

University of Alberta

Dissolution of Salts Encapsulated with Elemental Sulfur

by

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ABSTRACT

Encapsulating solid salts with elemental sulfur and simultaneous disposal of them into tailing ponds is a brand new idea in managing the large volume of the two oilsands industrial byproducts. The dissolution of encapsulated salts and the environmental impact are the two concerns relating to the disposal.

Measurements of pH, electric conductivity, dissolved oxygen, alkalinity, and ion concentration were conducted during the laboratory research. Analytical and numerical models were developed to determine the diffusion coefficients of dissolved salts through elemental sulfur caps.

Neutral pH conditions were found at the interface of salt-sulfur solid and CT release water. The back-calculated salt diffusion coefficients through a layer of porous elemental sulfur were in the order of that in unsaturated soils. Encapsulating solid salts with elemental sulfur and simultaneous disposal of them into tailing ponds was concluded to be a viable method of managing solid salts and elemental sulfur.

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LIST OF SYMBOLS

c	Concentration of solutes [M/L^3]
c_b	Concentration of boundary input [M/L^3]
C_B	Total carbonate alkalinity [M/L^3]
C_T	Total carbon [M/L^3]
c_i	Concentration of ion i [M/L^3]
D	Diffusion coefficient [L^2/T]
D^*	Effective diffusion coefficient [L^2/T]
D_i	Free solution diffusion coefficient of ion i [L^2/T]
D_{ij}	Dispersion coefficients [L^2/T]
D_{ij}^m	Mechanical dispersion coefficients [L^2/T]
G	Generic reaction term, i.e. mass produced/ consumed per unit volume of porous medium and per unit time [$M/L^3/T$]
J_i	Total flux in one direction [$M/L^2/T$]
n	Porosity for saturated media, volumetric water content for unsaturated media
P	Vapor pressure of water [N/L^2]
P_0	Barometric pressure (mm Hg)
q_i	Macroscopic fluid flux [$M/L^2/T$]
S^*	Oxygen solubility [M/L^3]
S^*_{760}	Saturation value at 760 mm Hg
S_y	Salinity [M/L^3]
t	Time [T]
T	Absolute temperature (K)

x_j	Fluid flow directions [dimensionless]
z_i	Charge of ion i [dimensionless]
μ	Viscosity [centipoises]
τ	Tortuosity of the flow path [dimensionless]
ε	Porosity of the medium [dimensionless]
γ	Activity coefficient of ions [dimensionless]

LIST OF ABBREVIATIONS

AEGRF	Applied Environmental Geochemistry Research Facility
APHA	American Public Health Association
CBE	Charge balance error
CT	Composite tailings
DBL	Diffusion boundary layer
DI	Deionized
DO	Dissolved oxygen
EC	Electrical conductivity
EDR	Electrodialysis Reversal
IC	Ion chromatography
L	Liter
MFT	Mature fine tailings
NST	Non-segregated tailings
SRB	Sulfate reducing bacteria
TDS	Total dissolved solid
XRD	X-ray diffraction
ZLD	Zero liquid discharge

1.0 INTRODUCTION

1.1 General Background

Until a new energy revolution emerges, the non-renewable fossil fuel, represented by petroleum, will remain the most important energy source for humankind. Sustainable economic and societal development requires current generations to seek a reasonable and environmentally acceptable use of these natural resources.

The province of Alberta, Canada, holds one of the largest oil sand reserves in the world. In all, Albertan oil sands contain 1.7 to 2.5 trillion barrels of bitumen, of which approximately 315 billion barrels are potentially recoverable under current technological and economic conditions (EUB, 2002). To date, only about 2% of the bitumen reserve has been exploited, indicating that the oil sands industry will play a very influential role in the future economy and environment of Alberta and Canada.

The crude bitumen of Alberta's oil sand deposits contains 5% to 7% sulfur. During the process of bitumen extraction and upgrading, 90% of the sulfur is recovered in elemental sulfur form or remains within the coke byproducts (EUB, 2002). Three hundred thousand tons of sulfur (EUB, 2003), including 27 thousand tons from Syncrude Canada Ltd. alone, are generated in Alberta each month. However, only a small fraction of this sulfur is shipped to offshore markets. Elemental sulfur, once an industrial material in high demand, has almost no market for the Alberta oilsands industry due to high costs of shipping it south and its oversupply on the international market.

Generation of sulfur from the industrial process is unavoidable, and the ever-increasing stockpiles of excess sulfur demand proper management. Currently, the common method of sulfur management is outdoor block storage without shelter or containment (Fig.1.1). Potential for contact and interaction of sulfur with surrounding soils and air as time passes is possible. Such contact will certainly impact the environment. Finding a technically safe storage method for the waste sulfur that is both economically and environmentally acceptable is a challenge facing the oilsands industry today.

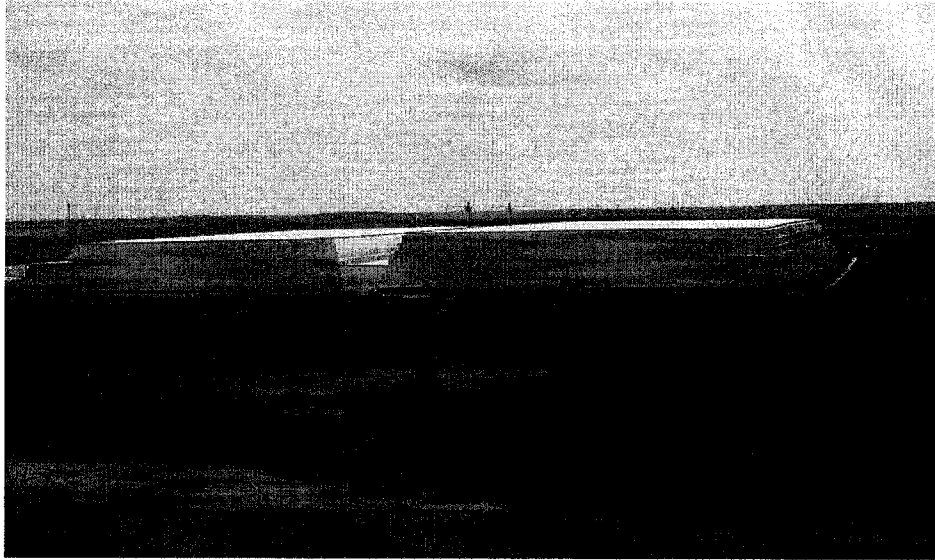


Fig.1.1 Sulfur Stockpiles (source: the author's field trip to Fort McMurray, 2003.)

“(Oilsands) Industry has made significant progress on reclamation of overburden waste piles and the sand deposits, but has yet to achieve the larger goals of reclamation: development of sustainable ecosystems, returning disturbed land to equivalent land capabilities, or the ability to progressively reclaim tailings ponds and deposits” (CANMET, 2002)

Meanwhile, the Albertan oilsands industry has been producing and continues to produce enormous amounts of tailings daily. After the sand settles out, the surface water clarifies and is recycled back to the plant. The remaining material is a mixture of clay, water, and other fines called MFT (Mature Fine Tailings, List and Lord, 1996). The MFT is not predicted to consolidate into stable materials for several centuries (Mikula et al. 1996, 1997). One method being used to improve the tailing performance, eliminate MFT accumulation and provide the opportunity to reclaim existing tailing disposal areas is called Nonsegregating Tailings (NST). This method consists of reblending MFT with coarse sand and coagulants (chemical additives) resulting in Consolidated/ Composite Tailings (CT). Currently, CT is amended by the addition of gypsum, producing the most favorable release water quality (Matthews et al. 2002).

The CT release water, containing mainly sodium, chloride and sulfate, requires management through recycling, storage, or treatment followed by discharge. The release water is discharged because it undergoes geochemical and biochemical interactions within the

tailings environment, resulting in pH changes, bacterially catalyzed redox reactions and gas genesis. Presently, research on the CT release water is focused on the impact of dissolved ions on the northern environment (CANMET 2002).

At the moment, the CT release water and elemental sulfur generated by the oilsands industry need to be properly managed. One option is to manage them together, i.e., manage waste by making use of waste. Natural resources are always limited. Any so-called “waste” at this time can be valuable sometime in the future. Therefore, a proper management of these two byproducts implies that they should be recoverable and reclaimable in the future. A research team at the University of Alberta conceived a conceptual model of disposing sulfur and salt together in a mined-out pit (see Fig. 1.2). The CT release water can be treated using Reverse Osmosis (RO) which results in treated water and a small volume of concentrated salts in the form of brine (RCCI Report). If the waste heat of the oilsands processing system can evaporate RO brine, the leftover material will be solid salts. The salts can then be crushed and mixed with molten elemental sulfur and discharged to a specially designed block in a mined-out pit. This mixture could then be encapsulated with sulfur, which restrict the access of water to the encapsulated salt and thus sequestered the salt within the sulfur. The sulfur encapsulation and the sulfur-salt mixture are then covered by several meters thick CT water as the pit is in-filled and finally disposed of or stored for possible future use of the sulfur. The use of CT that surrounds the in-pit block is to buffer any future release of acidity from the sulfur.

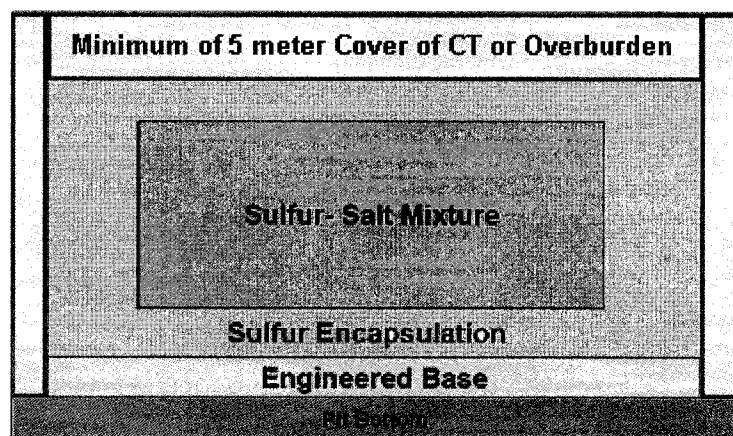


Fig. 1.2 Conceptual Model of Sulfur and Salt Disposal in a Mined-out Pit

The above conceptual design includes several questions that need to be answered: Can the CT water efficiently buffer acidity released from sulfur? Can the encapsulated salts be dissolved and return to the environment and how fast? The purpose of this research is to explore these questions by conducting carefully designed laboratory experiments.

1.2 Objectives

Unlike naturally created sulfur crystals which are molecularly compacted, industrially formed elemental sulfur solid has built-in pores (see details in coming sections). If the salts are encapsulated within elemental sulfur ($S^{(0)}$), water may penetrate and saturate the porous $S^{(0)}$ and dissolve the contained salts. The dissolved salts will then transport into the surrounding environment. The fundamental mechanisms governing the transport processes must be examined; therefore, this research program was designed with the following objectives:

- Assessing the disposal of solid salts by encapsulating them with elemental sulfur and covering this mass using CT release water;
- Inspecting the pH changes of different encapsulation conditions;
- Measuring the rates of diffusion of salts through porous elemental sulfur into water under different encapsulation conditions;
- Determining the effective diffusion coefficients of salts through porous elemental sulfur via analytical modeling.

The diffusion of aqueous salt ions through porous, molecular sulfur is different from the diffusion of aqueous salt ions through typical porous media. Measurement of electrochemical change of the aqueous solution and chromatographic detection of ions and their concentrations were conducted in this research program. Both analytical and numerical models were used to evaluate the laboratory data.

1.3 Methodology

This research program included a literature review, description of test methods, development of experimental procedures and analytical methods, and general laboratory testing.

The literature review in Chapter 2 reviews existing information on material transport in porous

media including the determination of diffusion and dissolution coefficients in water solutions, salt dissolution reaction kinetics, and biogeochemical reactions in S-H₂O-O₂ systems. Chapter 3 provides an overview of the physical and chemical properties of the materials and the methods used in the laboratory tests. Chapter 4 presents the time-dependent test results. Chapter 5 interprets the test results, including the buffer capacity of the CT release water, the effect of sulfur encapsulation and salt fluxes, and mathematically modeled test results. Chapter 6 summarizes the key findings and makes recommendations for use in engineering practices.

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2.0 LITERATURE REVIEW AND BACKGROUND INFORMATION

Industrial elemental sulfur can be viewed as a porous material through which dissolved salts transport into a water reservoir. The properties of the materials used in this research, such as elemental sulfur, solid salts and water, will be introduced in Chapter 3. Theories pertaining to fluid transport in porous media and water chemistry are reviewed in this chapter.

2.1 Transport Theory

2.1.1 Advection-Dispersion Model

The general form of the advection-dispersion equation describing physical transport of solute in porous media is presented below:

$$\frac{\partial}{\partial t}(n \cdot c) + \frac{\partial}{\partial x_i}(q_i \cdot c) - \frac{\partial}{\partial x_i}(n \cdot D_{ij} \cdot \frac{\partial c}{\partial x_j}) = \pm G, \quad i, j = 1, 2, 3 \quad (2.1)$$

where,

n — porosity for saturated media, volumetric water content for unsaturated media
[dimensionless]

c — concentration of solutes [M/L³]

t — time

q_i — macroscopic fluid flux [M/L²/T]

D_{ij} — dispersion coefficients [L²/T]

x_i — fluid flow directions [dimensionless]

G — generic reaction term, i.e., mass produced/consumed per unit volume of porous medium and per unit time [M/L³/T]

The total mass flux can be expressed as:

$$J_i = q_i \cdot c - n \cdot (D_{ij}^m + D) \cdot \frac{\partial c}{\partial x_j} \quad i, j = 1, 2, 3 \quad (2.2)$$

where,

J_i — total flux in one direction [M/L²/T]

D_{ij}^m — mechanical dispersion coefficients [L²/T]

D — diffusion coefficient [L²/T]

If the following assumptions are made:

- Porosity of the medium is constant in time and space

- One-dimensional flow
- Fluid is static, i.e. only diffusions of the ions or molecules are activated by chemical potential difference of the solute
- The medium is water saturated
- The fluid is essentially incompressible
- No reactions,

Equations 2.1 and 2.2 can be simplified to:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (2.3)$$

$$J = D \frac{\partial c}{\partial x} \quad (2.4)$$

2.1.2 Transport Coefficients

2.1.2.1 Diffusion Coefficients of Strong Electrolytes

The most common basis for estimating diffusion coefficients in liquids is the Stokes-Einstein equation or its empirical parallels (Reid et al., 1977). Table 2.1 shows some ion diffusion coefficients in water.

Table 2.1 Diffusion Coefficients in Water for Selected Ions*

Anion	D_0 ($\times 10^{-6}$ cm ² /s)	Cation	D_0 ($\times 10^{-6}$ cm ² /s)
Cl ⁻	20.3	Na ⁺	13.3
SO ₄ ²⁻	10.7	K ⁺	19.6
F ⁻	14.7	Ca ²⁺	7.9
Br ⁻	20.8	Mg ²⁺	7.1

* Values correspond to infinite dilution in water at 25 °C

Source: Li and Gregory (1974).

Strong electrolytes are completely disassociated in water and have their own free solution diffusion coefficients, but they are tied together electrostatically and transport in the same diffusion coefficients that can be calculated by Equation 2.5 (Harned and Owen, 1950), presented below:

$$D = \frac{D_1 D_2 (|z_1| + |z_2|)}{D_1 |z_1| + D_2 |z_2|} \quad (2.5)$$

where

D_i — free solution diffusion coefficient of ion i [L^2/T]

z_i — charge of ion i [dimensionless]

Diffusion coefficients measured in concentrated solutions frequently vary by several hundred percent from those measured in pure liquids. Equation 2.6 (Cussler, 1997) indicates the empirical adjustment of diffusion coefficients between infinitely dilute solutions and concentrated solutions.

$$D = D_0 \left(1 + \frac{\partial \ln \gamma}{\partial \ln c} \right)^{0.6} \quad (2.6)$$

where

γ — activity coefficient [dimensionless]

D_0 — free solution diffusion coefficient [L^2/T]

For a multicomponent system in a concentrated solution, the fluxes and concentration profiles deviate significantly from binary solutions. In addition, “multi-component diffusion coefficients are difficult to estimate and experimental values are fragmentary” (Cussler, 1997).

An effective diffusion coefficient in a porous medium is a function of the free water diffusion coefficients and the physical properties of the solid matrix. Mathematically, the effective diffusion coefficient is defined as:

$$D^* = D_0 \frac{\varepsilon}{\tau} \quad (2.7)$$

where

τ — tortuosity of the flow path within material [dimensionless]

D^* — effective diffusion coefficient [L^2/T]

ε — porosity of the material [dimensionless]

For a medium containing a single mobile phase, the effective diffusion coefficient may be estimated by the relationship derived by Millington and Quirk (1961):

$$D^* = D_0 \varepsilon^{4/3} \quad (2.8)$$

2.1.2.2 Oxygen Flux in Water

The physical process of oxygen transfer across a water surface in contact with the atmosphere is described by the simple reaction:



This process tends to restore the thermodynamic equilibrium which is reached when the chemical potential (or fugacity) of oxygen is equal in both phases. At equilibrium, the water is oxygen saturated with respect to the atmosphere. The reaction proceeds to the right as long as the water is under-saturated, and conversely to the left in the case of over-saturation. The dissolution reaction is fast; hence, the concentration at the surface becomes saturated as soon as the atmosphere is applied. However, the movement of O_2 into the water body is limited by diffusion away from its surface. The governing equations of the one-dimensional diffusion are given in Equation 2.3 and Equation 2.4.

Estimates of the oxygen diffusion coefficient in liquids often use a correlation developed by Wilke and Chang (1955), which is based on the Stokes-Einstein equation and given as:

$$D_{\text{O}_2-\text{H}_2\text{O}} = 7.4 \times 10^{-8} \frac{T \sqrt{\Psi_{\text{H}_2\text{O}} M_{\text{H}_2\text{O}}}}{\mu V_{\text{O}_2}^{0.6}} \quad (2.10)$$

where

T = the absolute temperature (K);

$\Psi_{\text{H}_2\text{O}}$ = an "association" parameter for the solvent water: 2.26 (Reid et al., 1977)

$M_{\text{H}_2\text{O}}$ = the molecular weight of water: 18g/mole

μ = viscosity of water [centipoises].

V_{O_2} = the molar volume of oxygen = 25.6 cm³/g-mole (Welty et al., 1984)

Equation 2.10 lacks the rigorous theoretical foundation used to develop the equations for gas mixtures and is usually accurate to $\pm 10\%$ for dilute solutions of non-dissociating solutes (Bird, et al., 1960). In addition, Equation 2.10 neglects the effects that dissolved substrates and microorganisms may have on diffusion.

The concentration of dissolved oxygen (DO) in water is a function of the temperature of the air and water, the salinity of the water, and the demand for oxygen within the body of water.

The relationship between temperature, salinity, and dissolved oxygen is approximated with the following exponential equation (URL Ref No.: 1):

$$\ln(C_{\text{sat}}) = -139.34 + \frac{1.5757 \times 10^5}{T} - \frac{6.6432 \times 10^7}{T^2} + \frac{1.2438 \times 10^{10}}{T^3} - \frac{8.6219 \times 10^{11}}{T^4} - S_y \left(1.7674 \times 10^{-2} - \frac{10.754}{T} + \frac{2.1407 \times 10^3}{T^2} \right) \quad (2.11)$$

where,

T = Temperature (K)

S_y = Salinity (g/L)

C_{sat} = Saturated oxygen concentration in water (mg/L)

2.2 Salt Dissolution Reaction Kinetics

2.2.1 Salt Dissolution Kinetics

Without further chemical reaction in the solution, two processes control the dissolution of solids into an aqueous solution: a) the dissolution of solute molecules on the solid surface through surface reaction, which depends on the chemical composition of the solution at the surface (such as the presence of trace metals and ion concentrations); and b) the subsequent diffusion of the disintegrated solute molecules toward the bulk liquid phase across a diffusion boundary layer (DBL) with thickness δ (Richard and Sjöberg, 1983). The mass flux of the two processes is equal, i.e. both processes simultaneously control the effective dissolution rate. There exist two extreme limits: a) surface controlled dissolution: for infinitely small values of δ , transport by diffusion is so effective that the concentration of the ion at the surface equals that in the bulk of the solution; and b) transport controlled dissolution: if the dissolution rate of the solid at the surface is extremely high, as with rock salt, transport will be entirely controlled by molecular diffusion (Jeschke et al., 2000). However, a rigorous treatment of conventional analysis that is almost always based on the extreme cases shows that neglecting the effect of surface reaction in the dissolution kinetics may lead to a significant deviation from real conditions (Hsu and Liu 1992).

2.2.2 Solubility of Salt Solids

The solubility of some selected salts in water at 25°C is listed in Table 2.2.

Table 2.2 Solubility of Selected Salts (25°C)

Salt Species	Solubility mol/(kg water)	Salt Species	Solubility mol/(kg water)
NaCl	6.15	Na ₂ SO ₄	1.97
KCl	4.5	K ₂ SO ₄	0.65
MgCl ₂	5.7	MgSO ₄	2.6
CaCl ₂	9.4	CaSO ₄	3.6×10 ⁻⁴

Temperature is a major factor affecting the solubility of inorganic materials. As shown in Table 2.3 (Stephen, 1963), the solubility of Na₂SO₄ is strongly temperature dependent. Cragg and Graham (1954) point out that below a temperature of 32.4°C, the one solid phase that can exist in equilibrium with a solution of sodium sulfate is the decahydrate, Na₂SO₄·10H₂O.

Table 2.3 Solubility of Salt in Pure Solution and at Different Temperatures

NaCl			Na ₂ SO ₄ ·10H ₂ O			Na ₂ SO ₄	
Temp. (°C)	Solubility g/(kg H ₂ O)	Solubility g/(kg H ₂ O)	Temp. (°C)	Solubility g/(kg H ₂ O)	Solubility mol/(kg H ₂ O)	Solubility g/(kg H ₂ O)	Solubility mol/(kg H ₂ O)
-15	320.13	5.48	0	194.74	0.60	49.98	0.35
20	358.70	6.14	20	440.92	1.36	194.74	1.37
25	359.43	6.15	25	529.05	1.63	280.41	1.97
30	360.91	6.17	33			506.02	3.56
60	371.18	6.35	60			453.49	3.19
80	380.26	6.51	75			436.78	3.08

Note: the data of solubility shown by Stephen, 1963 were at same temperature for Na₂SO₄·10H₂O and Na₂SO₄ but at different temperature for Na₂SO₄·10H₂O and NaCl.

Common ions decrease salt solubility. The solubility of a salt mixture can be found from a phase equilibrium diagram. In some cases, both hydrated and anhydrous salts can be formed; this occurs with the NaCl-Na₂SO₄-H₂O system between 17.9°C and 32.4°C. The equilibrium diagram at 25°C is shown in Fig. 2.1. Along AC the solid phase is NaCl, and along CD anhydrous Na₂SO₄ separates, whereas along DB the solution is in equilibrium with Na₂SO₄·10H₂O. At the invariant points C and D, the two solids are NaCl and Na₂SO₄, and Na₂SO₄ and Na₂SO₄·10H₂O, respectively. It is of interest to observe that in the ternary system the anhydrous salt is stable at a temperature below the normal transition point for the binary system Na₂SO₄-H₂O; the ternary transition point, at which the three solids, Na₂SO₄,

$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and NaCl , can all be in equilibrium with solution is 17.9°C . Above 32.4°C , the binary transition point, the decahydrate can no longer exist, and so at higher temperature there are only two parts to the solubility curve, the solid phases being NaCl and anhydrous Na_2SO_4 . At an equilibrium state, McHale (1992) shows that weight percentage of NaCl and Na_2SO_4 in saturated solutions with the existence of solid phase halite and thenardite is 24.99 and 4.68, respectively, at 75°C for a $\text{NaCl-Na}_2\text{SO}_4\text{-H}_2\text{O}$ system, i.e. the solubility of NaCl : $355.32 \text{ g}/(\text{kg}\cdot\text{H}_2\text{O})$ and Na_2SO_4 : $66.54 \text{ g}/(\text{kg}\cdot\text{H}_2\text{O})$. Both are lower than their solubility in pure solutions. At room temperature, the equilibrated solubility of dissolved NaCl should be lower than $355.32 \text{ g}/(\text{kg}\cdot\text{H}_2\text{O})$ at 75°C .

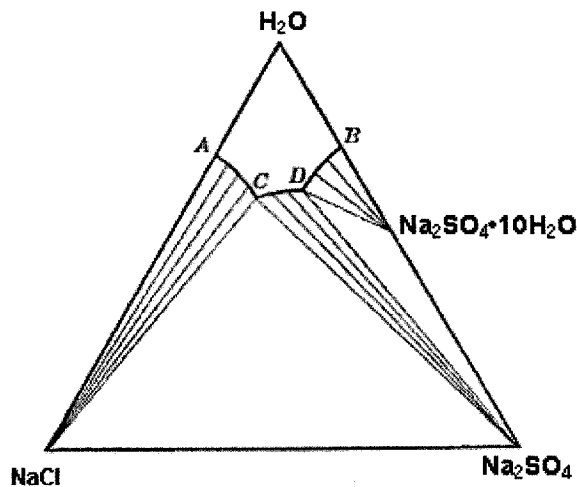


Fig. 2.1 The System $\text{NaCl-Na}_2\text{SO}_4\text{-H}_2\text{O}$ at 25°C (Modified after: Glasstone, 1940)

2.3 Biogeochemical Reactions in the S-H₂O-O₂ System

Biogeochemical processes of sulfur include microbial redox reactions and acid-base reactions, which, in contrast to abiotic reactions of sulfur, occur at ambient temperatures (Wainwright, 1984; Chapman, 1989). $\text{S}^{(0)}$ was used to encapsulate solid salts in this research, and one of the main components of the CT release water used in the tests was sulfate. Therefore, it's necessary to briefly introduce the biogeochemical reactions in an S-H₂O-O₂ system to understand the mechanism of pH changes and dissolved oxygen fluctuations for this research study.

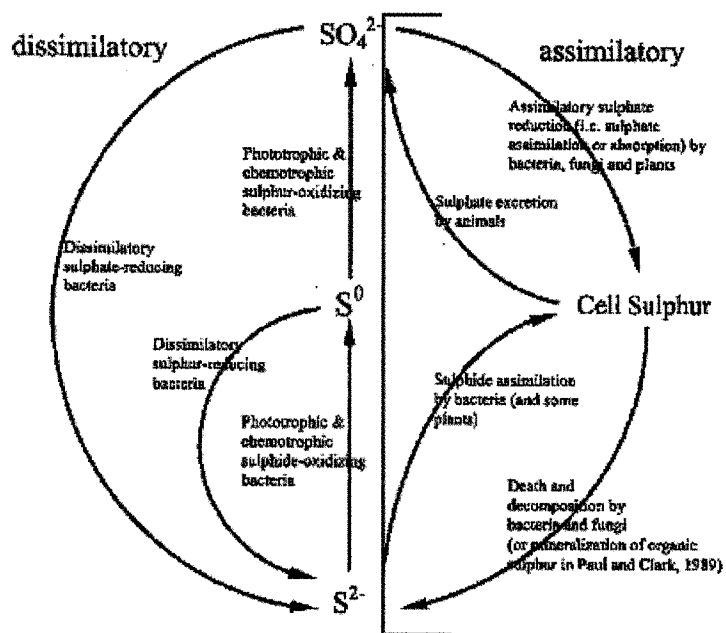


Fig 2.2 The Biogeochemical Sulfur Cycle (Modified after Truper, 1984)

Reactions of the biogeochemical sulfur cycle shown in Fig. 2.2 can be divided mainly into two types: redox and acid-base reactions (Langmuir, 1997a). The dominant redox reactions might be sulfate reduction and $\text{S}^{(0)}$ oxidation because the main species in the test are $\text{S}^{(0)}$ and sulfate (left side of Fig. 2.2). The redox reactions produce or consume protons in the $\text{S-H}_2\text{O-O}_2$ system and decrease or increase the pH of the system.

2.3.1 Redox Reactions of Sulfurs

Sulfur Reduction

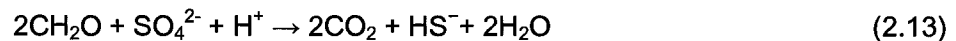
Inorganic sulfate can act as an electron acceptor in the process of oxidation of organic materials by bacteria. The sulfate will be reduced to sulfide with acetate as the final metabolized product. The reaction is presented in Equation 2.12 below (Langmuir, 1997a).



Some sulfate reducing bacteria (SRB) prefer a pH between 6.0 and 8.0, but can function between pH 4.2 and 9.9 and can operate at a temperature as low as 0°C and as high as 110°C (Jorgensen et al. 1992). Sulfate is used as the terminal electron acceptor in oxidation of organics (anaerobic respiration) in this reaction. Sulfate reduction produces alkalinity. Sulfide (S^{2-}) produced may precipitate metal sulfides and give sediment a characteristic black color (and bad smell if disturbed) (URL Ref. No.2)

Contrary to the traditional belief that SRB are strict anaerobes, active sulfate reduction has also been observed in the presence of dissolved oxygen in the photosynthetic zone of microbial mats (Canfield and Des Marais, 1991).

Langmuir (1997b) presents a common equation of sulfate reduction that indicates pH increase of the solution. The reaction may be written:

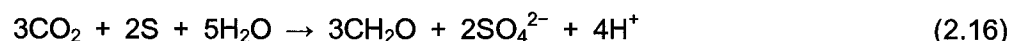


Some bacteria, such as *acetoxidans*, can reduce $\text{S}^{(0)}$ anaerobically by oxidizing acetate to CO_2 via the tricarboxylic acid cycle (URL Ref. No.2)



Sulfur Oxidation

$\text{S}^{(0)}$ in soil may be oxidized to SO_4^{2-} under both aerobic and anaerobic conditions by chemotrophic and phototrophic bacteria. Besides these heterotrophs, autotrophs also exist by gaining energy from oxidizing $\text{S}^{(0)}$ and using CO_2 as their carbon source (Vitolins and Swaby, 1969). The reactions are presented in Equations 2.15 and 2.16. Note that Equation 2.16 is a photoautotrophic reaction. Research in soils from different areas (such as Canada and Australia) shows that $\text{S}^{(0)}$ oxidation may be dominated by either autotrophs or heterotrophs (Watkinson and Bolan, 1998):



The oxidation of $\text{S}^{(0)}$ as an agricultural fertilizer applied to fields for the improvement of crop growth has been well researched since the 1970s. The reported $\text{S}^{(0)}$ oxidation rates range from $4.8 \mu\text{g}/\text{cm}^2/\text{day}$ to $84 \mu\text{g}/\text{cm}^2/\text{day}$, depending on soil types, $\text{S}^{(0)}$ particle sizes and temperatures (Janzen and Bettany 1987a, 1987b; Watkinson, 1989; Chapman, 1989). However, the $\text{S}^{(0)}$ microbial redox reaction in this S-H₂O-O₂ system has not been identified because it is beyond the scope of the research objectives.

The most reduced sulfur, hydrogen sulfide, can be oxidized to $\text{S}^{(0)}$ through both a biotic reaction (Equation 2.17 and 2.18) and a simultaneous abiotic reaction in the presence of oxygen (Equation 2.17) (URL Ref. No.2).



2.3.2 Acid-base Reactions

Protons are produced during the sulfur oxidation reactions (Equations 2.15 and 2.16). Therefore, these continuous reactions will result in a decreasing pH in the water reservoir. The dissociation constants of some acids are listed in Table 2.4.

Table 2.4 the Dissociation Constant of the Acids and Their Conjugate Bases

Acid	Base	pK ₁	pK ₂
H ₂ SO ₄	HSO ₄ ⁻ , SO ₄ ²⁻	~-3	1.99
H ₂ SO ₃	HSO ₃ ⁻ , SO ₃ ²⁻	1.93	7.36
H ₂ S	HS ⁻ , S ²⁻	7.03	(18.51)*
H ₂ CO ₃	HCO ₃ ⁻ , CO ₃ ²⁻	6.35	10.33
CH ₃ COOH	CH ₃ COO ⁻	4.76	-

* The parenthesis value is estimated. Source: Langmuir, 1997a

Analogous to the distribution of carbonate species as a function of pH (Langmuir, 1997b), the acid itself dominates below pH = pK₁; its second conjugate base dominates above pH = pK₂. Between pH = pK₁ and pH = pK₂, its first conjugate base dominates. The pH of the solution is independent of the total concentration of acid and its conjugate bases. Therefore, the products of reactions (Equations 2.12 to 2.16) are pH dependent. They may be weak acids or their conjugate bases.

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Date accessed: Aug. 4, 2004

Colorado School of Mines,

Microbes and Redox Course Notes

<http://www.mines.edu/Academic/envsci/courses/esgn513/Microbes&redoxnotes.doc>

3.0 MATERIALS AND METHODS

3.1 Introduction

CT release water has the capacity to buffer pH change when being used to cap the elemental sulfur. On the other hand, DI has zero capacity to buffer any pH change. As a comparison, both CT release water and DI water are used in this research to inspect the pH changes under different encapsulation conditions. Elemental sulfur ($S^{(0)}$) can be used to encapsulate salts and then be disposed of together, possibly at the base of a mined-out pit that is then covered with tailings. In this laboratory study, $S^{(0)}$ was melted, mixed with solid salts, cast in layers in plastic cylinders, and encapsulated with pure molten sulfur. The finished samples were then immersed in deionized water or CT release water. Electrical conductivity (EC), dissolved oxygen (DO) and pH of these solutions were measured to quantify the salt dissolution and diffusion from within the sulfur and assess the reactions occurred in the solutions. The sampled solutions were analyzed using aqueous ion chromatography (IC) and alkalinity titration to determine ion concentrations and salt fluxes. Both analytical and numerical models were developed to simulate the laboratory test results and used to predict the salt dissolution and diffusion in different situations.

Prior to dealing with the above issues, it is essential to understand the physical, chemical and biological properties of the materials used during this research, i.e., elemental sulfur, solid salts, CT release water and deionized water.

3.2 Materials

3.2.1 Elemental Sulfur

Pure elemental sulfur at room temperatures is a bright yellow, odorless, tasteless and brittle solid. The color of sulfur often indicates its purity. Bright yellow sulfur is over 99% pure. The pure sulfur used in this laboratory research was obtained from Syncrude Canada Ltd.

Sulfur is a non-metal element with an atomic number of 16 and an atomic weight of 32.064. It generally exhibits valences of $-II$, 0 , IV and VI . ^{32}S is the dominant isotope with a proportion of 95.1%. ^{33}S , ^{34}S and ^{36}S are the other three naturally occurring isotopes (Tuller, 1970). $S^{(0)}$

exists in a large number of forms, i.e. allotropes, but only two physical forms are of practical interest in this study: 1) Orthorhombic or α sulfur, the most stable form at room temperature and up to 96°C; and 2) Monoclinic or β sulfur, the stable form at its melting point. These two sulfur crystal allotropes convert to each other at 96°C. Both α and β $S^{(0)}$ crystals contain crown shaped S_8 molecules stacked in a complex array (see bottom right of Fig. 3.1). Bottom left of Fig. 3.1 illustrates a natural sulfur crystal containing no pores. The top of Fig. 3.1 shows a laboratory-made sulfur crystal containing void space. Some physical and chemical data of elemental sulfur are listed in Table 3.1 below.

Table 3.1 Physical and Chemical Properties of α and β Sulfur*

Properties	α sulfur	β sulfur
Density (g/cm^3) at 20°C/138°C	2.07/1.79	1.96/1.79
Melting point (°C)	112.8	119.6
Ignition point (°C, liquid) in air	168 ~ 261	
Enthalpy of formation, ΔH_f^0 (kJ/mol)	0	0.33
Standard entropy (S^0 , J/k/mol) at 25°C	32.054 \pm 0.050	-

* The data are cited from *The CRC Handbook of Chemistry and Physics*.

Elemental sulfur at room temperature is insoluble in water, but readily dissolves in liquid ammonia and carbon disulphide and some organic solvents. At room temperature, $S^{(0)}$ reacts with amines and nucleophilic reagents, but not with hydrocarbons. Above 150°C, it reacts violently when in contact with oxidizing agents or powdered metals (Environmental Canada, 1984). Heat, light and other catalysts can initiate reactions of sulfur with organic compounds.

$S^{(0)}$ occurs naturally in the vicinity of volcanoes and hot springs. Mineral $S^{(0)}$, often containing impurities like arsenic and selenium, can be a light yellow, semi-transparent compact crystal. Industrial $S^{(0)}$ crystal generally creates internal pores during the solidifying process (see Fig. 3.1 and 3.2). The porosities of samples made in the laboratory are summarized in Table 4.4.

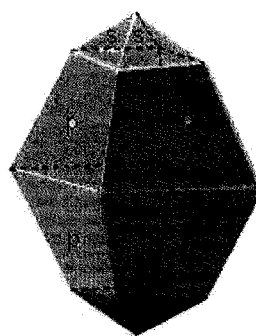
Elemental sulfur burns with a pale blue flame. The reaction described by Equation 3.1 is exothermic ($\Delta H_r^0 = -297.04 \text{ kJ/mol}$) and spontaneous ($\Delta G_r^0 = -300.19 \text{ kJ/mol}$). However, its abiotic oxidation is extremely slow at ambient temperatures in any medium (Wainwright, 1984; Chapman, 1989; Nor and Tabatabai, 1977).



Industrial Sulfur 3"x 3"



Natural Sulfur Crystal



Sulfur Crystal Structure

Fig. 3.1 Sulfur Crystals (Modified after Internet (URL Ref. 1))

3.2.2 Solid Salts

Syn crude Canada Ltd. has been working to fulfill a full-scale zero liquid discharge (ZLD) system to recover recycle water at the Mildred Lake site in Alberta. The proposed ZLD system uses Electrodialysis Reversal (EDR) to recover approximately 85% of the water for reuse. The EDR reject (brine) is concentrated further in a Brine Concentrator. The highly concentrated brine from the Brine Concentrator is then processed in a forced circulation crystallizer to recover the remainder of the water and reduce the brine stream to dry solids. The solids produced by the ZLD system will be suitable for disposal (RCCI report, 2001).

In this research, the brine shipped from Syncrude Canada Ltd. was put into an oven at a temperature of about 140°C in order to evaporate the water. The solid salt was then crushed to mix with S⁽⁰⁾ for disposal in a bench scale study. The leftover solid salts can be easily crushed into different sizes. Sieve analysis was done on the crushed solid salts used in the bench test. The crushed salts were in granule form with a brown color. Salt density of 2.23 g/cm³ was determined by the specific gravity method (see Appendix A1.4). A sample of dissolved salt solution was sent to Norwest Labs in Edmonton to check the salt components by using APHA (American Public Health Association) Standard Methods for the Examination of Water and Wastewater. Lafarge Canada Inc. did a semi-quantitative analysis on the salt cake. Resources Conservation Company International (RCCI) reported their analysis on the solid salt they produced during their study. All these test results are shown in Table 3.2.

Table 3.2 Solid Salt Components

Mass fraction of ions %	Source 1	Source 2	Source 3 *
SO ₄ ²⁻	19.1	19.0	20.6
Cl ⁻	42.8	44.0	43.0
HCO ₃ ⁻	**	-	-
Na ⁺	36.7	36.5	34.6
K ⁺	0.5	-	0.7
Mg ²⁺	0.5	0.44	0.4
Ca ²⁺	0.4	0.33	0.9

Source 1: Test Report on Salt Cake, by Lafarge Canada, Inc. The reported percentage of oxides was converted to percentage of ions.

Source 2: RCCI test report — Bench-scale Crystallizer Testing, Concentration and Crystallization of EDR and Evaporator Pre-concentrated Recycle Water.

Source 3: Analytical Report on Dissolved Salt Solution, by Norwest Labs.

Note: * the University of Alberta produced the samples of Source 3.

** Undetected

In Table 3.2, the concentrations of main ions from the three sources were close to each other. Including an XRD (X-ray diffraction) test done by Department of Earth and Atmosphere Sciences, University of Alberta, sources indicated that the main minerals in the solid salts were halite (NaCl) and thenardite (Na₂SO₄) and that these two minerals account for about 72% and 24% by mass according to Table 3.2. Besides the main cations and anions shown in Table 3.2, some trace ions like fluoride, organic and inorganic carbon, aluminum, boron,

lithium and strontium were also detected.

3.2.3 CT Release Water

CT release water, a large volume byproduct of tailings disposal, has a light yellow color with no discernible odor. It is cloudy due to suspended clay particles (Material Safety Data Sheet from Syncrude Canada Ltd.) and can be clarified by long-term quiescent placement.

The measured pH and EC of the CT release water shipped to the University of Alberta from Syncrude Canada Ltd. in June 2003 were 8.2 and 4.3 mS/cm, respectively. A continuous increase of pH to above 9.0 after three weeks' exposure to the atmosphere was measured in an incubated 3.0 liters of the CT release water sample. Analytical chemical tests were conducted on the water both by the University of Alberta and Norwest Labs in Edmonton (shown in Table 3.3).

Table 3.3 CT Release Water Components

Ion concentration (mg/L)	Source 1	Source 2
SO ₄ ²⁻	255.6	288.7
Cl ⁻	882	1051.6
NO ₃ ⁻	8.4	25
F ⁻	-	2.98
HCO ₃ ⁻	761	663.6
Na ⁺	968	1005.9
K ⁺	14.0	14.3
Mg ²⁺	12.0	16.3
Ca ²⁺	10.5	16.1
Sum	2911.5	3099.5
pH	8.8	8.2
EC (mS/cm)	4.97	4.3
Charge Balance %	1.36	-2.88

Source 1: Test done by Norwest Labs, Edmonton, submitted by the University of Alberta

Source 2: Test done by the Applied Geochemistry Laboratory of Department of Civil and Environmental Engineering, University of Alberta

Table 3.3 reveals that the two sources showed a similar concentration of the major ions. A main difference between the salt solids and the CT release water was the bicarbonate content. The salt solids were the leftover from the evaporation of the recycle water. RCCI

(2001) finds that the pH of the solutions stayed at 5.5 after the Brine Concentrator. In solutions at a pH of 5.5, most bicarbonate changed to carbonic acid (H_2CO_3) (see Section 3.3.2.4) which finally emitted to the atmosphere as CO_2 because of its low solubility in water at normal air pressure and temperature.

3.2.4 Deionized Water

The deionized (DI) water used in the test was collected from the ultra-pure water system (Barnstead International, Model No.: D11901) in the AEGRF (Applied Environmental Geochemistry Research Facility) laboratory. The measured EC of the water was less than 5 $\mu\text{S}/\text{cm}$. Using a commercial handheld pH probe (Accumet catalog No. 13-620-299), the measured pH of the DI water ranged from 5.5 to 6.3 during tests. Due to the close-to-zero buffer capacity of the high quality water, it is difficult to obtain a stable pH reading close to 7.0. The dissolution of atmospheric CO_2 into DI water forms carbonic acid and consequently causes a pH of less than 7.0. Any disturbance of the dissolved CO_2 can seriously affect the pH measurement of DI water (URL Ref. 2).

3.3 Methods

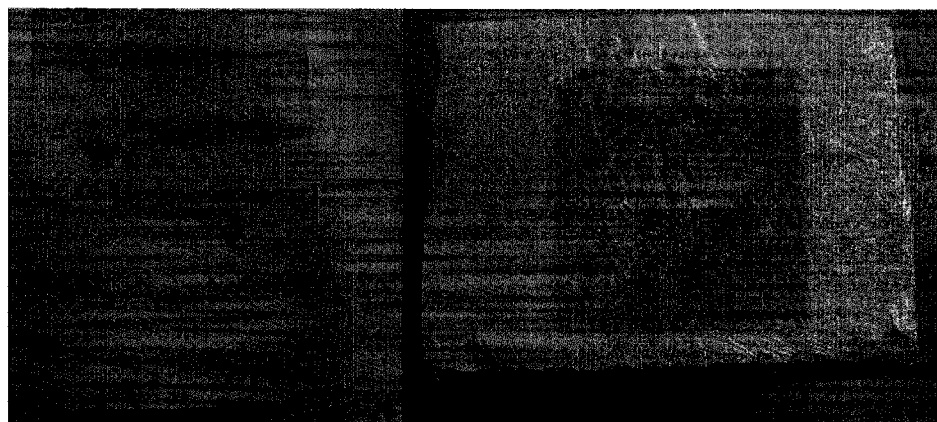
3.3.1 Sample Preparation

$\text{S}^{(0)}$, solid salts, CT release water and DI water were used to prepare test samples. Two batches, layered samples (open to the atmosphere) and core samples (closed in a nitrogen-filled gas bag, see Fig. 3.2), were prepared in May and November 2003, respectively. The samples were encapsulated with sulfur under different conditions. In field, when sulfur and salt are covered with several meters thick water, the materials will be isolated from the atmosphere and oxygen. As a comparison in this research, the layered samples were open to the atmosphere. The core samples were a modified design which had better encapsulation conditions and was considered to be more realistic in field and similar to the conceptual model shown in Fig 1.2.

