	4.80
0Ha	0	1.9	1	1.9	10		19.00	6.00	2.40
0Hb	0	0.8	1	0.8	10		8.00	17.00	6.80
5TB	5	7.2	1	7.2	10	72			
5U	5	8.4	1	8.4	10		84.00	-12.00	-4.80
5Ha	5	2.3	1	2.3	10		23.00	49.00	19.60
5Hb	5	3.2	1	3.2	10		32.00	40.00	16.00
10TB	10	9.5	1	9.5	10	95			
10U	10	12	1	12	10		120.00	-25.00	-10.00
10Ha	10	4.6	1	4.6	10		46.00	49.00	19.60
10Hb	10	4.2	1	4.2	10		42.00	53.00	21.20
25TB	25	26	1	26	10	260			
25U	25	27	1	27	10		270.00	-10.00	-4.00
25Ha	25	10.3	1	10.3	10		103.00	157.00	62.80
25Hb	25	14	1	14	10		140.00	120.00	48.00

Appendix Table C4.1 continued

Sample ID	Approx. Conc. mg/L	Dilute Equil. Concentration mg/L	Dilution Factor	Equilibrium Soln. Conc. mg/L	Solution Volume ml	Total Solute Mass µg	Equil. Solute Mass in Soln. µg	Equil. Sorbed µg	Solute Mass Sorbed mg/kg
50TB	50	52	1	52	10	520			
50U	50	53	1	53	10		530.00	-10.00	-4.00
50Ha	50	22	1	22	10		220.00	300.00	120.00
50Hb	50	20	1	20	10		200.00	320.00	128.00
75TB	50	77	1	77	10	770			
75U	50	73	1	73	10		730.00	40.00	16.00
75Ha	50	34	1	34	10		340.00	430.00	172.00
75Hb	50	37	1	37	10		370.00	400.00	160.00
100TB	100	99	1	99	10	990			
100U	100	97	1	97	10		970.00	20.00	8.00
100Ha	100	52	1	52	10		520.00	470.00	188.00
100Hb	100	50	1	50	10		500.00	490.00	196.00
200TB	200	206	1	206	10	2060			
200U	200	190	1	190	10		1900.00	160.00	64.00
200Ha	200	114	1	114	10		1140.00	920.00	368.00
200Hb	200	117	1	117	10		1170.00	890.00	356.00

Sample ID explanation
10TB (test blank) - no zeolite and 10 mg/L sulfate solution
10a and 10b - duplicate HDTMA-zeolite samples and 10 mg/L sulfate solution
10U - natural (unmodified) zeolite and 10 mg/L sulfate solution

Appendix Table C4.2. Sulfate Desorption from HDTMA-zeolite

02/17/93 sorption isotherm samples

Zeolite: St. Cloud
Tailoring agent: HDTMA
Date: 12/17/93
Solution volume: 10 mL
Zeolite mass: 2.5 g

Sample Number	Soln. Conc. (ppm)	Mass Removed (µg)	Solute Mass Sorbed (µg)	Solute Mass Sorbed (mg/kg)
10 ppm				
10a	0.04	249.60	249.60	99.84
10a.1	3	29.80	219.80	87.92
10a.2	2.4	9.00	210.80	84.32
10a.3	2.6	14.00	196.80	78.72
10b	0.7	243.00	243.00	97.20
10b.1	2.7	23.50	219.50	87.80
10b.2	2.3	9.50	210.00	84.00
10b.3	2.2	10.50	199.50	79.80
25 ppm				
25a	10.30	147.00	147.00	58.80
25a.1	8.2	30.50	116.50	46.60
25a.2	5.6	15.00	101.50	40.60
25a.3	4.5	17.00	84.50	33.80
25a.4	3.7	14.50	70.00	28.00
25b	14	110.00	110.00	44.00
25b.1	7.9	9.00	101.00	40.40
25b.2	5.3	13.50	87.50	35.00
25b.3	4	13.50	74.00	29.60
25b.4	4.3	23.00	51.00	20.40

Appendix Table C4.2 continued

Sample Number	Soln. Conc. (ppm)	Mass Removed (µg)	Solute Mass Sorbed (µg)	Solute Mass Sorbed (mg/kg)
50 ppm				
50a	22	280.00	280.00	112.00
50a.1	14	30.00	250.00	100.00
50a.2	9.8	28.00	222.00	88.80
50a.3	11	61.00	161.00	64.40
50a.4	6.2	7.00	154.00	61.60
50b	20	300.00	300.00	120.00
50b.1	14	40.00	260.00	104.00
50b.2	9	20.00	240.00	96.00
50b.3	7.3	28.00	212.00	84.80
50b.4	7.2	35.50	176.50	70.60
100 ppm				
100a	52	480.00	480.00	192.00
100a.1	32	60.00	420.00	168.00
100a.2	19	30.00	390.00	156.00
100a.3	14	45.00	345.00	138.00
100a.3	10	30.00	315.00	126.00
100b	50	500.00	500.00	200.00
100b.1	32	70.00	430.00	172.00
100b.2	19	30.00	400.00	160.00
100b.3	13	35.00	365.00	146.00
100b.3	10	35.00	330.00	132.00

Appendix Table C4.3. pH Values for Sulfate Sorption Isotherm

Initial Concentration mg/L	Initial solution	Natural zeolite	100% modified HDTMA-zeolite
0	6.60	5.99	6.96
0			6.87
5	6.56	6.05	6.36
5			6.49
10	6.38	6.05	6.88
10			6.97
25	6.22	6.04	6.49
25			6.36
50	6.45	6.24	6.23
50			6.14
75	6.71	6.23	6.23
75			6.14
100	6.68	6.45	7.02
100			7.00
200	6.60	6.40	6.42
200			6.38

Attachment C4

pH-eH Stability Diagrams for Sulfate

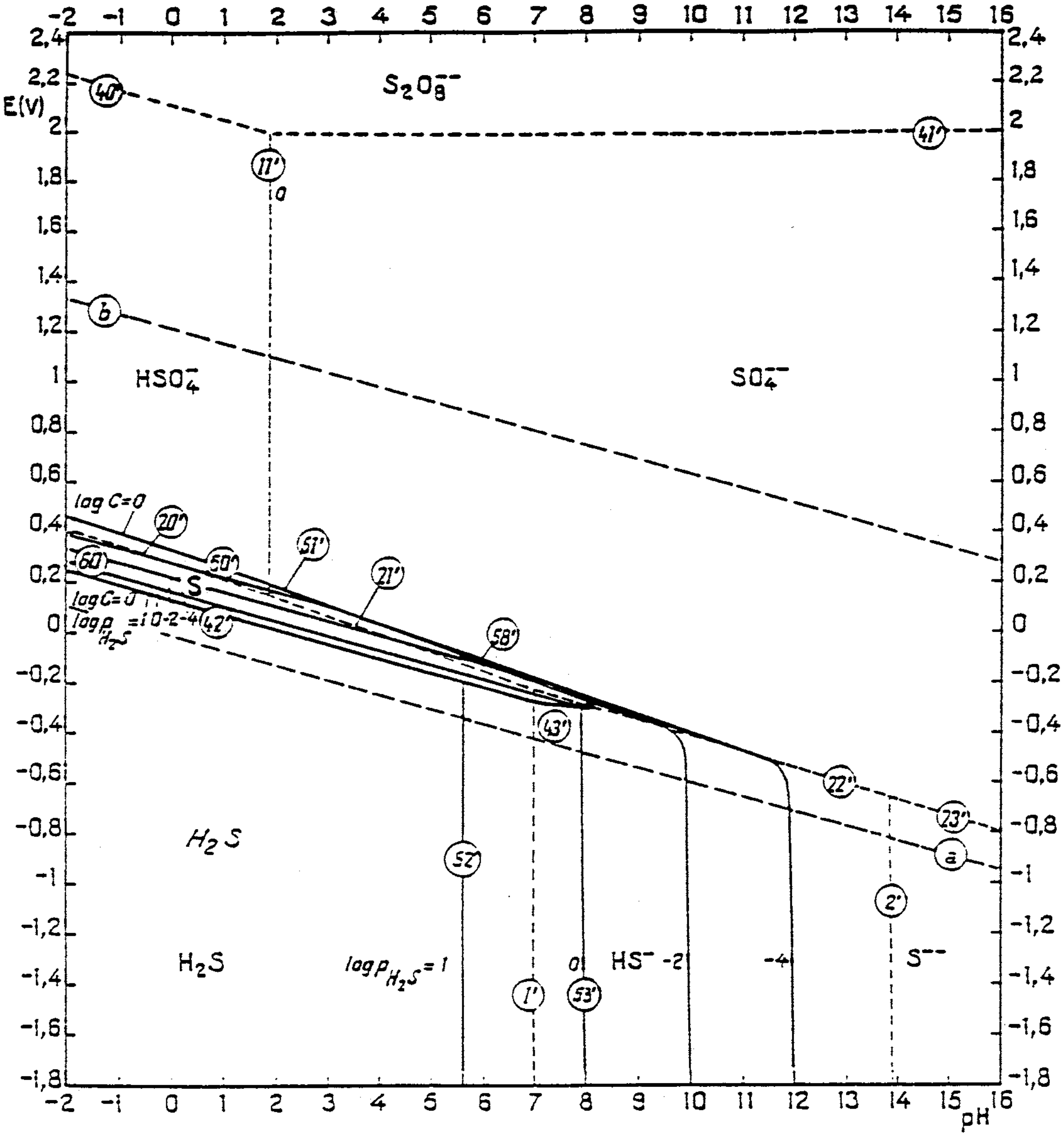


FIG. 1. Potential–pH diagram for the stable equilibria of the system sulphur–water, at 25°C.

The part of this diagram lying outside the line log C = 0 refers to solutions which are not saturated with solid sulphur but which contain 1 g-at/l (32 g/l) of sulphur, dissolved in the forms $H_2S + HS^- + S^{--} + HSO_4^- + SO_4^{--} + S_2O_8^{--}$. The part inside this line refers to solutions saturated with solid sulphur.