3.3.1.1 Preparation of Layered Samples

For the layered samples, $\text{S}^{(0)}$ was melted at a temperature of 137°C , and the salt was heated

to a temperature of 147°C. These temperatures were set at the mid-range of the melting point and ignition point of S⁽⁰⁾ in air (see Table 3.1). The salt was heated at a higher temperature to improve the mixing of salt and liquid sulfur. The salt and sulfur were mixed together in a bowl. The mixture was then placed into an oven at 147°C for approx. 20 min. It was then poured into a 152 × 305 mm (diameter × height) plastic cylindrical mold, one layer after another as they solidified, for a total of four layers with slightly varying thickness. Samples with the same salt content composed one group, resulting in five groups of samples, each with different salt content. The four layers of different groups had the same mass of salt but a different mass of sulfur. The salt content of each group is shown in Table 3.4. The R group with zero salt content had six samples; each other group had eight samples. Among the eight samples of each group, four samples were covered by 470 g, 1.25 cm thick sulfur caps while the other four samples were not covered. For R group, there were no caps. After the sulfur solidified in plastic molds, three liters of CT release water shipped from Syncrude Canada Ltd. were placed on the top surface of two samples with sulfur caps and two samples without sulfur caps from each group. Three liters of DI water was placed on the top surface of two samples with sulfur caps and two samples without sulfur caps from each group. Samples with the same salt content and water overlay were thus duplicated. For R group, three samples were covered with CT water and three with DI water. The DI water was deaerated for about 30 minutes at pressures of 200 to 500 mm Hg and the measured DO was less than 5mg/L prior to being used.



The layered sample

The core sample

Fig.3.2 Layered and Core Samples (The left sample: 20% salt, the right sample: 40% salt)

In short, the layered samples had three different encapsulations: different salt contents (five

different percentage), different caps and different water overlay (DI or CT). In total, 38 samples were tested. Fig. 3.3 illustrates the typical profiles of the finished layered samples.

Table 3.4 Salt Content of the Layered Samples

Group #	Salts Mass (g)	Sulfur Mass** (g)	Total Mass (Sulfur+Salts)	Sulfur / Total Mass (%)	Salts / Total Mass (%)
R	0	3441	3441	100.0	0.0
F	127.6	3441	3568.6	96.4	3.6
L	127.6	1912	2039.6	93.7	6.3
U	127.6	1274	1401.6	90.9	9.1
S*	127.6	384	511.6	75.1	24.9

* One sample contained 30.7% salts.

** Excluded the mass of the sulfur cap.

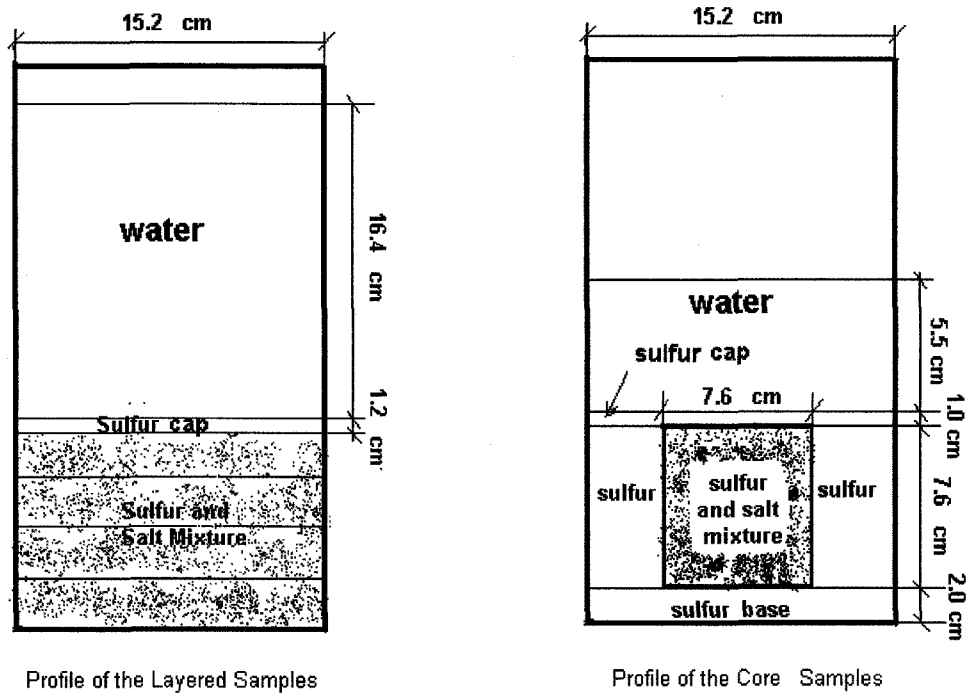


Fig. 3.3 Conceptual Profiles of Samples

3.3.1.2 Preparation of Core Samples

Instead of the layered sulfur and salt mixture used in the layered samples, the core samples contained 76× 76 mm (diameter × height) cylindrical sulfur and salt mixture as cores which were made in 76×152 mm plastic cylinders with different salt contents (see Table 3.5). During the creation of cylindrical cores, it was found that salt settled at the bottom for the cores made

with 10%, 20% and 30% salt content. For the samples made with 40% and 50% salt content, the salt mixed well with sulfur (see Fig.3.2). To make the core samples, initially, a 2 cm-thick sulfur base was placed in the cylindrical mold, and then a solidified, previously prepared core was placed in the upside down position to allow the salt to contact the sulfur cap. A predetermined mass of liquid sulfur was then poured around the core sample to cover it with a cap as shown in Fig. 3.3. The designed cap thickness of sulfur was 1.0 cm. After the sample solidified, to detect the expected lower salt dissolution rate, only one liter of CT release water or DI water was placed over the surface of the sulfur cap.

In short, the core samples had two different encapsulations: different salt contents (5 different percentage), and different water overlay (DI or CT). Each sample was duplicated. In total, 20 samples were tested. Fig. 3.3 illustrates the typical profiles of the finished core samples.

Table 3.5 Salt Content of Cores (Core Samples)

Core #	S ⁽⁰⁾ mass (g)	Salt mass (g)	S ⁽⁰⁾ content (%)	Salt content (%)
N	652.07	72.46	90.0	10.0
E	583.81	146.00	80.0	20.0
W	514.61	220.54	70.0	30.0
H	444.33	296.25	60.0	40.0
Y	373.04	373.05	50.0	50.0

3.3.1.3 Sample Layout and Designation

The layered samples were exposed to the atmosphere in the laboratory to examine the sulfur response to oxidizing conditions. The core samples were placed into nitrogen filled gas bags to simulate the conditions without oxygen. Fig. 3.4 illustrates the sample collection. Each layered sample was capped with a plastic bonnet and a wooden disc to reduce water evaporation and exposure to light. Nitrogen gas in the plastic bags on the right was refilled daily. Oxygen levels in these bags were measured using a portable multi-gas detector (PKI Instrumental Inc. Part No.: 71-0028RK).

To identify this large number of samples easily, a new designation was used in the research. The air condition – salt content – water overlay – sulfur cap – sample number is the general

form used to label these samples. “A” at the beginning of the designation for all layered samples indicates that these samples were exposed to the atmosphere, and that oxygen and carbon dioxide exchange could occur between the fluid cap and the atmosphere. “N” at the beginning of the designation of the core samples indicates that these samples were separated from the atmosphere via containment in nitrogen filled bags, preventing oxygen and carbon dioxide exchange at the surface of the liquid. For a layered sample, for example, A-9.1-CT-C-2 indicates a sample exposed to the atmosphere, with 9.1% salt content, a CT release water overlay and a sulfur cap, sample No. 2. A-6.3-DI-N-1 means exposed to atmosphere, 6.3% salt content, DI water and no sulfur cap, sample No. 1. All core samples were capped with sulfur. The designation is therefore simpler. For example, N-20-CT-2 means no air, 20% salt, CT release water overlay of sample No. 2. In this research, hereafter, all the samples will be identified by this system. The old designations of S, U, L, F, R and N, E, W, H, Y used in Table 3.4 and 3.5 are not used anymore.

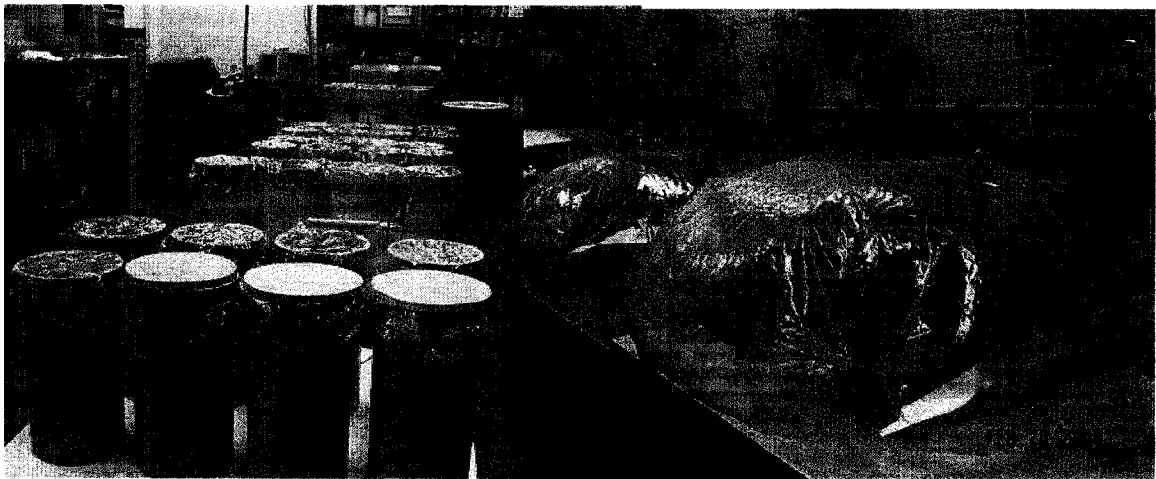


Fig. 3.4 Layout of Layered (left) and Core (right) Samples

3.3.2 Test Methods

EC measurement indicated the total dissolved solid (TDS) contained in the liquid overlay. This method was chosen due to continuous dissolution and diffusion of solid salts into the liquid. pH measurement suggested the presence of acid-base reactions in the solutions occurring as a result of the biogeochemical reaction in the S-H₂O-O₂ system. DO measurements showed the amount of dissolved O₂, which was a balance of the influx of oxygen and its consumption by biogeochemical reactions in the solutions. Alkalinity titration, together with the pH measurement, displayed the total carbon in the solutions. Ion

chromatography (IC) quantified the concentration of each dissolved ion in the overlay liquid. Tests of materials, such as porosity of $S^{(0)}$ and specific gravity of salt, were also briefly described in this chapter.

3.3.2.1 Material Tests

To start, the properties of each material were tested, such as solubility and density of salts, along with the porosity of $S^{(0)}$.

Solid salt used in the test was a mixture of different salts. A test modified from the soil specific gravity test (Bowles, 1992) was conducted with paraffin oil instead of water to determine the density of the salt solids (see Appendix A1.4).

After evaporating the brine to produce the solid salts, they were crushed into small granules. Sieve analysis was conducted on the crushed product by using ASTM method D421-85: Standard Practice for Dry Preparation of Soil Samples for Particle-size Analysis and Determination of Soil Constants.

To quantify the insoluble mass present in the salt solid, a small amount of salts was dissolved into DI water. A vacuum was then used to filter the solution through a 0.22 μm filter paper. The residual of the un-dissolved salt was collected, dried and weighed. The test was repeated three times with different amounts of salt.

As discussed in Section 2.2.2, the solubility of a salt mixture is not equal to the sum of the separate solubility of its components in the binary system. IC analysis at room temperature was carried out to establish the solubility of the salt mixture used in this research. Salt with mass of 59.3g, 74.6g and 120.6g were mixed with 200mL of DI water, respectively, stirred at about 1000rpm for about 8 hours and then left to stand overnight. On the second day, the samples were filtered through a 0.22 μm filter paper. The filtered solutions was sampled and diluted to form a solution of 1000 mL. A 10.0 mL of sample of this dilute solution was then used for IC analysis.

In order to understand the salt diffusion through porous $S^{(0)}$, the porosity of the sulfur samples was measured. Because the densities of salt and $S^{(0)}$ were known, the theoretical volume of a certain mass of salt, $S^{(0)}$, or their mixture could be calculated. The actual volume of the

samples did not equal their theoretical values because pores were formed as the sample cooled. The porosity of the samples was the difference between the theoretical volumes and the measured volumes. The measured volumes of the core samples were obtained by making three separated measurements of each sample.

3.3.2.2 EC Measurement

Electrical conductivity, k , is a measure of the ability of an aqueous solution to conduct an electric current. This ability depends on the presence of dissolved ions, their total concentration and valence as well as the temperature of the solution being measured.

EC measurement approximates the concentration of the TDS in the solution using an empirical equation, such as Equation 3.2:

$$\text{TDS} = A \cdot \text{EC} \quad (3.2)$$

where TDS is in mg/L; EC is in $\mu\text{S}/\text{cm}$ and A is a correlation factor, usually between 0.5 to 0.75. In this research, the relationships between EC and the TDS in the DI water and the CT release water were established as shown in Fig. 3.5.

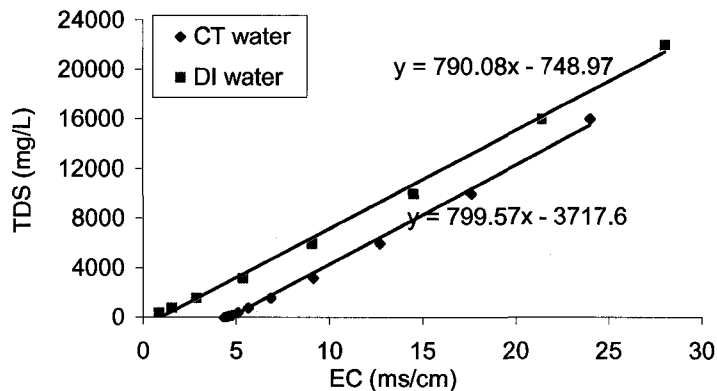


Fig. 3.5 The relationship between TDS and EC

The difference in the slopes of the two curves was due to the alkalinity of the CT release water. The solid salts contain a small amount of carbonate. The CT release water contains a large amount of bicarbonate (>20% of TDS, see Table 3.3). The intercept of the DI water curve indicates low accuracy of the relationship at the low concentration where it is not linear. The measured EC of the CT release water and the DI water was 4.3 mS/cm and less than 5 $\mu\text{S}/\text{cm}$, respectively, in June 2003. Distilled water produced in a laboratory generally has

conductivity in the range of 0.5 to 3 $\mu\text{S}/\text{cm}$. The conductivity increases shortly after exposure to the atmosphere due to CO_2 gas dissolution into DI water.

Prior to measuring the solution, the EC probe (Accumet catalog No. 13-620-160) was calibrated using a commercial EC calibration solution whose EC value was accurately known (see Appendix A1.1). When calibrating, Equation 3.3 determines the cell constant, k :

$$K = \frac{k(\text{Standardsolution})}{k(\text{Display})} \quad (3.3)$$

This calculation was carried out automatically and the cell constant was stored for the subsequent test evaluation. Compared to the slope of the pH electrodes, the cell constant had more long-term stability. Most changes occurred as a result of microscopic deposits and damage associated with the electrode surface.

3.3.2.3 pH Measurement

pH measurements are based on the response of a pH sensor to the logarithmic concentration of hydrogen ions in solution. Most pH sensors are designed to produce a 0 mV signal at pH 7.0, with a (theoretically ideal) slope sensitivity of $-59.16 \text{ mV}/\text{pH}$ at 25°C (see Fig. 3.6). In practice, however, a new electrode may have a slope of only -57 to $-58 \text{ mV}/\text{pH}$. As the electrode ages, its slope usually decreases.

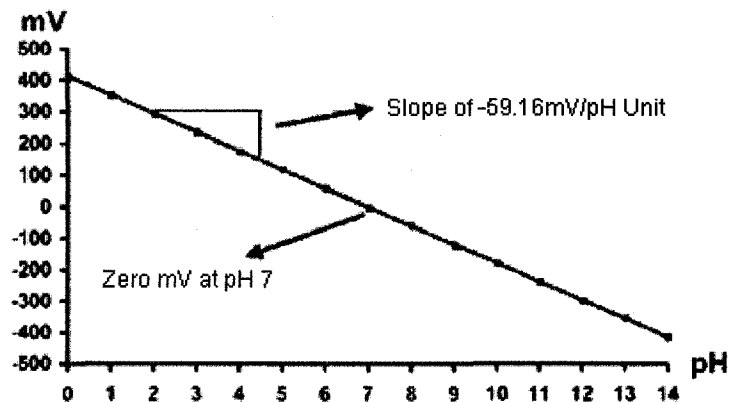


Fig. 3.6 pH Slope (Modified after The Theory of pH Measurement URL Ref. 3)

$$E = A - B (T + 273.15) (\text{pH} - 7) \quad (3.4)$$

Equation 3.4 presents a temperature compensation equation on pH. E is the cell voltage. The slope of the line is $-B (T + 273.15)$, where T is the temperature in $^\circ\text{C}$, and the y-intercept is A . The closer the pH is to 7.0, the less important is the temperature compensation.

The pH probe must be calibrated by using buffers having pH values that bracket the pH of the samples being tested. For example, if the expected pH is between 5.0 and 9.0, calibrate with pH buffers of 4.0 and 10.0 (Theory and Practice of pH Measurement, URL Ref. 4).

At pH values below 1.0, the glass pH electrode can be subject to acid error. Alkali ion error, i.e., sodium ion error, occurs at a high pH. This error results in a reading that is lower than the actual pH. However, the pH values of the solutions in this research were found to lie between 4.0 and 10.0. Thus, the errors associated with the extremes in pH were not a concern.

If the solute's concentration is above 15% by weight, the solute may dry the pH electrode, requiring periodic rewetting of the sensor with water. The highest salt content of the solutions in this research was less than 10%.

An Accumet® combination pH electrode (catalog No. 13-620-299) was used in the pH measurement of this research. It was calibrated with standard pH buffers of 4.0, 7.0 and 10.0.

3.3.2.4 DO Measurement

The concentration of dissolved oxygen (DO) in natural water and wastewater is a function of the temperature of the air and water, the salinity of the water, and the demand for oxygen in the body of water.

For barometric pressures other than 760 mmHg (sea level), the oxygen solubility can be computed from Equation 3.5 (Colt, 1984):

$$S^* = \frac{S_{760}^*(P_0 - P)}{760 - P} \quad (3.5)$$

where

S^* — oxygen solubility [M/L³]

S_{760}^* — saturation value at 760 mm Hg (see URL Ref. 5)

P_0 — barometric pressure (mm Hg)

P — vapor pressure of water (see URL Ref. 5)

Edmonton stands about 600 meters above sea level; therefore, the calibration value for the altitude is 0.93 (see URL Ref. 5). Table 3.6 shows that at the room temperature oxygen solubility in water is 7.3~8.3 mg/L.

Table, 3.6 DO Calibration Values for the Edmonton Area

Temp. (° C)	Oxygen Solubility (mg/L)	Temp. (° C)	Oxygen Solubility (mg/L)
21	8.28	25	7.66
22	8.11	26	7.52
23	7.96	27	7.39
24	7.81	28	7.26

The higher the salinity of the water is, the lower the DO. The flux of oxygen into water at various temperatures can be calculated by combining Equations 2.4 and Table 3.6.

$$J = D \frac{\partial c}{\partial x} \quad (2.4)$$

Two incompatible objectives were required via manual operation; i.e., to measure DO, the probe should be stirred, but to maintain diffusion, the 16cm-deep solution should not be disturbed. Therefore, a new method was developed. The DO probe was attached to a supporting lab stand. When an operator gently wobbled the supporting stand, the probe stirred the solutions at a more stable speed (see Fig. 3.7) compared to naked hand operation. Several comparative tentative tests during the early stages of the laboratory research indicated that a relatively ideal reading was obtainable. However, the optimum flow rate for the solution passing the probe membrane is about 30cm per second, and accuracy is not affected by a rate higher than this. However, lower ones, like those obtained with this new method, affect it. Thus, the new method was relatively accurate and applicable to this test. The DO test procedure is presented in Appendix A1.2.



Fig. 3.7 DO Measurement Using a Supporting Stand

Other gases in solution, such as H₂S, can seriously interfere with the DO measurement by reacting with the cathode of the probe.

3.3.2.5 Alkalinity Titration

If total carbonate, C_T, is defined as in Equation 3.6 below:

$$C_T = \text{H}_2\text{CO}_3 + \text{HCO}_3^- + \text{CO}_3^{2-} \quad (3.6)$$

then the concentration of each component will be a function of the pH as represented by Equations 3.7 to 3.10 below:

$$(\text{CO}_3^{2-}) = \frac{C_T}{\alpha_H} \quad (3.7)$$

$$(\text{HCO}_3^-) = \frac{C_T(\text{H}^+)}{K_2\alpha_H} \quad (3.8)$$

$$(\text{H}_2\text{CO}_3) = \frac{C_T(\text{H}^+)^2}{K_1K_2\alpha_H} \quad (3.9)$$

$$\alpha_H = (\text{H}^+)^2 10^{16.68} + (\text{H}^+) \cdot 10^{10.33} + 1 \quad (3.10)$$

where $K_1 = 10^{-6.35}$ is the first dissociation step of the carbonic acid; $K_2 = 10^{-10.33}$ is the second dissociation step of the carbonic acid. Both K_1 and K_2 are present at 25°C (also see Table 2.4). Fig. 3.8 plots the relationship between the carbonate species concentration and the pH. The plot features a pH's independence with respect to C_T and the occurrence of the curve crossovers at pH = pK for each dissociation step (Langmuir 1997b). The pH's independence with respect to C_T implies that regardless of C_T, the titration inflection points discussed below are applicable to any solution.

The total alkalinity, C_B, of wastewater typically includes both the carbonate alkalinity (HCO₃⁻ + 2CO₃²⁻) and the caustic alkalinity (OH⁻):

$$C_B = \text{HCO}_3^- + 2\text{CO}_3^{2-} + \text{OH}^- - \text{H}^+ \quad (3.11)$$

Because carbonate species are weak bases, the titration curve shows several inflection points (see Fig. 3.8).

Fig. 3.8 shows a titration curve with a pH range of 3 to 12. The caustic alkalinity titration endpoint occurs near a pH of 11, where HCO₃⁻ ≈ OH⁻, indicating a free OH⁻ from a strong base. Two main reactions occur at this stage:

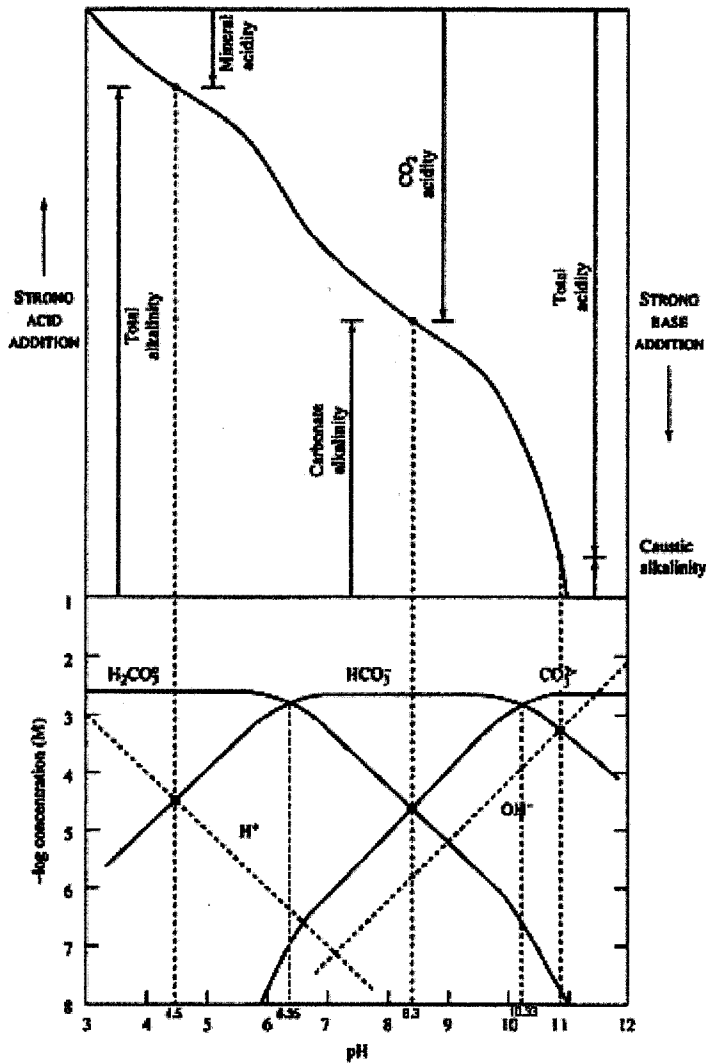


Fig. 3.8 Alkalinity Titration Curves (Modified from Langmuir, 1997b)

At the carbonate alkalinity endpoint, pH = 8.3, the equilibrium constant of the reaction shown in Equation 3.15 is $K_{\text{eq}} = 1 / K_2$. The ratio of $(\text{HCO}_3^-) / (\text{CO}_3^{2-}) = (\text{H}^+) / K_2 = 10^{2.03} \approx 107$ indicates that below a pH of 8.3 the (CO_3^{2-}) is negligible, and the reaction shown in Equation 3.14 below will be the main reaction at this stage:



The total alkalinity titration endpoint near pH 4.5 is defined exactly by



and is determined by the C_T of the solution as below (Langmuir, 1997b):

$$(H^+) = 10^{-3.18} C_T^{1/2} - 10^{-6.65} \quad (3.16)$$

The alkalinity titration of 121 samples was completed in this research by using a HACH® digital titrator model 16900. The procedure is described in Appendix A1.3. No titration was carried out on the samples with a pH of less than 5.0 because of the negligible alkalinity of these samples. The endpoint was a pH of 4.5 for all titrated samples determined by $C_T \approx 10^{-2}$ M and Equation 3.16.

3.3.2.6 Ion Chromatography (IC)

EC measurement provides no information about either the ions present in the water sample, or the concentration of any of the individual ion contained in the samples. However, the ion chromatography (IC) method can simultaneously determine all anions or cations of interest in a sample during a single pass through the test column.

In total, 261 water solution samples were analyzed in the AEGRF of the Department of Civil and Environmental Engineering, University of Alberta. In this test, the analyte concentration for the IC test was limited to less than 2 mS/cm. Therefore, samples were diluted by multiples of 0 to 40, depending on the measured EC values. Before dilution, the original samples were filtered through a 0.45 μ m membrane to remove solid particles with a detrimental effect on the IC column.

3.3.3 Sampling and Storage

Water sampling was conducted on samples open to the atmosphere at intervals of 14, 29, 52, 100, 143, 172 and 202 days, and on the samples in the gas bags at intervals of 28, 49, 98 days after the start of the testing.

After collecting a 50 mL sample from the solutions at a depth of approximately 9 cm in the layered samples (with a 3-liter, 16.5 cm-deep water column) and at a depth of approximately 3 cm depth in the core samples (with a 1-liter, 5.5 cm-deep water column) by using a plastic syringe, the same volume (50 mL) of CT release water or DI water was remitted to the samples. To avoid cross-contamination, several plastic syringes were used and cleaned with DI water prior to each sample collection.

The 50 mL solution samples were transferred to plastic bottles and labeled with sample numbers and dates. Finally, the bottles were stored in a cold room maintained at a constant temperature of 4°C prior to analysis.

Though the layered samples were covered with both plastic and wooden caps (see Fig. 3.4), water loss was still measured. The lost water was replaced after each sampling event.

3.3.4 Analytical Methods

3.3.4.1 Ion Concentrations

The IC results were multiplied by the appropriate diluting factors and adjusted according to the mass loss of the sampled salt and evaporated water. The total salt concentration of each sample was then the sum of the concentration of all ions in the sample.

3.3.4.2 Charge Balance

The quality of analytical data from water analysis can be checked by computation of the ionic charge balance error (CBE). The ionic charge balance equation is defined as

$$CBE = \frac{\Sigma \text{cations} - \Sigma \text{anions}}{\Sigma (\text{cations} + \text{anions})} \times 100. \quad (3.17)$$

In this equation, meq/L concentrations of cations and anions are used. If the CBE of a chemical data set is more than 10%, this error makes the quality of analysis questionable (Peden, 1983). Any sample that did not meet the charge balance criteria in this research was considered contaminated and either reanalyzed or discarded.

3.3.4.3 Salt Fluxes

The salt flux was calculated by using Equation 3.18. The determination of effective diffusion coefficients and the modeling of the salt diffusion will be discussed in Chapter 5.

$$\text{SaltFlux} = \frac{\text{SaltConcentration}_i - \text{SaltConcentration}_{i-1}}{\text{ElapsedTime}} \times \text{Point Depth} \quad (3.18)$$

where i means times of sampling. The solutions were sampled three to five times to determine salt concentration and diffusion rate at different times.

3.3.4.4 Analytical and Numerical Modeling

If the salt concentrations and fluxes were determined, models could be developed to predict the concentration and flux for similar situations in engineering practice. In this study, the

encapsulated salt dissolution could be viewed as a two-layer, one-dimensional diffusion in a closed system. The two-layer model was analogous to the samples with sulfur caps. For samples without sulfur caps, after the salt at the interface of the solid and liquid dissolved, the salt will then be transported through two layers, i.e., the leftover porous sulfur and water. Therefore, this diffusion could also be viewed as two-layer diffusion. In the plastic cylinder, water was placed on the top of the solid. After the water penetrated into and saturated the sulfur caps, the dissolved salt diffused vertically into the water reservoir through the sulfur caps where the salt concentration was low. The salt transport in the media, thus, was just one-dimensional. The partial differential equations controlling one-dimensional diffusion were discussed in Section 2.1.1. Because no mass was exchanged between the samples and surroundings, it was a closed system.

Liu et al. (1997) present an analytical solution to the one-dimensional, closed solute advection-dispersion equation in multi-layer porous media. Choy and Reible (1999) illustrate some diffusion models using MathCAD worksheets. The analytical solutions and MathCAD program were combined together in this research to build analytical models of the two-layer, one-dimensional salt diffusion in a closed system (see Appendix C and D). To prove the analytical models, numerical models were built using the program *ChemFLUX*[®], and the same parameters as those used in the analytical models were applied to the numerical models. The salt concentration profiles of the two models were compared to validate the agreement between the two approaches (see Section 5.8).

3.3.5 Quality Assurance and Quality Control (QA/QC)

Measurement error is always associated with analytical results. The objective of a QA/QC program is to control this error and ensure data reliability. In this research, the QA/QC of the sampling and laboratory tests was conducted.

Sampling QA/QC

- Plastic containers and syringes were used to avoid cross contamination and match the job (see Table 3.7).
- The sample numbers, sampling dates and container series were labeled continuously.
- The sampling locations were clearly recorded and correlated with sample numbers.
- The testing notes were recorded in a hardcover book.

Laboratory QA/QC

- The diluting multiples of the samples were designed to match the IC test requirements.
- Blank samples and blind analytical duplicates were run by the lab.
- Internal monitoring of accuracy and precision was carried out by the lab.
- Individual pieces of QA/QC data were used to assess the quality of the data; the average relative standard deviations for the analytical duplicate pairs were < 20% (See Table 3.8).

Table 3.7 Typically Recommended Containers, Preservatives and Maximum Holding Times (CCME, 1993)

Compounds	Containers; Volume	Preservatives	Maximum Holding Time
Major cations	P, G; 100-1000 mL	HNO ₃ to pH<2	6 months
Major anions	P, G; 100-1000 mL	Cool, 4°C	14 to 28 days
Chloride	T, P, G; 50 mL	Cool, 4°C	7 days
Sulfate	T, P, G; 50 mL	Cool, 4°C	7 days
Sodium	T, P; 1000 mL	HNO ₃ to pH<2	6 months

Note: T= Teflon; S= stainless steel; P = PVC, polypropylene, polyethylene; G = borosilicate glass.

Table 3.8 the Average Relative Standard Deviations for Analytical Duplicates

Sample #	Analyzer	Concentration (mg/L)	Average relative standard deviation
CT water 1		2711.4	
CT water 2	AEGRF, University of Alberta	3400.4	11.0%
CT water 3		3369.2	
CT water 4	Norwest Lab	2911.5	

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4.0 TEST RESULTS

4.1 Introduction

Table 4.1 shows the actual test schedule. A total of thirty-eight samples were open to the atmosphere. The pH, EC and DO tests on the first twenty-four samples began on June 25, 2003. Testing on fourteen additional samples began on July 16, 2003. All tests on the samples open to the atmosphere were completed on January 12, 2004, so that the testing on the first twenty-four samples and the additional fourteen samples lasted about 200 days and 180 days, respectively. Initial pH, EC and DO measurements were taken at weekly intervals, which were increased to monthly intervals after September 2003. The pH and EC tests on twenty samples in the nitrogen gas bags started on November 25, 2003 and ended on March 2, 2004, lasting 98 days. The pH and EC measurements were conducted every 7 to 10 days. IC analyses on all the samples were completed from February to April 2004. Alkalinity titrations were carried out in April 2004. Solutions sampled in September and December 2003 were not submitted to the IC or alkalinity analyses.

Table 4.1 Actual Test Schedule

Samples and Tests			06/03	07/03	08/03	09/03	10/03	11/03	12/03	01/04	02/04	03/04	04/04	
Samples open to the atmosphere	First 24 samples	pH	_____											
		EC	_____											
		DO	_____											
	Additional 14 samples	pH		_____										
		EC		_____										
		DO		_____										
Samples in gas bags	pH								_____					
	EC								_____					
IC analyses										_____				
Alkalinity analyses												_____		

The samples open to the atmosphere had 16.5 cm-deep water columns. In order to know the physical and chemical changes throughout the whole water column, the pH, EC and DO were measured at 4 different depths: 2cm, 5cm, 10cm and 15cm. The measurements showed

some depth-related differences when the disturbance of the water column was minimized.

The results and conclusions of these tests, including the material tests, are presented in this chapter. The interpretation of the results and conclusions will be presented in Chapter 5.

4.2 Test Results of Materials

4.2.1 Density of Salt Solids

The specific gravity of the solid salt and the density of the paraffin oil were tested by using the test methods described in Appendix A1.4. The results are shown in Table 4.2 below. The salt density was 2.23g/cm^3 . The density of the paraffin oil was 0.85g/cm^3 .

Table 4.2 Specific Gravity of Salt Solid

(1) M_{bo} (g)	(2) M_s (g)	(3) M_{bos} (g)	(4)Specific Gravity	Density (g/cm^3)	Average (g/cm^3)
623.05	60.05	659.95	2.59	2.20	2.23
623.22	65.05	663.81	2.66	2.26	

(1) Mass of flask + oil to the volume mark on the flask

(2) Mass of salt particles

(3) Mass of flask + oil + salt particles to the volume mark on the flask

(4) Compare to paraffin oil instead of water

4.2.2 Grain-Size of Salt Solids

Sieve analysis was conducted on two salt samples (see Fig. 4.1). The grain-size distributions of the salt solids are similar to those of medium or fine sand.

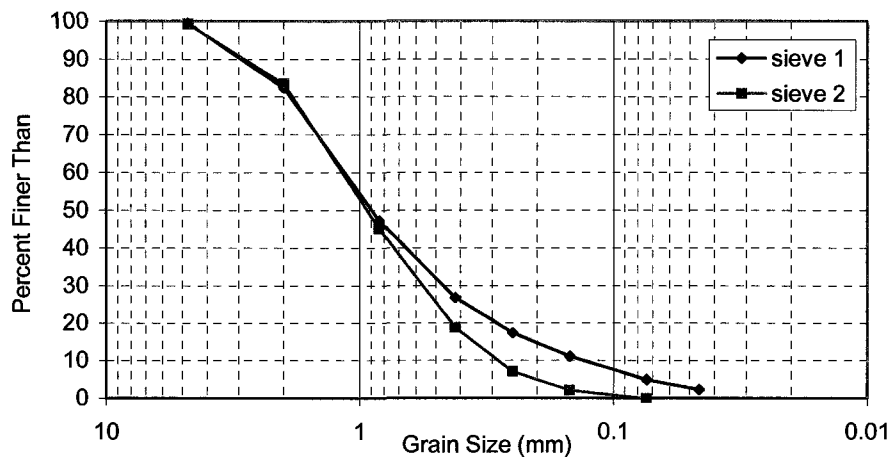


Fig. 4.1 Sieve Analysis of Salt Solid

4.2.3 Quantification of Insoluble Materials in Salt and Solubility of Salt

Three tests at low salt concentrations were completed to quantify the insoluble materials in the salt mixture (the solutions with high salt concentrations were difficult to filter). The insoluble parts in the salt were found to be 0.36%, 0.25% and 0.18%, small enough to be neglected.

Different amounts of salt were dissolved in DI water to determine its solubility, as discussed in Section 3.3.2.1. Three samples were found to have some un-dissolved parts in the glass bottles. Table 4.3 summarizes the dissolved salt concentrations determined from IC analysis. One sample with completely dissolved salt was designated D₀. The other three samples with non-dissolved portion in the water were designated D₁, D₂ and D₃. Note that the non-dissolved portion was dissolvable but did not dissolve into the solution due to saturation.

Table 4.3 shows that from Sample D₀ to D₃, the measured concentrations of the major ions, SO₄²⁻, Cl⁻ and Na⁺, increased and the CBE of the four analyses were within ±10%.

Table 4.3 Concentration (mg/L) of Dissolved Salt

Ion	D ₀	D ₁	D ₂	D ₃
Cl ⁻	126.68	244.47	311.01	388.31
Br ⁻	0	0	0.13	0.10
SO ₄ ²⁻	64.16	109.90	131.94	152.09
Li ⁺	0.02	0.04	0.05	0.07
Na ⁺	96.16	187.85	222.05	287.40
K ⁺	2.12	4.08	5.27	8.14
Mg ²⁺	1.36	2.80	3.48	4.65
Ca ²⁺	2.53	1.30	0.59	0.26
Charge error (%)	-4.68	-3.45	-6.52	-3.72

4.2.4 Measured Porosity of Samples

The measured porosities of the samples in the gas bags are shown in Table 4.4. The height, diameter of the cores and the thickness of the cylinder wall were measured at three to four different points. The average values were used to calculate the porosity for each sample.

Table 4.4 Porosity of the Samples in the Gas Bags

Sample	Porosity of Cap %	Thickness of Cap (mm)	Porosity of Core %	Height of Core (mm)
N-10-DI-1	12.9	17.0	11.5	82.3
N-10-DI-2	10.9	15.2	12.4	82.9
N-10-CT-1	11.0	12.3	13.1	82.3
N-10-CT-2	16.9	16.0	12.1	82.5
Ave.	12.9	15.1	12.3	
N-20-DI-1	11.1	13.0	10.6	81.4
N-20-DI-2	10.9	16.2	12.1	81.7
N-20-CT-1	9.2	15.9	12.0	80.4
N-20-CT-2	10.3	12.2	12.3	81.6
Ave.	10.4	14.3	11.7	
N-30-DI-1	10.8	12.6	10.8	81.6
N-30-DI-2	10.0	12.8	9.6	80.6
N-30-CT-1	10.7	13.7	10.2	80.2
N-30-CT-2	10.0	10.8	10.8	83.3
Ave.	10.4	12.5	10.4	
N-40-DI-1	10.9	13.3	11.1	80.8
N-40-DI-2	9.2	10.7	12.0	83.0
N-40-CT-1	10.8	13.0	11.4	81.1
N-40-CT-2	10.2	11.6	11.4	82.5
Ave.	10.3	12.1	11.5	
N-50-DI-1	9.6	10.9	12.2	82.9
N-50-DI-2	7.9	10.3	13.0	84.9
N-50-CT-1	9.0	10.5	13.0	82.9
N-50-CT-2	8.7	10.3	13.7	84.3
Ave.	8.8	10.5	13.0	

4.3 EC Measurement Results

The measured EC data are presented in Table B1.1 and Fig.B1.1 to Fig.B1.24, in Appendix B1.0. The observations made during the EC measurements are summarized below.

The EC values of the samples with caps and without caps both increased continuously with time. The slope of the EC-Time curves was unique for each sample and was particularly noticeable for the core samples in the gas bags. The samples with zero salt content (i.e., in a pure $S^{(0)}$ condition) presented nearly horizontal lines (even for different depths). See Fig. 4.2

and Fig. 4.3 for examples (also see Table B1.1 and Fig.B1.1 to Fig.B1.24 in Appendix B1.0).

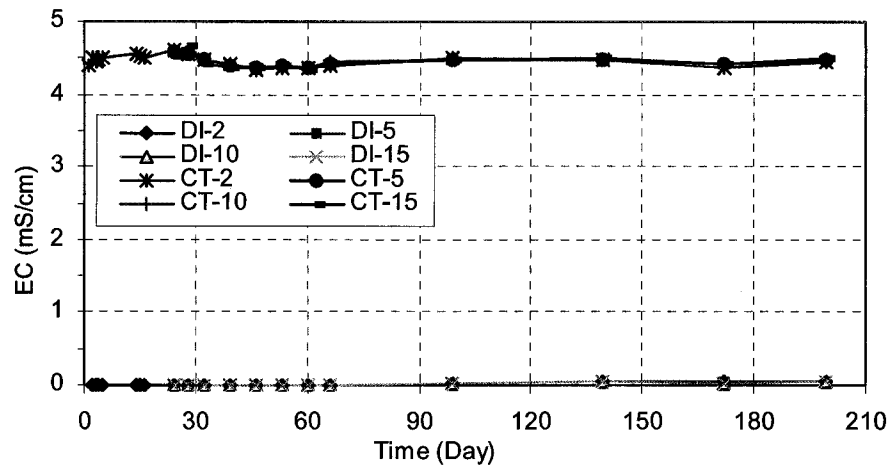


Fig. 4.2 EC vs. Time (Sample A-0-CT-2 and A-0-DI-2)

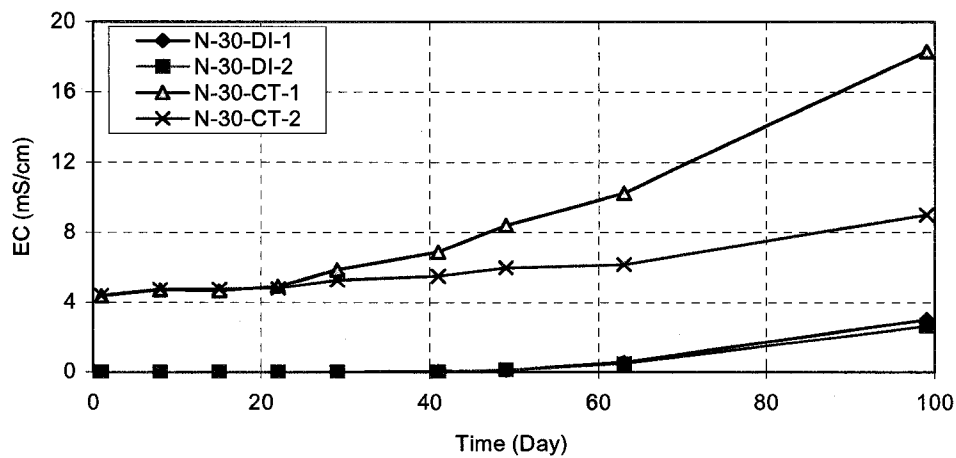


Fig.4.3 EC vs. Time (30% salt, in nitrogen bags)

In all samples except those of pure $S^{(0)}$ the EC measurements at the beginning of the test were strongly dependent on the depth for the samples without $S^{(0)}$ caps. Over time, the depth-related differences gradually disappeared. Fig. 4.4 shows the EC measured at different depths in one CT solution and one DI solution (also see Fig.B1.4 to Fig.B1.19 in Appendix B1.0). For the samples in the nitrogen gas bags, just one EC point was measured in the 5.5 cm-deep water column. The depth of the measurement point was around 3.0 cm.