Appendix C5

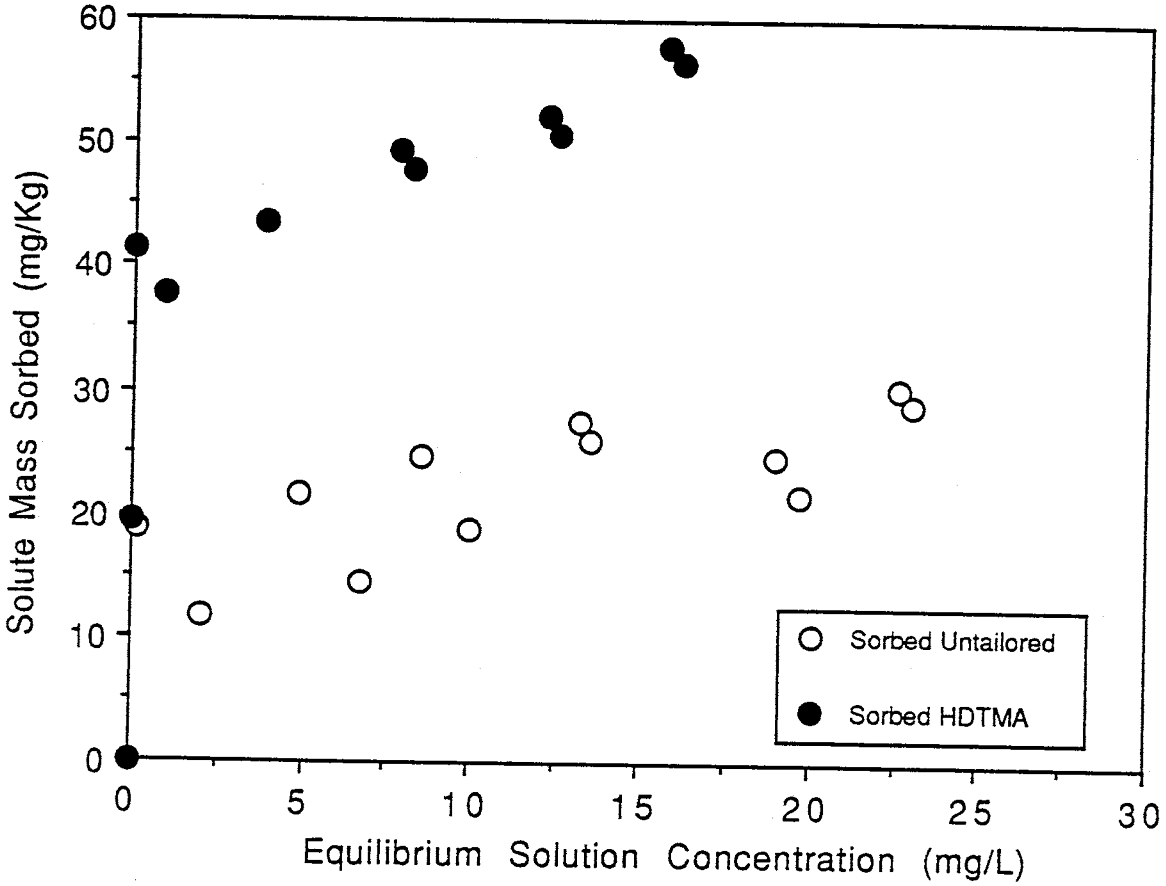
Arsenate Results

C5-1. Arsenate Isotherm Results

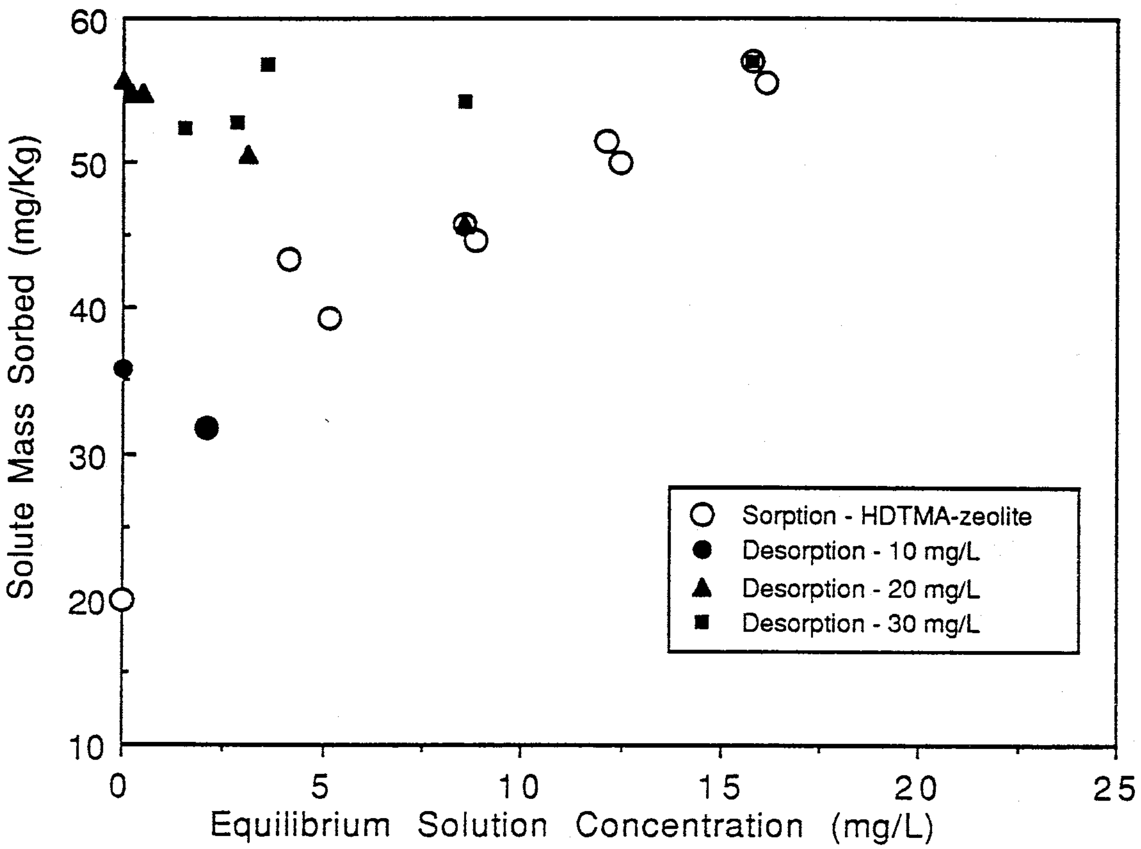
Results for the arsenate sorption isotherms with natural and HDTMA-zeolite are contained in Appendix Tables C5.1 and C5.2. Appendix Figure C5.1 shows the sorption isotherm results graphically. The results for arsenate desorption at initial concentrations of 10, 15, and 20, 25, and 30 mg/L are summarized in Appendix Table C5.3 and C5.4. Appendix Figure C5.2 shows the desorption results for 10, 20 and 30 mg/L. Experiments with arsenate were performed in June, 1992, using HDTMA chloride and were not repeated using HDTMA bromide (as was done for chromate, selenate, and sulfate). I discovered the concentration of the HDTMA chloride solution was less than originally believed, and therefore, surface modification of the zeolite used in the summer of 1992 was at less than 100% of the external CEC. While the data contained in this appendix shows sorption by the HDTMA-zeolite of arsenate did occur, it is not possible to quantify sorption due to the uncertainty in the surfactant loading on the zeolite.

C5-2. pH Measurements

Anion solutions used in the isotherm experiments were unbuffered. The pHs of the equilibrated supernatant were not measured for these experiments. Attachment C5 contains a diagram on the stability of arsenate species in aqueous solution from the *Atlas of Electrochemical Equilibria in Aqueous Solutions* (Marcel Pourbaix, 1974).



Appendix Figure C5.1. Sorption of Arsenate by Natural and HDTMA-zeolite



Appendix Figure C5.2. Arsenate Desorption for 10, 20 and 30 mg/L

Appendix Table C5.1. Arsenate Sorption by Natural Zeolite

Type of Zeolite : St. Cloud
Mass of Zeolite : 5.0 grams
Date of Analysis : 6/23/92

Sample ID	Approx. Conc. mg/L	Dilute Equil. Concentration mg/L	Dilution Factor	Equilibrium Soln. Conc. mg/L	Solution Volume ml	Total Solute Mass µg	Equil. Solute Mass in Soln. µg	Equilibrium Mass Sorbed µg	Solute Mass Sorbed mg/Kg
TB	0	0	1	0	20	0			
1	0	0	1	0	20		0	0	0
2	0	0	1	0	20		0	0	0
TB	5	4.89	1	4.89	20	97.8			
5	5	1.99	1	1.99	20		39.8	58	11.6
6	5	0.18	1	0.18	20		3.6	94.2	18.84
TB	10	10.32	1	10.32	20	206.4			
9	10	6.7	1	6.7	20		134	72.4	14.48
10	10	4.89	1	4.89	20		97.8	108.6	21.72
TB	15	14.66	1	14.66	20	293.2			
13	15	9.96	1	9.96	20		199.2	94	18.8
14	15	8.51	1	8.51	20		170.2	123	24.6
TB	20	20.1	1	20.1	20	402			
17	20	13.22	1	13.22	20		264.4	137.6	27.52
18	20	13.58	1	13.58	20		271.6	130.4	26.08
TB	25	25.16	1	25.16	20	503.2			
21	25	19.01	1	19.01	20		380.2	123	24.6
22	25	19.73	1	19.73	20		394.6	108.6	21.72
TB	30	30.23	1	30.23	20	604.6			
25	30	22.63	1	22.63	20		452.6	152	30.4
26	30	22.99	1	22.99	20		459.8	144.8	28.96

Appendix Table C5.2. Arsenate Sorption by HDTMA-zeolite

Type of zeolite : St. Cloud
Mass of zeolite : 5.0 grams
Date of analysis : 6/23/92

Sample ID	Approx. Conc. mg/L	Dilute Equil. Concentration mg/L	Dilution Factor	Equilibrium Soln. Conc. mg/L	Solution Volume ml	Total Solute Mass µg	Equil. Solute Mass in Soln. µg	Equilibrium Mass Sorbed µg	Solute Mass Sorbed mg/Kg
TB	0	0	1	0	20	0			
3	0	0	1	0	20		0	0	0
4	0	0	1	0	20		0	0	0
TB	5	4.89	1	4.89	20	97.8			
7	5	0	1	0	20		0	97.8	19.56
8	5	0	1	0	20		0	97.8	19.56
TB	10	10.32	1	10.32	20	206.4			
11	10	0.9	1	0.9	20		18	188.4	37.68
12	10	0	1	0	20		0	206.4	41.28
TB	15	14.66	1	14.66	20	293.2			
15	15	3.8	1	3.8	20		76	217.2	43.44
16	15	3.8	1	3.8	20		76	217.2	43.44
TB	20	20.1	1	20.1	20	402			
19	20	8.15	1	8.15	20		163	239	47.8
20	20	7.78	1	7.78	20		155.6	246.4	49.28
TB	25	25.16	1	25.16	20	503.2			
23	25	12.13	1	12.13	20		242.6	260.6	52.12
24	25	12.49	1	12.49	20		249.8	253.4	50.68
TB	30	30.23	1	30.23	20	604.6			
27	30	16.11	1	16.11	20		322.2	282.4	56.48
28	30	15.75	1	15.75	20		315	289.6	57.92

Appendix Table C5.3. Arsenate Desorption from Natural Zeolite

Zeolite: St. Cloud
Tailoring agent: HDTMA
Date of analysis: 6/26/92
Solution volume: 20 mg Zeolite mass: 5 gms

Sample Number	Soln. Conc. (ppm)	Mass Removed (µg)	Solute Mass Sorbed (µg)	Solute Mass Sorbed (mg/kg)
5 ppm				
5	0	100.00	100.00	20.00
6	0	100.00	100.00	20.00
10 ppm				
9	6.5	70.00	70.00	14.00
9.1	1.79	-29.20	99.20	19.84
9.2	1	2.10	97.10	19.42
9.3	0	-10.00	107.10	21.42
9.4	0	0.00	107.10	21.42
10	6.21	75.80	75.80	15.16
10.1	2.83	-5.50	81.30	16.26
10.2	0.5	-18.30	99.60	19.92
10.3	0	-5.00	104.60	20.92
10.4	0	0.00	104.60	20.92
15 ppm				
13	11.16	76.80	76.80	15.36
13.1	5.95	7.40	69.40	13.88
13.2	2.3	-13.50	82.90	16.58
13.3	0	-23.00	105.90	21.18
13.4	0	0.00	105.90	21.18
14	10.381	92.38	92.38	18.48
14.1	4.9	-5.81	98.19	19.64
14.2	1.8	-13.00	111.19	22.24
14.3	0	-18.00	129.19	25.84
14.4	0	0.00	129.19	25.84

Appendix Table C5.3 continued

Sample Number	Soln. Conc. (ppm)	Mass Removed (µg)	Solute Mass Sorbed (µg)	Solute Mass Sorbed (mg/kg)
20 ppm				
17	14.8	104.00	104.00	20.80
17.1	6	-28.00	132.00	26.40
17.2	4.65	33.00	99.00	19.80
17.3	2.04	-5.70	104.70	20.94
17.4	0	-20.40	125.10	25.02
18	14.8	104.00	104.00	20.80
18.1	6.73	-13.40	117.40	23.48
18.2	3.34	-0.50	117.90	23.58
18.3	1.78	2.20	115.70	23.14
18.4	0.48	-8.20	123.90	24.78
25 ppm				
21	17.9	142.00	142.00	28.40
21.1	8.55	-8.00	150.00	30.00
21.2	6.21	38.70	111.30	22.26
21.3	1.79	-26.30	137.60	27.52
21.4	0.22	-13.50	151.10	30.22
22	17.15	157.00	157.00	31.40
22.1	7.52	-21.10	178.10	35.62
22.2	2.3	-29.20	207.30	41.46
22.3	0.744	-8.12	215.42	43.08
22.4	0	-7.44	222.86	44.57
30 ppm				
25	22.6	148.00	148.00	29.60
25.1	10.12	-23.60	171.60	34.32
25.2	5.17	2.20	169.40	33.88
25.3	1.26	-26.50	195.90	39.18
25.4	0.22	-8.20	204.10	40.82
26	24.44	111.20	111.20	22.24
26.1	11.42	-16.00	127.20	25.44
26.2	6.47	15.20	112.00	22.40
26.3	0	-64.70	176.70	35.34
26.4	0	0.00	176.70	35.34

Appendix Table C5.4. Arsenate Desorption from HDTMA-zeolite

Zeolite: St. Cloud
Tailoring agent: HDTMA
Date of analysis: 6/26/92
Solution volume: 20 mg Zeolite mass: 5 gms

Sample Number	Soln. Conc. (ppm)	Mass Removed (µg)	Solute Mass Sorbed (µg)	Solute Mass Sorbed (mg/kg)
5 ppm				
7	0	100.00	100.00	20.00
8	0	100.00	100.00	20.00
10 ppm				
11	2.04	159.20	159.20	31.84
11.1	0	-20.40	179.60	35.92
11.2	0	0.00	179.60	35.92
11.3	0	0.00	179.60	35.92
11.4	0	0.00	179.60	35.92
12	2.05	159.00	159.00	31.80
12.1	1	-0.50	159.50	31.90
12.2	0	-10.00	169.50	33.90
12.3	0	0.00	169.50	33.90
12.4	0	0.00	169.50	33.90
15 ppm				
15	5.17	196.60	196.60	39.32
15.1	2.31	-5.50	202.10	40.42
15.2	0.74	-8.30	210.40	42.08
15.3	0.48	2.20	208.20	41.64
15.4	0.22	-0.40	208.60	41.72
16	4.13	217.40	217.40	43.48
16.1	2.05	-0.30	217.70	43.54
16.2	0.22	-16.10	233.80	46.76
16.3	0	-2.20	236.00	47.20
16.4	0	0.00	236.00	47.20

Appendix Table C5.4 continued

Sample Number	Soln. Conc. (ppm)	Mass Removed (µg)	Solute Mass Sorbed (µg)	Solute Mass Sorbed (mg/kg)
20 ppm				
19	8.56	228.80	228.80	45.76
19.1	3.09	-23.80	252.60	50.52
19.2	0.48	-21.30	273.90	54.78
19.3	0	-4.80	278.70	55.74
19.4	0.22	4.40	274.30	54.86
20	8.82	223.60	223.60	44.72
20.1	3.09	-26.40	250.00	50.00
20.2	1.53	-0.30	250.30	50.06
20.3	1.53	15.30	235.00	47.00
20.4	0.74	-0.50	235.50	47.10
25 ppm				
23	12.13	257.40	257.40	51.48
23.1	5.43	-12.70	270.10	54.02
23.2	1.79	-18.50	288.60	57.72
23.3	0.74	-3.10	291.70	58.34
23.4	1.01	12.80	278.90	55.78
24	12.49	250.20	250.20	50.04
24.1	5.69	-11.10	261.30	52.26
24.2	1.53	-26.30	287.60	57.52
24.3	1.79	20.50	267.10	53.42
24.4	0	-17.90	285.00	57.00
30 ppm				
27	16.11	277.80	277.80	55.56
27.1	8.82	15.30	262.50	52.50
27.2	6.21	36.00	226.50	45.30
27.3	3.35	4.90	221.60	44.32
27.4	0	-33.50	255.10	51.02
28	15.75	285.00	285.00	57.00
28.1	8.56	13.70	271.30	54.26
28.2	3.61	-13.40	284.70	56.94
28.3	2.83	20.50	264.20	52.84
28.4	1.53	2.30	261.90	52.38