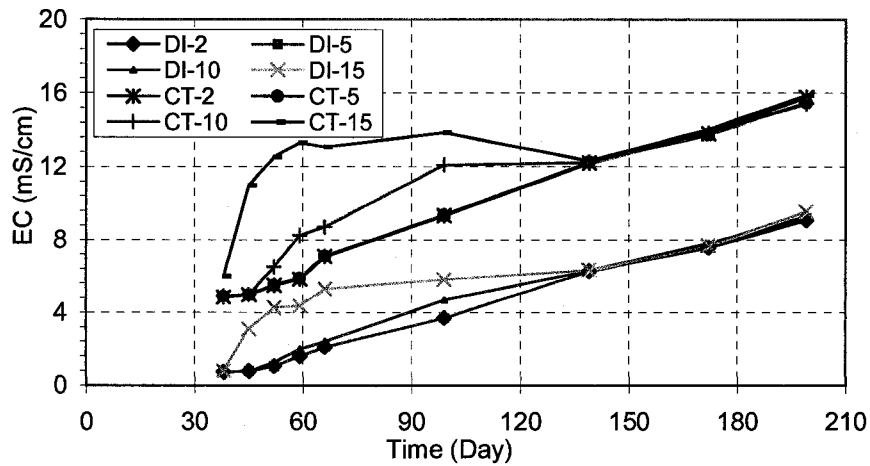


Fig. 4.4 EC vs. Time (Sample A-9.1-CT-N-1 and A-9.1-DI-N-1)

The measured EC values were affected by the use of sulfur caps. For the same salt content, the EC measurements for the samples with caps were generally smaller than those for the samples without caps (see Table 4.5). Note that the EC of the CT water and the DI water at the beginning of the test was around 4.3 mS/cm and 5.0 μ S/cm, respectively.

The EC values were also related to the content of the encapsulated salt to some degree. The samples with higher salt content generally had higher EC values (see Table 4.5), but there were some exceptions. The samples with 40% salt content had a lower measured EC than the samples with 20% salt content (see Table 4.6; also see Table B1.1 in Appendix B1.0).

Table 4.5 EC (mS/cm) of Samples at the End of Testing

Salt content (%)	CT release water overlay		DI water overlay		Porosity (%)
	With cap	Without cap	With cap	Without cap	
0		4.5		0.03~0.05	
3.6	6.3~10.0	11.7~12.4	2.9	7.5~9.0	
6.3	10.2~11.3	14.6~15.2	2.6~7.0	10.3~12.5	
9.1	8.8~10.3	15.7	1.4~12.0	9.5~11.6	
24.9	13.3~14.5	39.8~40.1	9.7	40.0~41.0	
10		9.1~9.9		2.0~24.2	12.9
20		11.0~12.0		3.6~6.0	10.4
30		9.0~18.3		2.7~3.1	10.4
40		7.2~8.8		0.2~2.9	10.3
50		13.1~15.2		3.2~10.4	8.8

The EC measurements were not obviously affected by the porosity of the sulfur caps. The samples with 50% salt had relatively higher EC but less porosity of the cap. See Table 4.5.

The EC readings of some samples with 24.9% salt content were not taken for a period of time (from August 2003 to September 2003, see Table B1.1 in Appendix B1.0).

4.4 pH Measurement Results

The pH measurements are listed in Table B2.1 and figures B2.1 to B2.24, in Appendix B2.0. Observations regarding the pH measurement are summarized below. To clearly narrate these observations, samples were divided into two groups: the samples open to the atmosphere and samples in the gas bags. Both groups were again subdivided into two conditions: CT water and DI water.

For the samples open to the atmosphere, the CT release water solutions at the upper layers (2cm, 5cm) started at a pH of 8.2 and increased to a pH of around 9.0 at the first 2 months of encapsulation, then decreased to a pH of around 8.4 after 180 to 200 days of encapsulation. At the lower layers (10cm, 15cm) of the CT solutions, the pH slightly increased at the first 4 weeks of encapsulation, then decreased and tended to stabilize at higher than a pH of 7.0 after 180 to 200 days encapsulation. See Fig. 4.5 for an example (also see Table B2.1 and Fig.B2.1 to Fig.B2.19 in Appendix B2.0).

For the samples open to the atmosphere, no depth-related difference was found in the DI water solutions. The pH values in the DI solutions started at 6.6 and continuously decreased until they stabilized at a pH slightly above 4.0 after 180 to 200 days of encapsulation. See Fig. 4.5 for an example (also see Table B2.1 and Fig.B2.1 to Fig.B2.19 in Appendix B2.0).

For the samples open to the atmosphere with pure $S^{(0)}$ conditions, the pH experienced a similar pattern of increase and decrease. The difference was that no depth-related pH differences were found in the CT water solutions, and their pH stabilized around 8.7. See Fig. 4.6 for examples (also see Table B2.1 and Fig.B2.1 to Fig.B2.19 in Appendix B2.0).

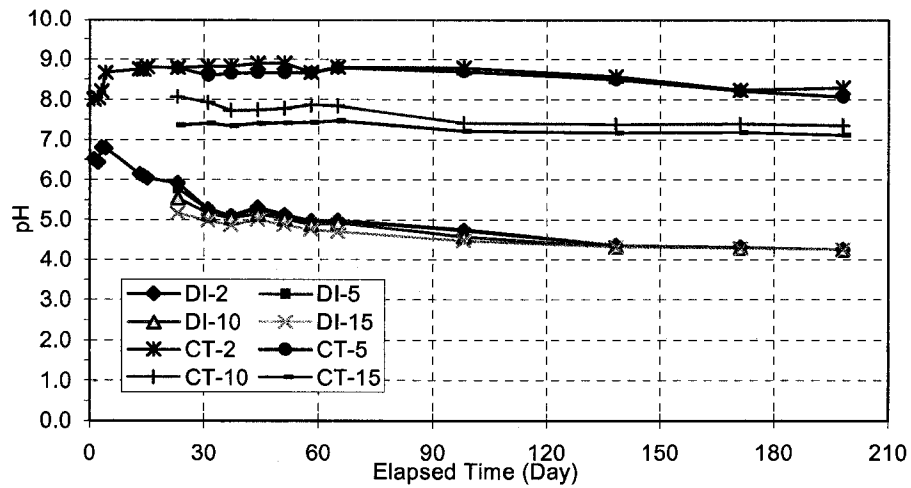


Fig.4.5 pH vs. Time (Sample A-9.1-CT-N-2 and A-9.1-DI-N-2)

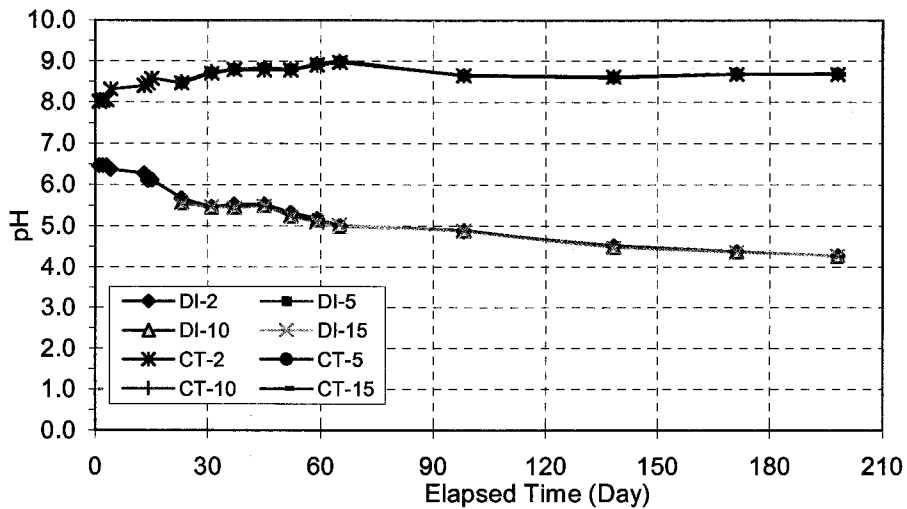


Fig.4.6 pH vs. Time (Sample A-0-CT-1 and A-0-DI-1)

For the samples in the gas bags, the CT solutions started at a pH of 8.3, increased to a pH of approximately 9.3 during the first 4 weeks of encapsulation, and then decreased slightly to a pH of 9.0 after 100 days encapsulation. The trend of the pH change in the DI water solutions was different. The pH in the DI water started at 5.8, decreased to around 4.3, and then increased with time. See Fig. 4.7 for an example (also see Table B2.1 and Fig.B2.20 to Fig.B2.24 in Appendix B2.0). Just one pH point was measured in the 5.5 cm-deep-water column in the gas bags at a depth of around 3.0 cm.

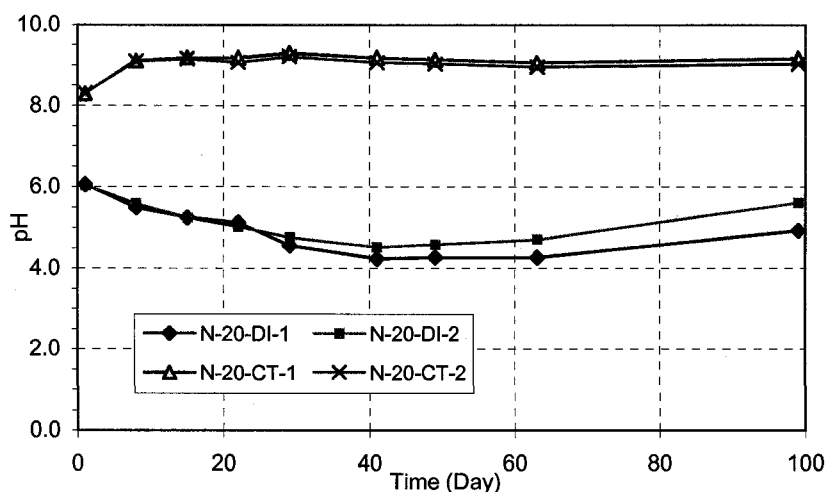


Fig. 4.7 pH vs. Time (20% salt in nitrogen bags)

Table 4.6 pH of Samples (at water /solid interface and at the end of the test)

Salt content (%)	CT release water overlay		DI water overlay	
	With cap	Without cap	With cap	Without cap
0	8.7		4.1~4.3	
Samples open to the atmosphere	3.6	7.0~8.3*	4.5~4.8	4.2
	6.3	7.1~7.2	4.4~4.8	4.2~4.3
	9.1	7.1~7.2	4.3	4.3
	24.9	7.1	4.5~4.6	5.0
Samples in gas bags	10	9.2	4.7~5.6	
	20	9.0~9.2	4.9~5.6	
	30	9.0~9.2	4.8	
	40	9.2	4.2~4.8	
	50	9.1	4.9~5.6	

* Sample 3.6-CT-C-2 had a high pH

The pH changes in the samples were not obviously related to the use of sulfur caps or to the salt content. The two different pH conditions for the samples open to the atmosphere included a pH of approximately 7.2 for the CT solutions and the pH of approximately 4.3 for the DI solutions. Two different pH states for the samples in the gas bags included a pH of around 9.1 for the CT solutions and the pH ranging from 4.9 to 5.6 for the DI solutions (see Table 4.6).

4.5 DO Measurement Results

The measured DO data are presented in Table B3.1 and Fig.B3.1 to Fig.B3.19, in Appendix B3.0. The observations made during the DO measurement are summarized below.

The initial DO in the DI water was around 5.0 mg/L after deaerating; in the CT water, it was around 2.0 mg/L when measured in the sealed container. For the pure $S^{(0)}$ condition, the measured DO in the water columns increased continuously with time until the DO reached its saturation level. The saturated DO in the DI water was around 8.0mg/L at room temperature at Edmonton's sea level. The DO in the CT water tended to saturate at 7.0mg/L. In both the CT water and the DI water, the DO was homogenous with depth. See Fig.4.8 for an example (also see Fig.B3.1 to Fig.B3.3 in Appendix B3.0).

Generally, the DO in the DI water was higher than in the CT water, but its fluctuation in the CT water was larger than in the DI water, and no stabilized DO reading was made in the CT water column. See Fig.4.9 for an example (also see Fig.B3.4 to Fig.B3.19 in Appendix B3.0).

The deeper the measurement in the CT water solution, the lower the DO, and the greater the DO fluctuation (see Samples 6.3-CT-C-2 and 9.1-CT-C-2 in Fig.B3.11 and Fig.B3.15 in Appendix B3.0). The DO at 15 cm depth was close to zero for most samples with the CT water (see Fig.4.9) except for the pure $S^{(0)}$ conditions (see Fig.4.8, Table B3.1 and Fig.B3.4 to Fig.B3.19 in Appendix B3.0).

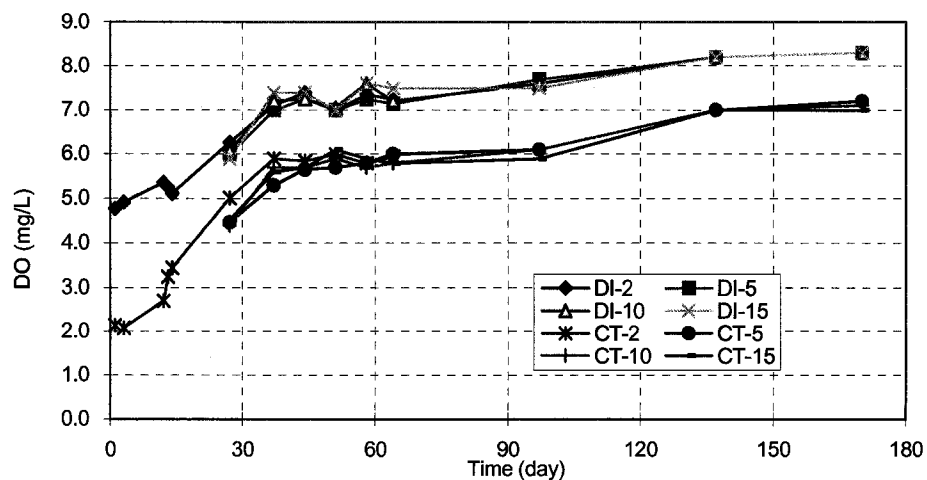


Fig. 4.8 DO vs. Time (Sample A-0-CT-2 and A-0-DI-2)

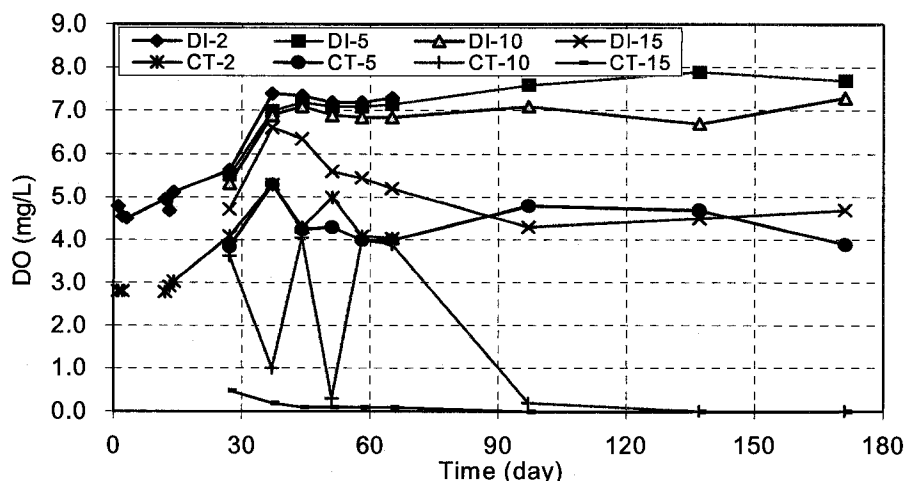


Fig. 4.9 DO vs. Time (Sample A-6.3-CT-C-2, A-6.3-DI-C-2)

The measured DO of the samples in the nitrogen-filled gas bags ranged from 1.2 to 1.5mg/L, which indicated a small air leakage had occurred in the gas bags throughout the experimental study.

4.6 Alkalinity Titration Results

The titrated alkalinity data are presented in Table B4.1 and Fig.B4.1 to Fig.B4.7, in Appendix B4.0. Observations about the alkalinity titration are summarized below.

The average bicarbonate alkalinity of five CT release water samples was 663.6 mg/L. The alkalinity of all the DI water solutions was small enough to be neglected. The alkalinity of both solutions was obviously related to neither the salt contents nor the $S^{(0)}$ caps. See Table B4.1 and Fig.B4.1 to Fig.B4.7 in Appendix B4.0.

For the samples open to the atmosphere, the alkalinity of the CT water solutions increased to 700~750 mg/L in the first 2 to 4 weeks and equilibrated with atmospheric CO_2 . The alkalinity then decreased to 400 mg/L to 500 mg/L according to the measurements taken at the end of the test. The final alkalinity was dependent on the pH of the solutions, with a low pH corresponding to low bicarbonate concentrations. See Fig.4.10 for an example (also see Table B4.1 and Fig.B4.1 to Fig.B4.5 in Appendix B4.0).

For the samples in the gas bags, the alkalinity of the CT water solutions decreased to about 500 mg/L to 600 mg/L according to the final measurements and was also dependent on the pH of the solutions, with a low pH corresponding to low bicarbonate concentrations. See Table B4.1 and Fig.B4.6 to Fig.B4.7 in Appendix B4.0.

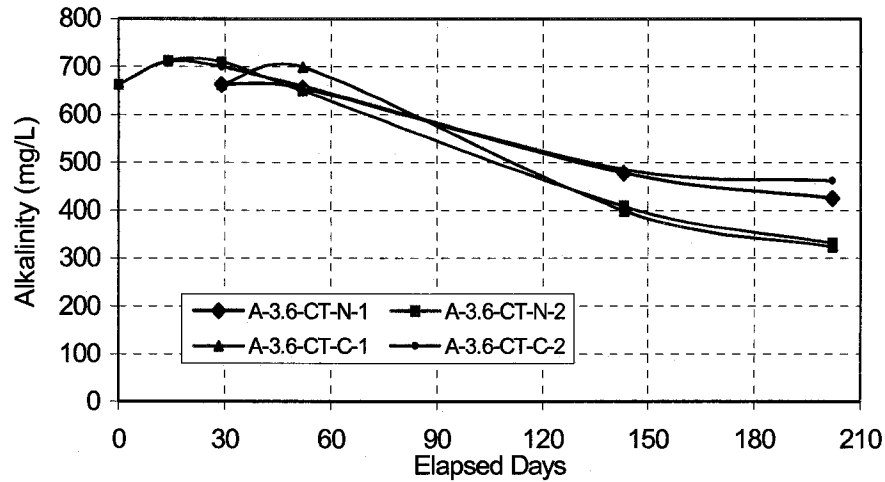


Fig.4.10 Alkalinity vs. Time (3.6% salt in nitrogen bags)

4.7 IC Test and Analytical Results

The results of the IC analyses were multiplied by appropriate dilution factors and adjusted according to mass loss due to the sampled salt and evaporated water. The concentration of each ion and the total salt concentration of each sample are presented in Table B5.1 to Table B5.29 and Fig.B5.1 to Fig.B5.15, attached in Appendix B5.0. Besides the major ions, SO_4^{2-} , Cl^- and Na^+ , some trace cations and anions such as Li^+ and NH_4^+ and F^- , Br^- , NO_3^- , and NO_2^- are also presented.

The total salt concentration of each sample increased with time. The shapes of the curves also implied that the dissolution of the salt increased with time. See Fig. 4.11 for an example (also see Fig.B5.1 to Fig.B5.15 in Appendix B5.0).

The CBE of each sample was calculated by using Equation 3.17. The calculations showed that the CBE of most samples were within $\pm 10\%$ except for three samples with the pure $\text{S}^{(0)}$ and the DI water encapsulation. The distribution of the CBE is shown in Fig.4.12, which

shows that total salt concentrations of most samples were less than 0.4M. When the concentrations were low, the CBE were low.

The ratios of measured total salt concentration (i.e., the total dissolved salt, TDS) to the critical TDS are listed in Table 4.7. The critical TDS is the calculated total salt concentration if all the encapsulated salt of each sample is dissolved or the solution reaches its salt solubility, whichever is less. (Some samples encapsulated an amount of salt higher than its solubility.) The critical TDS of the samples are shown in Table 4.7. The ratio indicates the percentage of salt that dissolved or the percentage of the salt that could be dissolved.

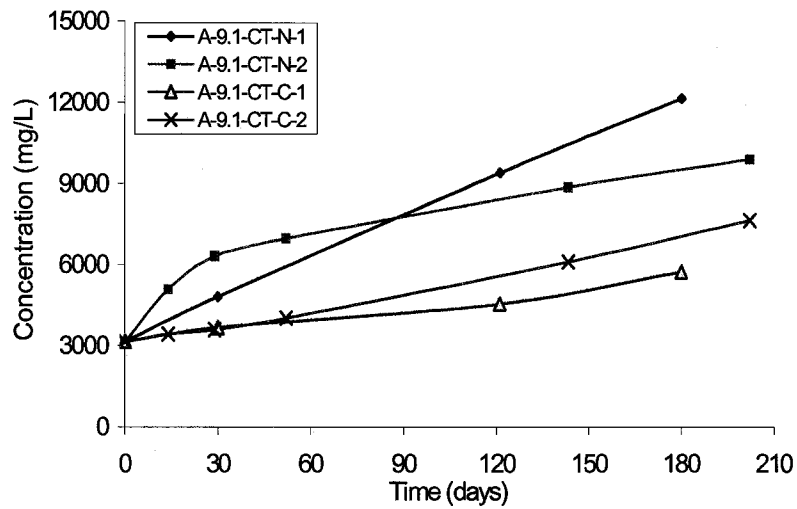


Fig.4.11 Total Concentration vs. Time

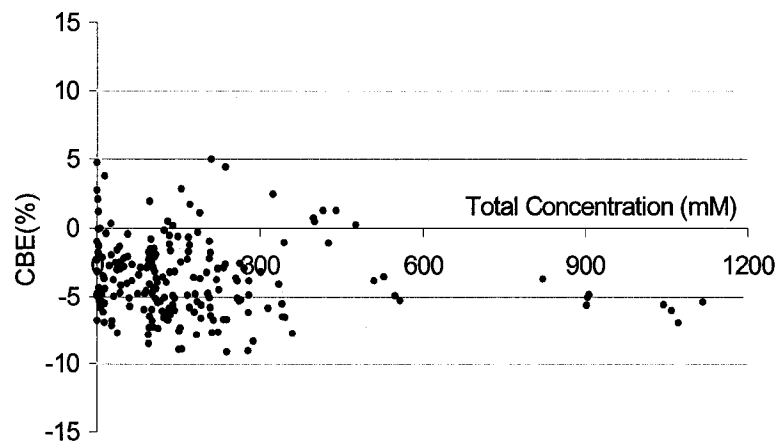


Fig.4.12 Distribution of CBE
(63.3% samples with less than 5% CBE)

Table 4.7 Ratios (%) of TDS to Critical Concentration of Samples

Salt content (%)	CT release water overlay		DI water overlay		Critical concentration (mg/L)*
	With cap	Without cap	With cap	Without cap	
24.9	25.0~26.8	86.4~88.4	14.7~16.1	83.2~84.8	42,533
9.1	13.5~18.0	23.3~28.6	2.0~17.1	15.3~18.3	42,533
6.3	16.0~20.4	26.1~27.0	2.8~10.8	16.1~20.5	42,533
3.6	10.7~17.6	20.5~22.3	4.2~4.4	10.5~13.9	42,533
50	3.0~3.5		0.5~2.4		337,300
40	1.6~2.0		0.03~0.6		275,210
30	2.5~5.8		0.6~0.7		220,544
20	4.7~5.3		1.3~2.4		145,996
10	7.7~8.6		1.4~23.0		72,456

* For the samples with 30%, 40% and 50% salt, the critical concentration was their salt solubility, which is determined through an IC test (see Table 4.3)

4.8 Salt Fluxes

Using Equation 3.18, the salt flux of each sample was calculated, and the results are presented in Table B6.1 to Table B6.7 and Fig.B6.1 to Fig.B6.13, in Appendix B6.0.

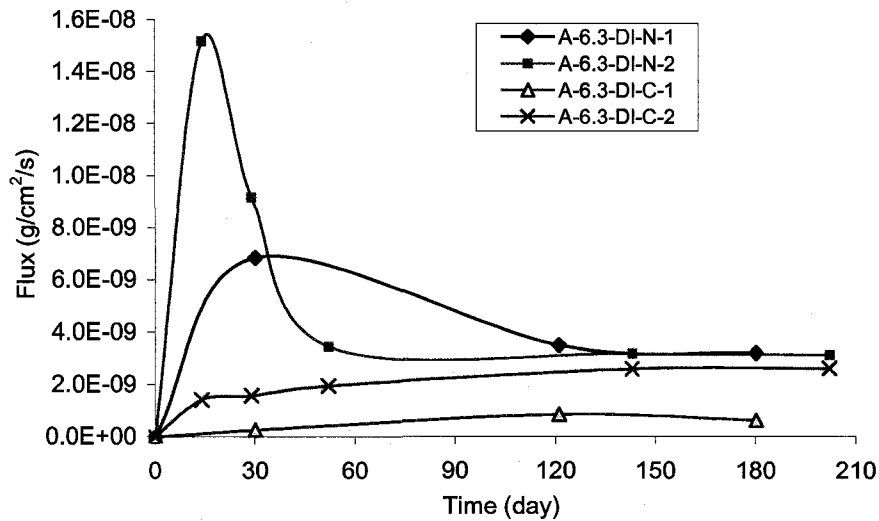


Fig. 4.13 Salt Flux (6.3% salt)

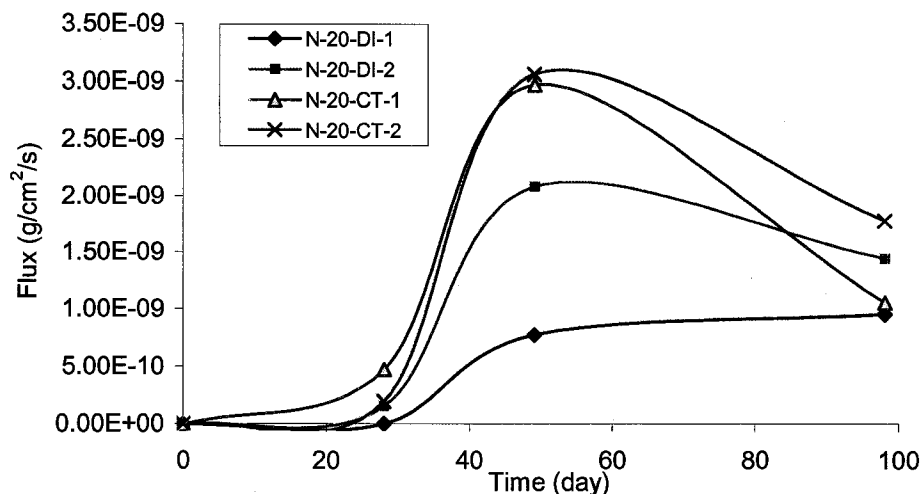


Fig. 4.14 Salt Flux (20% salt)

The layered samples open to the atmosphere without sulfur caps showed similar flux curves displaying the peak values of the salt flux about two to four weeks after encapsulation. See Fig. 4.13 for an example (also see Fig.B6.1 to Fig.B6.6 in Appendix B6.0). The samples with sulfur caps showed much lower peak values.

For the core samples in the gas bags, all the salt fluxes showed a 15 to 25 day delay at the beginning of the test when compared with the layered samples. See Fig.4.14 for an example (also see Fig.B6.7 to Fig.B6.13 in Appendix B6.0). The maximum salt flux of the samples in the gas bags and the corresponding porosity of the sulfur caps are presented in Table 4.8, which indicate no obvious correlation between salt flux and cap porosity.

In extreme conditions, the sulfur cap could decrease the salt flux by two orders of magnitude (see Sample A-24.9-CT-N-2 and Sample A-9.1-DI-C-1 in Table 4.8). According to this study, the effectiveness of the caps might vary by two orders of magnitude (see Sample N-10-DI-1 and Sample N-40-DI-1 in Table 4.8). However, the maximal salt fluxes more typically range 1~5g/cm²/s.

Table 4.8 Maximal Fluxes and Cap Porosities of Samples

Sample #	Max. Flux ($\times 10^{-9}$ g/cm ² /s)	Porosity %	Sample #	Max. Flux ($\times 10^{-9}$ g/cm ² /s)	Porosity %
A-24.9-DI-N-1	56.8		A-3.6-DI-C-1	1.2	
A-24.9-DI-N-2	66.8		A-3.6-DI-C-2	1.0	
A-24.9-DI-C-1	4.0		A-3.6-CT-N-1	5.5	
A-24.9-DI-C-2	3.5		A-3.6-CT-N-2	14.3	
A-24.9-CT-N-1	60.4		A-3.6-CT-C-1	1.1	
A-24.9-CT-N-2	75.3		A-3.6-CT-C-2	2.2	
A-24.9-CT-C-1	4.7		N-10-DI-1	13.4	12.9
A-30.7-CT-C-2	4.7		N-10-DI-2	0.6	10.9
A-9.1-DI-N-1	3.9		N-10-CT-1	2.8	11.0
A-9.1-DI-N-2	9.6		N-10-CT-2	2.0	16.9
A-9.1-DI-C-1	0.7		N-20-DI-1	0.96	11.1
A-9.1-DI-C-2	5.9		N-20-DI-2	2.1	10.9
A-9.1-CT-N-1	5.8		N-20-CT-1	3.0	9.2
A-9.1-CT-N-2	14.5		N-20-CT-2	3.1	10.3
A-9.1-CT-C-1	1.8		N-30-DI-1	0.87	10.8
A-9.1-CT-C-2	2.4		N-30-DI-2	0.74	10.0
A-6.3-DI-N-1	6.9		N-30-CT-1	6.9	10.7
A-6.3-DI-N-2	15.2		N-30-CT-2	1.9	10.0
A-6.3-DI-C-1	0.86		N-40-DI-1	0.05	10.9
A-6.3-DI-C-2	2.4		N-40-DI-2	0.84	9.2
A-6.3-CT-N-1	6.7		N-40-CT-1	0.85	10.8
A-6.3-CT-N-2	11.0		N-40-CT-2	1.4	10.2
A-6.3-CT-C-1	2.3		N-50-DI-1	0.8	9.6
A-6.3-CT-C-2	3.6		N-50-DI-2	4.1	7.9
A-3.6-DI-N-1	6.6		N-50-CT-1	3.9	9.0
A-3.6-DI-N-2	18.4		N-50-CT-2	5.2	8.7

5.0 INTERPRETATION AND ANALYSIS

This chapter provides an interpretation of the test data presented in Chapter 4. Analytical models of the salt diffusion are presented in this chapter and are compared with numerical models of the salt diffusion by using the program *ChemFLUX*[®]

5.1 Analysis of the Test Results of Materials

5.1.1 Density of Salt Solids

The reported densities of halite and thenardite were 2.165g/cm^3 and 2.68g/cm^3 , respectively. Halite and thenardite accounted for 72% and 24% of the salt mixture, therefore, the measured salt density of 2.23g/cm^3 was acceptable. However, the salt density might vary with the salt components and the process of formation.

5.1.2 Grain-Size of Salt Solids

Fig. 4.1 shows that the grain-size distribution of the crushed salt solids is similar to that of fine or medium sand. The fine parts of the two samples showed the most difference because the salt crystals were fragile, and the salt-solids were easily crushed into smaller sizes depending on the amount of crushing. The process used to make the salt sulfur mixture also resulted in grain breakage and caused variations in the salt grain-size distribution.

5.1.3 Solubility of Salt Solids

Less than 0.5% of the salt solid was found to be insoluble. The insoluble matter was observed to be brown in color.

Table 4.3 shows that from Samples D_0 to D_3 the major ion concentration increased, and the solubility of the solids moved toward the invariant point C where both NaCl and Na_2SO_4 were saturated (see Fig.2.1). The solubility of the salt solids was 420.5 g/L or higher for Sample D_3 .

5.1.4 Measurement of Porosity

Fig. 3.1 and Fig. 3.2 show that pores were present in the industrial sulfur crystal. For the samples in the gas bags, the porosities of the cores and the pure sulfur caps were found to be around 10%. Table 4.4 summarizes the porosity data for the core samples in the gas bags.

Pores formed in the sulfur due to the dissolved gases in the liquid sulfur and the density differences between liquid and solid sulfur. The density of liquid sulfur is temperature-dependent and is approximately 1.8 g/cm^3 at 138°C , a value which is about 90% of the density of solid sulfur (2.07 g/cm^3). During the process of cooling of the molten sulfur, a hard skin formed on the tops of the samples, preventing volume change. As the liquid sulfur solidified, the dissolved gases were prevented from escaping by the hard skin formed on the tops of the samples. The trapped gas created bubbles which resulted in pore formation in the solidifying sulfur. The time and order of sample creation caused temperature differences in the liquid sulfur, and resulted in the porosity differences.

The porosity of the $S^{(0)}$ is believed to have significantly enhanced the salt flux in this research. It influenced the water infiltration time and the salt dissolution rate. To control the dissolution of the encapsulated salt, reducing the porosity of the sulfur caps should be considered.

5.2 Analysis of the EC Test Results

For the samples open to the atmosphere, the EC values measured at the beginning of the test were strongly related to the depth where the measurement was taken within the samples. Gradually, this relationship disappeared (see Fig. 4.3; also see Fig.B1.4 to Fig.B1.19 in Appendix B1.0). The dissolution and transport of the salt in the water changed the EC profiles of the samples. The frequent measurements at the beginning of the test caused mixing in the overlying water columns, increasing the salt dissolution. The mixing caused by the sampling process contributed to the relationship of the EC values with the depth.

The EC values for samples with and without sulfur caps are compared in Table 4.6. The values were consistent with the prediction that the sulfur caps would reduce the salt dissolution. However, the effectiveness of encapsulation on the salt dissolution varied between samples (see Table 5.1).

The effectiveness of encapsulation was calculated as the ratio of the EC of the sample with a sulfur cap to the EC of the sample without a sulfur cap. Table 5.1 shows that the effectiveness of encapsulation ranged from 0.72 to 0.24; i.e., the sulfur caps reduced the EC of the overlying water solutions by 28% to 76% for the layered samples.

Table 5.1 Sulfur Cap's Influence on Salt Diffusion

Salt Content	24.9%	9.1%	6.3%	3.6%
Average EC* (DI-N**) (mS/cm)	40.5	10.6	11.4	8.2
Average EC (DI-C**) (mS/cm)	9.7	6.7	4.8	2.9
Effectiveness of Encapsulation***	0.24	0.63	0.42	0.35
Average EC (CT-N) (mS/cm)	40	15.7	14.8	12.0
Average EC (CT-C) (mS/cm)	13.9	9.2	10.7	8.1
Effectiveness of Encapsulation	0.35	0.58	0.72	0.67

* at the end of the test; ** N – No sulfur cap, C – Sulfur cap

*** defined as C / N

The measured EC values were higher for some samples with lower salt contents than for some samples with higher salt contents because of the different salt-diffusion rates between the samples. Samples with high EC values indicated high dissolution rates. The salt-dissolution rates were related to the porosity of the caps, and the tortuosity and continuity of the flow path. Therefore, the diffusion rates shown in Table 4.5 cannot be determined solely based on porosity.

5.3 Analysis of the pH Test Results

The redox reactions in the S-H₂O-O₂ system are affected by many factors such as pH, light, (organic) carbon, inorganic compounds, oxygen and temperature. The exact reactions occurring in the samples have not been identified and are beyond the scope of this research. The analysis of the pH is based on observations made during the testing program.

5.3.1 Analysis of pH Increase

The pH was measured for two kinds of samples: those with pure sulfur and those with sulfur encapsulated salt. Although increases in pH were observed for both types of samples, the rate and magnitude of the increases differed depending on the exposure to the atmosphere during the test.

The CT water stayed at a pH of around 8.2 when sealed in the Syncrude bulk container shipped to the University of Alberta laboratory. A three-liter sample of the CT water had a pH above 9.0 after being exposed to the atmosphere for three weeks. All the CT water samples

showed a slight increase in a pH from 8.2 to 9.0 after approximately eight weeks of exposure to the atmosphere and after approximately four weeks in the sealed gas bags. Many factors contributed to the increase in the pH under different conditions. Some are discussed below.

1) When a solution with mineral carbonates is exposed to the atmosphere and allowed to equilibrate with atmospheric CO₂, the minerals tend to raise the pH to values from 9 to 10 or even higher (Langmuir, 1997b). PHREEQC 2.10 (A USGS program that performs aqueous geochemical calculations) was used to calculate the pH of the CT water solutions with 500 ~ 800 mg/L of bicarbonate. The pH for the CT water solutions was predicted to be around 9.1.

2) Sulfides were produced through the reduction of sulfates (see Equation 2.12 and Equation 2.13; also see Fig. 2.3) in the sealed container shipped from Syncrude Canada and at the bottom of the CT water solutions in this research where DO was close to zero. The abiotic oxidation of hydrogen sulfide by oxygen (see Equation 3.7) after exposure to the atmosphere might have resulted in the pH increase for the pure CT water and the pure sulfur encapsulation condition:



When the CT water from the Syncrude shipping container was sampled, the pH was around 8.2. According to Table 2.4, between pH = pK₁ = 7.03 and pH = pK₂ > 14, its first conjugate base, HS⁻, dominates sulfides. The consumption of H₂S forced the reaction below (Equation 5.1) to move to the right:



By combining Equations 3.7 and 5.1, the H₂S can be eliminated:



The consumption of H⁺ results in the increase of pH of the solutions.

If the oxygen was depleted, the reaction described by Equation 5.2 stopped. The depletion of the oxygen might explain the shorter time observed for the pH increase for the samples in the gas bags with the CT water overlay (see Fig. 4.7; also see Table B2.1 and Fig.B2.20 to Fig.B2.24 in Appendix B2.0)

3) For the samples with encapsulated salt, the salt could increase the pH of the solution because the solid salt contained a small amount of carbonate. The increase in the pH could be observed in some of the samples in the gas bags with the DI water overlay (see Fig. 4.7;

also see Table B2.1 and Fig.B2.20 to Fig.B2.24 in Appendix B2.0). The increase in the EC occurs together with the increase in the pH (see Fig. 5.1). Sulfate reduction might also contribute to the pH increase (also see Section 5.6.2).

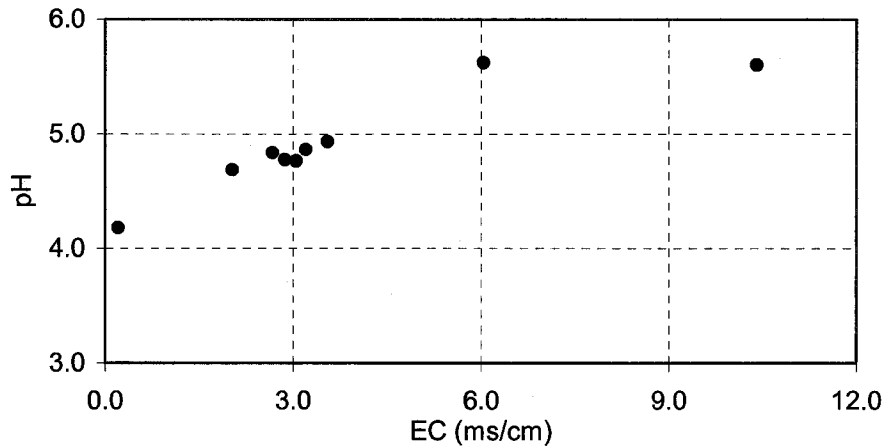
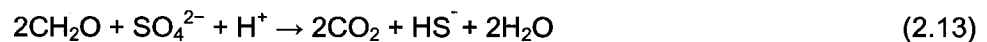
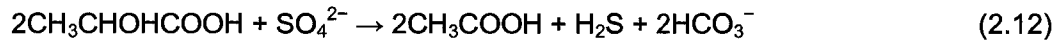


Fig. 5.1 EC vs. pH
(Samples in gas bags with DI water encapsulation)

4) If enough organic matter was present in the CT water, the growth of SRB (sulfate reducing bacteria) could be supported. SRB in the solution would reduce the sulfate to H_2S and HCO_3^- (see Equations 2.12 and 2.13, Fig. 2.3) and HCO_3^- would increase the alkalinity and the pH of the solution.



The increase in the alkalinity of the CT water samples at the beginning of the encapsulation supported this analysis (see Section 4.6 and Section 5.5 below).

Sulfate reduction is a strictly anaerobic reaction; i.e., organisms in a solution cannot tolerate the presence of O_2 . They obtain energy and carbon from reduced carbon compounds using sulfate as the terminal electron acceptor. DO values that were close to zero and nearly neutral pH conditions occurred together at the bottom of the water columns of some samples (see Table 5.2), for example, Sample A-3.6-CT-C-2. The production of sulfide (S^{2-}) gave the water column a characteristic black color and unpleasant smell if disturbed. The colors of Sample A-24.9-CT-N-2 at the beginning and end of the test are shown for comparison in Fig. 5.2.

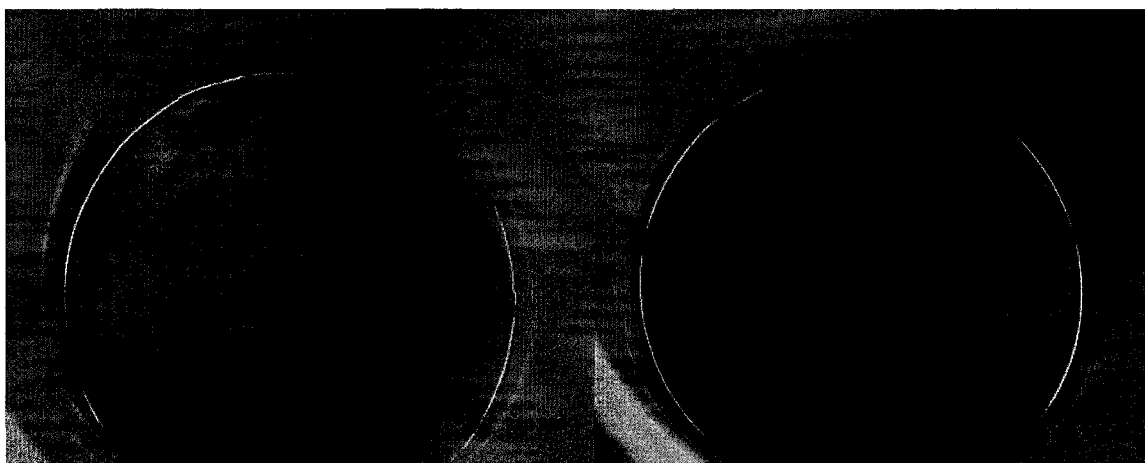


Fig. 5.2 Color of Sample A-24.9-CT-N-2 at the Beginning (Left) and End (Right) of the Test

Table 5.2 Measured EC, pH and DO at the End of the Test

Sample #	EC (mS/cm)	pH		DO (mg/L)	
		5 cm deep	15 cm deep	5 cm deep	15 cm deep
A-0-DI-1	0.03	4.29	4.29	8.20	8.20
A-0-DI-2	0.05	4.08	4.07	8.30	8.30
A-0-DI-3	0.03	4.47	4.45	8.30	8.20
A-0-CT-3	4.54	8.73	8.74	7.20	7.10
A-3.6-DI-N-1	9.12	4.15	4.16	7.40	4.10
A-3.6-DI-N-2	7.08	4.17	4.16	7.50	3.70
A-3.6-DI-C-1	2.78	4.87	4.76	7.80	5.80
A-3.6-DI-C-2	2.92	4.54	4.48	7.80	5.40
A-3.6-CT-N-1	11.76	8.56	7.17	2.50	1.60
A-3.6-CT-N-2	12.47	8.10	7.02	2.30	0.30
A-3.6-CT-C-1	6.20	8.80	8.26	6.10	4.60
A-3.6-CT-C-2	9.95	8.56	7.09	3.90	0.00
A-6.3-DI-N-1	10.66	4.20	4.20	7.40	3.50
A-6.3-DI-N-2	12.65	4.28	4.31	7.20	2.30
A-6.3-DI-C-1	2.61	4.78	4.77	7.80	6.60
A-6.3-DI-C-2	7.06	4.35	4.35	7.70	4.70
A-6.3-CT-N-1	15.7	8.53	7.28	3.80	0.00
A-6.3-CT-N-2	14.55	8.25	7.10	2.80	0.00
A-6.3-CT-C-1	10.23	8.37	7.22	2.70	0.00
A-6.3-CT-C-2	11.31	8.39	7.07	3.90	0.00
A-9.1-DI-N-1	9.57	4.33	4.31	7.40	2.80
A-9.1-DI-N-2	11.74	4.27	4.26	7.10	1.70

Table 5.2 Measured EC, pH and DO at the End of the Test (Continued)

Sample #	EC (mS/cm)	pH		DO (mg/L)	
		5 cm deep	15 cm deep	5 cm deep	15 cm deep
A-9.1-DI-C-1	1.42			8.10	6.00
A-9.1-DI-C-2	11.97	4.44	4.34	7.40	1.90
A-9.1-CT-N-1	15.89	8.44	7.20	2.10	0.00
A-9.1-CT-N-2	15.64	8.08	7.13	1.50	0.00
A-9.1-CT-C-1	8.91	8.75	7.25	3.30	0.20
A-9.1-CT-C-2	10.40	8.61	7.08	3.70	0.70
A-24.9-DI-N-1	40.00	5.13	5.02	5.70	0.70
A-24.9-DI-N-2	41.40	5.17	5.00	7.30	0.60
A-24.9-DI-C-1	9.85	4.62	4.54	7.50	2.40
A-24.9-DI-C-2	9.49	4.76	4.63	7.20	3.40
A-24.9-CT-N-1	40.70	8.44	7.32	2.80	0.00
A-24.9-CT-N-2	39.80	8.23	7.38	2.80	0.00
A-24.9-CT-C-1	13.22	8.24	7.08	2.70	0.00
A-30.7-CT-C-2	14.77	8.38	7.10	3.40	0.00

Table 5.2 reveals that for all samples with encapsulated salt and CT water (except for Sample A-3.6-CT-C-1), DO was less than 2.0 mg/L and pH was around 7.0 at the bottom of the water columns (at a depth of 15 cm). At a depth of 5 cm, the samples showed a DO larger than 2.0 mg/L and a pH around 8.0. In addition to salinity, possible $S^{(0)}$ oxidation affected the DO levels in the solutions. Sulfate reduction is strictly anaerobic, and sulfur oxidation is aerobic; therefore, sulfate reduction at the bottom of the water column, and a corresponding increase in the pH should have occurred. However no pH increase was observed for these samples. The color change and the smell of the solution implied that the sulfate reduction reaction occurred. However, the sulfate reduction reaction must have been either very slow or masked by a sulfur oxidation reaction, resulting in a neutral pH condition. If so, the neutral pH condition at the bottom of the water columns of these samples might be a long-term phenomenon. For most of the samples with encapsulated salt and the DI water, the measured DO was higher than 2.0 mg/L, and the pH was between 4.0 and 5.0, values which were 1 to 2 units lower than those of the pH at the beginning of the test. The pH decrease was similar to that in the CT-water-encapsulated samples. The pH decrease observed in the DI water solutions will be discussed in next section.

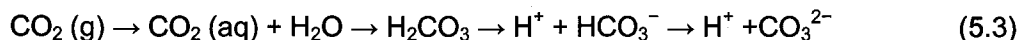
For samples without encapsulated salt, the measured DO in the CT water at the end of the

test was 7.0 mg/L, which was close to saturation. The pH was slightly lower than the peak value of 9.0, indicating that the sulfur oxidation was very slow under these conditions. This result will also be discussed in next section.

5.3.2 Analysis of the pH Decrease

As was the case for the pH increases in this research, more than one factor forced the pH to decrease in the solutions.

1) The pH decrease in the CT water solutions differed from that in the DI water solutions. When DI water was exposed to the atmosphere for a period of time, the measured pH was lower than 7.0, as a result of CO₂ dissolving into water and forming carbonic acid (see Equation 5.3). The pH of CO₂-saturated DI water can be calculated using Equation 5.4 (Langmuir, 1997b)



$$[\text{H}^+] = \frac{K_{\text{CO}_2} K_1 P_{\text{CO}_2}}{[\text{HCO}_3^-]} \quad (5.4)$$

The geochemistry program PHREEQC (A USGS free program conducting geochemistry analysis) was used, setting the pure water to be in equilibrium with atmospheric CO₂. The result showed that the pH could be as low as 5.7. This factor partially explained why the pH of the samples without encapsulated salt and DI water gradually decreased to 4.2 after 200 days encapsulation (see Table B2.1 and Fig.B2.1 to Fig.B2.3).

2) The abiotic oxidation of S⁽⁰⁾ is extremely slow at ambient temperatures in any medium (as discussed in Section 2.3.1). The photoautotrophic oxidation of S⁽⁰⁾ (see Equation 2.16) might exist but was slow, and the samples were capped by wooden disks most of the time. For samples in the gas bags with DI water, the O₂ and CO₂ gases were replaced by N₂ gas. The photoautotrophic oxidation of S⁽⁰⁾ might occur but was very slow. However, the pH of these samples still decreased by one to two units. Except for the dissolution of atmospheric CO₂ into the DI water solutions due to air leakage, other reactions causing this pH decrease were unclear.

3) The pH decrease for the samples with the CT water can be quantitatively analyzed. The continuous decrease of pH in the CT water samples with encapsulated salt might be mainly a

result of the oxidation of $S^{(0)}$ (see Equation 2.15):



For the samples open to the atmosphere, the total buffer capacity from a pH of 9.0 to 7.0 was 1.45×10^{-2} eq/L (see Table 5.3). At a pH of 7.0, $(H^+) = 10^{-7}$ eq/L, the total proton produced can be assumed to be 1.45×10^{-2} eq/L \times 1.0 L = 14.5 mmols. According to Equation 2.15, 7.3 mmols or 0.23 g $S^{(0)}$ and 10.9 mmols or 0.35 g O_2 were consumed to produce 14.5 mmols of protons. The amount of consumed O_2 was larger than the maximal amount of oxygen that could diffuse into the water during the 200-days of encapsulation (about 100mg, see Section 5.4.1), which suggests that other unknown factors contributing to the decrease of pH in these solutions might exist. The amount of $S^{(0)}$ oxidized in the period of testing was also small.

The oxidation of sulfur and the dissolution of CO_2 in the water column shaped the pH profile of the solutions (see Fig.B2.1 to Fig.B2.24 in Appendix B2.0).

5.3.3 Buffer Capacity of CT Water Tested Samples

The alkalinity of the CT water solutions included OH^- ; weak acid ions such as HCO_3^- , CO_3^{2-} , S^{2-} , HS^- , and CH_3COO^- ; and oxyhydroxides of some metals, such as Al and Fe. The buffer capacity is pH-dependent. Below a pH of 10.0, the concentrations of OH^- , S^{2-} and CO_3^{2-} were too low to contribute to the solutions' buffer capacity. The concentrations of HS^- and CH_3COO^- were not measured or detected in the solutions. The tests showed very small amounts of Al and Fe ions in the solution. Therefore, not all of these ions contributed to the solutions' buffer capacity. Only the bicarbonate controlled the buffer capacity of the CT release water solutions due to the bicarbonate's high concentration (400 to 700 mg/L, see Table 3.4 and Table B5.1 to Table B5.29 in Appendix B5.0) and suitable pH condition (pH 4.0 to pH 9.0). The pH buffering reaction is shown in Equation 3.14:



In this research, some samples were exposed to the atmosphere, which could be viewed as an open system with constant CO_2 pressure. Other samples were sealed in the nitrogen gas bags, which could be viewed as closed systems with constant total carbon. Langmuir (1997b) presents the calculation of buffer capacity, β , both in an open system and in a closed system as shown in Equations 5.5 to 5.7 and Equation 5.8, respectively.

$$\beta_{open} = 2.3 \left[(HCO_3^-) + 4(CO_3^{2-}) + (H^+) + (OH^-) \right] \quad (5.5)$$

$$(\text{HCO}_3^-) = (K_1 K_{\text{CO}_2} P_{\text{CO}_2}) \cdot 10^{\text{pH}} \quad (5.6)$$

$$(\text{CO}_3^{2-}) = (K_1 K_2 K_{\text{CO}_2} P_{\text{CO}_2}) \cdot 10^{2 \cdot \text{pH}} \quad (5.7)$$

$$\beta_{\text{close}} = 2.3 \left[(\text{H}^+) + (\text{OH}^-) + \frac{C_T 10^{10.3} (\text{H}^+) \cdot [10^{16.7} (\text{H}^+)^2 + 10^{7.0} (\text{H}^+) + 1]}{[10^{16.7} (\text{H}^+)^2 + 10^{10.3} (\text{H}^+) + 1]^2} \right] \quad (5.8)$$

For the closed system, i.e., for the samples in the gas bags, the average measured alkalinity, C_B , for a pH around 9.3 was 656 mg/L, i.e., 1.07×10^{-2} eq/L. The calculated buffer capacity from a pH of 9.0 to 4.0 is presented in Table 5.3 by using Equation 5.8. For the open system, the calculated buffer capacity at pH 9.0 to pH 4.0 is also presented in Table 5.3 by using Equations 5.5 to 5.7.

Table 5.3 shows that the open system had a higher total buffer capacity (from a pH of 9.0 to 4.0) than the closed system. For the open system, the CT water solutions had the largest buffer capacity, which occurred at a pH of 9.0. For the closed system, the largest buffer capacity of the CT solutions occurred at a pH of around 6.0.

Therefore, disposal of the encapsulated salt and $\text{S}^{(0)}$ together with the CT water, opening the CT water to the atmosphere, might be a viable option to maintain a neutral pH condition.

Table 5.3 Buffer Capacities of Samples

pH	H^+ (eq/L)	OH^- (eq/L)	CO_3^{2-} (eq/L)	Open System			Closed System	
				HCO_3^- (eq/L)	β_{open}	$\log(\beta_{\text{open}})$	β_{closed}	$\log(\beta_{\text{closed}})$
9.0	1.0E-09	1.0E-05	4.9E-04	5.3E-03	1.3E-02	-1.9	1.2E-03	-2.9
8.0	1.0E-08	1.0E-06	4.9E-06	5.3E-04	1.2E-03	-2.9	7.2E-04	-3.2
7.0	1.0E-07	1.0E-07	4.9E-08	5.3E-05	1.2E-04	-3.9	4.0E-03	-2.4
6.0	1.0E-06	1.0E-08	4.9E-10	5.3E-06	1.4E-05	-4.8	5.0E-03	-2.3
5.0	1.0E-05	1.0E-09	4.9E-12	5.3E-07	2.4E-05	-4.6	9.3E-04	-3.0
4.0	1.0E-04	1.0E-10	4.9E-14	5.3E-08	2.3E-04	-3.6	3.3E-04	-3.5
Sum					1.5E-02		1.9E-03	

Note that the unit of buffer capacity in Table 5.3 is eq/L/pH.

5.4 Analysis of the DO Test Results

5.4.1 Calculation of the DO in Water

According to Equation 2.11, the calculated solubility of oxygen at 25 °C and 0, 9.0 g/L and 18.1 g/L salinity is 8.26 g/L, 7.85 mg/L and 7.46 mg/L, respectively. As the test was carried out at a location 600meters above sea level, the solubility of oxygen would be around 7.66 mg/L, 7.30 mg/L and 6.94 mg/L (also see Table 3.6). According to Equation 2.10, the calculated diffusion coefficient of oxygen at 25 °C in pure water is $2.3 \times 10^{-5} \text{ cm}^2/\text{s}$. Given the water salinity, the diffusion coefficient of oxygen would be reduced to around $2.0 \times 10^{-5} \text{ cm}^2/\text{s}$.

Table 5.2 reveals that the mean saturated concentration of oxygen at the upper surface of the samples without encapsulated salt was 8.3 mg/L for the DI water solutions and 7.2 mg/L for the CT water solutions. These values were close to the calculated saturation values of 8.26 mg/L to 6.94 mg/L (based on Equation 2.11 and the salinity of the solutions). The measured DO difference between the upper surface and the bottom of the water column ranged from 1.5 mg/L to 7.5 mg/L. According to Equation 2.4, the simplest calculation of oxygen fluxes and the total mass of oxygen transported within 200 days of encapsulation are presented in Table 5.4. This calculation assumed that the oxygen transport distance was 5 cm (see Fig. B3.19 for an example)

$$J = D_{\text{O}_2-\text{H}_2\text{O}} \frac{dc}{dx} \quad (2.4)$$

According to the above calculations, up to 94.6 mg of oxygen could diffuse into the water column during 200 days of encapsulation and thus be available to be consumed by oxygen-demanding reactions. The effect of bacterial activity on the oxygen diffusion in the solutions was not considered in the above calculation. In fact, for zero-order kinetics and a constant reaction rate with depth, the depth of the oxygen penetration (or oxygen transport distance) is determined by both metabolic activity and the rate of the diffusive supply of oxygen to the reservoir.

Table 5.4 Oxygen Fluxes in 200 Days*

Concentration Difference (mg/L) in 5cm depth	1.5	3.0	4.5	6.0	7.5
Oxygen Flux (mg/cylinder area/day)	9.46E-02	1.89E-01	2.84E-01	3.78E-01	4.73E-01
Total Mass Transported (mg/cylinder)	18.9	37.8	56.7	75.7	94.6

* $D_{\text{O}_2-\text{H}_2\text{O}}$, was assumed to be $2 \times 10^{-5} \text{ cm}^2/\text{s}$,

5.4.2 Analysis of the DO Results

DO measurements are used to indicate the oxygen balance required for oxidation reactions and the oxygen transport in water. If the oxidation reactions consume oxygen faster than the oxygen transport for a particular location, the measured DO will decrease to zero.

The DI water was deaerated to a DO level less than 5.0 mg/L before being placed in contact with the solid samples. If the oxidation reactions in the solution are very slow, the oxygen will remain at a saturated concentration (for DI water at room temperature this level is around 7.66 mg/L) and will be homogeneously distributed in the solution. The samples containing pure sulfur left open to the atmosphere were homogeneously oxygen-saturated (see Fig.B3.1 to B3.3 in Appendix B3.0), indicating that the oxygen demanding reactions in these samples were very slow. Had the oxygen-demanding biotic reactions been active, more oxygen would have been consumed. Consequently, the DO would have decreased with depth, as observed in most of the encapsulated samples (see Fig.B3.4 to Fig.B3.19 in Appendix B3.0). The DO profile of the water columns implied a balance between the oxygen fluxes in the water solution and the oxidation reactions.

Fig.B3.1 to Fig.B3.3 in Appendix B3.0 reveal that the measured DO in some CT water solutions with an EC of less than 5.0 mS/cm, were about 1.0 mg/L less than that in DI water solutions with an EC of less than 0.1mS/cm. Fig.B3.4 to Fig.B3.19 in Appendix B3.0 show that the measured DO differences in most CT water solutions and DI water solutions were much more than 1.0 mg/L. Therefore, the solubility of oxygen was obviously affected by the salinity of the solution (see Table 5.2). In short, both the oxidation reactions and the salinity of the solutions affected the ongoing oxygen balances.

Gases such as H₂S could react with the cathode of the DO probe, causing fluctuations in the DO readings. DO fluctuations were observed at a depth of 10 cm in Sample A-6.3-CT-C-2 and at a depth of 5cm in Sample A-9.1-CT-N-2 (see Fig.B3.11 and Fig.B3.13 in Appendix B3.0). The fluctuating DO readings in the CT release water compared to those in the DI water also indicated that oxidation reactions occurred more readily in the CT water (see Fig.B3.10 and Fig.B3.14 in Appendix B3.0).

The DO concentration in the solutions reflected the scale of the ongoing redox reactions.

Both the magnitude of the redox reactions and the salinity of the solution affected the dissolving of oxygen. Maximum 0.5 mg oxygen dissolved into the cylinders per day.

5.5 Analysis of the Alkalinity Titration Results

As discussed in Section 5.2.3, the oxyhydroxides of some metals and weak acid ions contributed to the total alkalinity of the solutions. However, when the pH was below 10.33, bicarbonate mainly controlled the alkalinity of the solution.

Alkalinity titration was conducted only on the samples using the CT release water and with a pH higher than 5.0. Samples with a pH of less than 5.0 indicated only negligible amounts of alkalinity (see Fig. 3.8). The initial total carbon, C_T , of the CT release water was used to determine the total alkalinity of the samples (see Table 5.5). The encapsulated salts contained a small amount of carbonate (0 to 6%). Trial titration of these samples with the DI water revealed a bicarbonate concentration ranging from 0~20 mg/L. The alkalinity of the DI water solutions was negligible when compared to the bicarbonate alkalinity of the samples with CT release water which ranged from 300~700 mg/L (see Table B4.1 in Appendix B4.0). All titration tests were assumed to be conducted in a closed system.

The total alkalinities in samples with CT water increased slightly during the first several weeks of exposure to the atmosphere because the samples were in equilibrium with atmospheric CO_2 (see Table 5.5; also see Fig.B4.1 to Fig.B4.7 in Appendix B4.0). The samples in the N_2 filled gas bags did not show the same increase in alkalinity (see Table 5.5). By combining this observation with the analysis in Section 5.2.1, it was concluded that the SRB reaction should be very slow at this time.

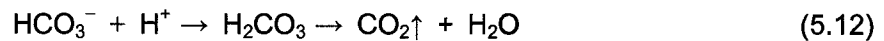
Table 5.5 Average Total Alkalinities of CT Water Samples at Different Time

open to the atmosphere	Elapsed Days	0	14	29	52	143	202
	Alkalinity (mg/L)	663.6	709.7	699.7	665.8	501.5	449.5
in gas bags	Elapsed Days	0	28	49	98		
	Alkalinity (mg/L)	663.6	655.6	633.4	582.7		

In an open system, the CO_2 gas pressure is assumed to remain constant. Under normal atmospheric pressure, the CO_2 gas pressure is $10^{-3.48}$ bar. The water in an open system can

contain more dissolved CO₂ when the CO₂ produced by decay or other reactions is greater than the amount of CO₂ degassing. The calculated amount of dissolved CO₂ in the CT solutions with the bicarbonate alkalinity shown in Table 5.5 indicated that the CO₂ gas pressures were between 10^{-1.17} bar and 10^{-3.17} bar for pH's ranging from 7.0 to 9.0, values which were larger than the normal atmospheric pressure of 10^{-3.48} bar. In fact, the highest bicarbonate concentration below a pH of 9.0 in an open system with normal atmospheric pressure is 5.3×10⁻³ eq/L (equal to 323 mg/L) (see Table 5.3). Table 5.5 shows that the bicarbonate concentrations of all the samples with the CT solutions were greater than 323 mg/L. This finding indicated a higher gas pressure in the solutions.

The pH of the CT water solutions decreased from above 9.0 to around 7.0, strongly reducing the alkalinity of the solutions due to the reaction of HCO₃⁻ to H₂CO₃ to CO₂ (g) (see Equation 5.12). Therefore, water alkalinity is pH-dependent.



Most of the alkalinity in the water solutions was derived from the initial alkalinity contained in the CT release water. The total alkalinity was mainly in the form of bicarbonate alkalinity, and it decreased with pH. Exposing the CT water to the atmosphere increased its alkalinity.

5.6 Analysis of the Salt Dissolution

Molar concentrations are approximately equal to the molal concentrations for water with a TDS of up to about 7000 mg/L. Below a TDS of 7000 mg/L, the density of water solutions is approximately 1 kg/L, and the difference between the molar (M) and molal (m) concentration can be ignored (Langmuir, 1997d). In cases where TDS is higher than 7000 mg/L, common for the solutions used in the current research, the appropriate units are mass per volume.

5.6.1 Analysis of the Trace Ions

The absence or presence of trace ions such as NO₃⁻, NO₂⁻ and NH₄⁺ (see Table B5.3 and Table B5.4 in Appendix B5.0), revealed the redox conditions within a given solution. Nitrate, nitrite or both were detected in five CT release water samples collected from the same bulk sample shipped from Syncrude Canada Ltd. but at different times. Bacterial reduction of NO₃⁻ to NH₄⁺ has been studied in microbiology, but the dominant process in contaminant hydrogeology appears to be a reduction of NO₃ to N₂. Intermediate elements such as nitrite,

resulting from nitrate reduction, can be measured in ground water at low concentrations and indicates ongoing nitrate reduction (Appelo and Postma, 1993). The dilution of samples may decrease concentrations of some trace ions below the detection limit. However, the detailed biotic reactions occurring in test solutions have not been studied at this time.

5.6.2 Analysis of the Sulfate Concentration

The sulfate concentration increased with time due to the salt dissolution and sulfur oxidation reactions. The percentage of sulfate with respect to other dissolved ions in the solution would have remained unchanged if no sulfate reduction or sulfur oxidation occurred. The changes in the percentage of sulfate thus reflected the redox conditions of the solution. Along with the pH and the DO measured at a depth of 15 cm, the sulfate concentrations for elapsed times ranging from 29 to 202 days are presented in Table 5.6.

The change in sulfate concentration, C_c , for the DI water solutions was calculated as the difference between the percentage of sulfate in the first sample, P_o , and the percentage of sulfate in the current sample, P_i , multiplied by the total salt concentration of the current sample, C_i , as shown in Equation 5.13. For the CT water tested samples, the initial concentration was subtracted from the total salt concentration in CT water (C_o). The remainder of the calculation is the same as that for the DI water samples (see Equation 5.14).

$$C_c = (P_i - P_o)C_i \quad (5.13)$$

$$C_c = (P_i - P_o)(C_i - C_o) \quad (5.14)$$

Table 5.6 reveals that the sulfate content decreased for most of the samples in the gas bags, indicating a sulfate reducing condition. Generally, the change was less than 1.0 mM. In contrast, increase of sulfate content was observed in most of the samples open to the atmosphere indicating possible sulfur-oxidizing conditions (see Equation 2.15):

The buffer capacity of the CT water samples with pH values ranging from 9.0 to 7.0 was 14.5 meq/L protons (see Table 5.3). According to Equation 3.5 and Table 5.6, 3 mM to 20 mM of sulfate were produced, along with 6.0 to 40 meq/L protons. This amount approximated the buffer capacity of the CT water when the pH values range from 9.0 to 7.0.

Table 5.6 Sulfate Concentration Change (mM)

Sample #	Elapsed Time (day)			
	29	52	143	202
A-24.9-DI-N-1	1.07	2.66	14.26	19.81
A-24.9-DI-N-2	1.11	3.99	11.71	14.02
A-24.9-DI-C-1	-0.10	-0.16	0.23	1.23
A-24.9-DI-C-2	-0.01	0.12	0.75	1.89
A-24.9-CT-N-1	0.12	6.89	18.71	20.29
A-24.9-CT-N-2	1.75	5.99	16.63	18.86
A-24.9-CT-C-1	0.17	0.67	4.48	7.23
A-24.9-CT-C-2	-0.14	0.18	3.05	4.52
A-9.1-DI-N-1			-1.54	-2.63
A-9.1-DI-N-2	1.90	2.09	3.71	4.71
A-9.1-DI-C-1			-0.27	-0.45
A-9.1-DI-C-2	0.38	0.34	3.16	5.13
A-9.1-CT-N-1			3.62	6.17
A-9.1-CT-N-2	1.68	2.73	4.91	6.68
A-9.1-CT-C-1			0.76	2.43
A-9.1-CT-C-2	0.10	0.32	2.39	3.79
A-6.3-DI-N-1			0.71	1.35
A-6.3-DI-N-2	2.39	2.85	4.05	3.91
A-6.3-DI-C-1			-1.08	-1.21
A-6.3-DI-C-2	-0.30	-0.72	-1.13	-1.99
A-6.3-CT-N-1			3.97	5.15
A-6.3-CT-N-2	1.78	2.95	4.77	5.86
A-6.3-CT-C-1			0.40	0.84
A-6.3-CT-C-2	0.04	0.41	2.50	2.55
A-3.6-DI-N-1			1.92	1.68
A-3.6-DI-N-2	0.38	0.93	1.02	0.55
A-3.6-DI-C-1			0.02	0.18
A-3.6-DI-C-2	-0.04	-0.16	-0.62	-0.87
A-3.6-CT-N-1			3.55	4.26
A-3.6-CT-N-2	-0.03	0.52	3.03	3.05
A-3.6-CT-C-1			0.58	1.14
A-3.6-CT-C-2	0.06	0.40	2.71	4.03
A-0-DI-1	0.01	0.01	0.05	0.05
A-0-DI-2	0.02	0.03	0.06	0.07
A-0-DI-3			0.01	0.01
A-0-CT-1	0.05	0.15	0.16	0.23
A-0-CT-2	0.04	0.13	0.23	0.08
A-0-CT-3			-0.17	-0.21

Table 5.6 Sulfate Concentration Change (mM) (Continued)

Sample #	Elapsed Time (day)	
	49	98
N-10-DI-1	3.38	2.63
N-10-DI-2	0.03	0.11
N-10-CT-1	0.71	1.19
N-10-CT-2	0.32	0.47
N-20-DI-1	-0.31	-1.41
N-20-DI-2	-0.46	-1.09
N-20-CT-1	0.37	0.41
N-20-CT-2	0.35	0.15
N-30-DI-1	-0.20	-0.87
N-30-DI-2	-0.18	-0.92
N-30-CT-1	0.12	-0.92
N-30-CT-2	0.17	0.02
N-40-DI-1	0.01	0.01
N-40-DI-2	-0.45	-2.06
N-40-CT-1	0.16	0.13
N-40-CT-2	0.12	-0.11
N-50-DI-1	-0.11	-0.97
N-50-DI-2	0.34	-0.78
N-50-CT-1	0.26	-0.16
N-50-CT-2	0.35	-0.29

Some odd results were observed in Samples A-3.6-DI-C-2 and A-6.3-DI-C-2 where the amount of sulfate decreased under aerobic condition. The increase in the amount of sulfate in the pure sulfur samples might have been due to cross-contamination in the measurements. CBE of the three DI water tested samples were larger than $\pm 10\%$, likely due to the missing carbonates from the IC analysis.

5.6.3 Checking the Mass of Dissolved Salt

More than 80% of the encapsulated salt in Samples A-24.9-DI-N-1, A-24.9-DI-N-2, A-24.9-CT-N-1 and A-24.9-CT-N-2 dissolved (see Table B5.1, Table B5.3 in Appendix B5.0 and Table 4.4). In order to confirm these results, a cross section of sample A-24.9-CT-N-1 was obtained in order to examine the salt-dissolution features inside the sample. The mass of dissolved salt was also checked by evaporating the water in an oven at a temperature of 120°C. The result showed that the mass of the dissolved salt was 84.6% of sulfur encapsulated salt (see Table 3.4) and that the concentration of salt in the solution was about 36 g/L (close to the salt concentration of 37.6 g/L measured in the IC test). A photo of Sample

A-24.9-CT-N-1 is shown in Fig. 5.3.

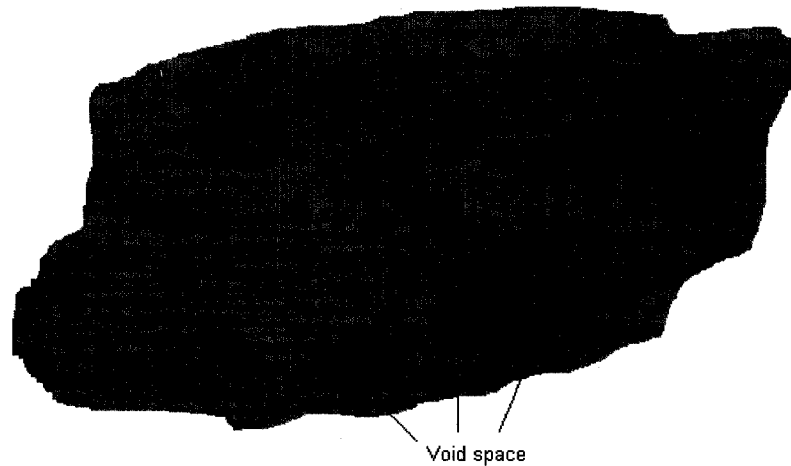


Fig. 5.3 The Dried Salt and Sulfur Mixture
(Sample A-24.9-CT-N-1, around 1.5 times the original size)

5.7 Influence of the Sulfur Caps

5.7.1 Effectiveness of Encapsulation

Similar to EC measurements, the TDS also indicated the influence of the sulfur caps on the salt dissolution, i.e., the effectiveness of encapsulation. Table 5.7 shows the effectiveness of encapsulation, indicated by the ratio of the average critical ratio of the TDS of the samples with sulfur caps to the average critical ratio of the samples without sulfur caps. The average critical ratio was taken from Table 4.7.

On average, the salt dissolution rates of the samples open to the atmosphere with sulfur caps were 18.3% to 68.4% of the salt dissolution rates for the samples without caps. Therefore, the sulfur caps reduced the salt dissolution by approximately 30~80%. At the end of the test, Sample A-9.1-DI-C-1 had the smallest concentration increase of 0.83 g/L (see Table B5.6 in Appendix B5.0), which was just 2.3% of the largest concentration increase of 36.08 g/L in Sample A-24.9-DI-N-2 (see Table B5.1 in Appendix B5.0).

Table 5.7 shows that the encapsulated samples with more salt generally had higher average critical ratios. More salt would cause more salt diffusion channels to be left behind after the salt dissolved, resulting in higher rates of dissolution.

Table 5.7 Effectiveness of Salt Encapsulation

Salt content	24.9%	9.1%	6.3%	3.6%
Ave. critical ratio (DI-N)	84.0	16.8	18.3	12.2
Ave. critical ratio (DI-C)	15.4	9.6	6.8	4.3
Effectiveness of encapsulation	18.3	57.1	37.2	35.2
Ave. critical ratio (CT-N)	87.4	26.0	26.6	21.4
Ave. critical ratio (CT-C)	25.9	15.8	18.2	14.2
Effectiveness of encapsulation	29.6	60.7	68.4	66.4

Note: N—No cap, C—Cap

The measured TDS for the samples in the gas bags also indicated the effectiveness of encapsulation (see Table 4.7). Sample N-40-DI-1 had the lowest salt concentration of 77.8 mg/L (see Table B5.26 in Appendix B5.0) after about 100 days of encapsulation, which was only 0.03% of its critical concentration. Sample N-10-DI-1 had the highest salt concentration of 16,668 mg/L (see Table B5.20 in Appendix B5.0), which was 23% of its critical concentration. These two samples showed that the effectiveness of encapsulation varied by more than two orders of magnitude.

The designed cap thickness was 1.25 cm for the layered samples open to the atmosphere and 1.00 cm for the core samples in the gas bags. Pores were created in the sulfur caps during the fabrication process, resulting in slightly larger thicknesses. Any continuous pores also provided pathways for the surface water to penetrate through the cap to the encapsulated salt, resulting in higher salt dissolution rates. The cap design was thus crucial in effectively encapsulating the salt within the elemental sulfur. The two most important factors in selecting the correct cap design included the most appropriate cap thickness and ensuring that the porosity remained low as the molten cap cooled.

The sulfur caps could significantly reduce the rate of salt dissolution. However, the effectiveness of salt encapsulation might vary and was highly dependent on the design and construction of the caps.

5.7.2 Analysis of Salt Fluxes

For the samples open to the atmosphere, a decrease in the salt flux was observed in the 16 samples with the sulfur caps compared to the other 16 samples without the sulfur caps (see Table 4.8 and Table 5.8). A decrease in the salt flux indicated that the sulfur caps were more

effective in encapsulating the salt.

Table 5.8 Average Maximal Salt Fluxes of Samples

Samples	with caps ($\times 10^{-9}$ g/cm ² /s)	without caps ($\times 10^{-9}$ g/cm ² /s)
Open to the atmosphere	2.6	23.9
In the gas bags	2.8	

All the samples in the gas bags showed an obvious time delay in releasing salt (see Fig.B6.9 to Fig.B6.13 in Appendix B6.0). Generally, the delay was around 20 days. For samples with very low salt fluxes, such as Sample N-50-DI-1, the delay was as long as four weeks. This phenomenon suggested that water needed time to penetrate and saturate the sulfur caps. Longer delay times indicated that some sulfur caps had fewer well-connected pores and thus smaller salt flux.

5.7.3 Influence of Salt Content and Caps on Salt Encapsulation

For the layered samples with the sulfur caps and the core samples in the gas bags, the average maximum salt flux are compared to the various salt contents (see Table 5.9), revealing a correlation between them. A large difference in salt content caused small changes in salt flux. Furthermore, the influence of sulfur caps was greater than that of the salt content. For example, the salt flux of Sample N-10-DI-1 (which encapsulated just 10% salt) was 13.4×10^{-9} g/cm²/s. This flux was hundreds of times higher than that of Sample N-40-DI-1, 0.05×10^{-9} g/cm²/s, which encapsulated 40% salt. The sulfur caps were therefore the most crucial factor controlling salt dissolution.

Table 5.9 Salt Fluxes and Encapsulated Salt Content

Salt Content (%)	Average Maximum Salt Flux ($\times 10^{-9}$ g/cm ² /s)	Salt Content (%)	Average Maximum Salt Flux ($\times 10^{-9}$ g/cm ² /s)
24.9	4.2	50	3.5
9.1	2.7	40	0.8
6.3	2.3	30	2.6
3.6	1.4	20	2.3
		10*	1.8

*Exclude the flux of Sample 10-DI-1, which has an extremely high flux: 13.4×10^{-9} g/cm²/s. When a cap had large pores, it failed to reduce salt dissolution.

5.8 Numerical and Analytical Modeling

Both analytical and numerical models were built to simulate the salt dissolution in a one-dimensional, two-layer, closed system. The modeling results and discussion are presented in this section. Appendix C displays the MathCAD worksheets for the analytical models. Appendix D presents the math development of the analytical models.

5.8.1 Parameter Setup

5.8.1.1 Dimensions of the Model

A one-dimensional diffusion model was created by using a two-layer closed system (discussed in Section 3.3.4.4). The geometry used in the various models is shown in Appendix C and D (also see Fig.5.4). The depth of water reservoirs was 16.45cm and 5.5cm, respectively. When the water penetrated the pores, the depth of the reservoir decreased slightly; however, this small decrease could be neglected at the beginning of the test. As discussed in Section 3.3.4.4, the diffusion boundary at the bottom of the samples without sulfur caps required a moving boundary condition. For the samples with the sulfur caps, after the encapsulated salt dissolved, the bottom of the sample also required a moving boundary condition. Therefore, the thicknesses of the caps were adjusted slightly as required.

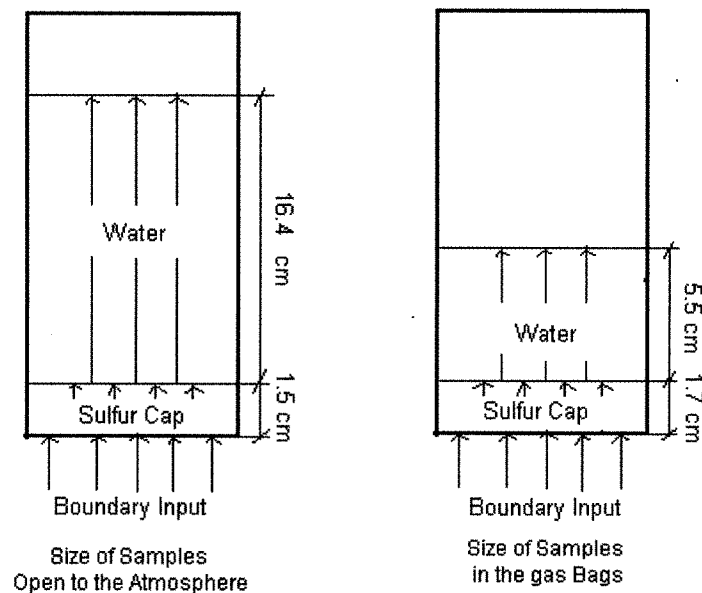


Fig. 5.4 Size of Samples

5.8.1.2 Diffusion Coefficients

The major ions in the salt from the CT release water are Na^+ , Cl^- and SO_4^{2-} . As diffusion progresses, Na^+ , Cl^- and SO_4^{2-} speciate and move via the same diffusion coefficients as NaCl and Na_2SO_4 (Harned and Owen, 1950). The amount of solid salt in the blank samples indicates that the main minerals are NaCl and Na_2SO_4 . The dissolution rate at a halite surface is extremely high, and the transport is entirely controlled by molecular diffusion (Alkattan et al., 1997). The diffusion of NaCl and Na_2SO_4 can represent the salt diffusion. The calculated NaCl and Na_2SO_4 diffusion coefficients in a dilute solution, using Table 2.1 and Equation 2.5, are $1.61 \times 10^{-5} \text{ cm}^2/\text{s}$ and $1.14 \times 10^{-5} \text{ cm}^2/\text{s}$, respectively. The diffusion coefficient of salt in water can be assumed to be $1.46 \times 10^{-5} \text{ cm}^2/\text{s}$ if the interaction among the ions is neglected. If the salt solution is concentrated, the salt diffusion will be slower when compared with a dilute solution because of the interactions among ions (Cussler, 1997). The effective diffusion coefficient may be orders of magnitude smaller in a concentrated solution than in a dilute solution. Additional unknowns arise when predicting the diffusion coefficient of the sulfur caps, including the tortuosities of the pores within the caps, whether the pores are homogeneously distributed, and if the pores are inter-connected (see Fig. 3.1 and Fig. 3.2). Therefore, the effective diffusion coefficients cannot be predicted directly by using Equations 2.6 to 2.8 and have to be found through modeling.

5.8.1.3 Constant Boundary Input

Using Equation D-17 (see Appendix D) results in a condition where the salt concentration at the inlet boundary is not constant. The salt concentration in the water column is also a function of the salt concentration at the inlet boundary. To simplify the problem, the salt concentration at the inlet is initially assumed to be constant. A more precise salt concentration is then found through modeling techniques (see discussion in Appendix D):

$$- \int \frac{dc'}{c'} = \frac{k_a}{D_2} \int dz \quad . \quad (\text{D-17})$$

5.8.2 Results from the Analytical Model

As discussed in Section 3.3.4.4, the salt transported through the porous media is modeled by using a two-layer, one-dimensional, closed system. Analytical models were built to simulate

the salt flux curves through this system. The results of some of the modeling and measurements are shown in Table 5.10.

The modeled results and the measured results of maximal flux and concentration of dissolved salt showed a good consistency. The modeled and the measured flux curves of Sample N-40-DI-1 and N-20-DI-2 are presented in Fig. 5.5 and Fig. 5.6 as examples.

Table 5.10 Results of Salt Flux Modeling

Sample	Delay Time (day)		Maximal Flux (g/cm ² /s)		Conc. (g/L) ⁽¹⁾		D* ⁽²⁾ (×10 ⁻⁷ cm ² /s)	C _b ⁽³⁾ (g/L)	Porosity %
	Modeled	Msd ⁽⁴⁾	Modeled	Msd	Modeled	Msd			
A-3.6-DI-C-1	5		1.2×10 ⁻⁹	1.2×10 ⁻⁹	1.8	1.8	2.2	17.7	
N-40-DI-1	15	22	4.89×10 ⁻¹¹	4.83×10 ⁻¹¹	0.055	0.078	0.66	3.5	10.9
N-40-CT-1	25	18	8.20×10 ⁻¹⁰	8.52×10 ⁻¹⁰	4.6	4.3	5.1	5.9	10.8
N-20-DI-2	25	12	2.04×10 ⁻⁹	2.08×10 ⁻⁹	3.6	3.4	5.4	13.8	10.9
N-10-DI-1	21	5	1.02×10 ⁻⁸	1.34×10 ⁻⁸	16.6	16.7	14.0	29.0	12.9

(1) Final concentration at the sampling point. (2) D*: Calculated effective diffusion coefficient in sulfur caps.

(3) C_b: Constant boundary input.

(4) Msd: Measured

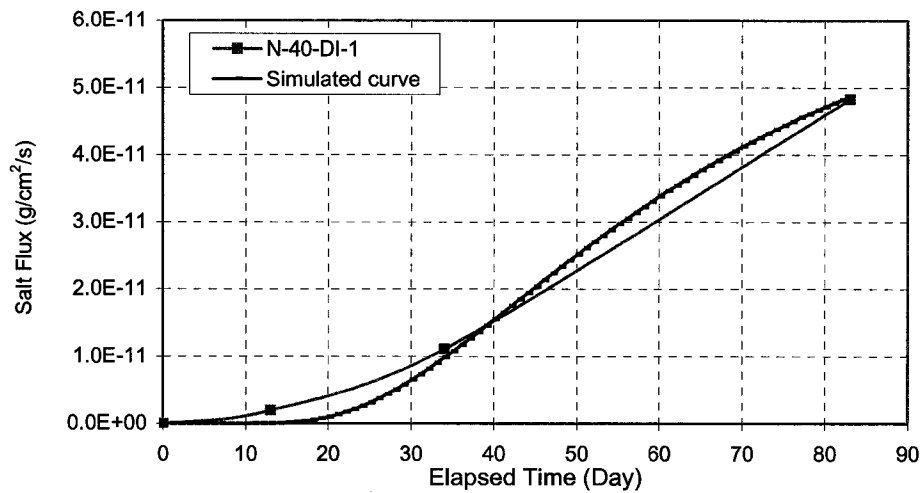


Fig. 5.5 Sample N-40-DI-1 Salt Flux Modeling

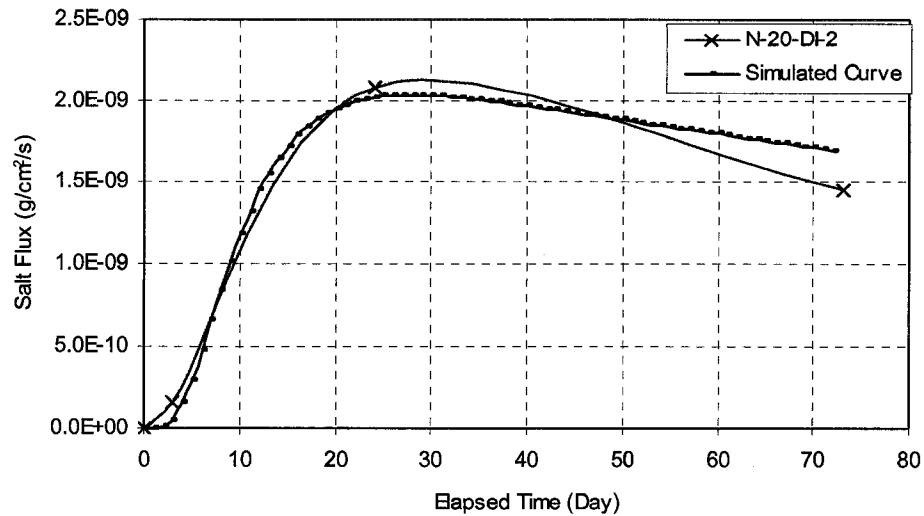


Fig. 5.6 Sample 20-DI-2 Salt Flux Modeling

Table 5.10 shows that the salt diffusion coefficients through centimeter-thick sulfur caps are generally 2 orders of magnitude lower than in water. If the salt diffuses through meter-thick and well engineered sulfur caps to reduce the porosity, the difference will be even larger. Mehta et al. (1995) report that the ratio of diffusion of salt in soil to the diffusion of salt in bulk water varies from 0.31 to 2.98×10^{-3} as water content of soils decreases from 60.89% to 20.22%. It can be seen that sulfur caps can function like unsaturated soils in encapsulating solid salt. Practically, soils will be saturated and diffuse salt more readily when used to encapsulate solid salt in tailing ponds. Therefore, encapsulation of salt with elemental sulfur and disposing them together in an appropriate location such as a mined-out pit and then covering with tailings is a viable measure in managing both salt and elemental sulfur.

5.8.3 Comparison of Analytical Modeling to Numerical Modeling

In order to confirm the analytical modeling, numerical models were built by using the program *ChemFLUX*[®]. The same geometrical and physical parameters, boundary conditions, and initial conditions used in the analytical model were applied to the numerical model. Two samples with different flux curves, Sample N-40-DI-1 and Sample N-20-DI-2, were modeled numerically. The modeling results show that the final concentration profiles determined by the numerical and analytical models were in agreement (see Fig. 5.7 and Fig. 5.8).