Attachment C5

pH-eH Stability Diagrams for Arsenate

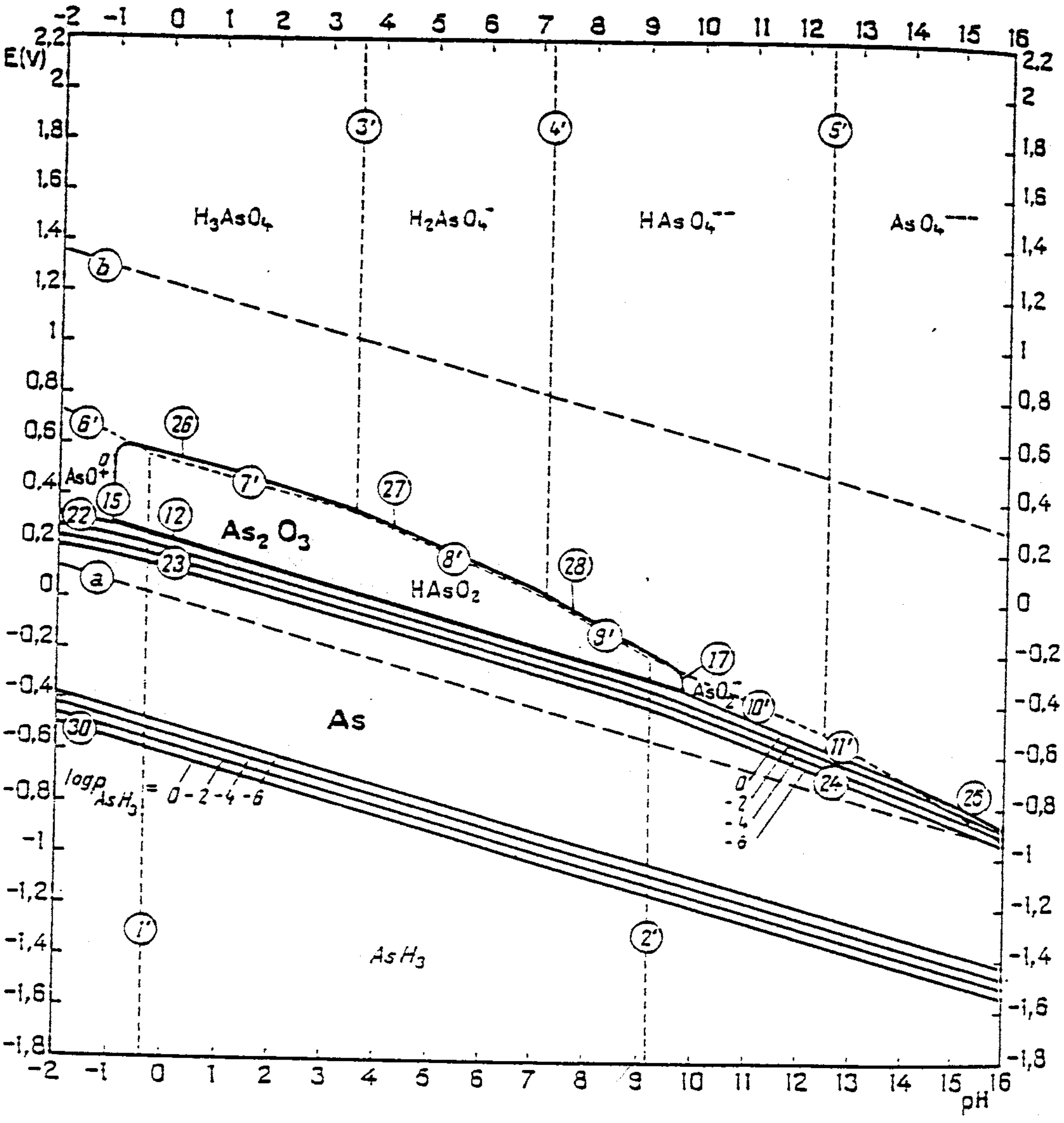


FIG. 1. Potential–pH equilibrium diagram for the system arsenic–water, at 25°C.

APPENDIX D

BIODEGRADATION EXPERIMENTS

D1-1. Introduction

A preliminary biodegradation study was conducted to determine the potential for microbial interaction with HDTMA-zeolite and HDTMA in aqueous solution. Potential uses for cationic surfactants in environmental applications such as permeable barriers or water treatment systems may make the organic cation accessible for degradation by naturally occurring microbes. Biodegradation may decrease the sorption capacity of the organo-zeolite (or organo-clay). Additionally, the toxicity and biodegradability of cationic surfactants must be known if they are to be used in-situ for aquifer remediation.

Consumption of cationic surfactants, primarily as components of textile softeners and detergents, is estimated to have been about 190,000 metric tons in 1987 in the U.S (Boethling, 1993). Most of this quantity eventually ends up as sewage and is potentially released to receiving waters. This may be cause for environmental concern. Removal of cationic surfactants from effluent may occur by sorption, complexation, and/or biodegradation. Cationic surfactants are strongly and rapidly sorbed to mineral particles. They also form 1:1 complexes with anionic surfactants, which are present in far greater quantities in effluents than cationics. Finally, biodegradation of surfactants probably occurs in acclimated systems such as a waste treatment plant.

Boethling (1993) cites a number of studies addressing the toxicity and biodegradability of cationic surfactants. In general, these studies indicate that greater than 90 percent of mono and dialkyl-quaternary amines are degraded in the water column (Boethling, 1993). However, biodegradation of quaternary amines ranging from 0 to 100 percent have been reported. Acclimation appears to profoundly affect the biodegradability of the amines. The fate of cationic surfactants which are sorbed to sediments is not as well characterized.

Although studies have been conducted on alkyl trimethylammonium compounds in waste streams, not much is known of the fate of cationic surfactants in soils and groundwater (Boethling, 1993). HDTMA, at concentrations below 1 mg/L, were found to degrade in river water with a half-life of 2 to 3 days. For several types of aerobic soils, half-lives of a C18 quaternary amine was found to range from 1 to 8 days. Other studies indicated that acclimation strongly affects biodegradation. Therefore, pristine environments may inherently be at risk to surfactant contamination (Boethling, 1993).