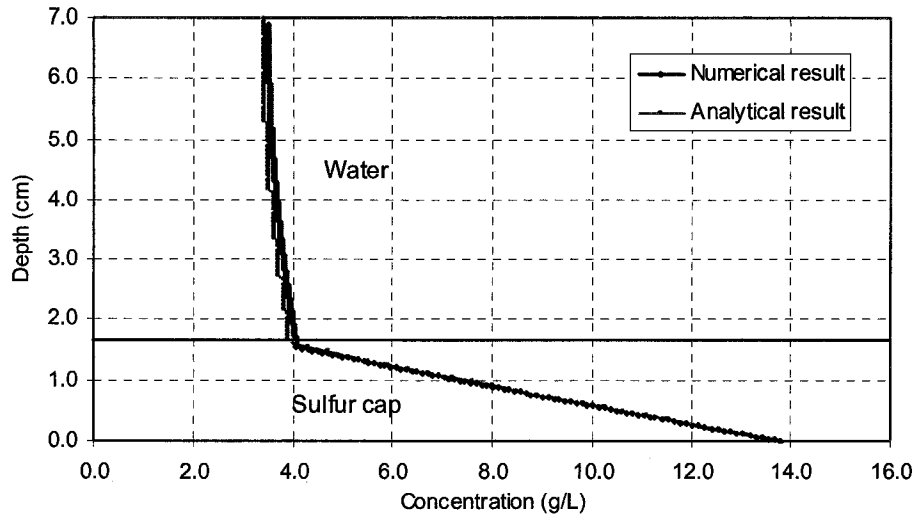


Fig. 5.7 Modeling Result of Final Concentration (Sample N-20-DI-2)

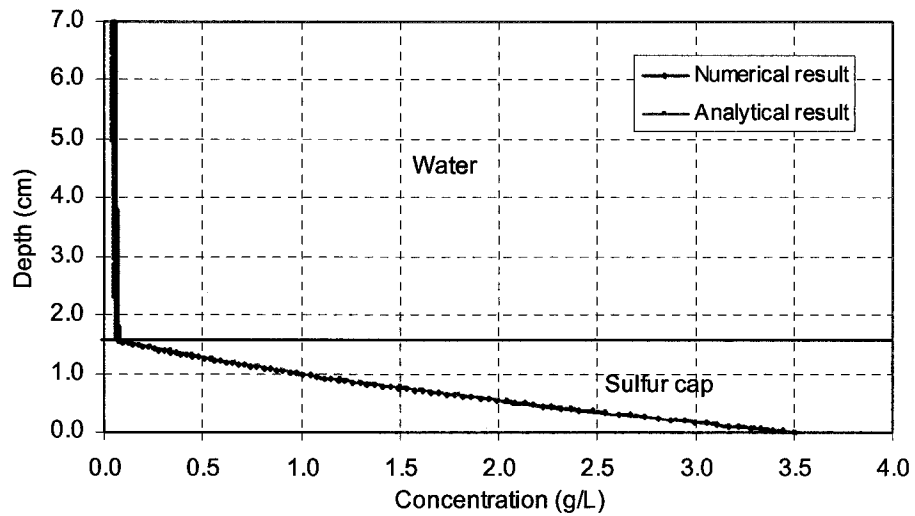


Fig. 5.8 Modeling Result of Final Concentration (Sample N-40-DI-1)

5.8.4 Sensitivity Analysis of C_b and D^*

The sensitivity analysis was focused on studying the effect of the constant boundary input C_b and the effective diffusion coefficient of the sulfur cap D^* on the shape of the flux curves. When D^* was fixed, the modeled flux curve was shown with half C_b . When C_b was fixed, the modeled flux curve was shown with double D^* . The results indicated that the effective diffusion coefficient D^* controlled both the slope of the flux curve and the location of the peak

of the curve. The constant boundary input C_b influenced only the maximum flux values (see Fig. 5.9 and Fig. 5.10).

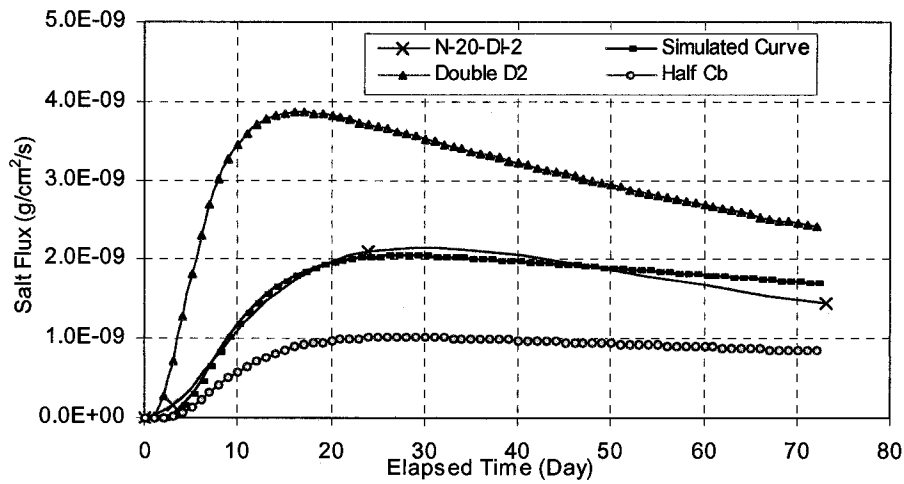


Fig.5.9 Sensitivity Analysis of Salt Flux Modeling

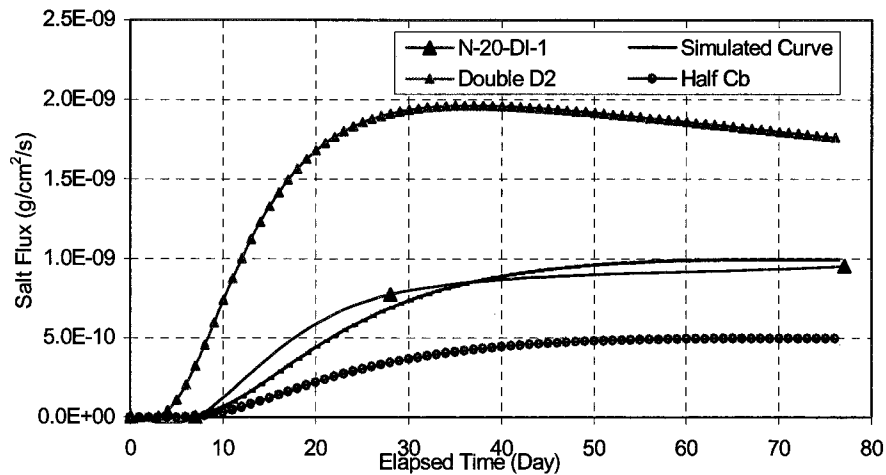


Fig.5.10 Sensitivity Analysis of Salt Flux Modeling

5.8.5 Discussion on the Results of Modeling

The modeled effective diffusion coefficient D^* for the porous sulfur caps varied two orders of magnitude ranging from $0.66 \times 10^{-7} \text{ cm}^2/\text{s}$ to $14 \times 10^{-7} \text{ cm}^2/\text{s}$. Smaller D^* and C_b values correspond with a lower salt flux as shown in Table 5.10.

The effective diffusion coefficient is obviously a function of the salt flux. However, the relationship between the salt flux and the boundary input constant was hidden by the distribution of pores within the sulfur caps. One of the assumptions in Equation 2.4 (the flux equation) is that the porosity of the medium is constant in time and space. The pores for the samples used in this research were not homogeneously distributed within the sulfur caps. As shown in Figs. 3.1 and 3.4, the pore volume was dominated by large voids in the sulfur caps. Nevertheless, to simplify the computer models, the pores were assumed to be homogeneously distributed within the sulfur caps. In reality, the boundary input could be different for the samples with different porosities and pore distributions. Therefore, the so-called “constant boundary input” is just an average boundary input for the testing time and the area of the cylinder.

The modeled results indicate that the effective diffusion coefficients for the porous sulfur caps were approximately two orders of magnitude smaller than the coefficients in free water. The final concentration profiles showed that the difference in the salt concentration along the water column was very small (see Fig. 5.8 and Fig. 5.9). Therefore, the salt concentration along the water column could be viewed as one value that describes the concentration at the water solid interface and the water layer could be removed from the two-layer model, resulting in a one-layer system. The salt and sulfur mixture can be viewed as an additional layer with a moving boundary to be included in future modeling studies.

5.8.6 Limitations of the Models

Several simplifications made in the models caused the modeling results to deviate from the measured results. These simplifications and limitations include:

- The thickness of the sulfur cap strongly influences the salt flux and should be modeled with a moving input boundary. The model was simplified with a stationary input boundary, yet the exact location of the boundary was unknown.
- The salt concentration at the input boundary is not constant but a function of time, the porosity of the cap, and the salt concentration in the reservoir.
- The diffusion coefficient is not a constant. In reality, diffusion in concentrated solutions with

multiple components is slower than in dilute solutions.

- The porosity in the sulfur cap is not homogeneous, so the salt diffusion determined experimentally deviated from the idealized modeling predictions.

5.9 References

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6.0 SUMMARY AND RECOMMENDATIONS

The objective for the research was to assess the encapsulation of salt with sulfur. Test data were collected, analyzed and modeled to determine the effective diffusion coefficients for salt diffusion through a sulfur cap. This chapter summarizes the key issues and findings as well as provides recommendations for future engineering practice.

6.1 Testing Methods

6.1.1 Key Findings of Material Tests

- The measured salt density was 2.23g/cm^3 . The salt density may vary with the salt composition and the formation process.

- The resulting grain-size distribution of the crushed salt solids was similar to that of fine to medium sand. The salt crystals were fragile and the salt solids were easily crushed into smaller sizes.

- Less than 0.5% of the salt was found not to dissolve in water. The solubility of the salt mixture containing halite and thenardite was 420.5 g/L or higher.

- The porosities of the cores and the pure sulfur encapsulant, for the samples in the gas bags, were found to be around 10%. The measured thicknesses of the sulfur caps were approximately 1.5 cm, 50% greater than the designed thicknesses.

6.1.2 Key Findings of EC Measurements

- The measured EC of the initial CT water was around 4.3 mS/cm. The measured EC of the initial DI water was less than 5.0 $\mu\text{S/cm}$.

- At the end of the test, the measured EC values were reduced by 28% to 76% when the sulfur caps were used. This finding was consistent with the prediction at the start of testing that the sulfur caps should reduce the salt dissolution. However, the influence of caps on the salt dissolution varied between samples.

- The measured EC values were related to the encapsulated salt content within the sample. The samples with higher salt content generally had higher EC values but some exceptions occurred.
- The salt dissolution rates were dependent on the porosity of the sulfur caps, the tortuosity of the flow path and the continuity of the flow path. Therefore, using the porosity alone was not sufficient when calculating the diffusion rate.

6.1.3 Key Findings of pH Measurements

- The measured pH of the initial CT water was around 8.2. The measured pH of the initial DI water ranged from 5.3 to 6.6.
- For the samples open to the atmosphere, the pH of the upper layer of the CT solutions increased to around 9.0 after two months of encapsulation and then decreased, stabilizing at around 8.0. The pH at the solid and liquid interface tended to stabilize above 7.0. The pH of the DI water solutions was homogeneous and continually decreased, stabilizing at a pH of slightly above 4.0.
- For the samples in the gas bags, the initial pH of the CT solutions was 8.2, increasing to about 9.3 after the first four weeks of encapsulation and then decreasing slightly to about 9.0 after 100 days encapsulation. The pH in the DI water started at 5.8, decreased to about 4.3 and then increased with time to 5.6 at the end of the test.
- For the pure $S^{(0)}$ condition, the pH experienced a similar pattern of increase and decrease. The difference was that no depth-related pH difference occurred in the CT water solutions, and the pH stabilized at around 8.7.
- The pH changes within the samples were not obviously related to either the use of sulfur caps or the salt content.
- The pH increase in the solutions might have occurred for several reasons, including: (1) when a CT solution with mineral carbonates was exposed to the atmosphere and allowed to equilibrate with atmospheric CO_2 , the minerals tended to raise the pH to values of 9 or

10, or even higher; (2) the abiotic oxidation of hydrogen sulfide by oxygen could raise the pH; (3) the continuous dissolution of the salt, which contained some carbonates, could increase the pH of the solutions; (4) SRB in the solution could reduce the sulfate to H₂S as well as to HCO₃⁻ and increase the alkalinity and pH of the solutions. However, this reaction must have been either very slow or masked by a sulfur oxidation reaction

- Elemental sulfur oxidation with air in the CT water and the dissolution of the atmospheric CO₂ into the DI water solutions controlled the pH decrease in the solutions.
- The open system had a higher total buffer capacity (pH 9.0 to pH 4.0) than the closed system. For the open system, the CT water solutions had the largest buffer capacity and existed at a pH of 9.0 whereas the closed system existed at a pH of around 6.0.

6.1.4 Key Findings of DO Measurements

- The initial DO in the DI water was around 5.0 mg/L after de-aeration. The initial DO in the CT water was around 2.0 mg/L when measured in the container. The saturated DO in the DI water was around 8.0mg/L at a room temperature accounting for the elevation of the Edmonton area. The DO in the CT water tended to saturate at 7.0 mg/L.
- Generally, the DO in the DI water was higher than in the CT water, but the fluctuation in the CT water was larger than in the DI water. No stabilized DO reading was taken in the CT water column.
- The deeper the measurement in the CT water solution, the lower the DO and the greater the DO fluctuation.
- Calculations showed that after 200 days of encapsulation, approximately 95 mg of oxygen could diffuse into a water column to be consumed by oxygen-demanding reactions. This finding suggested that about 0.5 mg of oxygen dissolved into the cylinder per day.
- Both the oxidation reactions and salinity of the solutions affected the ongoing oxygen balances in the water solutions.

6.1.5 Key Findings of Alkalinity Titration

- The average bicarbonate alkalinity of the five CT release water samples was 663.6 mg/L.
- Most of the alkalinity in the water solutions was derived from the initial alkalinity contained in the CT release water. The total alkalinity was mainly bicarbonate alkalinity and decreased with pH. Exposing the CT water to the atmosphere increased its alkalinity.
- For the samples open to the atmosphere, the alkalinity of the CT water solutions increased from 663.6 mg/L to 700~750 mg/L during the first two to four weeks, was equilibrated with atmospheric CO₂ and then decreased to approximately 400~500 mg/L, depending on the pH of the samples.
- For the samples in the gas bags, the alkalinity of CT water solutions decreased to about 500~600 mg/L at the last measurement, depending on the pH of the samples.
- The alkalinity of the DI water solutions was negligible. Also, the CT water solutions with a pH below 5.0 indicated a negligible amount of alkalinity.

6.1.6 Recommendations

- The sulfur caps reduced the EC by 28% to 76% on average for the layered samples open to the atmosphere; therefore, the use of sulfur caps to encapsulate a sulfur and salt mixture provides a favorable measure to reduce the salt-dissolution rates.
- The pH at the solid liquid interface in the CT water-encapsulated samples tended to stabilize above 7.0. Exposing the CT water to the atmosphere increased its alkalinity and buffered the pH changes. Therefore, to maintain a neutral pH condition, the encapsulated salt and sulfur can be disposed of together with the CT water, leaving the CT water open to the atmosphere.

6.2 Analytical Results

6.2.1 Key Findings

- The CBE of most samples were located within $\pm 10\%$. When concentrations were low, the

CBE were low.

- The samples open to the atmosphere without sulfur caps showed similar flux curves and displayed peak salt fluxes about two to four weeks after encapsulation.
- For the samples in the gas bags, the maximum salt fluxes were delayed by 15 to 25 days from the beginning of the test.
- The maximum salt fluxes in the layered samples ranged from 10^{-10} g/cm²/s to 10^{-8} g/cm²/s while the maximum salt fluxes in the cored samples in the gas bags ranged from 10^{-11} g/cm²/s to 10^{-9} g/cm²/s.
- The sulfate content for most samples in the gas bags decreased, indicating a sulfate-reducing condition. Generally, the reduced sulfate was less than 1.0 mM. However, for the samples open to the atmosphere, most samples presented increasing sulfate content, indicating a sulfur-oxidizing condition.
- The salt flux was related to the encapsulated salt content. However, the change in the salt flux was small for large variations in the salt content. The influence of caps was greater than that of the salt content.
- In extreme conditions, a sulfur cap could decrease the salt flux by two orders of magnitude. The influence of the sulfur caps was found to vary by two orders of magnitude in this study. The design and construction of the caps was the most important factor in controlling the salt dissolution rate.
- No obvious relationship was found between the salt flux and cap porosity.

6.2.2 Recommendations

- The influence of caps on salt flux was greater than that of the salt content. Therefore, the proportions of sulfur and salt in the mixtures were not an important factor when trying to control the salt flux.

- The sulfur caps may decrease the salt flux by two orders of magnitude. The influence of the sulfur caps was found to vary by two orders of magnitude in this study. Therefore, the careful design and construction of the sulfur caps is very important. Any perforated cracks or voids in the caps could have tremendous impact on salt encapsulation. Research is required in order to determine how to build sulfur caps with the smallest possible porosity. The cap thickness and construction are the main factors that will control the containment.

6.3 Modeling Results

6.3.1 Key Findings

- The results of the analytical models satisfied both the flux curves and the final concentration values.
- Both the analytical model and the numerical model displayed similar salt-concentration profiles. This finding suggests that the analytical model can be used to confidently predict the salt dissolution in similar conditions.
- The results of the analytical model showed that the effective diffusion coefficient, D_2 , was the primary factor controlling the slope of the flux curves and the location of the peak of the curve. The constant boundary inputs, C_b , only influenced the maximum flux value.
- The diffusion coefficient of the salt in the porous sulfur caps ranged from 10^{-8} to 10^{-6} cm^2/s , which was two to three orders of magnitude smaller than the diffusion coefficient of salt in water. Sulfur caps function like unsaturated soils in encapsulating solid salt. Therefore, encapsulation salt with elemental sulfur and disposing them together in a mined-out pit and then covering with tailings is a viable measure in managing both salt and elemental sulfur.
- The smaller the salt flux is, the smaller the effective diffusion coefficient and constant boundary inputs.
- Both the analytical and numerical models showed that only small differences occurred in the salt concentration along the water column when compared to the difference in the

sulfur caps. Therefore, a one-layer diffusion model is acceptable. However, the limitations of the current model must be kept in mind.

6.3.2 Recommendations

- The limitations of the current model could be overcome by using a moving boundary and non-constant boundary input.

- Encapsulating salt with elemental sulfur, disposing them together in a mined-out pit and covering with tailings is a viable measure in managing both salt and elemental sulfur.

APPENDIX A

A1.0 Laboratory Measurements

All the measurement used in our laboratory research: EC, DO, alkalinity titration and specific gravity of salt solids measurements, except pH and IC test, are attached here. pH measurement is such a common laboratory practice that it is not necessary to attach its operation method and it was discussed in some degree in Chapter 3. Practical IC test is complicated and generally conducted by a qualified laboratory technician.

A1.1 EC Measurement

Two EC probes were used in the test: Accumet® 13-620-162 two cell probe with nominal cell constant of 10.0/cm. One probe was calibrated by using standard solution with 1mS/cm; the other was calibrated by using standard solution with 10mS/cm. The optimal conductivity range for the second probe is 1~200mS/cm. Because most measurements were taken using the second probe, the introduction here is focused on it.

OPERATING INSTRUCTIONS

Installation -The conductivity cell should be placed into service as follows:

Prior to use, soak the conductivity cell in distilled or deionized water for 5 to 10 minutes. Connect the conductivity cell to the conductivity meter and follow the meter manual instructions for standardizing the cell for use at a given temperature. The cell constant value stated is nominal. It is only with standardization using a solution of known conductivity that an actual cell constant is calculated.

Note: When standardizing the conductivity cell, use a standard solution as close to the conductivity value of the sample as possible.

Sample measurement

1. Rinse the conductivity cell sensing elements with distilled or deionized water between samples.
2. Best results will be obtained if the cell is rinsed with a small portion of sample before measurement.
3. Dip cell up and down in sample 2-3 times to completely wet surface.
4. Allow air bubbles to escape from conductivity cell side holes by tilting cell slightly.

5. It is important to control sample temperature since readings will continue to drift until the temperature has stabilized. A good rule of thumb is to allow 5 times the amount of time it takes for the thermistor to respond to allow the reading to stabilize. Any sudden dips or peaks should be ignored during this time.

STORAGE

It is best to store the conductivity probe so that the electrodes are immersed in deionized water. If the conductivity probe is stored dry, it should be soaked in deionized water for 5 to 10 minutes before its use to assure complete wetting of the electrodes.

CLEANING For best results follow these procedures

The single most important requirement for accurate and reproducible results in conductivity measurement is a clean cell. A dirty cell will contaminate the solution and cause the conductivity to change. Grease, oil, fingerprints, and other contaminants on the sensing elements can cause erroneous measurements and sporadic responses.

1. For most applications, a hot solution of water with a mild laboratory detergent can be used for cleaning.
2. A 1% dilute nitric acid may be used. Dip the cell in the 1% nitric acid and agitate for two to three minutes. Other dilute acids (e.g. sulfuric, hydrochloric, chromic) may be used for cleaning except for aqua regia. Rinse the cell several times with distilled or deionized water.

WARNING: Aqua regia will dissolve platinum.

3. When a stronger cleaning solution is needed, prepare a solution of concentrated hydrochloric acid mixed into 50% isopropanol. Dip the cell in the acid/alcohol solution and agitate. Rinse the cell several times with distilled or deionized water.
4. For lime and other hydroxide containing solutions, clean with a 5 -10% solution of hydrochloric acid.
5. For solutions containing organic fouling agents (fats, oils, etc.), clean cell with acetone.
6. For algae and bacteria containing solutions, clean cell with a 10% chlorine bleach solution.
7. Platinum conductivity cells of cell constant 1.0 ~ 10.0 are coated with platinum black before calibration. This coating is extremely important to cell operation, especially in solutions of high conductivity. Cells are platinized to avoid errors due to polarization. Cells should be

inspected periodically and after each cleaning. If the black coating appears to be wearing or flaking off the cell, or if the cell constant of any cell has changed by 50%, the cell should be cleaned and electrodes replatinized.

REPLATINIZING

Care should be taken when performing this procedure as the chemicals used are potentially damaging to the conductivity cell.

1. The platinum electrode should first be cleaned thoroughly in aqua regia, being careful not to dissolve the platinum. If cell remains too long in aqua regia, the platinum elements will dissolve completely.
2. Prepare the solution of 0.025N HCl with 3% chloroplatinic acid (H_2PtCl_6) and 0.025% lead acetate.
3. Connect the cell to a rheostat or 3-4V battery to which a variable resistor has been connected.
4. Immerse the cell in the chloroplatinic acid solution and electrolyze at 10mA/cm for 10 to 15 minutes
5. Reverse the polarity to the cell every 30 seconds until platinum electrodes are covered with a thin black layer.
6. Disconnect the cell and save the platinizing solution. It may be conserved and reused many times and should not be discarded as it is expensive to make.
7. Rinse the electrode with tap water for 1 to 2 minutes, followed by distilled or deionized water rinse.

A1.2 DO Measurement

An YSI 550A DO instrument was used in our DO measurement. The instrument has a measuring range of 0~20mg/L and accuracy of ± 0.3 mg/L.

CALIBRATION IN MG/L

1. Power the instrument on and allow readings to stabilize. This may take 5 to 15 minutes, depending on the age of the instrument and condition of the probe.
2. Place the probe in a solution with a known mg/L reading. Continuously stir or move the probe through the sample at a rate of at least 1 foot per second (16cm per second) during

the entire calibration process. In our DO measurement, 500mL of DI water stirred and exposed to air at least 24 hours is used as the known 8.1mg/L DO solution.

3. Press and release both the UP ARROW and DOWN ARROW keys at the same time to enter the calibration menu.
4. Press the Mode key until "mg/L" is displayed on the right side of the screen for oxygen units. Presses ENTER.
5. CAL will now display in the lower left corner of the screen and the current DO reading (before calibration) will be on the main display. Once the current DO reading is stable, use the up and down arrow keys to select the mg/L value of the known solution, then press the ENTER button.
6. The LCD will prompt you to enter the approximate salinity of the water you are about to analyze. Enter any number 0 salinity (Calibrated with DI water). Use the arrow keys to increase or decrease the salinity setting. When the correct salinity appears on the, press the ENTER key. The instrument will return to normal operation.

STIRRING

It is important to recognize that a very small amount of oxygen dissolved in the sample is consumed during probe operation. It is therefore essential that the sample be continuously stirred at the sensor tip. If stagnation occurs, measurements will appear artificially low. Stirring may be accomplished by mechanically moving the sample around the probe tip, or by moving the probe through the sample. The YSI Model 550A has a flow dependence of <25%. The rate of stirring required is 1 foot per second (16cm per second).

MEASUREMENT PROCEDURE

1. Insert the probe into the sample to be measured.
2. Continuously stir or move the probe through the sample.
3. Allow temperature and dissolved oxygen readings to stabilize.
4. Observe/Record readings.
5. If possible, rinse the probe with clean water after each use.

PRECAUTIONS

1. Membranes last longer if properly installed and regularly maintained. Erratic readings can result from loose, wrinkled, damaged, or fouled membranes, large (more than 118"

- diameter) air bubbles in the electrolyte reservoir, or membrane coating by oxygen consuming (e.g. bacteria) or oxygen producing (e.g. algae) organisms. If unstable readings or membrane damage occurs, replace both the membrane cap and electrolyte solution.
2. Chlorine, sulfur dioxide, nitric oxide, and nitrous oxide can affect readings by behaving like oxygen at the probe.
 3. Avoid substances such as acids, caustics, and strong solvents, which may damage probe materials. Probe materials include the PE membrane, acrylic plastic, EPR rubber, stainless steel, epoxy, polyetherimide and the PVC cable covering.
 4. Always store the probe in the calibration/storage chamber with the moistened sponge.

A1.3 Alkalinity Titration

The standard titration method was modified by using pH meter measurement instead of buffer powder pillows, pH 8.3 and 4.5.

Equipment: HACH digital titrator model 16900-1; Erlenmeyer flask, 250mL; graduated cylinder, 100mL; pH meter; stirrer.

Reagents: Sulfuric acid titration cartridge, 1.600N; DI water.

Procedure

1. Select sulfuric acid titration cartridge corresponding to the expected alkalinity. In our test, only the 1.600N one was used.
2. Insert a clean delivery tube into the titration cartridge to the titrator body.
3. Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.
4. Dump the sample into a graduated cylinder and record its volume. Dilute the sample to 100 mL with DI water. Transfer the sample into a clean 250 mL Erlenmeyer flask.
5. Use the stirrer to mix the diluted sample and measure its pH value. If the pH is higher than 8.3, titrate to pH 8.3. Record the number of digits required.

$$P \cdot \text{alkalinity}(\text{mg} / \text{L} \cdot \text{as} \cdot \text{CaCO}_3) = \frac{\text{Digits} \cdot \text{required} \times 100\text{mL}}{\text{Sample} \cdot \text{volume}(\text{mL})}$$

6. Continue the titration until pH 4.5, and record the number of digits required.

$$\text{Total alkalinity (mg / L as CaCO}_3\text{)} = \frac{\text{Total} \cdot \text{digits} \cdot \text{required} \times 100\text{mL}}{\text{Sample} \cdot \text{volume (mL)}}$$

7. Calculate the alkalinity, using Table A1.1 below.

Table A1.1 Alkalinity Calculation Procedure

Row	Result of Titration	Caustic alkalinity is equal to	Carbonate alkalinity is equal to	Bicarbonate alkalinity is equal to
1	P alkalinity = 0	0	0	Total alkalinity
2	P alkalinity = T alkalinity	Total Alkalinity	0	0
3	P alkalinity < 1/2 T alkalinity	0	2 times the P alkalinity	T alkalinity – 2 times P alkalinity
4	P alkalinity = 1/2 T alkalinity	0	Total alkalinity	0
5	P alkalinity > 1/2 T alkalinity	2 times the P alkalinity – T alkalinity	2 times the difference between T and P alkalinity	0

A1.4 Specific Gravity of Salt Solid

This method is modified from the specific gravity method of soil solids test (Joseph E. Bowles: Engineering properties of Soils and Their Measurement, Fourth Edition, McGraw-Hill, Inc.) using paraffin oil instead of water because salt is insoluble in paraffin oil.

References

ASTM D 854, AASHTO T 100

Equipment

Volumetric flask, also called a pycnometer, preferably 250 or 500 mL (see Fig. A1.1)

Vacuum pump or aspirators for supplying a vacuum

Mortar and pestle Balances weighing to 0.1g

Supply of deaerated, temperature-stabilized

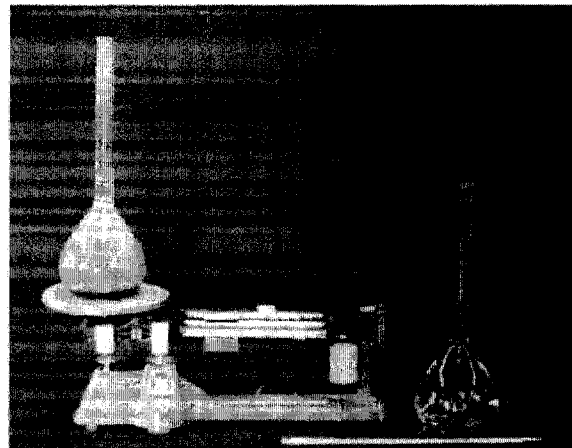


Fig. A1.1 Specific Gravity Test Equipments

paraffin oil.

General Discussion

The specific gravity of the salt particles will always be larger than the bulk specific gravity because the latter includes the salt voids in the computation. The specific gravity of any substance is defined as the density of the material divided by the density of distilled water at 4°C. Thus, if one is considering only the salt particles, one obtains specific gravity G_s as follows:

$$G_s = \frac{M_s / V}{M_w / V} \quad (1.4.1)$$

The specific gravity determination needs to obtain the volume of a known mass of salt particles and divide this by the mass of the same volume of paraffin oil, instead of water, that is, applying Equation 1.4.1. This form is easier to visualize as well as obtaining the necessary laboratory test data.

The volume of a known mass of salt particles can be obtained by using a container of known volume and the Archimedes Principle that a body submerged in a volume of water will displace a volume of water equal to the volume of the submerged body.

Since the laboratory work to determine the specific gravity of the soil using the volumetric flask is somewhat indirect it is instructive to derive the expression to compute the specific gravity:

1. Let M_{bo} = mass of flask + oil to the volume mark on the flask. Now empty the flask.
2. Next, place the mass of salt M_s into the flask and again fill the flask to the volume mark with oil and weigh. Let this mass value be M_{bos} .
3. Recalling that one is dealing with a constant volume, if no oil was displaced from the bottle when soil mass M_s was added the total mass would be

$$M_T = M_{bo} + M_s$$

However, since the volume of salt mass M_s occupies part of the space, the addition of M_{bo} to the flask would fill it above the volume mark. Since the volume mark is the reference point, the amount of oil that cannot be put into the flask because of the salt volume already there is

$$M_o = M_T - M_{bos} = M_{bo} + M_s - M_{bos}$$

4. Equation 1.4.1 can be directly solved since we have equal volumes of masses M_s and M_o now known, or $V_o = M_o / \rho_o = V_s$.

Rewriting Equation 1.4.1 with the mass values from Step 4 above into a form convenient to use in the order that the laboratory data is obtained gives

$$G_s = \frac{M_s}{M_{bo} + M_s - M_{bos}} \quad 1.4.2$$

A source of error, which can be important, is the use of masses obtained from poorly adjusted balances, or from not using the same balance for all weightings. The most serious error in this test will occur from not properly deaerating the salt-oil mixture. Any temperature error will be minor if the test is done between 18 and 22°C.

DEAERATION FOR THE TEST

Paraffin oil normally contains dissolved air. The soil particles will also contain air, and if the air is not removed from both of these materials, the volume of air will result in a decrease in the mass M_{bos} . This in turn will result in too small a computed value of G_s that is, $M_{bo} + M_s - M_{bos}$ will be too large.

Deaerating the salt-oil mixture is accomplished by applying a vacuum. The length of time the vacuum should be applied may range from a few minutes to several hours.

Procedure

1. Weigh a representative sample of salt. If using a 500 mL volumetric flask, this sample should be between 100 and 120g. Put this sample into the flask, being careful not to lose any salt, for the sample at this point is "representative". Then add oil to less than half full as washing salt out of the neck need some oil.
2. Attach the flask to a high vacuum for at least 10 min. During this time gently agitate the mixture by carefully shaking and turning the flask. Observe that the reduced air pressure in the flask causes the oil to "boil". This step can take several hours, however; in our laboratories, when up floating of bubbles almost disappear, start next step
3. When the deaerating process is complete, (or has been terminated), carefully add deaerated oil until the bottom of the meniscus is exactly at the volume mark. Be very careful not to reintroduce air into the flask when this oil is added. Carefully dry the neck of

the flask above the calibration mark with a rolled paper towel or by some other means.

4. Weigh the flask and its contents to the nearest 0.01g, (by estimation), to obtain M_{bos} . Repeat Steps 1 through this point for a second test.
5. Next, check that the flask is clean and then fill it two-thirds full of deaerated oil, apply vacuum for a short period, then completely fill to the volume mark. Be sure the temperature is within 1°C of the temperature used for obtaining M_{bos} . Weigh the flask with deaerated water as M_{bo} , and record on data sheet in the space provided.
6. Perform the necessary arithmetic on the data sheet entries to compute the two values G_s , using Equation 1.4.2.
7. Check if the two values of G_s just computed are within 3% of each other, defined as

$$\frac{LargerG_s}{SmallerG_s} \leq 1.03$$

Table B1.1 EC (mS/cm) vs. Time (day)

Sample#	6/24/03	6/25/03	6/26/03	6/27/03	6/28/03	7/7/03	7/8/03	7/9/03	7/17/03	7/21/03	7/25/03	8/1/03	8/8/03	8/15/03	8/22/03	8/28/03	9/30/03	11/9/03	12/12/03	1/12/04
Depth(cm)	1	2	3	4	5	14	15	16	24	28	32	39	46	53	60	66	99	139	172	203
A-0-DI-1				0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.02	0.03	0.06	0.03
									0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.03	0.06	0.03
									0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.04	0.05	0.03
									0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.04	0.05	0.03
A-0-DI-2		0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.04	0.04	0.05
									0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.04	0.04	0.05
									0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.03	0.04	0.04	0.05
									0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.04	0.04	0.05
A-0-DI-3												0.00	0.01	0.00	0.01	0.01	0.01	0.02	0.02	0.03
												0.00	0.01	0.00	0.01	0.01	0.01	0.02	0.02	0.03
												0.00	0.01	0.00	0.01	0.01	0.01	0.02	0.02	0.03
												0.00	0.01	0.00	0.01	0.01	0.01	0.02	0.02	0.03
A-0-CT-1	4.40	4.48	4.43	4.41	4.45	4.54	4.54	4.53	4.65	4.70	4.67	4.40	4.39	4.41	4.41	4.46	4.55	4.62	4.48	4.48
									4.62	4.63	4.58	4.42	4.40	4.42	4.41	4.46	4.54	4.63	4.54	4.50
									4.57	4.58	4.63	4.44	4.40	4.42	4.41	4.47	4.54	4.63	4.52	4.51
									4.50	4.58	4.60	4.43	4.33	4.41	4.40	4.45	4.48	4.63	4.57	4.51
A-0-CT-2	4.40	4.50	4.44	4.48	4.50	4.55	4.53	4.52	4.62	4.56	4.49	4.43	4.35	4.38	4.36	4.41	4.52	4.48	4.36	4.46
									4.58	4.55	4.47	4.40	4.37	4.40	4.36	4.42	4.47	4.48	4.43	4.47
									4.60	4.56	4.47	4.40	4.38	4.41	4.36	4.44	4.48	4.49	4.38	4.49
									4.53	4.66	4.43	4.38	4.37	4.39	4.35	4.42	4.47	4.50	4.43	4.50
A-0-CT-3												4.37	4.32	4.31	4.33	4.38	4.55	4.54	4.46	4.54
												4.39	4.32	4.32	4.33	4.36	4.55	4.54	4.47	4.55
												4.40	4.32	4.33	4.33	4.39	4.56	4.54	4.47	4.58
												4.40	4.32	4.32	4.31	4.38	4.51	4.54	4.49	4.54

Table B1.1 EC (mS/cm) vs. Time (day) (Continued)

Sample#	Depth(cm)	6/24/03	6/25/03	6/26/03	6/27/03	6/28/03	7/7/03	7/8/03	7/9/03	7/17/03	7/21/03	7/25/03	8/1/03	8/8/03	8/15/03	8/22/03	8/29/03	9/30/03	11/9/03	12/13/03	1/8/04
A-3.6-DI-N-1	DI-2												0.48	0.53	0.86	1.46	2.08	3.63	5.81	7.22	8.44
	DI-5												0.47	0.54	0.87	1.48	2.08	3.64	5.82	7.22	8.45
	DI-10												0.47	0.55	2.15	2.81	3.41	4.31	5.83	7.38	8.87
	DI-15												7.32	7.48	7.02	6.42	5.72	5.84	5.87	7.43	9.12
A-3.6-DI-N-2	DI-2		0.530	0.559	0.568	0.626	1.06	3.10	3.12	3.17	3.41	3.64	3.81	3.98	4.15	4.20	4.26	4.62	5.14	6.01	6.87
	DI-5									3.25	3.44	3.68	3.83	4.00	4.16	4.20	4.26	4.64	5.16	6.01	6.76
	DI-10									4.09	4.13	4.21	4.26	4.13	4.16	4.20	4.25	4.64	5.17	6.17	7.00
	DI-15									5.76	5.49	5.10	4.67	4.44	4.43	4.27	4.23	4.69	5.22	6.30	7.08
A-3.6-DI-C-1	DI-2												0.04	0.08	0.09	0.11	0.13	0.48	1.12	1.73	2.67
	DI-5												0.04	0.08	0.09	0.11	0.13	0.49	1.11	1.79	2.59
	DI-10												0.04	0.08	0.09	0.11	0.13	0.49	1.11	1.93	2.81
	DI-15												0.04	0.08	0.09	0.11	0.13	0.69	1.20	2.07	2.78
A-3.6-DI-C-2	DI-2		0.054	0.068	0.078	0.084	0.121	0.119	0.126	0.156	0.169	0.197	0.236	0.30	0.354	0.414	0.49	1.02	1.55	2.00	3.02
	DI-5									0.158	0.170	0.198	0.236	0.30	0.353	0.415	0.49	1.03	1.55	2.01	3.03
	DI-10									0.158	0.170	0.198	0.236	0.30	0.354	0.415	0.49	1.03	1.55	2.10	2.74
	DI-15									0.156	0.169	0.195	0.234	0.29	0.352	0.422	0.49	1.15	1.56	2.17	2.92
A-3.6-CT-N-1	CT-2												4.67	4.75	4.99	5.50	6.14	8.00	9.64	10.66	11.50
	CT-5												4.67	4.76	5.00	5.50	6.28	8.09	9.53	10.66	11.56
	CT-10												4.68	4.81	6.49	7.04	7.99	10.30	10.07	10.60	11.65
	CT-15												6.04	11.20	11.58	11.40	10.80	11.50	10.28	10.88	11.76
A-3.6-CT-N-2	CT-2	4.74	4.89	4.70	4.74	4.79	5.41	6.50	6.70	7.14	7.45	7.61	7.65	7.84	7.86	7.90	8.04	8.80	10.19	11.05	12.21
	CT-5									7.35	7.50	7.62	7.67	7.85	7.88	7.91	8.07	8.90	10.03	11.16	12.23
	CT-10									7.69	7.75	7.76	7.65	7.93	7.90	7.93	8.13	9.50	10.62	11.26	12.27
	CT-15									7.90	7.93	7.95	8.00	9.06	9.30	10.10	10.20	11.01	11.62	11.53	12.47
A-3.6-CT-C-1	CT-2												4.32	4.37	4.38	4.40	4.38	4.63	5.11	5.60	6.23
	CT-5												4.37	4.38	4.38	4.36	4.37	4.68	5.13	5.57	6.15
	CT-10												4.37	4.37	4.37	4.37	4.38	4.68	5.13	5.60	6.24
	CT-15												4.37	4.37	4.34	4.36	4.36	4.61	5.13	5.68	6.20
A-3.6-CT-C-2	CT-2	4.44	4.56	4.50	4.50	4.58	4.71	4.76	4.76	4.77	4.61	4.77	4.88	5.01	5.09	5.30	5.49	6.50	7.53	8.60	9.78
	CT-5									4.79	4.67	4.84	4.88	5.04	5.10	5.34	5.49	6.45	7.56	8.65	9.73
	CT-10									4.83	4.72	4.87	5.02	5.07	5.13	5.35	5.52	6.94	7.57	8.92	9.90
	CT-15									5.11	4.88	5.03	5.65	6.12	6.57	6.71	7.24	7.49	7.79	8.92	9.95

Table B1.1 EC (mS/cm) vs. Time (day) (Continued)

Sample#	Depth(cm)	6/24/03	6/25/03	6/26/03	6/27/03	6/28/03	7/7/03	7/8/03	7/9/03	7/17/03	7/21/03	7/25/03	7/31/03	8/8/03	8/15/03	8/22/03	8/29/03	9/30/03	11/9/03	12/13/03	1/12/04
		1	2	3	4	5	14	15	16	24	28	32	38	46	53	60	67	99	139	173	203
A-6.3-DI-N-1	DI-2												1.01	1.07	1.40	2.45	2.95	5.41	7.07	8.45	10.03
	DI-5												1.02	1.09	1.40	2.46	2.97	5.42	7.06	8.49	10.06
	DI-10												1.02	1.10	2.97	3.80	4.75	5.77	7.08	8.53	10.31
	DI-15												1.30	7.47	7.91	8.08	7.78	8.23	7.19	8.61	10.66
A-6.3-DI-N-2	DI-2		0.933	0.941	0.950	0.961	1.4	2.66	2.72	3.04	3.30	3.70	3.94	4.44	4.65	5.07	5.57	6.98	8.80	10.34	12.16
	DI-5									3.10	3.33	3.80	4.15	4.45	4.70	5.09	5.58	6.99	8.84	10.40	12.16
	DI-10									4.66	4.88	5.26	5.36	5.54	5.79	5.84	5.99	7.73	8.89	10.39	12.24
	DI-15									8.39	8.05	7.92	7.43	7.57	7.52	7.73	7.88	8.57	8.90	10.5	12.65
A-6.3-DI-C-1	DI-2												0.07	0.10	0.135	0.147	0.154	0.379	1.08	1.71	2.51
	DI-5												0.07	0.10	0.139	0.147	0.154	0.378	1.10	1.71	2.51
	DI-10												0.07	0.10	0.141	0.147	0.154	0.38	1.10	1.71	2.55
	DI-15												0.093	0.10	0.139	0.147	0.154	0.41	1.11	1.72	2.61
A-6.3-DI-C-2	DI-2		0.103	0.115	0.128	0.142	0.339	0.468	0.475	0.565	0.588	0.778	0.848	0.987	1.18	1.36	1.55	2.63	4.43	5.77	6.91
	DI-5									0.565	0.593	0.789	0.85	0.990	1.18	1.37	1.56	2.65	4.43	5.77	6.91
	DI-10									0.573	0.596	0.86	0.876	0.999	1.19	1.46	1.68	3.14	4.44	5.78	7.02
	DI-15									1.13	1.15	1.20	1.58	2.100	2.26	2.50	2.84	3.89	4.47	5.86	7.06
A-6.3-CT-N-1	CT-2												4.72	4.81	5.1	5.78	6.29	8.95	11.07	13	15.07
	CT-5												4.72	4.81	5.11	5.8	6.33	8.96	11.15	13.1	15.15
	CT-10												4.72	4.85	6.38	7.7	8.17	10.8	11.22	13.3	15.18
	CT-15												5.54	6.55	7.85	9.55	10.5	11.8	12.3	13.62	15.7
A-6.3-CT-N-2	CT-2	4.93	5.07	5.00	5.02	5.12	5.48	6.04	6.13	7.24	7.36	7.45	7.50	8.24	8.46	8.72	8.88	10.30	11.63	12.96	14.48
	CT-5									7.30	7.45	7.66	7.56	8.23	8.44	8.72	8.94	10.50	11.68	13.00	14.49
	CT-10									8.52	8.60	8.63	8.30	9.55	9.85	9.70	10.14	11.90	12.12	13.15	14.66
	CT-15									13.70	13.85	9.29	9.83	11.60	12.00	12.30	12.70	13.50	13.60	13.67	14.55
A-6.3-CT-C-1	CT-2												4.26	4.35	4.37	4.62	4.71	5.64	7.33	8.59	10.18
	CT-5												4.38	4.37	4.42	4.64	4.72	5.68	7.36	8.59	10.00
	CT-10												4.40	4.38	4.44	4.68	4.79	5.82	7.36	8.82	9.95
	CT-15												4.59	4.77	5.02	5.26	5.55	6.56	7.40	8.73	10.23
A-6.3-CT-C-2	CT-2	4.47	4.58	4.53	4.53	4.56	4.72	4.88	4.89	4.80	4.98	4.90	4.97	5.18	5.28	5.70	5.87	7.05	8.77	10.04	11.66
	CT-5									4.97	5.00	5.04	5.03	5.17	5.29	5.70	5.87	7.10	8.77	10.04	11.50
	CT-10									5.00	5.02	5.24	5.03	5.22	5.35	5.71	5.96	7.62	8.78	10.14	11.36
	CT-15									5.52	5.53	5.32	5.80	6.92	7.05	7.25	7.95	8.58	8.86	10.14	11.31

Table B1.1 EC (mS/cm) vs. Time (day) (Continued)

Sample#	Depth(cm)	6/24/03	6/25/03	6/26/03	6/27/03	6/28/03	7/7/03	7/8/03	7/9/03	7/17/03	7/21/03	7/25/03	7/31/03	8/7/03	8/14/03	8/21/03	8/28/03	9/30/03	11/9/03	12/12/03	1/12/04
A-9.1-DI-N-1	DI-2												0.74	0.79	1.06	1.61	2.11	3.71	6.29	7.60	9.10
	DI-5												0.74	0.79	1.06	1.63	2.11	3.72	6.29	7.70	9.22
	DI-10												0.74	0.79	1.29	2.01	2.42	4.70	6.33	7.84	9.33
	DI-15												0.80	3.09	4.27	4.36	5.30	5.82	6.36	7.70	9.57
A-9.1-DI-N-2	DI-2		0.700	0.720	0.722	0.753	1.16	1.82	1.88	2.27	3.85	4.23	4.24	4.37	4.52	4.71	5.00	6.42	8.12	9.55	11.23
	DI-5									2.32	4.10	4.23	4.25	4.39	4.61	4.71	5.02	6.50	8.19	9.68	11.32
	DI-10									3.94	4.40	4.47	4.29	4.58	4.73	4.95	5.15	7.26	8.32	9.80	11.60
	DI-15									7.01	4.97	4.93	5.44	5.89	6.15	6.42	6.99	8.77	8.35	9.82	11.74
A-9.1-DI-C-1	DI-2												0.04	0.10	0.16	0.18	0.20	0.29	0.57	0.91	1.40
	DI-5												0.04	0.10	0.17	0.18	0.20	0.30	0.57	0.91	1.41
	DI-10												0.04	0.10	0.17	0.18	0.20	0.30	0.57	0.91	1.41
	DI-15												0.07	0.10	0.17	0.18	0.20	0.29	0.57	1.11	1.42
A-9.1-DI-C-2	DI-2		0.104	0.118	0.139	0.178	0.303	0.619	0.640	0.87	0.97	1.19	1.52	1.79	2.10	2.48	2.99	4.87	7.30	9.01	11.53
	DI-5									0.88	0.98	1.20	1.52	1.80	2.10	2.48	3.00	4.93	7.31	9.04	11.55
	DI-10									1.26	1.61	1.88	2.07	2.37	2.74	3.10	3.48	6.09	7.35	9.32	11.90
	DI-15									3.55	3.76	3.50	4.09	4.65	5.22	5.29	5.70	7.03	7.36	10.00	11.97
A-9.1-CT-N-1	CT-2												4.85	4.96	5.50	5.83	7.09	9.35	12.22	13.84	15.80
	CT-5												4.88	4.97	5.50	5.89	7.11	9.37	12.26	13.77	15.48
	CT-10												4.90	4.97	6.50	8.25	8.71	12.10	12.26	13.84	15.41
	CT-15												6.01	11.00	12.55	13.33	13.10	13.88	12.34	14.05	15.89
A-9.1-CT-N-2	CT-2	4.99	5.12	5.07	5.11	5.32	5.68	6.82	6.92	7.36	7.40	7.64	7.75	8.43	8.80	8.86	9.23	10.00	12.19	13.55	15.30
	CT-5									7.48	7.69	7.80	7.96	8.55	8.87	8.85	9.24	10.40	12.20	13.55	15.30
	CT-10									9.14	9.50	8.88	8.62	10.30	10.20	9.97	11.70	13.10	12.31	13.55	15.49
	CT-15									15.00	14.00	10.00	9.78	11.30	11.80	12.10	12.60	14.19	12.39	13.87	15.64
A-9.1-CT-C-1	CT-2												4.35	4.41	4.30	4.48	4.69	5.14	6.23	7.28	8.51
	CT-5												4.38	4.43	4.44	4.50	4.69	5.15	6.24	7.45	8.53
	CT-10												4.42	4.43	4.47	4.52	4.69	5.17	6.27	7.47	8.66
	CT-15												4.49	4.52	4.72	4.68	4.94	5.78	6.30	7.51	8.91
A-9.1-CT-C-2	CT-2	4.47	4.60	4.58	4.63	4.72	4.82	4.85	4.88	5.00	5.02	4.90	4.83	5.01	5.12	5.17	5.37	6.18	7.67	8.78	10.10
	CT-5									4.95	4.99	4.92	4.82	5.01	5.12	5.18	5.38	6.25	7.67	8.78	10.20
	CT-10									4.98	4.99	4.90	4.80	5.03	5.14	5.19	5.39	6.47	7.70	8.78	10.30
	CT-15									4.95	5.03	4.90	5.02	5.45	5.80	6.40	6.87	7.40	7.72	8.89	10.40

Table B1.1 EC (mS/cm) vs. Time (day) (Continued)

Sample#	Depth(cm)	6/24/03	6/25/03	6/26/03	6/27/03	6/28/03	7/7/03	7/8/03	7/9/03	7/17/03	7/21/03	7/25/03	7/31/03	8/7/03	8/14/03	8/21/03	8/28/03	9/29/03	11/8/03	12/12/03	1/12/04
		1	2	3	4	5	14	15	16	24	28	32	38	45	52	59	66	98	138	172	203
A-24.9-DI-N-1	DI-2		0.353	0.359	0.390	0.427	1.79	6.9	7.13	9.12	9.67	9.94	11.00	12.00	14.00	14.30	16.00		28.70	33.50	39.20
	DI-5									9.29	10.10	10.20	11.50	12.60	14.10	15.00	16.40	23.20	29.20	34.00	39.50
	DI-10									13.10	13.40	14.10	16.10	17.60	19.40	20.20	21.50	26.20	30.70	34.90	39.60
	DI-15									22.00	22.60	23.20	25.60	27.90	29.10	29.40			31.30	35.20	40.00
A-24.9-DI-N-2	DI-2		1.61	1.63	1.67	1.69	3.87	3.86	12.6	13.80	13.90	14.00	15.30	16.70	17.70	18.60	20.10		33.90	35.60	41.00
	DI-5									14.30	14.50	14.70	15.90	17.20	18.20	19.00	20.50		33.90	35.60	41.10
	DI-10									17.30	17.70	18.30	20.20	21.40	23.40	23.80	24.90		34.10	36.00	41.20
	DI-15									27.00	27.60	27.80	29.20	29.90					34.20	36.20	41.40
A-24.9-DI-C-1	DI-2		0.070	0.090	0.107	0.120	0.329	0.348	1.03	1.15	1.22	1.36	1.52	1.70	2.02	2.29	2.54		6.48	7.81	9.36
	DI-5									1.17	1.22	1.36	1.52	1.71	2.03	2.30	2.57	3.84	6.48	7.75	9.44
	DI-10									1.18	1.35	1.71	1.83	2.25	2.35	2.60	3.12	4.84	6.51	7.81	9.57
	DI-15									2.45	2.71	2.80	3.26	4.10	4.31	4.49	4.98	5.32	6.55	7.88	9.85
A-24.9-DI-C-2	DI-2		0.060	0.072	0.095	0.102	0.320	0.844	0.857	1.08	1.14	1.26	1.41	1.59	1.90	2.26	2.49		6.08	7.41	9.03
	DI-5									1.08	1.14	1.26	1.42	1.60	1.91	2.27	2.50	3.86	6.09	7.41	9.08
	DI-10									1.08	1.18	1.44	1.72	1.86	2.09	2.40	2.80	4.33	6.11	7.79	9.11
	DI-15									1.95	2.28	2.34	3.00	3.47	3.62	3.85	4.34	4.82	6.15	8.16	9.49
A-24.9-CT-N-1	CT-2	5.04	5.33	5.29	5.38	5.41	6.14	15.4	15.5	16.30	15.80	16.10	16.80	18.00	18.10	18.90	20.20		32.30	34.40	39.40
	CT-5									16.20	15.80	16.00	16.50	18.30	18.40	19.60	20.50		32.30	36.00	39.60
	CT-10									16.70	17.50	17.70	18.90	22.20	23.10	24.10	24.90	27.80	32.50	36.00	40.60
	CT-15									25.00	25.20	23.40	24.00						32.50	36.10	40.70
A-24.9-CT-N-2	CT-2	5.48	5.69	5.67	5.69	5.78	7.04	7.49	17.5	18.20	18.00	18.20	19.30	20.30	20.50	20.80	21.90		34.70	35.50	39.10
	CT-5									18.60	18.20	18.30	19.30	20.30	20.30	20.90	22.00	27.70	35.00	36.30	39.30
	CT-10									19.80	19.60	20.00	21.10	23.70	24.10	25.90	27.70		35.70	36.70	39.40
	CT-15									25.90	26.20	25.90	26.10						36.50	37.20	39.80
A-24.9-CT-C-1	CT-2	4.42	4.53	4.46	4.52	4.64	4.79	4.77	4.83	5.14	5.33	5.12	5.38	5.81	6.04	6.36	6.81		10.60	11.84	13.34
	CT-5									5.18	5.35	5.15	5.38	5.85	6.05	6.36	6.80	8.12	10.60	11.78	13.16
	CT-10									5.29	5.46	5.42	5.61	6.33	6.60	6.95	6.88	9.29	10.70	11.91	13.34
	CT-15									7.81	7.96	6.36	6.97	8.11	8.41	8.87	10.10	10.40	10.90	12.00	13.22
A-30.7-CT-C-2	CT-2	4.45	4.57	4.53	4.61	4.61	4.80	4.87	4.88	4.90	5.23	5.16	5.62	6.05	6.46	6.70	7.00		11.30	12.65	14.65
	CT-5									4.98	5.26	5.33	5.65	6.10	6.46	6.71	7.02	8.73	11.30	12.65	14.29
	CT-10									5.42	5.93	5.72	5.66	6.40	6.50	6.87	7.15	9.55	11.40	12.65	14.50
	CT-15									8.25	7.76	6.60	7.30	8.55	9.20	9.40	10.12	10.73	11.40	12.84	14.77

Table B1.1 EC vs. Time (continued)

	11/25/03	12/2/03	12/9/03	12/16/03	12/23/03	1/4/04	1/12/04	1/26/04	3/2/04
Time (day)	1	8	15	22	29	41	49	63	99
N-10-DI-1	0.0064	0.202	1.21	2.85	5.55	9.2	11.87	14.8	24.2
N-10-DI-2	0.006	0.0062	0.0078	0.012	0.026	0.054	0.129	0.364	2.03
N-10-CT-1	4.42	4.67	4.85	4.88	5.64	5.97	6.53	6.91	9.91
N-10-CT-2	4.41	4.72	4.87	4.87	5.29	5.54	5.89	6.15	9.14
N-20-DI-1	0.0066	0.0059	0.0086	0.011	0.014	0.028	0.26	0.71	3.55
N-20-DI-2	0.0065	0.0072	0.0395	0.083	0.255	0.525	1.04	1.97	6.03
N-20-CT-1	4.44	4.77	4.93	4.96	5.5	5.87	6.26	6.94	11
N-20-CT-2	4.45	4.74	4.87	4.82	5.18	5.47	6.1	6.97	11.9
N-30-DI-1	0.0056	0.0067	0.0109	0.016	0.03	0.044	0.14	0.586	3.05
N-30-DI-2	0.0052	0.0055	0.0098	0.015	0.026	0.039	0.157	0.502	2.67
N-30-CT-1	4.36	4.72	4.67	4.94	5.88	6.9	8.43	10.28	18.33
N-30-CT-2	4.40	4.76	4.77	4.82	5.3	5.53	5.99	6.18	9.04
N-40-DI-1	0.0056	0.0084	0.0083	0.0093	0.022	0.031	0.046	0.063	0.207
N-40-DI-2	0.0058	0.0059	0.0133	0.0176	0.032	0.057	0.198	0.681	2.87
N-40-CT-1	4.43	4.68	4.65	4.71	5.18	5.25	5.25	5.51	7.17
N-40-CT-2	4.32	4.61	4.8	4.78	5.1	5.26	5.39	5.64	8.78
N-50-DI-1	0.0067	0.0059	0.0082	0.0125	0.019	0.047	0.384	0.56	3.2
N-50-DI-2	0.0055	0.0056	0.0457	0.283	0.775	1.78	2.89	4.4	10.4
N-50-CT-1	4.35	4.7	4.82	5.08	5.68	6.5	7.52	9.01	13.1
N-50-CT-2	4.36	4.8	5.06	5.46	6.53	7.73	8.61	9.72	15.2

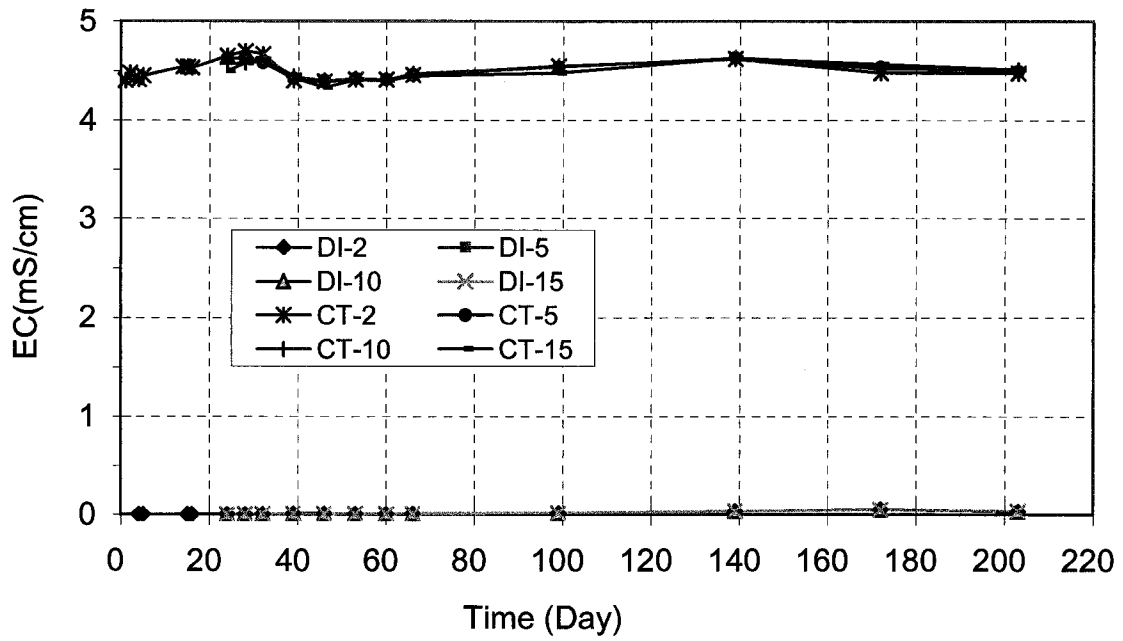


Fig. B1.1 EC - Time (A- 0-DI-1, A-0-CT-1)

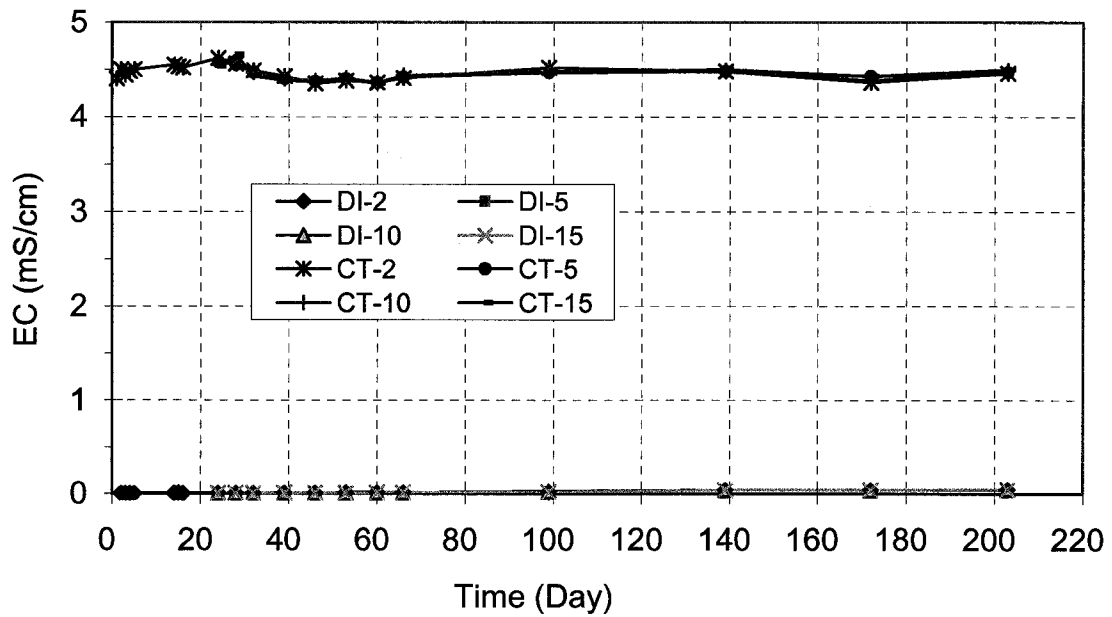


Fig. B1.2 EC - Time (A-0-DI-2, A-0-CT-2)

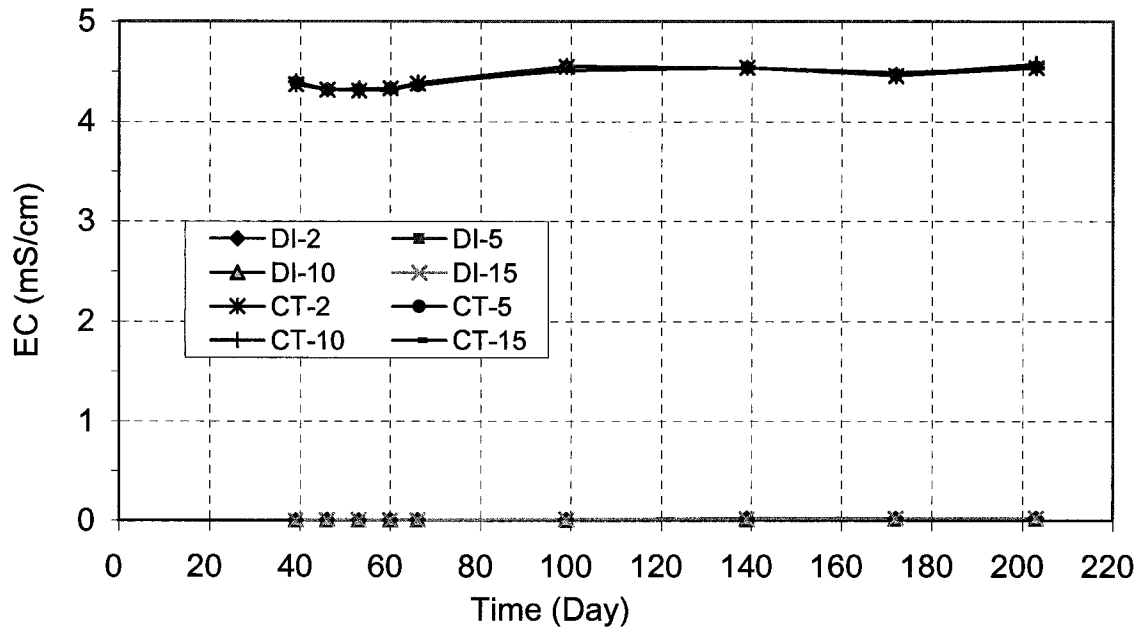


Fig. B1.3 EC - Time (A-0-DI-3, A-0-CT-3)

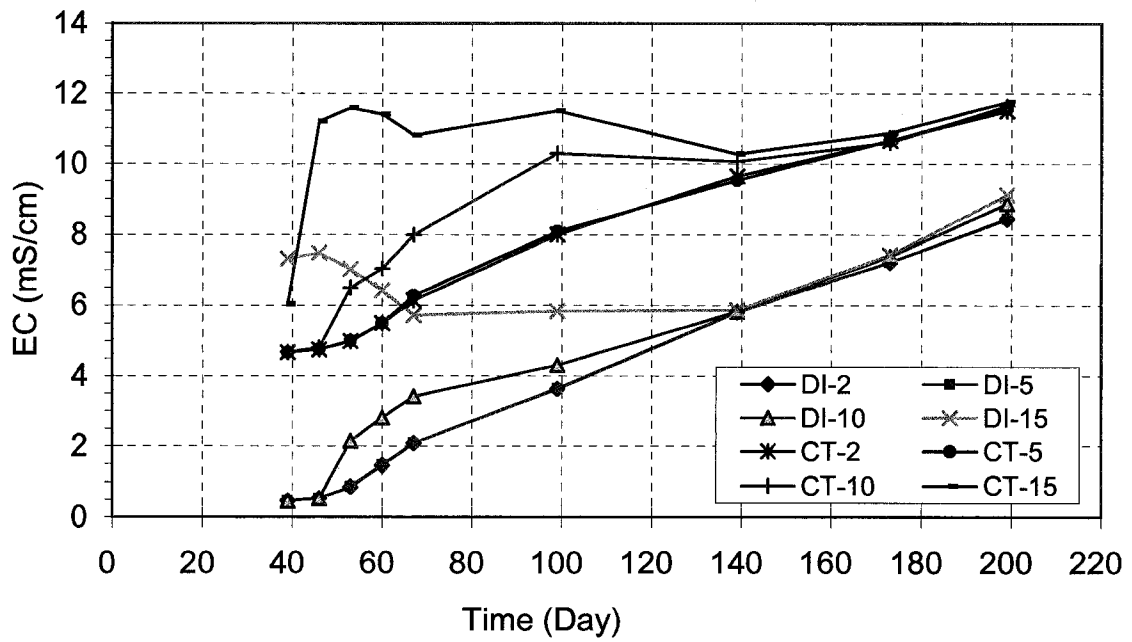


Fig. B1.4 EC - Time (A-3.6-DI-N-1, A-3.6-CT-N-1)

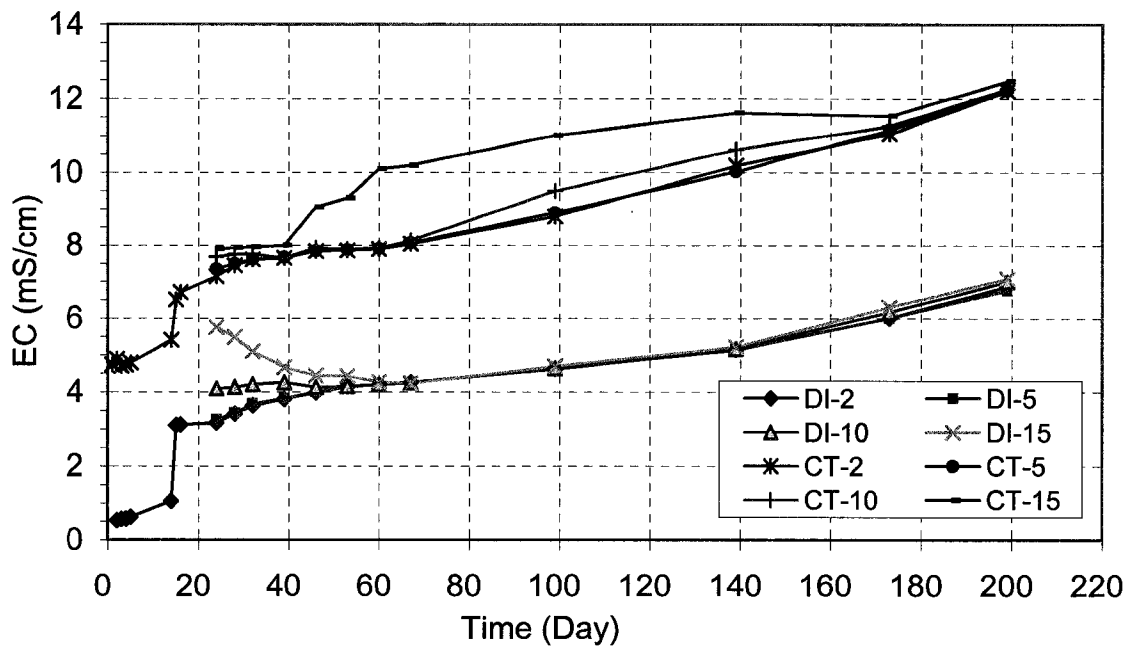


Fig. B1.5 EC - Time (A-3.6-DI-N-2, A-3.6-CT-N-2)

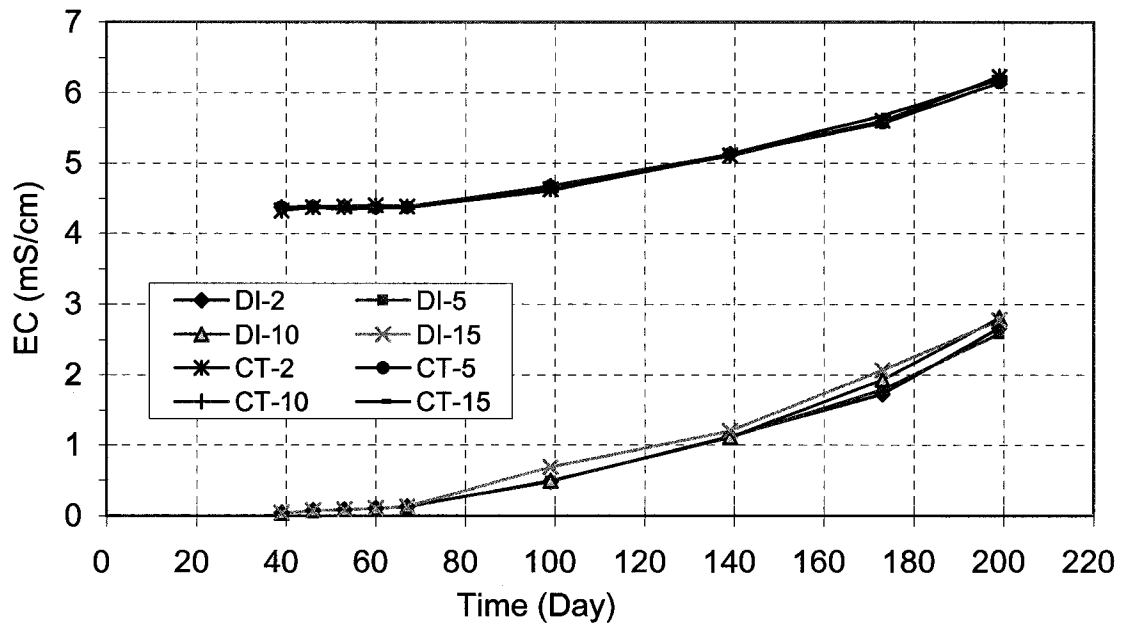


Fig. B1.6 EC - Time (A-3.6-DI-C-1, A-3.6-CT-C-1)

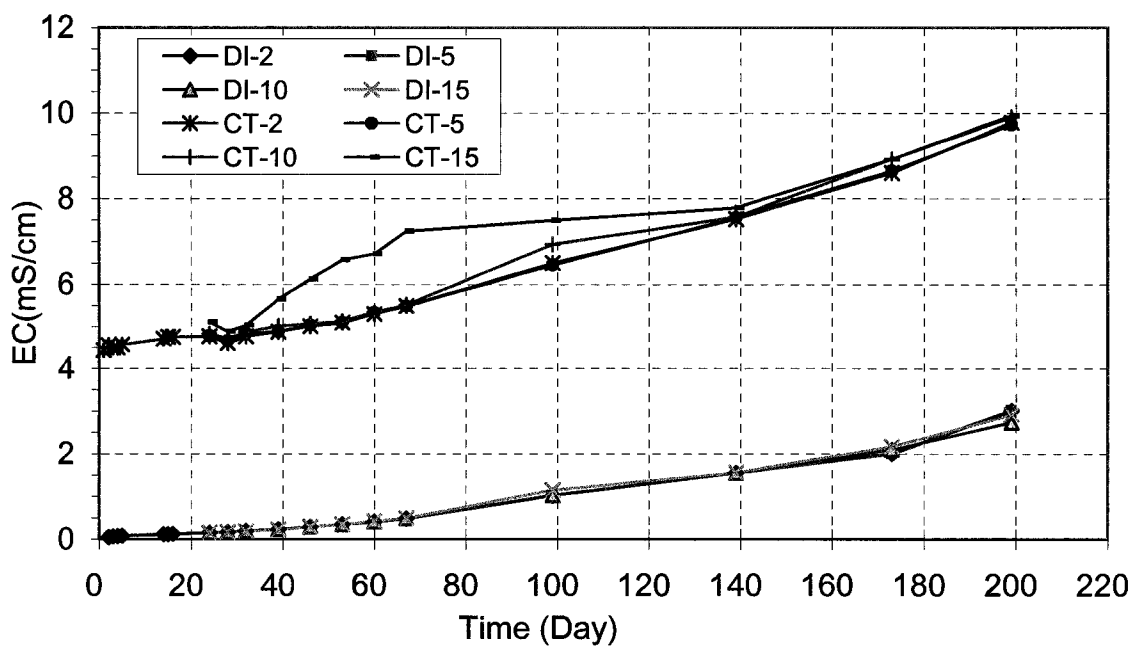


Fig. B1.7 EC - Time (A-3.6-DI-C-2, A-3.6-CT-C-2)

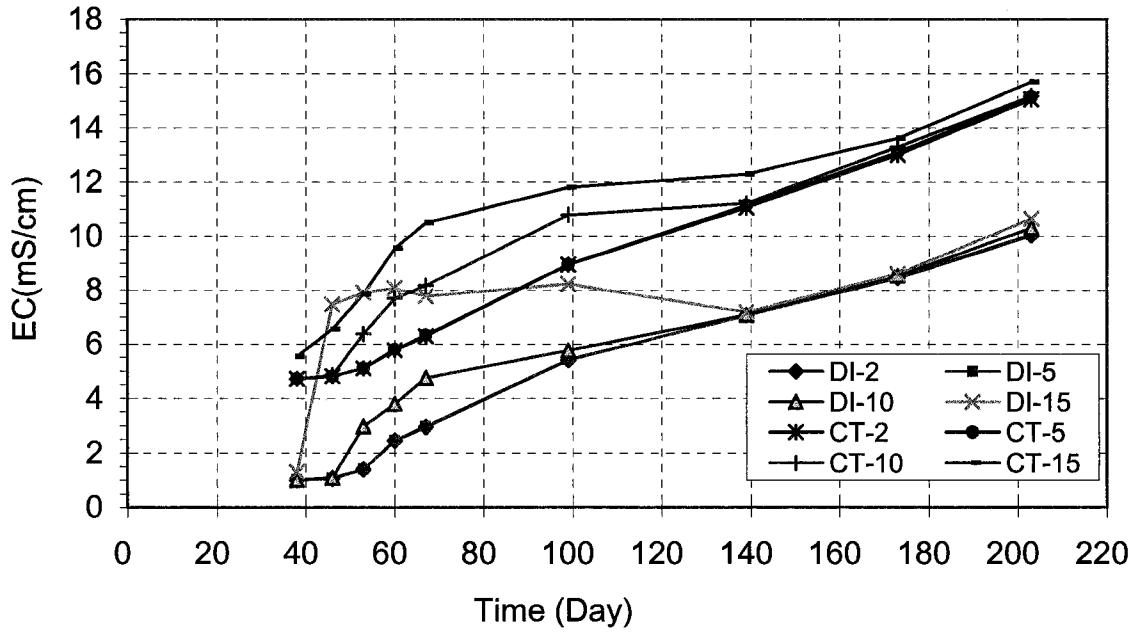


Fig. B1.8 EC - Time (A- 6.3-DI-N-1, A-6.3-CT-N-1)

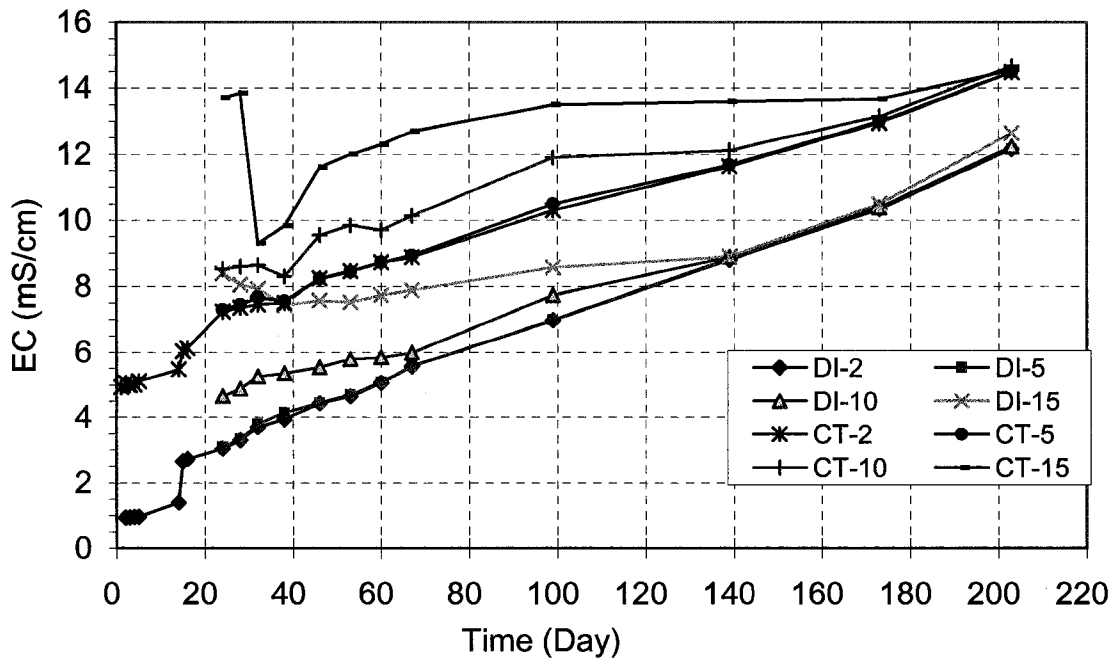


Fig. B1.9 EC - Time (A-6.3-DI-N-2, A-6.3-CT-N-2)

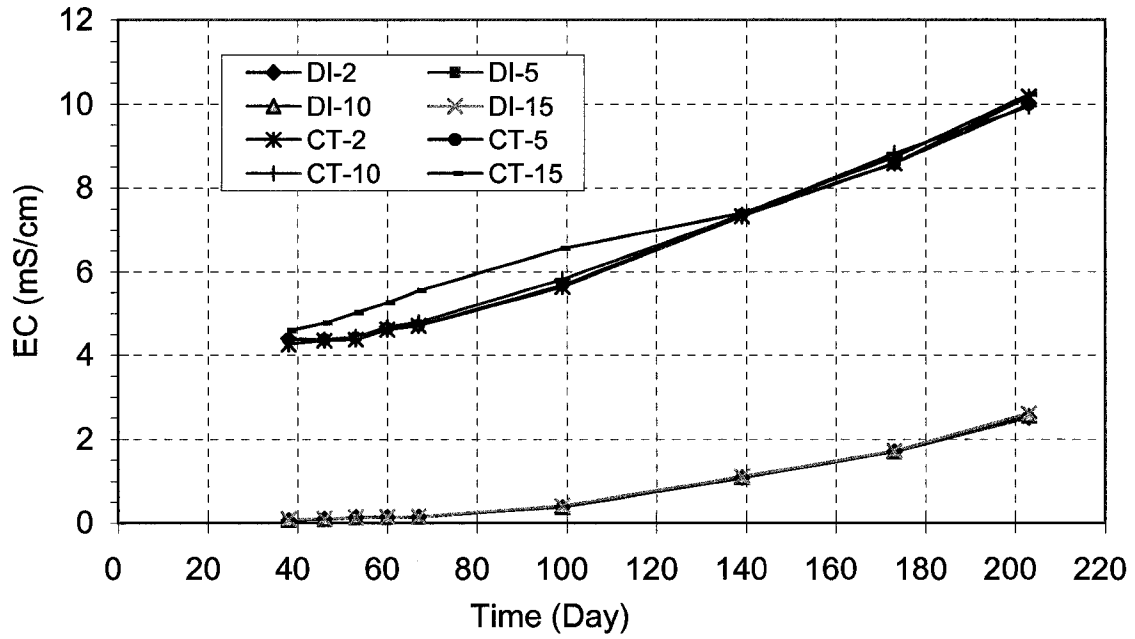


Fig. B1.10 EC - Time (A-6.3-DI-C-1, A-6.3-CT-C-1)

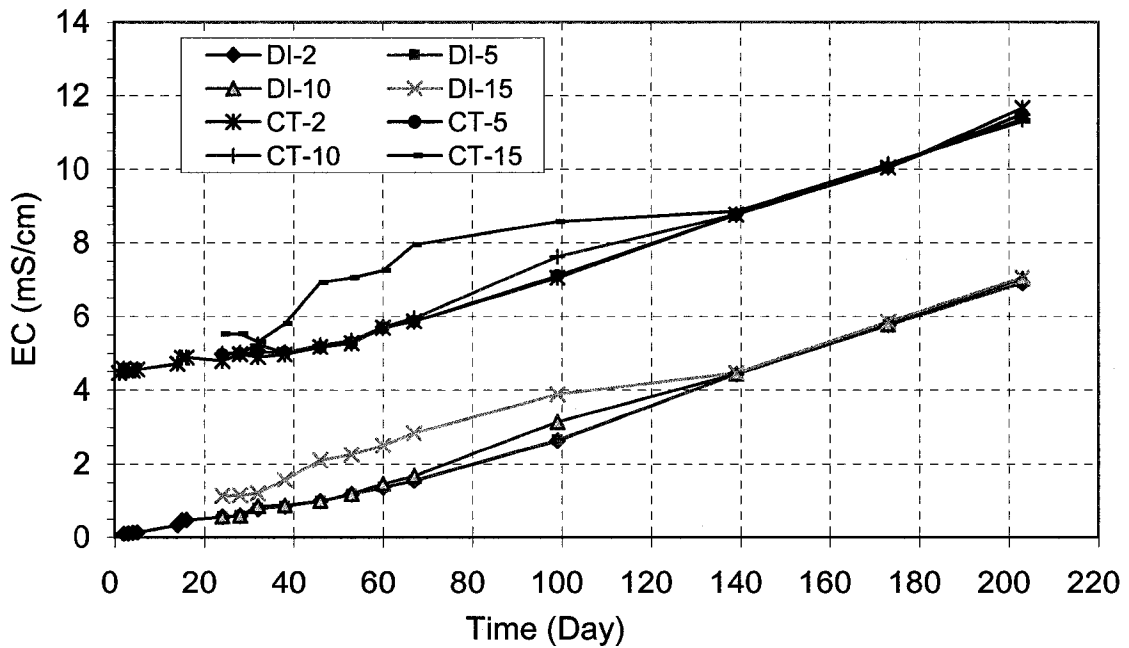


Fig. B1.11 EC - Time (A-6.3-DI-C-2, A-6.3-CT-C-2)

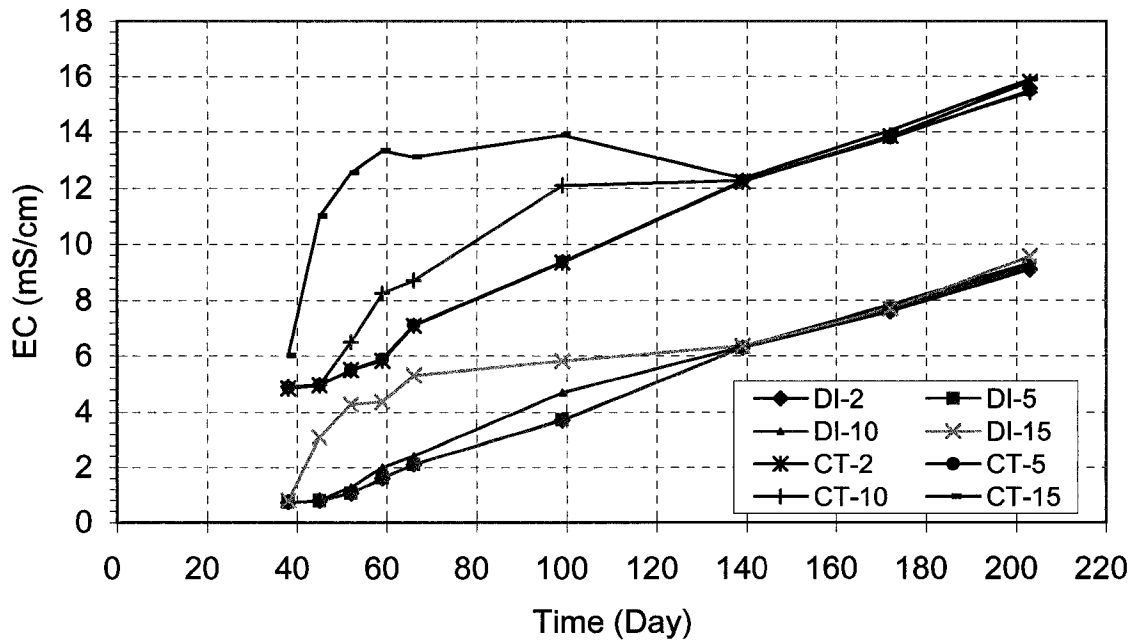


Fig. B1.12 EC - Time (A-9.1-DI-N-1, A-9.1-CT-N-1)

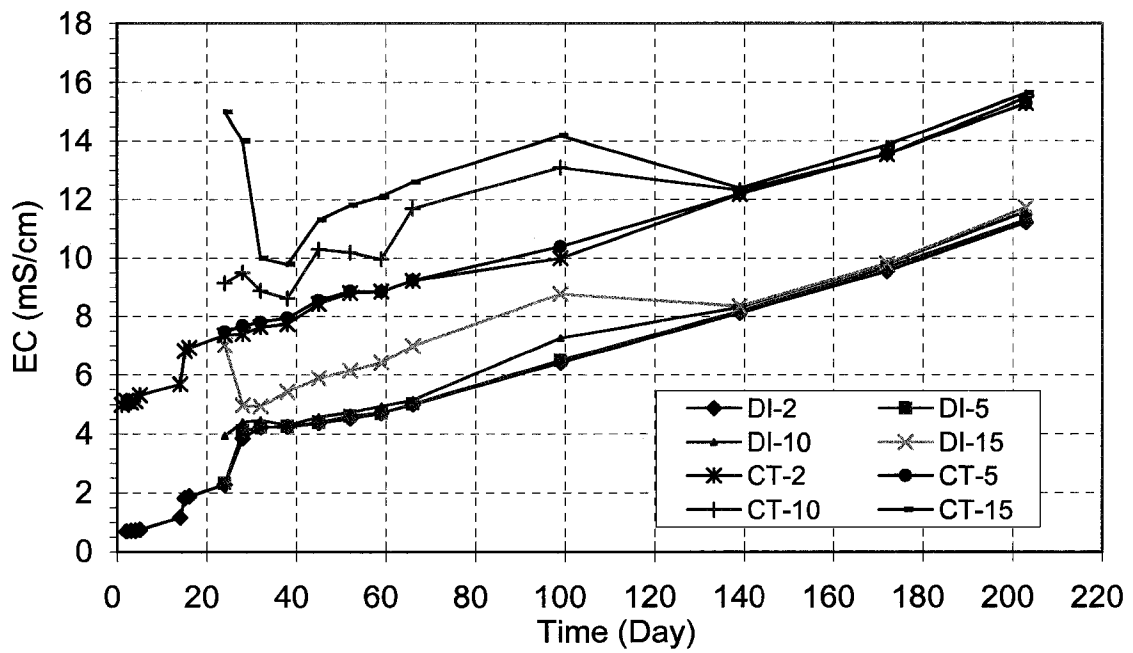


Fig. B1.13 EC - Time (A-9.1-DI-N-2, A-9.1-CT-N-2)