The acute toxicity (LC_{50}) of HDTMA (and other alkyl-TMAs) to fish and invertebrates is in the low mg/L range. Algal toxicity is also in the low mg/L range (Boethling, 1993).

Ginkel, et. al. (1992) found a strain of *Pseudomonas* sp. that can utilize HDTMA chloride as a sole source of carbon and energy. They also found that toxicity of the alkyltrimethylammonium compounds increased with increasing chain length, as evidenced by biodegradation rates. At least two organisms appeared mutually responsible for the total mineralization of HDTMA. One organism may break the alkyl chain and another may then break the N - C bonds. Formation of recalcitrant metabolites arising from incomplete biodegradation was thought to be impossible.

In recent work by researchers at Michigan State University (Crocker, et. al., 1992), the biostability of HDTMA-soils and the effects of HDTMA on the biodegradation of organic contaminants were studied. They found that the addition of HDTMA to an aquifer soil significantly reduced the rate and extent of mineralization of toluene and napthalene, and totally inhibited mineralization of phenanthrene. A reason for decreased biodegradation of the organic compounds in the presence of HDTMA was not provided in their abstract, however, W.F. Guerin (personal communication, 1992) speculated that this may have been due to reduced bioactivity due to the toxicity of HDTMA. Additionally, biodegradation experiments on HDTMA-soils indicated that the toxicity of the amine was reduced once it was bound to the soil. HDTMA-soil was biostable during a period of 12 months.

D1-2. Methods and Materials

A preliminary assessment of the biodegradability of HDTMA in aqueous solution and HDTMA-zeolite was performed using methods described by Anderson (1982) and Kieft (personal communication, 1992). In these methods, the rate of biodegradation of a specific organic compound is determined using a ^{14}C-labeled version of the compound. The amount of ^{14}C-labeled CO_2 is a measure of mineralization of the organic carbon to gaseous CO_2. This method does not measure the production of any organic intermediates (including possible volatile organics produced in the biodegradation process), the incorporation of labeled substrate into microbial cells, or methane production. A sterile or poisoned control is required to measure abiotic rates of mineralization.

^{14}C-labeled HDTMA was obtained from American Radiolabeled Chemicals, Inc. The ^{14}C is contained in one of the methyl groups surrounding the nitrogen. Appendix Table D1.1 contains a description of the samples that were prepared for this study. The biodegradation study was prepared in the following manner:

- A microcosm was prepared in a 125-mL glass bottle. The substrate (zeolite or solution), a carbon source (^{14}C-labeled HDTMA in aqueous solution), and activated sludge, as the inoculum, were added to the bottle. To some samples, inorganic nutrients and/or a poison (1 mL of 100 mg/L mercuric chloride) were also added.

- The microcosm was sealed with a rubber stopper and incubated at 22° C. Attached to the rubber stopper was a hanging cup containing 300 μL of an alkaline solution (0.3 *N* NaOH) which trapped gaseous CO_2. A strip of chromotagraphy paper was placed in the hanging cup to increase the surface area for CO_2 absorption.

- After a period of incubation (approximately 10 to 30 days, depending on the sample) the alkaline solution was transferred to scintillation vials and counted using a liquid scintillation counter to determine the amount of ^{14}C-labeled CO_2 which had been produced in the microcosm.

- The hanging cup was discarded and a new cup with fresh alkaline solution and paper was added to if incubation was to be continued.

A total of 11 samples were prepared for this study. Descriptions of the samples are provided in Appendix Table D1.1. For samples 1, 2, 3, 4, and 7, 5 g of natural St. Cloud zeolite was used as the substrate. Five mL of 0.5 N HDTMA solution, spiked with 0.1 uCi of ^{14}C-HDTMA, was added to samples 1 through 4 to achieve a surface modification of the zeolite to 100% of its external CEC. For sample 7, one mL of 0.1 N HDTMA solution, spiked with 0.1 uCi of ^{14}C-HDTMA, was added to the container and mixed with the zeolite. The zeolite was surface modified in this manner to permit a better determination of the initial amount of ^{14}C within the microcosm. The inoculum, activated sludge from the Socorro sewage treatment facility, was then added. A solution containing inorganic nutrients was added to some samples (as shown in Appendix Table D1.1). For the poison control samples, 100 mg/L of mercuric chloride was added to the microcosm. The composition of the nutrient solution is provided in Appendix Table D1.2.

Samples 5, 6, 8, 9, and 10 were microcosms in which various concentrations of aqueous solutions of HDTMA-Cl were tested for biodegradability. When the solutions were prepared I believed the concentrations were as stated above. However, since that time I found that the stock solution used (mixed by a previous researcher) was of a lesser concentration than identified on the container. As a result these solutions are more dilute than described above. How dilute is difficult to access since there is no means at our disposal to quantitatively determine the HDTMA concentration of a solution.

Sample 11 was a microcosm containing organo-zeolite as the substrate. The organo-zeolite was modified with radiolabeled HDTMA, rinsed, and air-dried, before it was added to the biodegradation container. Although this did not allow a quantitative determination of the amount of ^{14}C in the microcosm (due to wash off from the zeolite during rinsing) it prevented the possibility that direct application of HDTMA solution at high concentrations was killing the microorganisms.

Samples 1 through 7 were prepared on September 24, 1992, and the alkaline solution was collected monthly through December, 1992. Samples 8 through 11 were prepared on August 25, 1992, and the alkaline solution collected approximately every 10 days through December, 1992. The microcosms were also sampled in April, 1993.

D1-3. Results

Biodegradation was only apparent in samples 5 and 11. Data for these samples are presented on the following pages. Sample 5 was a dilute solution of HDTMA chloride (no zeolite) and sample 11 was HDTMA-zeolite.

Approximately 45% of the HDTMA was mineralized in sample 5 (Appendix Figure D1.1 and Appendix Table D1.3). However, the poison control sample also showed about the same amount of mineralization. Explanations for this include either survival and recovery of HDTMA-degrading microorganisms in the control sample or the occurrence of abiotic mineralization. Sample 8 was also a dilute aqueous solution of HDTMA chloride (0.001 *M*) prepared identically to sample 5 but on a different date. No mineralization was found to occur in this sample. Given these conflicting results, few conclusions can be made regarding the biodegradation of dilute HDTMA-Cl under these experimental conditions. From the lack of ^{14}C evolution in samples 6, 9, and 10, it appears certain that mineralization of HDTMA does not occur at high concentrations of the cationic surfactant in aqueous solution. This is an expected result based on the toxicity of quaternary amines to aquatic organisms at low mg/L ranges discussed in the previous section of this appendix.