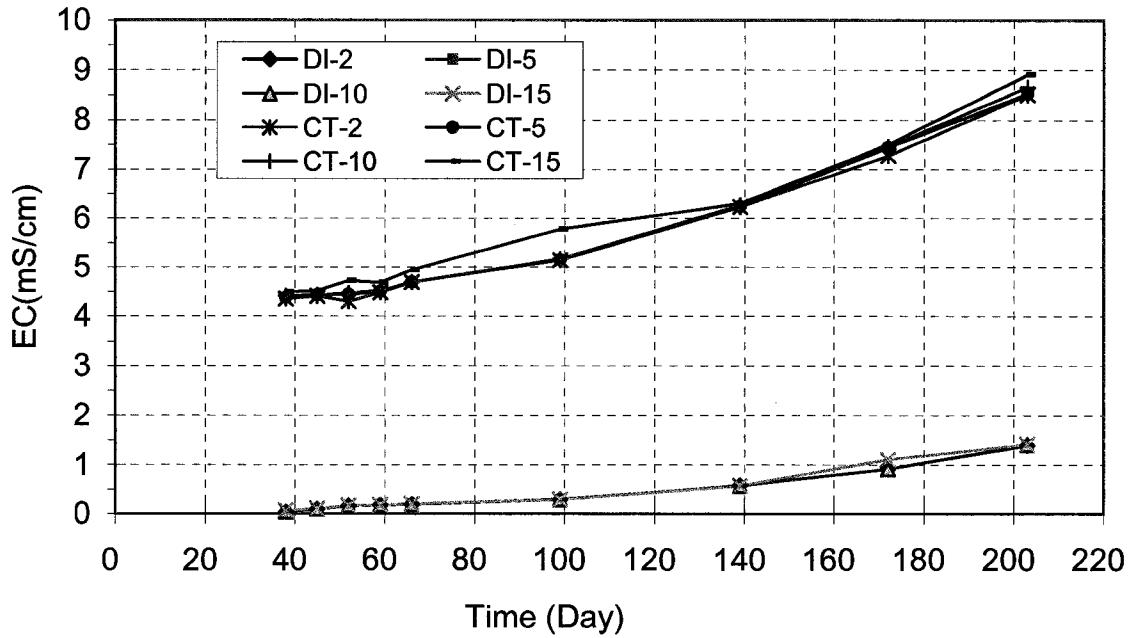


Fig. B1.14 EC - Time (A-9.1-DI-C-1, A-9.1-CT-C-1)

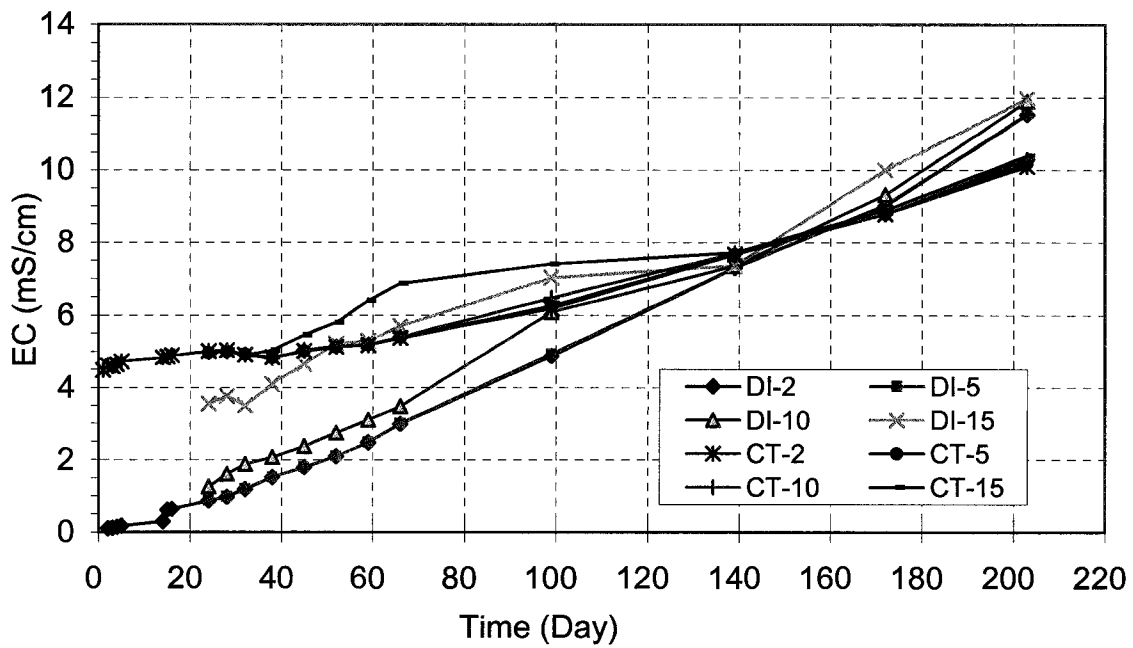


Fig. B1.15 EC - Time (A-9.1-DI-C-2, A-9.1-CT-C-2)

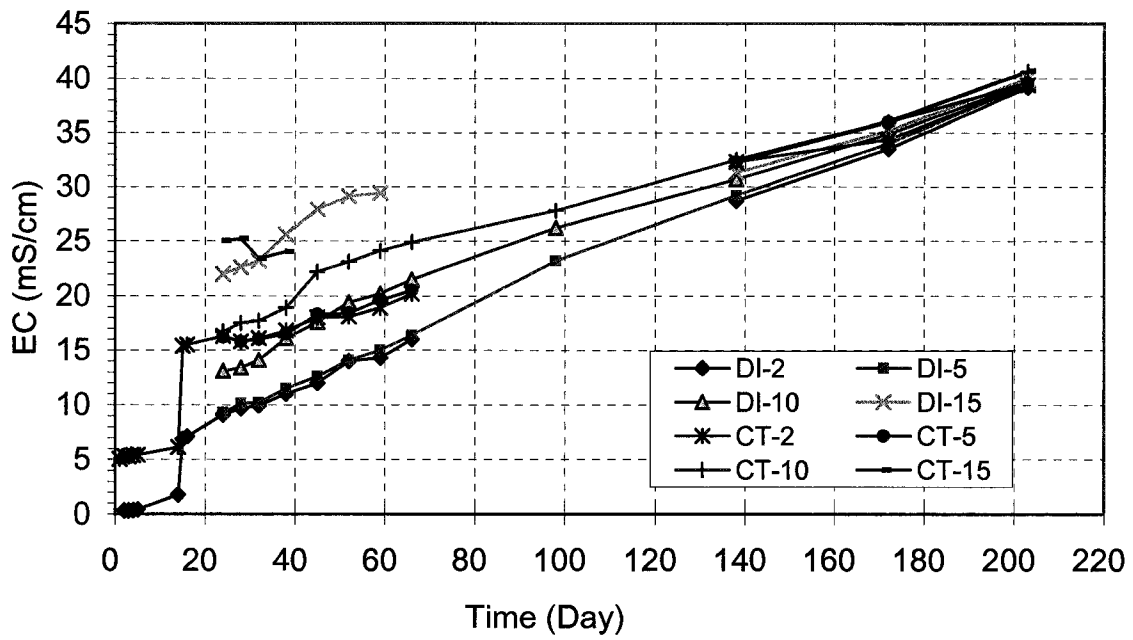


Fig. B1.16 EC - Time (A-24.9-DI-N-1, A-24.9-CT-N-1)

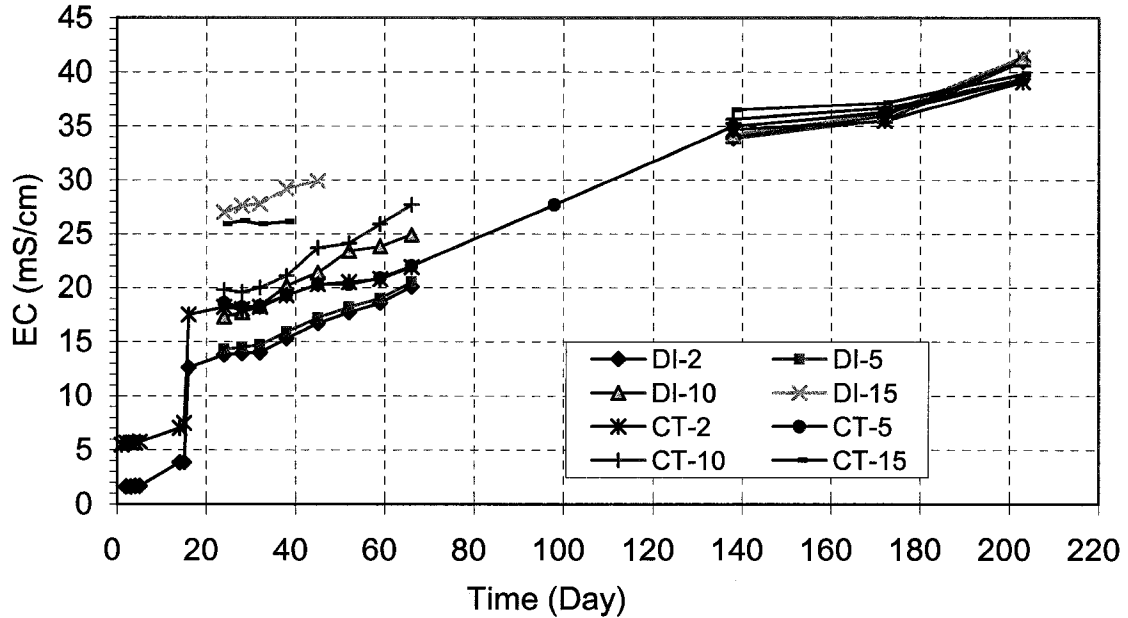


Fig. B1.17 EC - Time (A-24.9-DI-N-2, A-24.9-CT-N-2)

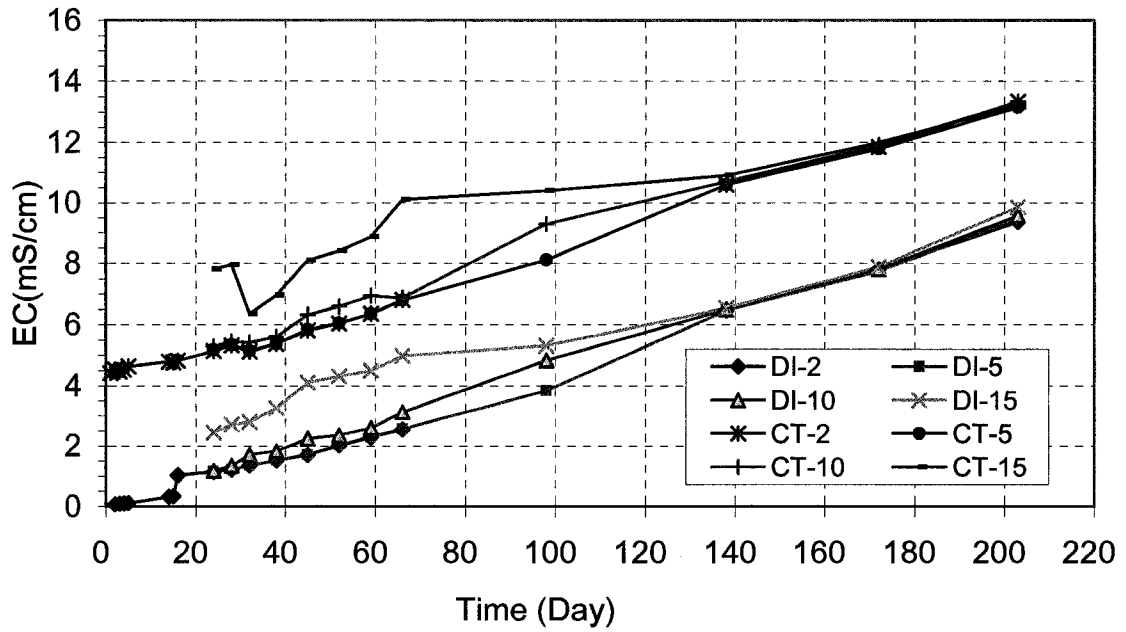


Fig. B1.18 EC - Time (A-24.9-DI-C-1, A-24.9-CT-C-1)

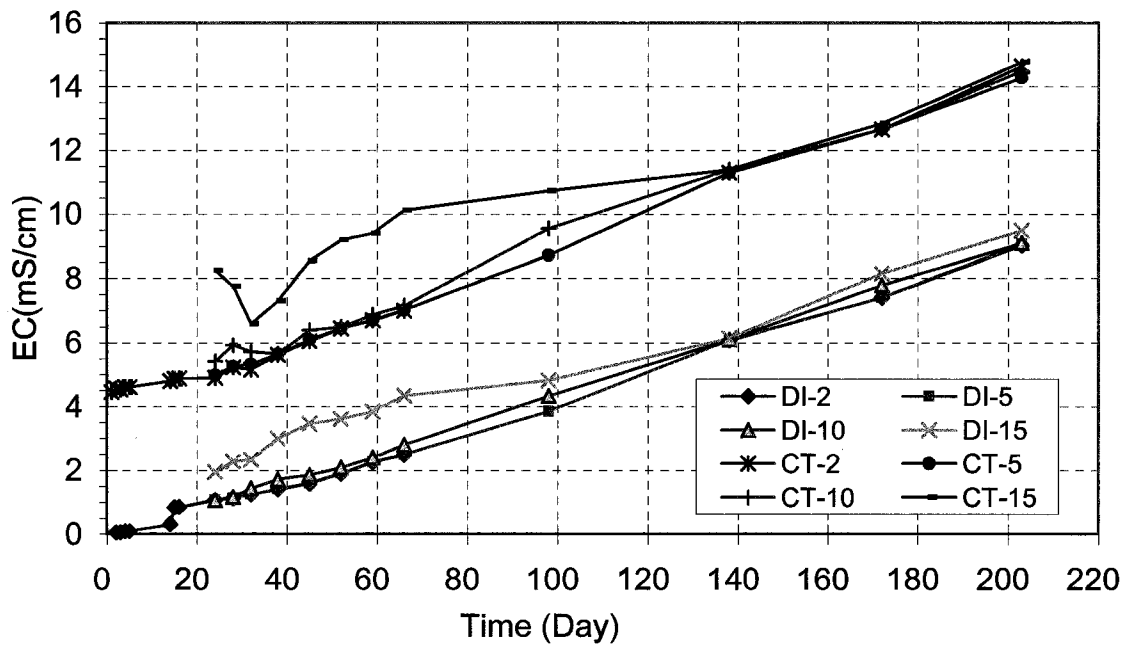


Fig. B1.19 EC - Time (A-24.9-DI-C-2, A-30.7-CT-C-2)

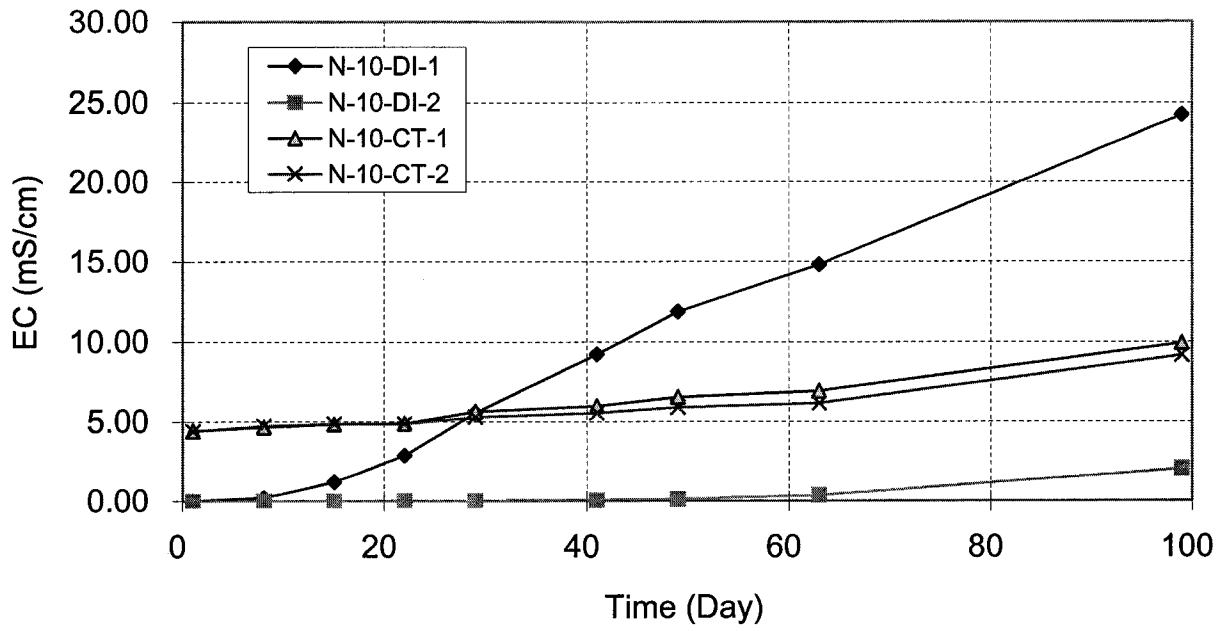


Fig. B1.20 EC -Time (10% Salt)

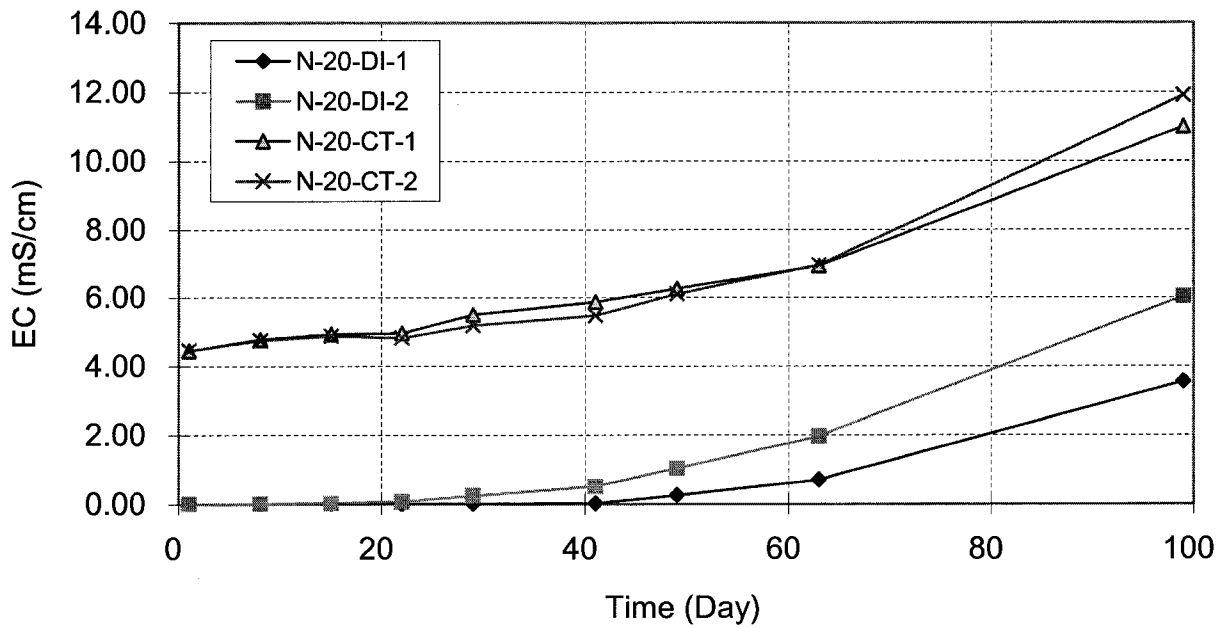


Fig. B1.21 EC -Time (20% Salt)

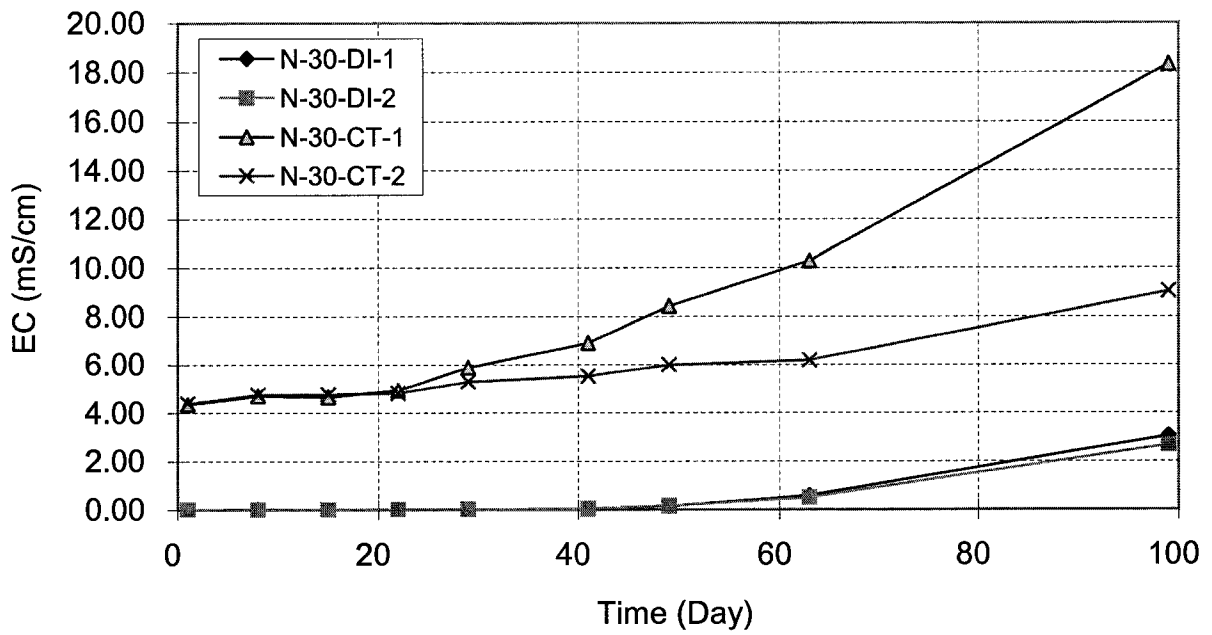


Fig. B1.22 EC -Time (30% Salt)

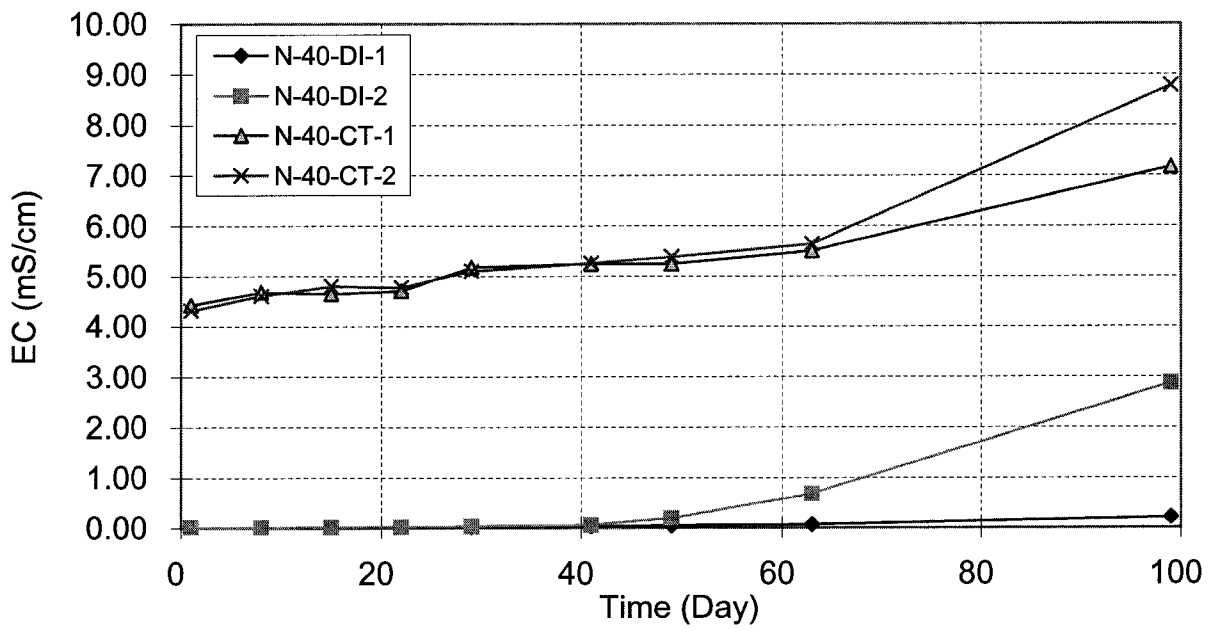


Fig. B1.23 EC -Time (40% Salt)

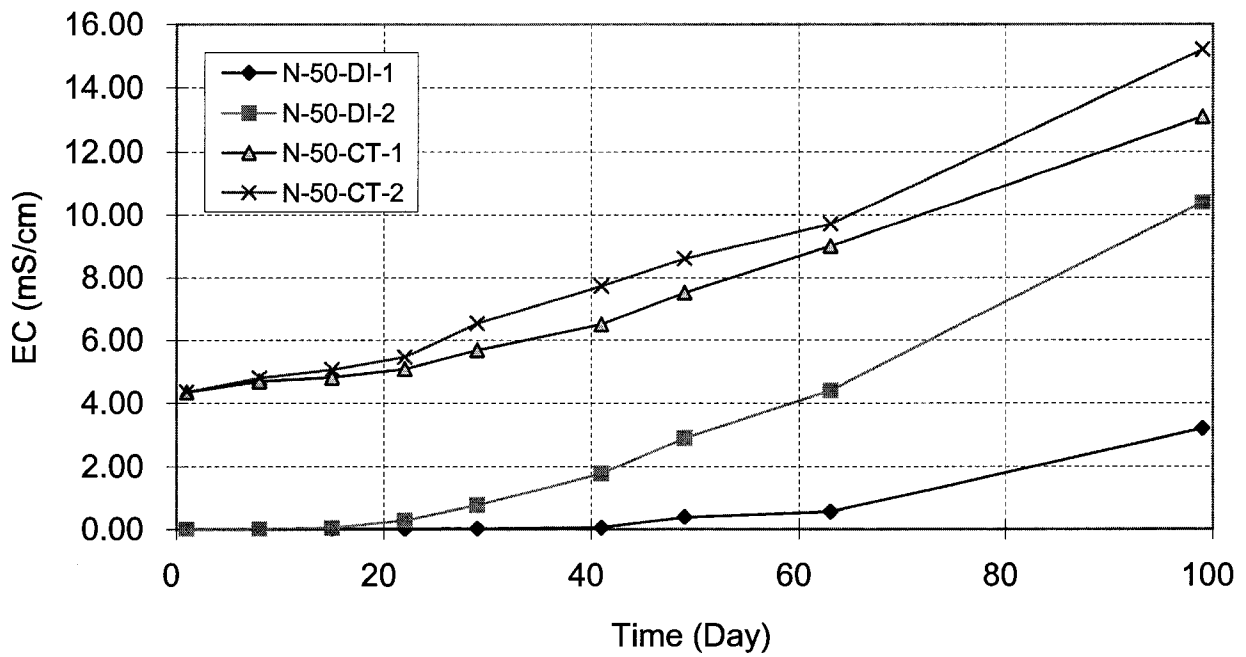


Fig. B1.24 EC -Time (50% Salt)

Table B2.1 pH vs. Time

Sample#	Depth(cm)	6/25/03	6/26/03	6/27/03	6/28/03	7/7/03	7/8/03	7/9/03	7/17/03	7/25/03	7/31/03	8/8/03	8/15/03	8/22/03	8/28/03	9/30/03	11/9/03	12/12/03	1/12/04
A-0-DI-1	DI-2	6.47	6.47	6.47	6.38	6.28	6.12	6.13	5.68	5.48	5.54	5.54	5.34	5.18	5.02	4.89	4.54	4.39	4.29
	DI-5								5.65	5.46	5.52	5.54	5.28	5.20	5.01	4.90	4.53	4.39	4.29
	DI-10								5.57	5.47	5.47	5.51	5.26	5.16	5.02	4.91	4.50	4.39	4.28
	DI-15								5.55	5.48	5.45	5.50	5.24	5.10	5.03	4.89	4.49	4.38	4.29
A-0-DI-2	DI-2	6.30	6.37	6.21	6.32	6.36	6.19	5.98	5.22	4.86	4.80	5.02	4.67	4.62	4.53	4.45	4.21	4.23	4.09
	DI-5								5.15	4.90	4.78	4.98	4.65	4.64	4.51	4.47	4.18	4.20	4.08
	DI-10								5.13	4.90	4.79	4.91	4.64	4.66	4.51	4.43	4.16	4.18	4.08
	DI-15								5.06	4.90	4.78	4.89	4.62	4.64	4.50	4.45	4.15	4.18	4.07
A-0-DI-3	DI-2										6.53	6.03	6.04	5.93	5.61	5.00	4.79	4.60	4.45
	DI-5										6.44	6.00	6.08	5.85	5.56	4.98	4.70	4.55	4.47
	DI-10										6.29	5.95	5.94	5.78	5.55	4.99	4.68	4.55	4.46
	DI-15										6.22	5.97	5.91	5.70	5.54	4.98	4.64	4.54	4.45
A-0-CT-1	CT-2	8.02	8.05	8.06	8.32	8.41	8.47	8.59	8.48	8.71	8.80	8.79	8.79	8.92	8.98	8.66	8.63	8.70	8.69
	CT-5								8.48	8.72	8.80	8.82	8.80	8.93	8.99	8.66	8.62	8.70	8.70
	CT-10								8.50	8.74	8.80	8.84	8.81	8.93	9.00	8.65	8.62	8.70	8.69
	CT-15								8.50	8.75	8.80	8.86	8.81	8.93	9.01	8.65	8.60	8.70	8.69
A-0-CT-2	CT-2	7.99	8.11	7.90	8.24	8.29	8.52	8.57	8.58	8.48	8.68	8.84	8.81	8.92	8.98	8.68	8.64	8.70	8.68
	CT-5								8.57	8.63	8.70	8.87	8.81	8.93	8.99	8.68	8.64	8.71	8.69
	CT-10								8.57	8.66	8.74	8.89	8.82	8.94	9.00	8.65	8.63	8.71	8.68
	CT-15								8.58	8.69	8.76	8.90	8.83	8.94	9.01	8.63	8.63	8.71	8.67
A-0-CT-3	CT-2										8.29	8.06	8.43	8.28	8.36	8.83	8.71	8.76	8.74
	CT-5										8.23	8.14	8.43	8.31	8.40	8.84	8.72	8.76	8.73
	CT-10										8.19	8.19	8.45	8.36	8.44	8.84	8.72	8.77	8.73
	CT-15										8.19	8.21	8.45	8.44	8.48	8.84	8.72	8.77	8.74

Table B2.1 pH vs. Time (Continued)

Sample#	Depth(cm)	6/25/03	6/26/03	6/27/03	6/28/03	7/7/03	7/8/03	7/9/03	7/17/03	7/25/03	8/1/03	8/8/03	8/15/03	8/22/03	8/29/03	9/30/03	11/9/03	12/13/03	1/12/04
A-3.6-DI-N-1	DI-2										6.10	5.96	5.82	5.79	5.36	4.61	4.46	4.21	4.16
	DI-5										6.10	5.98	5.82	5.77	5.31	4.60	4.41	4.22	4.15
	DI-10										6.07	6.00	5.70	5.37	4.96	4.57	4.39	4.22	4.15
	DI-15										6.05	5.93	5.38	4.83	4.68	4.55	4.32	4.22	4.16
A-3.6-DI-N-2	DI-2	6.36	6.18	6.26	6.13	6.20	6.15	6.12	5.90	5.48	5.06	4.80	4.52	4.53	4.47	4.42	4.30	4.20	4.18
	DI-5								5.87	5.44	5.02	4.77	4.50	4.51	4.44	4.41	4.26	4.20	4.17
	DI-10								5.47	5.00	4.68	4.66	4.46	4.51	4.43	4.40	4.24	4.20	4.17
	DI-15								5.18	4.64	4.54	4.59	4.45	4.48	4.42	4.34	4.26	4.22	4.16
A-3.6-DI-C-1	DI-2										6.23	5.97	6.20	5.69	5.27	5.21	5.16	5.13	4.88
	DI-5										6.26	5.90	6.10	5.54	5.23	5.20	5.14	5.03	4.87
	DI-10										6.27	5.95	5.85	5.27	5.23	5.19	5.10	4.99	4.82
	DI-15										6.23	5.95	5.87	5.45	5.23	5.14	5.10	4.92	4.76
A-3.6-DI-C-2	DI-2	6.05	6.22		6.21	5.80	5.78	6.06	6.20	5.80	5.52	5.38	5.12	5.20	5.28	5.12	4.82	4.62	4.56
	DI-5								5.89	5.58	5.42	5.28	5.17	5.12	5.19	5.05	4.80	4.61	4.54
	DI-10								5.70	5.45	5.30	5.21	5.20	5.08	5.11	5.03	4.73	4.60	4.52
	DI-15								5.46	5.33	5.25	5.15	5.02	5.04	5.05	4.90	4.75	4.58	4.48
A-3.6-CT-N-1	CT-2										8.16	8.25	8.34	8.72	8.86	8.79	8.61	8.56	8.56
	CT-5										8.16	8.26	8.38	8.74	8.80	8.69	8.60	8.56	8.56
	CT-10										8.17	8.25	7.92	8.12	8.14	7.77	7.60	7.60	7.64
	CT-15										8.06	7.90	7.77	7.88	7.94	7.37	7.20	7.22	7.17
A-3.6-CT-N-2	CT-2	8.16	8.20	8.22	8.36	8.55	8.61	8.75	8.70	8.73	8.70	8.70	8.61	8.62	8.63	8.76	8.57	8.24	8.26
	CT-5								8.69	8.55	8.70	8.72	8.63	8.60	8.64	8.78	8.57	8.19	8.10
	CT-10								8.07	8.19	8.24	8.40	8.59	8.59	8.58	7.87	7.49	7.30	7.25
	CT-15								7.35	7.55	7.50	7.51	7.40	7.46	7.40	7.20	7.14	7.09	7.02
A-3.6-CT-C-1	CT-2										8.15	8.29	8.27	8.48	8.57	8.76	9.05	8.90	8.80
	CT-5										8.17	8.30	8.31	8.51	8.59	8.77	9.06	8.85	8.80
	CT-10										8.17	8.31	8.33	8.53	8.60	8.77	8.92	8.61	8.61
	CT-15										8.16	8.31	8.33	8.53	8.61	8.77	8.67	8.29	8.26
A-3.6-CT-C-2	CT-2	8.18	8.23	8.31	8.58	8.64	8.47	8.71	8.75	8.92	8.83	8.94	8.90	8.90	8.90	8.58	8.57	8.55	8.54
	CT-5								8.72	8.87	8.84	8.96	8.90	8.90	8.91	8.58	8.55	8.56	8.56
	CT-10								8.68	8.74	8.68	8.78	8.17	8.11	8.06	7.65	7.65	7.69	7.75
	CT-15								7.95	7.96	7.47	7.53	7.39	7.41	7.45	7.18	7.10	7.07	7.09

Table B2.1 pH vs. Time (Continued)

Sample#	Depth(cm)	6/25/03	6/26/03	6/27/03	6/28/03	7/7/03	7/8/03	7/9/03	7/17/03	7/25/03	8/1/03	8/8/03	8/15/03	8/22/03	8/29/03	9/30/03	11/9/03	12/13/03	1/12/04
		1	2	3	4	13	14	15	23	31	38	45	52	59	66	98	138	172	202
A-6.3-DI-N-1	DI-2										6.51	6.30	6.02	5.76	5.41	4.46	4.44	4.31	4.18
	DI-5										6.41	6.13	5.95	5.74	5.38	4.47	4.42	4.31	4.20
	DI-10										6.34	6.16	5.93	5.49	5.05	4.46	4.38	4.28	4.20
	DI-15										6.27	6.00	5.45	4.97	4.71	4.45	4.31	4.26	4.20
A-6.3-DI-N-2	DI-2	6.34	6.30		6.38	6.20	6.12	6.18	5.98	5.50	5.48	5.49	5.34	5.07	4.93	4.47	4.31	4.36	4.28
	DI-5								5.90	5.46	5.42	5.46	5.19	4.98	4.80	4.47	4.31	4.35	4.28
	DI-10								5.57	5.30	5.16	5.17	4.88	4.80	4.68	4.45	4.30	4.32	4.28
	DI-15								5.20	5.02	4.93	4.85	4.66	4.67	4.61	4.44	4.33	4.35	4.31
A-6.3-DI-C-1	DI-2										6.35	6.10	5.96	5.48	5.32	4.70	4.69	4.75	4.79
	DI-5										6.33	6.03	5.78	5.38	5.25	4.68	4.68	4.75	4.78
	DI-10										6.29	6.14	5.70	5.35	5.14	4.67	4.68	4.75	4.78
	DI-15										6.16	6.03	5.68	5.32	5.12	4.65	4.61	4.77	4.77
A-6.3-DI-C-2	DI-2	6.03	6.09	6.56	6.50	6.09	6.00	6.26	6.01	5.25	5.31	5.31	5.06	4.98	4.81	4.53	4.50	4.39	4.38
	DI-5								5.95	5.19	5.24	5.30	5.04	4.96	4.80	4.55	4.50	4.39	4.35
	DI-10								5.88	5.17	5.20	5.20	5.04	4.86	4.74	4.54	4.48	4.39	4.34
	DI-15								5.60	5.10	5.13	5.04	4.78	4.75	4.66	4.56	4.48	4.41	4.35
A-6.3-CT-N-1	CT-2										8.15	8.34	8.49	8.84	8.92	8.62	8.58	8.61	8.58
	CT-5										8.21	8.33	8.55	8.83	8.92	8.65	8.50	8.57	8.53
	CT-10										8.19	8.30	8.14	8.22	8.28	7.97	7.73	7.63	7.67
	CT-15										8.10	7.97	7.84	7.95	7.95	7.64	7.45	7.28	7.28
A-6.3-CT-N-2	CT-2	8.06	8.09	8.20	8.73	8.73	8.83	8.94	8.81	8.88	8.94	8.98	8.82	8.79	8.81	8.60	8.57	8.52	8.32
	CT-5								8.81	8.88	8.75	8.97	8.68	8.72	8.83	8.62	8.56	8.29	8.25
	CT-10								8.06	7.97	7.85	7.78	7.82	7.84	7.80	7.56	7.32	7.33	7.35
	CT-15								7.35	7.44	7.40	7.47	7.38	7.44	7.40	7.25	7.18	7.15	7.10
A-6.3-CT-C-1	CT-2										8.06	8.23	8.46	8.73	8.78	8.92	8.62	8.48	8.45
	CT-5										8.10	8.27	8.48	8.78	8.82	8.92	8.60	8.43	8.37
	CT-10										8.13	8.28	8.49	8.81	8.86	8.41	8.14	7.53	7.42
	CT-15										8.15	8.13	8.05	8.18	8.21	7.70	7.46	7.27	7.22
A-6.3-CT-C-2	CT-2	8.19	8.20	8.37	8.60	8.63	8.66	8.70	8.79	8.80	8.93	8.89	8.72	8.83	8.82	8.84	8.70	8.40	8.43
	CT-5								8.78	8.80	8.90	8.91	8.72	8.82	8.82	8.84	8.68	8.40	8.39
	CT-10								8.78	8.38	8.56	8.60	8.37	8.40	8.33	7.56	7.69	7.58	7.34
	CT-15								8.00	7.69	7.50	7.49	7.54	7.48	7.40	7.17	7.38	7.12	7.07

Table B2.1 pH vs. Time (Continued)

Sample#	Depth(cm)	6/25/03	6/26/03	6/27/03	6/28/03	7/7/03	7/8/03	7/9/03	7/17/03	7/25/03	7/31/03	8/7/03	8/14/03	8/21/03	8/28/03	9/30/03	11/9/03	12/12/03	1/12/04
		1	2	3	4	13	14	15	23	31	37	44	51	58	65	98	138	171	202
A-9.1-DI-N-1	DI-2										6.03	6.13	6.32	6.16	5.97	5.17	4.37	4.44	4.34
	DI-5										6.06	6.15	6.23	6.14	5.53	5.13	4.66	4.44	4.33
	DI-10										6.06	6.18	6.18	5.79	5.15	4.77	4.58	4.39	4.31
	DI-15										6.03	5.95	5.95	4.96	4.80	4.58	4.51	4.30	4.31
A-9.1-DI-N-2	DI-2	6.53	6.44	6.81	6.80	6.15	6.11	6.05	5.93	5.28	5.11	5.32	5.14	4.98	5.00	4.75	4.37	4.34	4.27
	DI-5								5.79	5.26	5.11	5.27	5.08	4.96	4.99	4.73	4.37	4.34	4.27
	DI-10								5.56	5.17	5.06	5.16	5.04	4.89	4.94	4.59	4.34	4.31	4.26
	DI-15								5.17	4.99	4.87	5.01	4.88	4.76	4.70	4.48	4.32	4.30	4.26
A-9.1-DI-C-1	DI-2										6.72	6.03	5.83	5.60	5.46	7.12	6.40	5.39	5.07
	DI-5										6.57	5.97	5.73	5.55	5.32	7.01	6.30	5.35	5.05
	DI-10										6.42	5.97	5.69	5.52	5.24	6.92	6.13	5.28	5.05
	DI-15										6.36	5.94	5.68	5.50	5.25	6.88	5.40	5.19	4.95
A-9.1-DI-C-2	DI-2	6.08	6.07	6.35	6.35	6.65	6.26	6.39	5.88	5.94	5.87	5.32	5.15	5.15	4.98	4.90	4.75	4.61	4.44
	DI-5								5.87	5.80	5.74	5.33	5.12	5.09	4.88	4.82	4.73	4.57	4.44
	DI-10								5.70	5.60	5.38	5.09	5.00	5.06	4.86	4.75	4.66	4.55	4.40
	DI-15								5.49	5.30	5.12	4.96	4.95	4.94	4.84	4.70	4.64	4.52	4.34
A-9.1-CT-N-1	CT-2										8.15	8.27	8.70	8.76	8.90	8.86	8.59	8.49	8.49
	CT-5										8.17	8.26	8.71	8.79	8.95	8.69	8.60	8.30	8.44
	CT-10										8.18	8.25	8.26	8.28	8.33	7.64	7.46	7.47	7.53
	CT-15										8.09	7.87	8.02	8.01	8.05	7.23	7.22	7.24	7.20
A-9.1-CT-N-2	CT-2	8.02	8.05	8.21	8.68	8.77	8.76	8.82	8.81	8.84	8.84	8.92	8.92	8.69	8.82	8.81	8.59	8.25	8.31
	CT-5								8.80	8.61	8.66	8.67	8.67	8.68	8.81	8.71	8.51	8.23	8.08
	CT-10								8.07	7.93	7.73	7.75	7.78	7.87	7.85	7.41	7.38	7.40	7.36
	CT-15								7.37	7.41	7.35	7.41	7.43	7.44	7.48	7.23	7.18	7.20	7.13
A-9.1-CT-C-1	CT-2										8.12	8.00	8.16	8.70	8.74	8.94	9.06	8.68	8.79
	CT-5										8.15	8.05	8.24	8.74	8.78	8.98	9.04	8.76	8.75
	CT-10										8.15	8.10	8.31	8.74	8.84	8.82	8.10	7.91	7.62
	CT-15										8.15	8.03	8.09	8.39	8.44	8.32	7.61	7.34	7.25
A-9.1-CT-C-2	CT-2	8.07	8.21	8.34	8.39	8.69	8.67	8.61	8.55	8.82	8.81	8.76	8.95	8.96	8.94	8.67	8.60	8.58	8.63
	CT-5								8.54	8.81	8.82	8.80	8.96	8.97	8.97	8.68	8.40	8.50	8.61
	CT-10								8.50	8.79	8.83	8.81	8.97	8.97	8.97	7.94	7.52	7.55	7.60
	CT-15								8.54	8.77	8.59	8.37	7.65	7.55	7.53	7.21	7.11	7.10	7.08

Table B2.1 pH vs. Time (Continued)