Sample 11 was the only organo-zeolite that showed biodegradation. This sample was prepared differently from the other HDTMA-zeolite samples in that the zeolite was modified, rinsed, and air-dried prior to being added to the microcosm. For all other organo-zeolite samples, HDTMA was added to the zeolite directly into the microcosm to allow for greater control of the amount of ^{14}C actually in the system. As a result, no rinsing of excess HDTMA was possible and toxicity may have been acute for the microorganisms.

Good control on the initial ^{14}C concentrations of sample 11 was not possible. The initial ^{14}C amount was calculated as the initial concentration of ^{14}C-HDTMA added to the zeolite less the concentration of ^{14}C-HDTMA present in the rinsate. Based on this value, over a period of approximately three months, about 10.65% of HDTMA was mineralized (Appendix Figure D1.2 and Appendix Table D1.4). This indicates that HDTMA-zeolite is relatively biostable when sorbed to the zeolite.

D1-4. Discussion and Recommendations

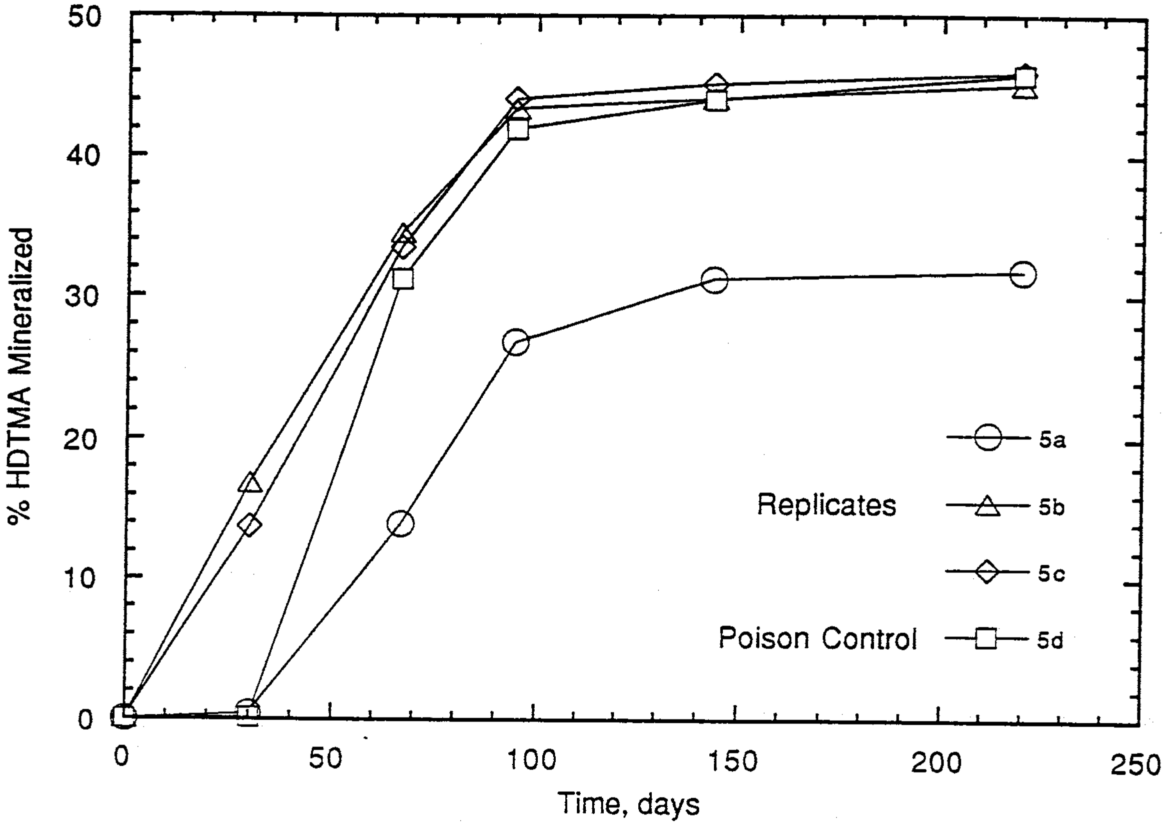
Other than using enrichment cultures, microorganisms in activated sewage will be good degraders of the sorbed cation because they have been acclimated to surfactants. The biodegradation observed in this study can probably be assumed to be a 'worst case'. This study was of too short a time length and too restricted in scope to fully evaluate conditions which could lead to biodegradation of HDTMA in the subsurface.

If organo-zeolites are to be used for environmental purposes several important considerations must be taken into account. The first is that the release of quaternary ammonium cations into the environment may threaten the health of organisms and contaminate drinking waters. The second is that the sorbed organic cation may be vulnerable to biodegradation and, as a result, the effectiveness of the modified material to sorb contaminants may be decreased. This preliminary study and a few other recent studies have shown that HDTMA-materials are fairly biostable under laboratory conditions. More work on the toxicity and biodegradability of cationic surfactants, especially when sorbed to a substrate, must be done before in-situ use of organo-zeolites is feasible. The following suggestions are just a few possibilities for future work in this field:

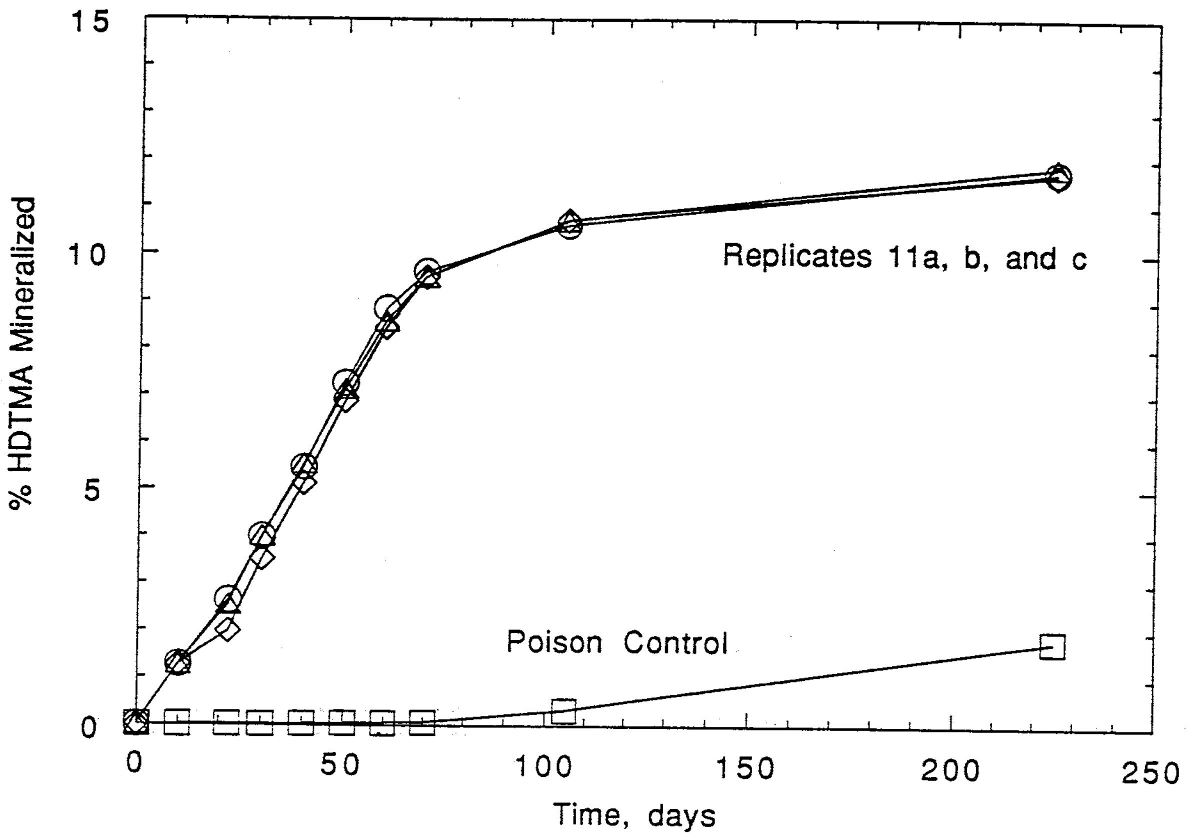
- Perform similar HDTMA-zeolite ^{14}C mineralization experiments using HDTMA bromide (HDTMA chloride was used in this study). Zeolite should be modified at various percentages of the external CEC. The zeolite should be prepared and dried before being added to the microcosm.

- Perform biodegradation experiments with other inoculums, such as river water, aquifer water and soils.

- In-situ biodegradation experiments are probably essential but difficult to achieve since the evolution of ^{14}C cannot be measured in an open system such as a soil column or aquifer. Direct measurement of HDTMA which is sorbed onto materials is also not possible so the removal rate from an organo-zeolite by bioactivity cannot be estimated by present analytical techniques. I don't have any answers to these difficult stumbling blocks but think that further work should be done to develop methods of estimating the fate of HDTMA in the subsurface.



Appendix Figure D1.1. Mineralization of 0.001 M ^{14}C-labeled HDTMA in aqueous solution by sewage microorganisms.



Appendix Figure D1.2. Mineralization of ^{14}C-labeled HDTMA-zeolite modified at below its external CEC. Activated sludge was the inoculum.

Appendix Table D1.1. Description of Biodegradation Samples

		Substrate				
Sample ID	Date began Sample interval	St. Cloud zeolite	^{14}C-labeled HDTMA	Activated Sludge	Nutrient solution	HgCl poison
1a,b,c	7/24/92 30 days	5 g	5 mL 0.5M	1 mL	1 mL	yes
2a,b,c	7/24/92 30 days	5 g	5 mL 0.5M	1 mL	1 mL	no
3a,b,c	7/24/92 30 days	5 g	5 mL 0.5M	1 mL	1 mL	no
4a,b,c	7/24/92 30 days	5 g	5 mL 0.5M	no	no	no
5a,b,c,d	7/24/92 30 days	no	5 mL 0.001M	1 mL	1 mL	5d only
6a,b,c,d	7/24/92 30 days	no	5 mL 0.5M	1 mL	1 mL	6d only
7a,b,c,d	7/24/92 30 days	5 g	5 mL 0.0001 M	1 mL	1 mL	7d only
8a,b,c,d	8/25/92 10 days	no	5 mL 0.001 M	1 mL	1 mL	8d only
9a,b,c,d	8/25/92 10 days	no	5 mL 0.01 M	1 mL	1 mL	9d only
10a,b,c,d	8/25/92 10 days	no	5 mL 0.1M	1 mL	1 mL	10d only
11a,b,c,d	8/25/92 10 days	5 g	premodified ^{14}C-HDTMA	1 mL	1 mL	11d only

Appendix Table D1.2. Composition of Nutrient Solution

Chemical constituent	Amount
K_2HPO_4	2g
K_2HPO_4	7g
$(NH_4)_2\ SO_4$	1g
$Mg_2SO_4{\bullet}7H_2O$	0.1g
$Fe_2SO_4{\bullet}5H_2O$	0.01g
H_2O	1 L

Appendix Table D1.3. Biodegradation Results for Sample 5

5a, b, and c are replicates of HDTMA-zeolite; 5d is the poison control

Approx. initial conc. 14-carbon in sample (cpm): 222000

Amount 14-carbon remaining (cpm)

Date:	8/18/92	9/24/92	10/22/92	12/10/92	4/17/93
5a	221145.2	191063.4	162591.2	152709.2	151457.2
5b	184599.4	145401.3	125725.6	124038.3	121869.1
5c	191488.3	147752.8	124141.3	121792	119947.4
5d	221728.9	152757.9	128903.3	124259.4	120202

Percent of radiolabeled substrate degraded

Date:	8/18/92	9/24/92	10/22/92	12/10/92	4/17/93
5a	0.39%	13.94%	26.76%	31.21%	31.78%
5b	16.85%	34.50%	43.37%	44.13%	45.10%
5c	13.74%	33.44%	44.08%	45.14%	45.97%
5d	0.12%	31.19%	41.94%	44.03%	45.85%

Appendix Table D1.4. Biodegradation Results for Sample 11

11a, b, and c are replicates of HDTMA-zeolite; 11d is the poison control

Initial conc. 14-carbon in sample (cpm): 1116816.9

Amount 14-carbon remaining (cpm)

Date:	9/5/92	9/17/92	9/26/92	10/6/92	10/16/92	10/26/92	11/5/92	12/10/92	4/17/93
11a	1102668.9	1087570.9	1072513.7	1055678.2	1035806.48	1018233.88	1009472.38	998407.08	985931.08
11b	1102664.9	1088425.2	1072332.4	1054970.1	1037302.8	1021063.9	1010708	997474.6	984619.6
11c	1102624.9	1094654.5	1077631.5	1059632.4	1040048.2	1022524.8	1010737.8	997245.8	986540.8
11d	1116682.8	1116607.6	1116537.7	1116480.9	1116389.9	1116313.1	1116197.9	1113223.8	1096834.8

Percent of radiolabeled substrate degraded

Date:	9/5/92	9/17/92	9/26/92	10/6/92	10/16/92	10/26/92	11/5/92	12/10/92	4/17/93
11a	1.27%	2.62%	3.97%	5.47%	7.25%	8.83%	9.61%	10.60%	11.72%
11b	1.27%	2.54%	3.98%	5.54%	7.12%	8.57%	9.50%	10.69%	11.84%
11c	1.27%	1.98%	3.51%	5.12%	6.87%	8.44%	9.50%	10.71%	11.66%
11d	0.01%	0.02%	0.02%	0.03%	0.04%	0.05%	0.06%	0.32%	1.79%

APPENDIX E

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