Sample#	Depth(cm)	6/25/03	6/26/03	6/27/03	6/28/03	7/7/03	7/8/03	7/9/03	7/17/03	7/25/03	7/31/03	8/7/03	8/14/03	8/21/03	8/28/03	9/29/03	11/8/03	12/12/03	1/12/04
A-24.9-DI-N-1	DI-2	6.11	5.99	6.20	6.42	6.32	6.44	6.47	6.28	6.30	6.48	6.28	6.20	6.34	6.33	6.10	5.81	5.38	5.17
	DI-5								6.21	6.15	6.17	6.15	6.15	6.34	6.20	5.93	5.70	5.34	5.13
	DI-10								6.05	5.98	5.91	5.90	5.92	5.98	5.93	5.69	5.49	5.21	5.07
	DI-15								5.88	5.95	5.90	5.89	5.82	5.89	5.91	5.68	5.49	5.16	5.02
A-24.9-DI-N-2	DI-2	6.04	5.80	5.98	6.10	5.92	6.14	6.23	6.35	6.28	6.45	6.29	6.22	6.23	6.15	6.12	5.78	5.36	5.28
	DI-5								6.22	6.11	6.15	6.00	6.02	6.15	6.10	5.93	5.62	5.35	5.17
	DI-10								6.02	5.92	5.92	5.78	5.85	5.88	5.85	5.47	5.26	5.16	5.07
	DI-15								5.93	5.89	5.90	5.66	5.83	5.81	5.82	5.60	5.24	5.14	5.00
A-24.9-DI-C-1	DI-2	6.02	5.91	6.25	6.19	5.89	6.00	5.98	5.84	5.64	5.63	5.74	5.78	5.78	5.81	5.52	5.12	4.82	4.65
	DI-5								5.80	5.62	5.60	5.71	5.76	5.71	5.76	5.40	5.10	4.80	4.62
	DI-10								5.77	5.67	5.60	5.64	5.67	5.63	5.68	5.25	4.83	4.65	4.56
	DI-15								5.58	5.58	5.58	5.58	5.62	5.60	5.61	5.01	4.67	4.56	4.54
A-24.9-DI-C-2	DI-2	6.08	6.07	6.21	6.36	5.91	6.04	5.88	6.17	5.80	5.74	5.79	5.94	5.80	5.80	5.62	5.14	5.10	4.80
	DI-5								6.00	5.80	5.73	5.78	5.88	5.79	5.86	5.52	5.14	5.10	4.76
	DI-10								6.10	5.72	5.65	5.70	5.84	5.70	5.80	5.42	5.00	4.83	4.70
	DI-15								5.91	5.66	5.59	5.63	5.76	5.66	5.71	5.22	4.81	4.70	4.63
A-24.9-CT-N-1	CT-2	8.01	8.22	8.30	8.45	8.52	8.48	8.54	8.77	8.78	8.88	8.76	8.96	8.95	8.97	8.80	8.61	8.56	8.58
	CT-5								8.71	8.75	8.78	8.67	8.90	8.90	8.90	8.48	8.54	8.46	8.44
	CT-10								8.40	8.45	8.43	8.10	8.16	8.10	8.08	7.66	7.65	7.69	7.70
	CT-15								7.94	7.70	7.54	7.46	7.53	7.57	7.53	7.39	7.32	7.37	7.32
A-24.9-CT-N-2	CT-2	8.01	8.15	8.42	8.54	8.69	8.65	8.45	8.70	8.68	8.85	8.76	8.55	8.90	8.95	8.70	8.63	8.59	8.56
	CT-5								8.61	8.65	8.74	8.70	8.84	8.89	8.79	8.45	8.47	8.34	8.23
	CT-10								8.27	8.32	8.20	8.14	7.97	8.08	8.00	7.67	7.57	7.62	7.68
	CT-15								7.90	7.76	7.50	7.48	7.49	7.57	7.56	7.33	7.31	7.38	7.38
A-24.9-CT-C-1	CT-2	8.14	8.15	8.32	8.64	8.88	8.85	8.89	8.91	8.90	8.83	8.88	8.98	8.76	8.96	8.86	8.68	8.64	8.58
	CT-5								8.91	8.91	8.84	8.89	8.97	8.92	8.97	8.82	8.57	8.64	8.24
	CT-10								8.68	8.48	8.15	8.20	8.38	8.42	8.34	7.74	7.47	7.50	7.34
	CT-15								7.54	7.52	7.50	7.40	7.44	7.43	7.50	7.18	7.14	7.14	7.08
A-30.7-CT-C-2	CT-2	8.16	8.22	8.36	8.51	8.88	8.81	8.85	8.92	8.88	8.62	8.82	8.84	8.84	9.04	8.90	8.56	8.56	8.56
	CT-5								8.92	8.90	8.66	8.82	8.83	8.87	9.06	8.85	8.55	8.46	8.38
	CT-10								8.48	8.14	8.47	8.19	8.45	8.24	8.53	7.60	7.72	7.53	7.45
	CT-15								7.50	7.53	7.42	7.38	7.47	7.52	7.57	7.12	7.14	7.14	7.10

Table B2.1 pH vs. Time (continued)

	11/25/03	12/2/03	12/9/03	12/16/03	12/23/03	1/4/04	1/12/04	1/26/04	3/2/04
Time (day)	1	8	15	22	29	41	49	63	99
N-10-DI-1	6.07	5.69	5.6	5.61	5.7	5.71	5.69	5.69	5.61
N-10-DI-2	6.08	5.67	5.24	4.94	4.65	4.35	4.33	4.27	4.69
N-10-CT-1	8.29	9.12	9.18	9.19	9.3	9.19	9.15	9.07	9.18
N-10-CT-2	8.28	9.12	9.17	9.19	9.3	9.19	9.13	9.08	9.18
N-20-DI-1	6.07	5.5	5.26	5.13	4.57	4.24	4.28	4.28	4.94
N-20-DI-2	6.05	5.6	5.26	5.03	4.77	4.53	4.6	4.72	5.63
N-20-CT-1	8.3	9.11	9.19	9.19	9.3	9.19	9.14	9.07	9.17
N-20-CT-2	8.31	9.1	9.16	9.07	9.21	9.07	9.04	8.96	9.04
N-30-DI-1	5.82	5.37	4.93	4.67	4.51	4.33	4.13	4.17	4.77
N-30-DI-2	5.77	5.3	4.89	4.62	4.64	4.3	4.14	4.18	4.84
N-30-CT-1	8.29	9.16	9.23	9.19	9.33	9.2	9.13	9.01	9.02
N-30-CT-2	8.28	9.16	9.23	9.22	9.35	9.23	9.21	9.07	9.2
N-40-DI-1	5.81	5.72	5.22	4.77	4.48	4.35	4.31	4.28	4.18
N-40-DI-2	5.84	5.6	5.0	4.7	4.54	4.27	4.21	4.22	4.78
N-40-CT-1	8.32	9.1	9.17	9.2	9.29	9.18	9.14	9.05	9.2
N-40-CT-2	8.31	9.1	9.18	9.19	9.29	9.19	9.15	9.1	9.16
N-50-DI-1	5.84	5.5	4.96	4.7	4.51	4.38	4.3	4.31	4.87
N-50-DI-2	5.86	5.43	4.97	4.87	4.85	5.1	5.41	5.4	5.61
N-50-CT-1	8.45	9.16	9.22	9.21	9.34	9.21	9.14	9.02	9.15
N-50-CT-2	8.46	9.19	9.2	9.2	9.32	9.21	9.18	9.01	9.11

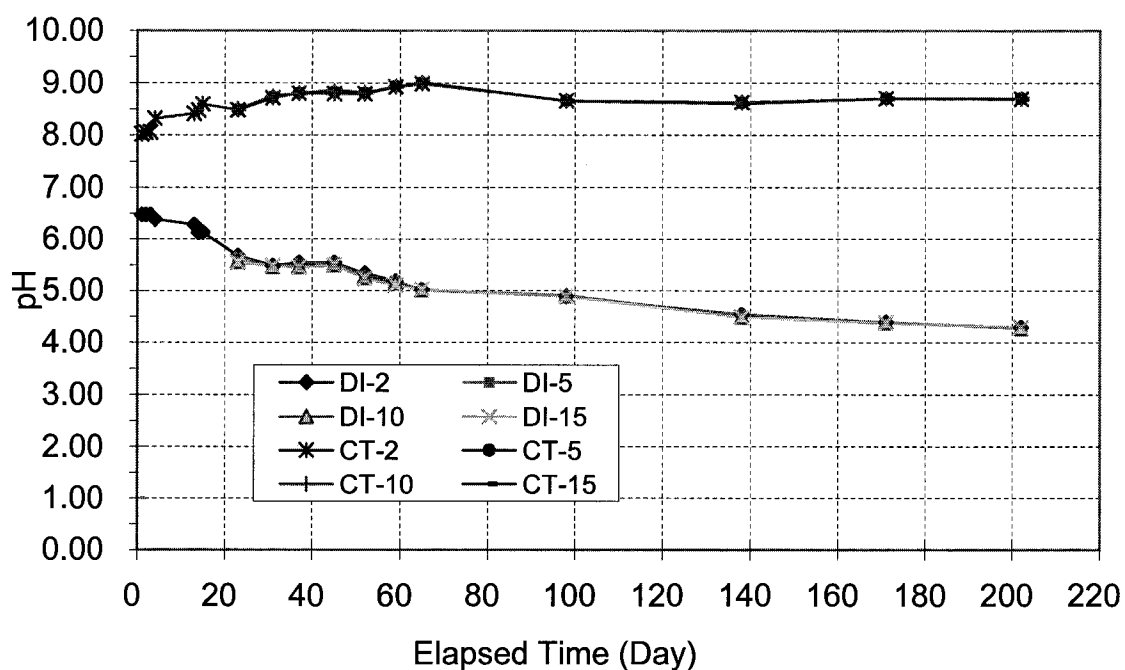


Fig.B2.1 pH - Time (A- 0-DI-1,A- 0-CT-1)

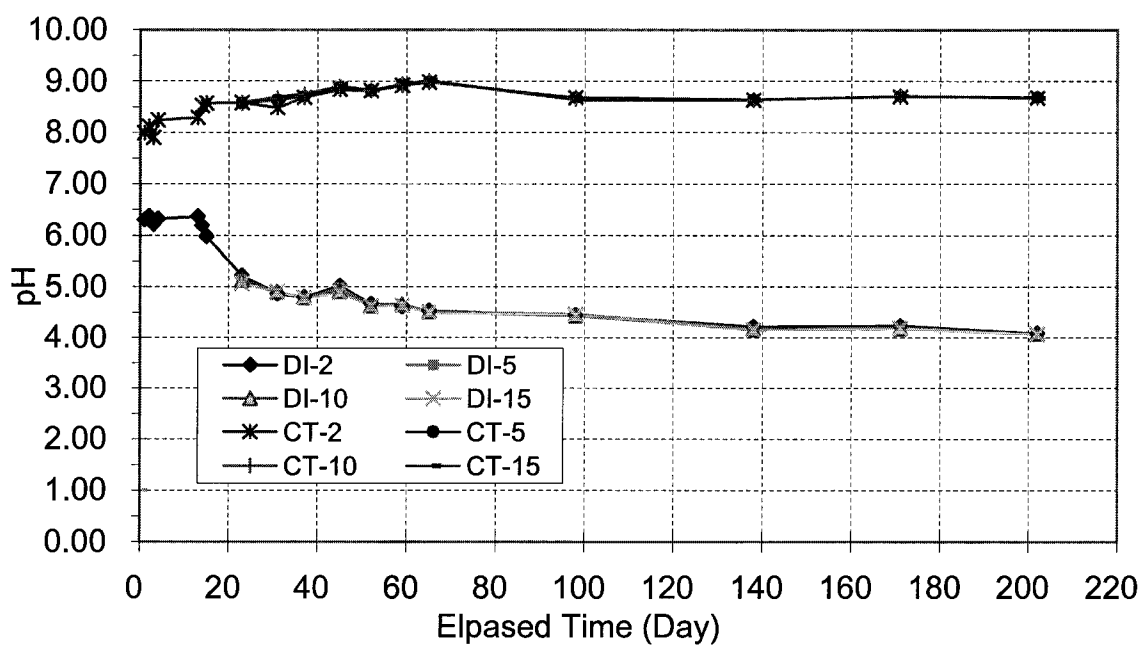


Fig. B2.2 pH - Time (A-0-DI-2, A-0-CT-2)

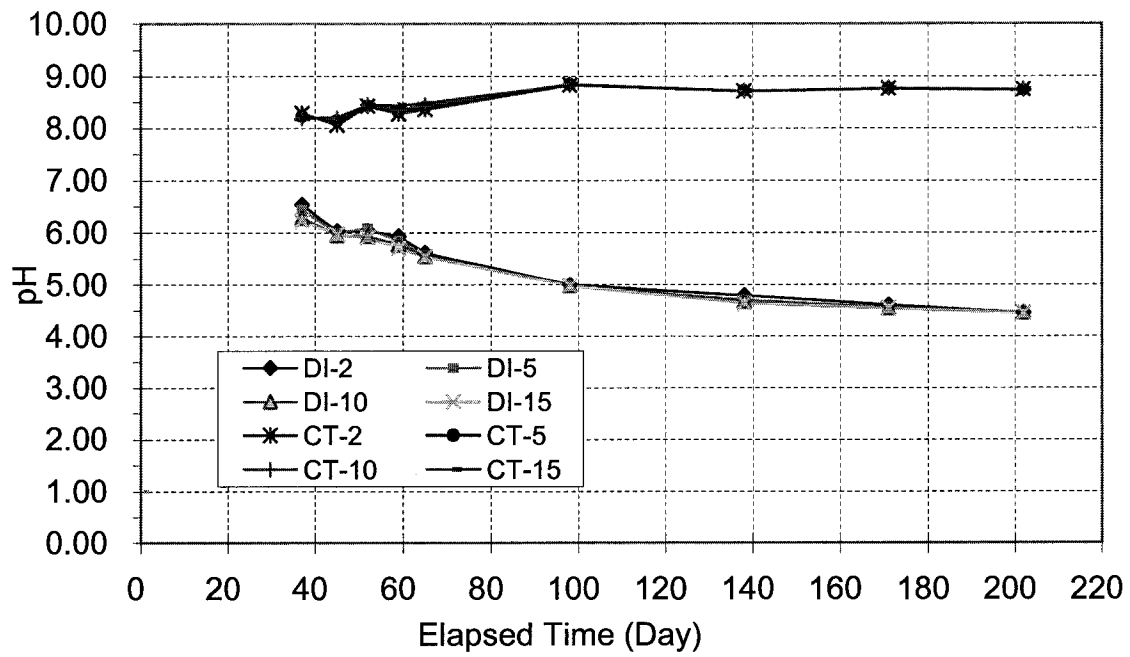


Fig. B2.3 pH - Time (A-0-DI-3, A-0-CT-3)

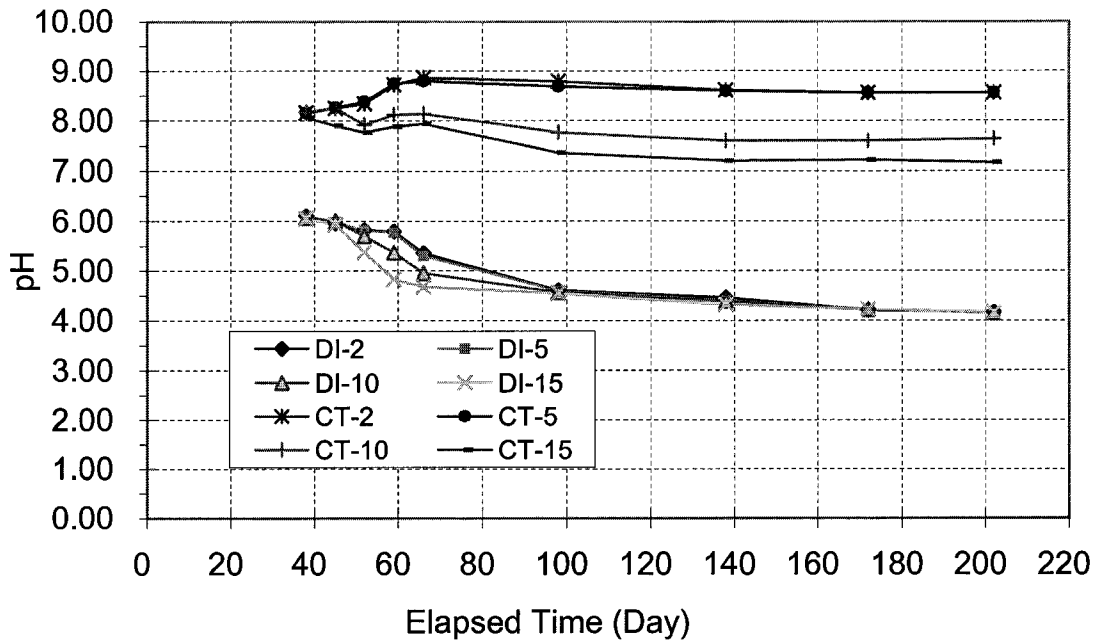


Fig.B2.4 pH - Time (A-3.6-DI-N-1, A-3.6-CT-N-1)

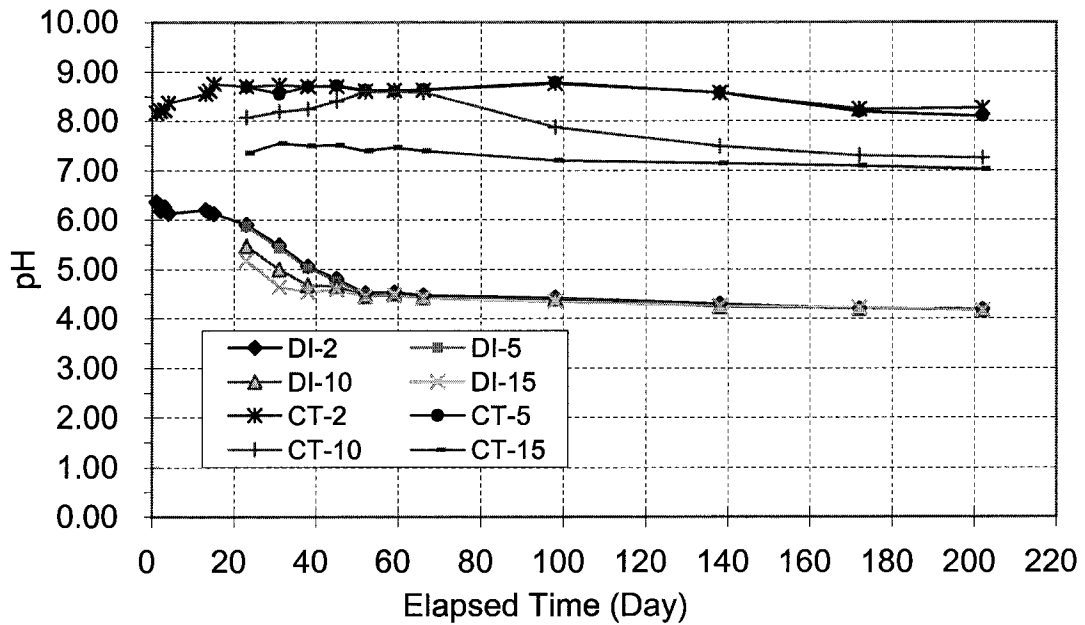


Fig. B2.5 pH - Time (A- 3.6-DI-N-2, A-3.6-CT-N-2)

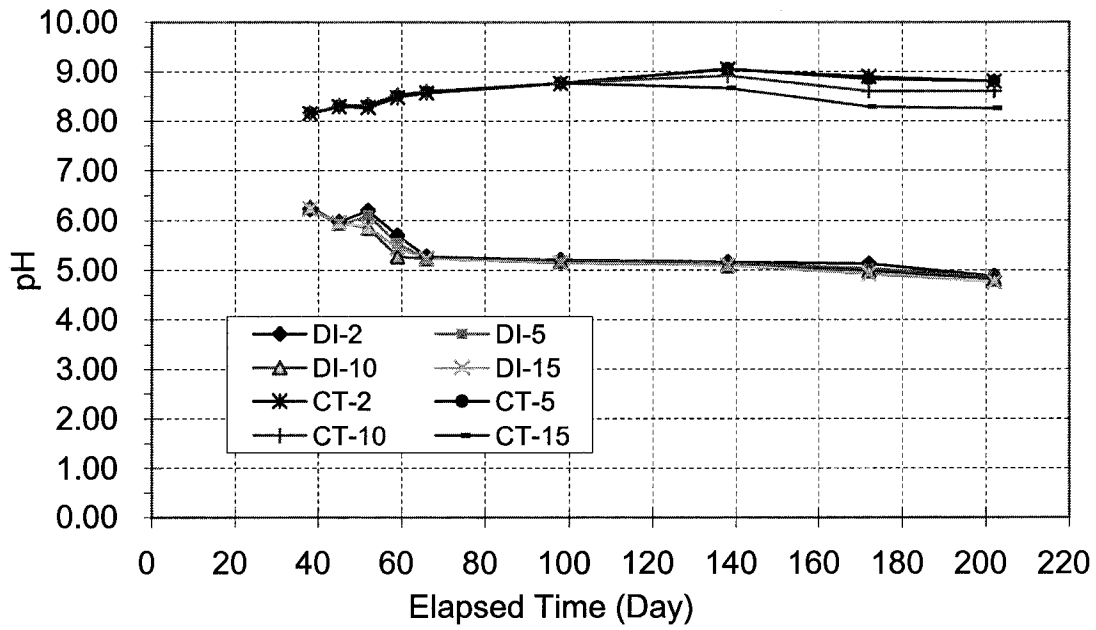


Fig. B2.6 pH - Time (A-3.6-DI-C-1, A-3.6-CT-C-1)

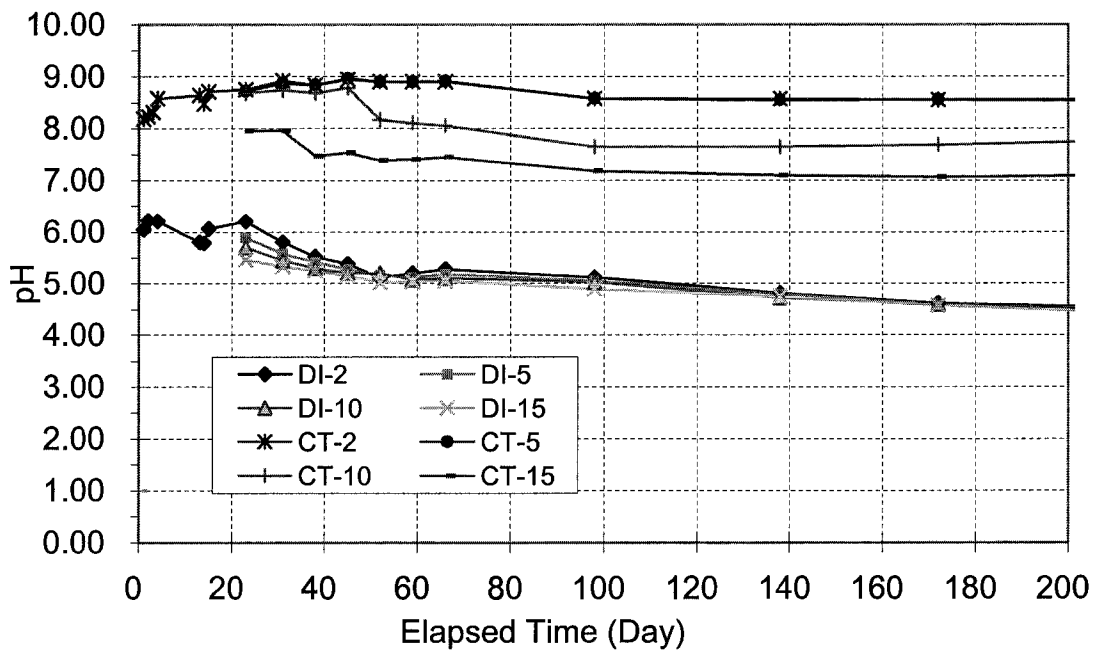


Fig. B2.7 pH - Time (A-3.6-DI-C-2, A-3.6-CT-C-2)

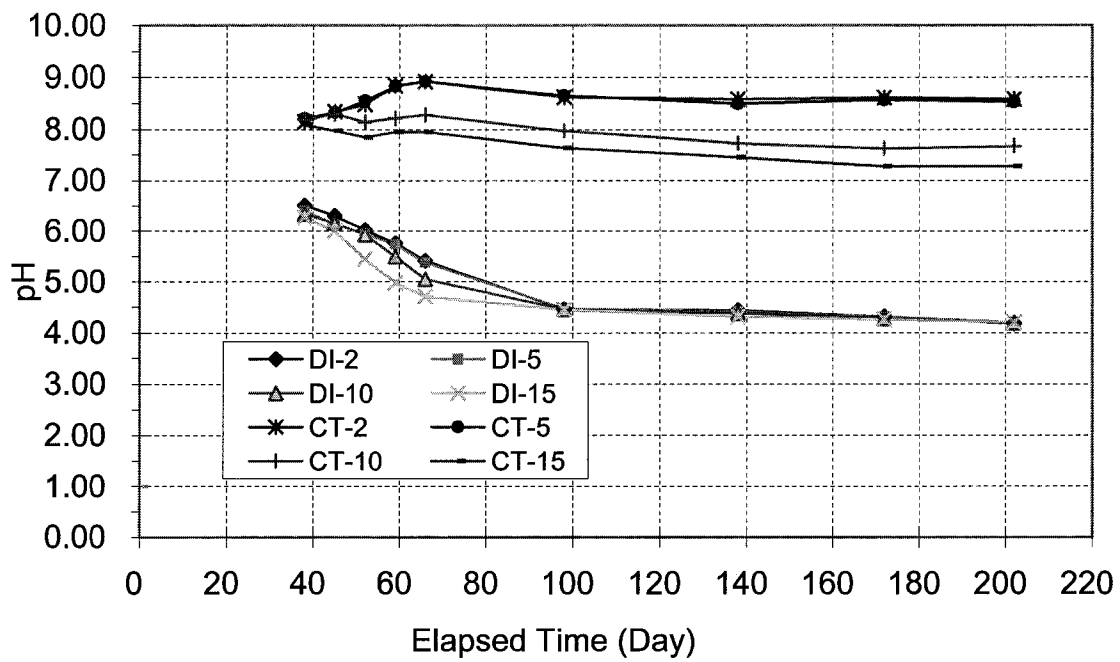


Fig. B2.8 pH - Time (A-6.3-DI-N-1, A-6.3-CT-N-1)

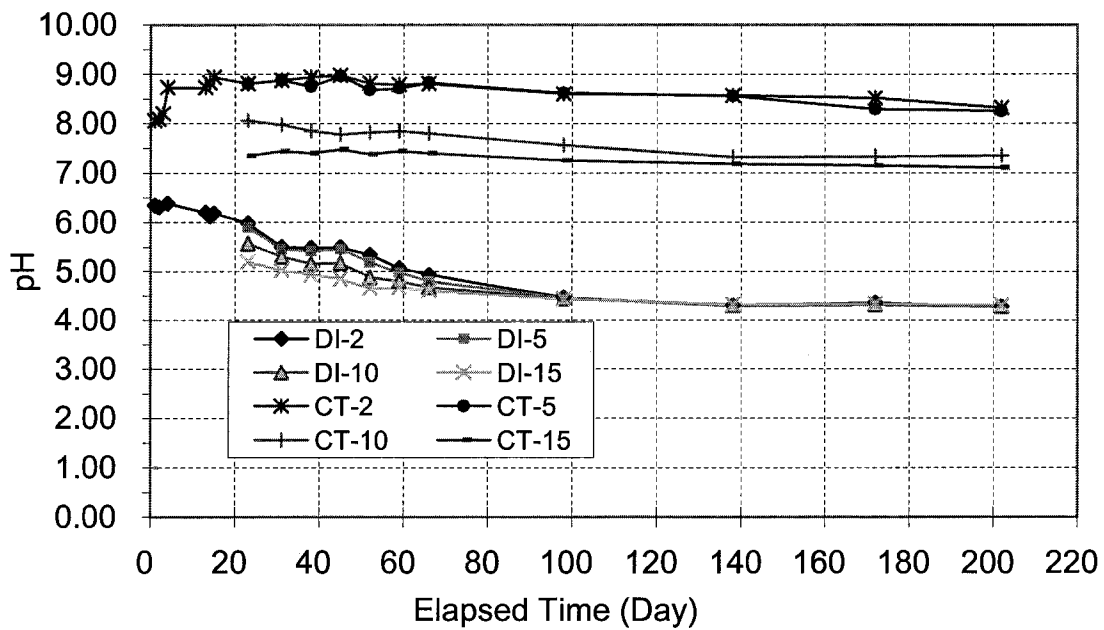


Fig. B2.9 pH - Time (A-6.3-DI-N-2, A-6.3-CT-N-2)

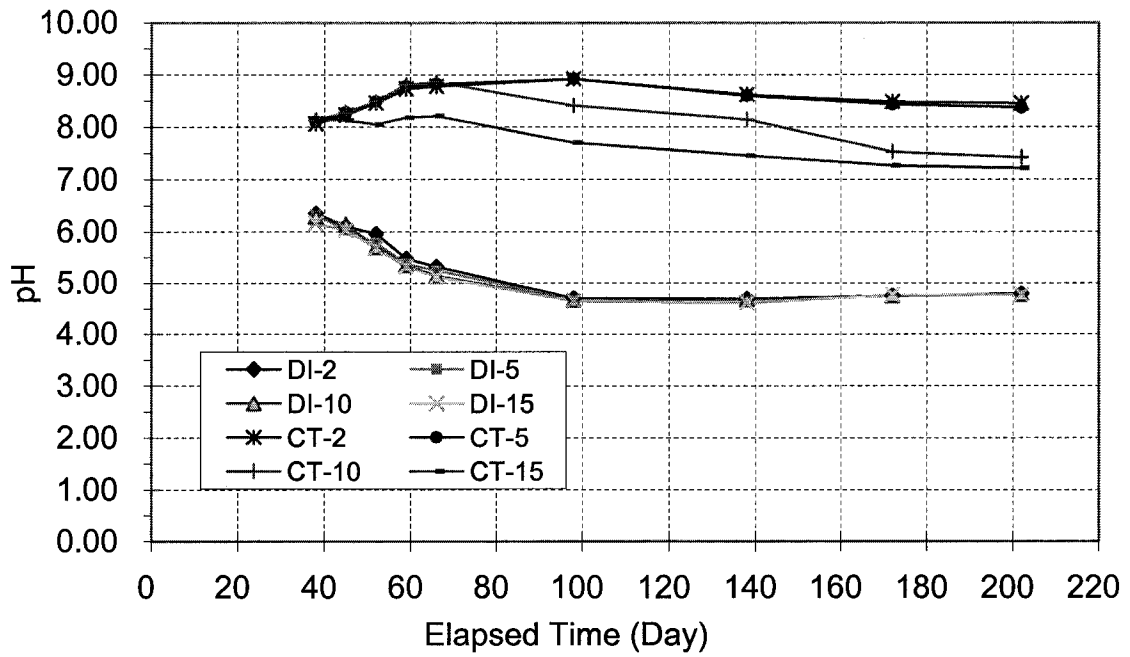


Fig. B2.10 pH - Time (A-6.3-DI-C-1, A-6.3-CT-C-1)

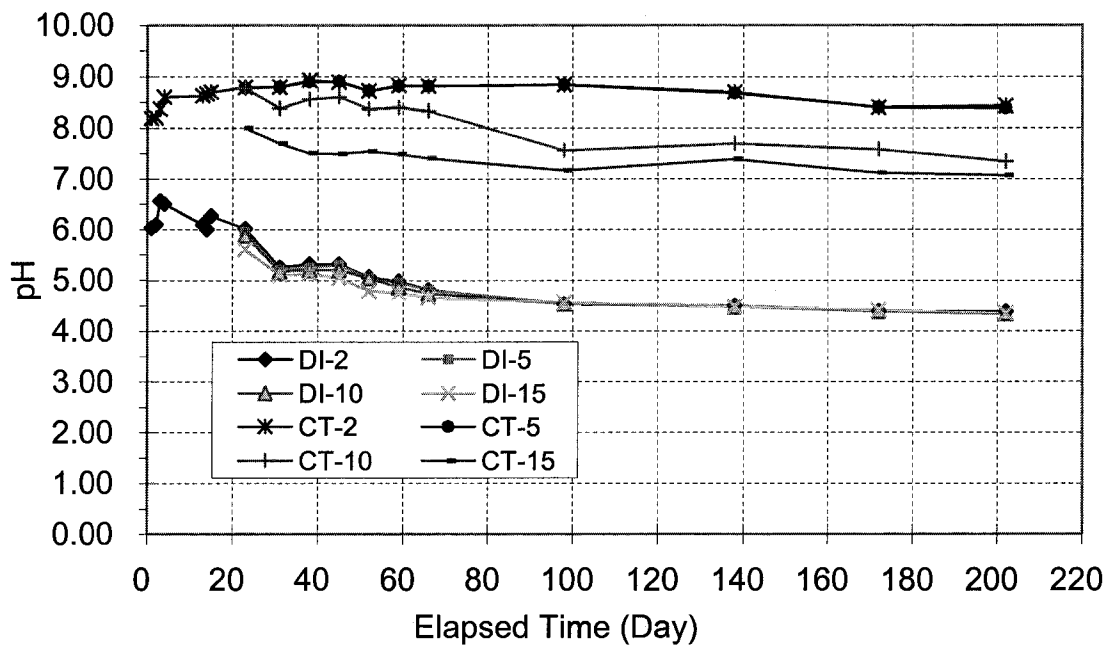


Fig. B2.11 pH - Time (A-6.3-DI-C-2, A-6.3-CT-C-2)

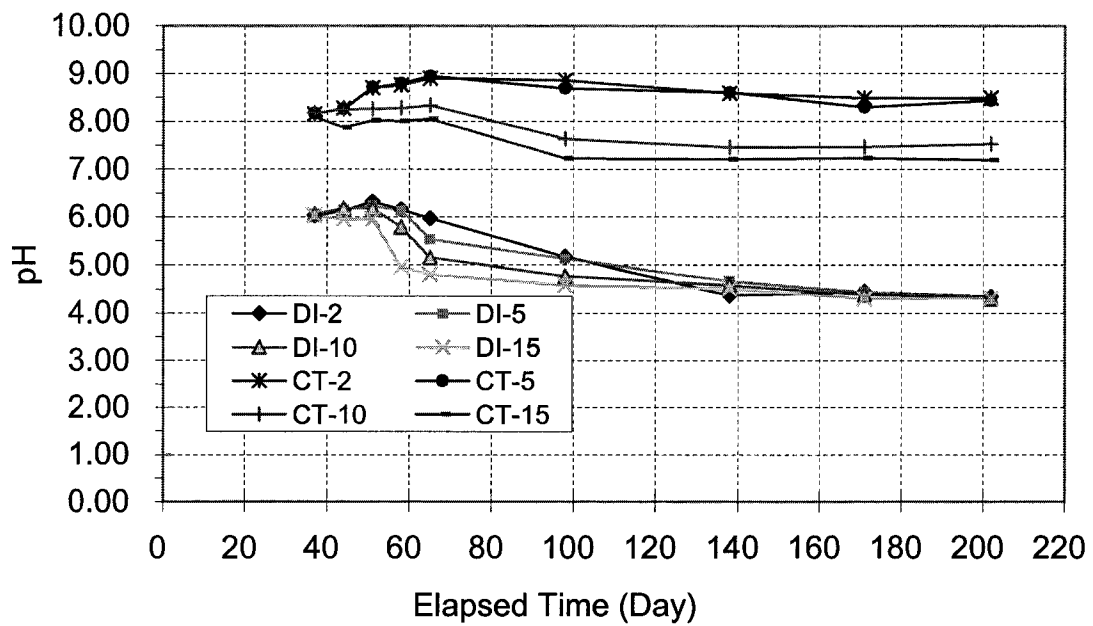


Fig.B2.12 pH - Time (A-9.1-DI-N-1, A-9.1-CT-N-1)

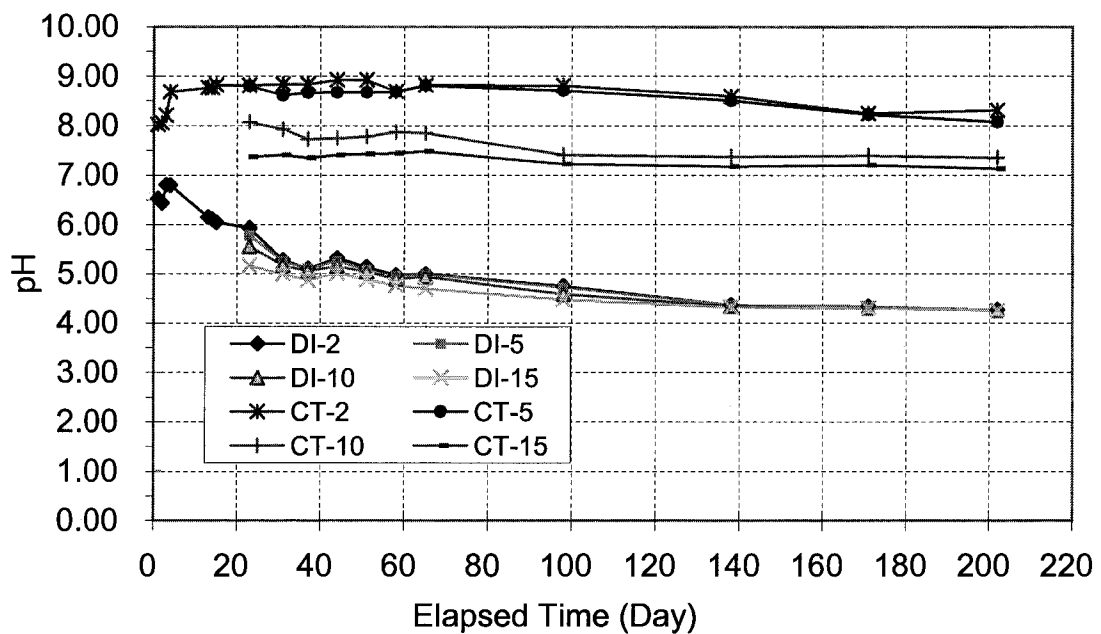


Fig. B2.13 pH - Time (A-9.1-DI-N-2, A-9.1-CT-N-2)

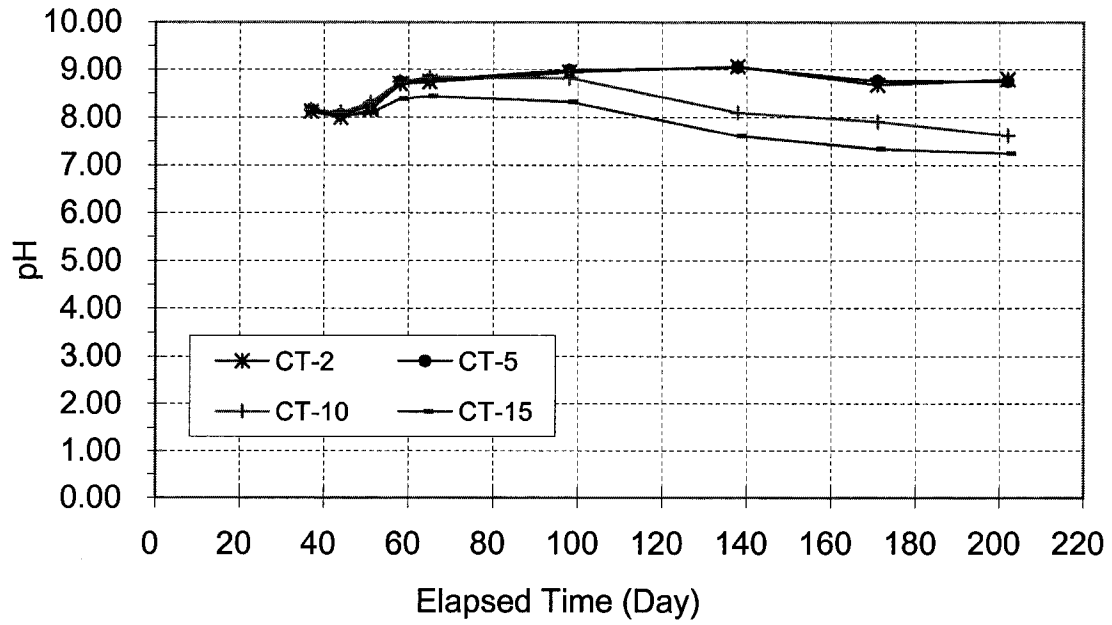


Fig. B2.14 pH - Time (A-9.1-CT-C-1)

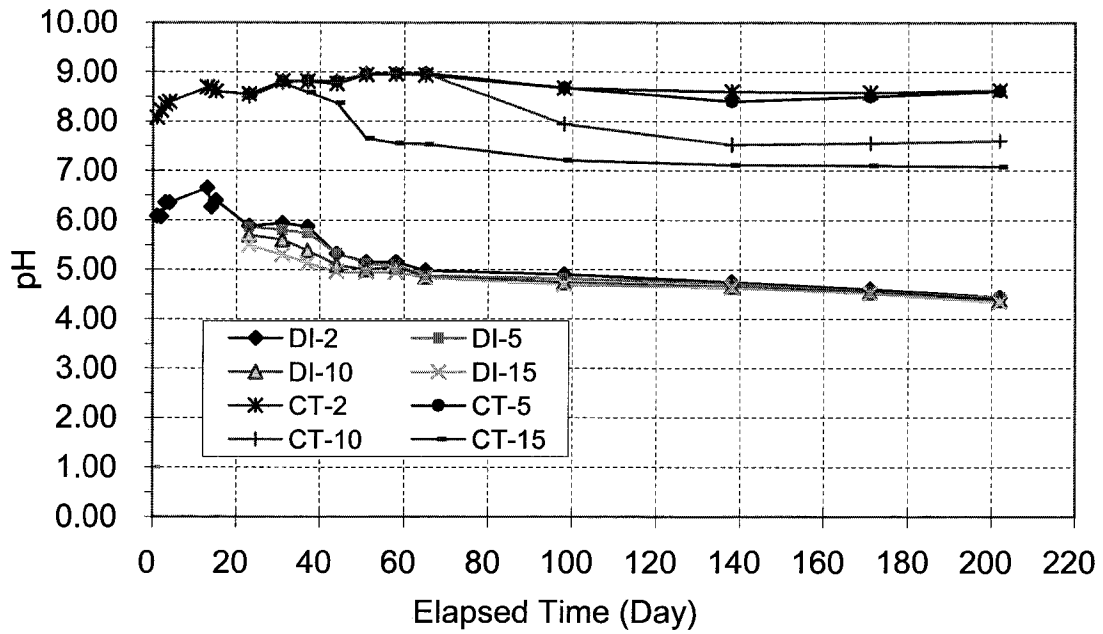


Fig. B2.15 pH - Time (A-9.1-DI-C-2, A-9.1-CT-C-2)

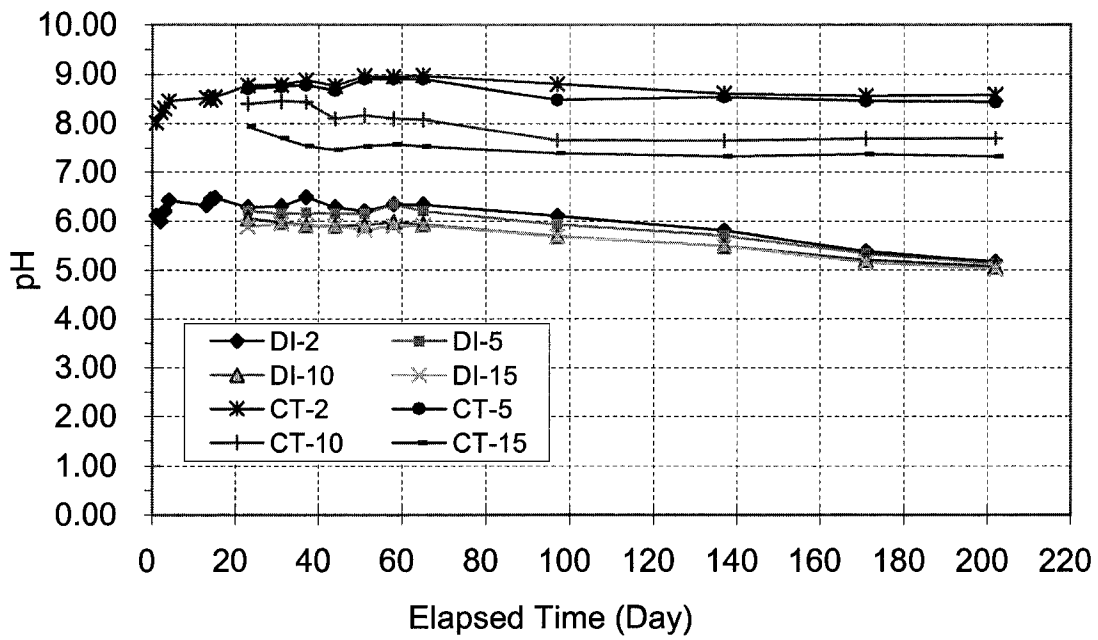


Fig. B2.16 pH - Time (A-24.9-DI-N-1, A-24.9-CT-N-1)

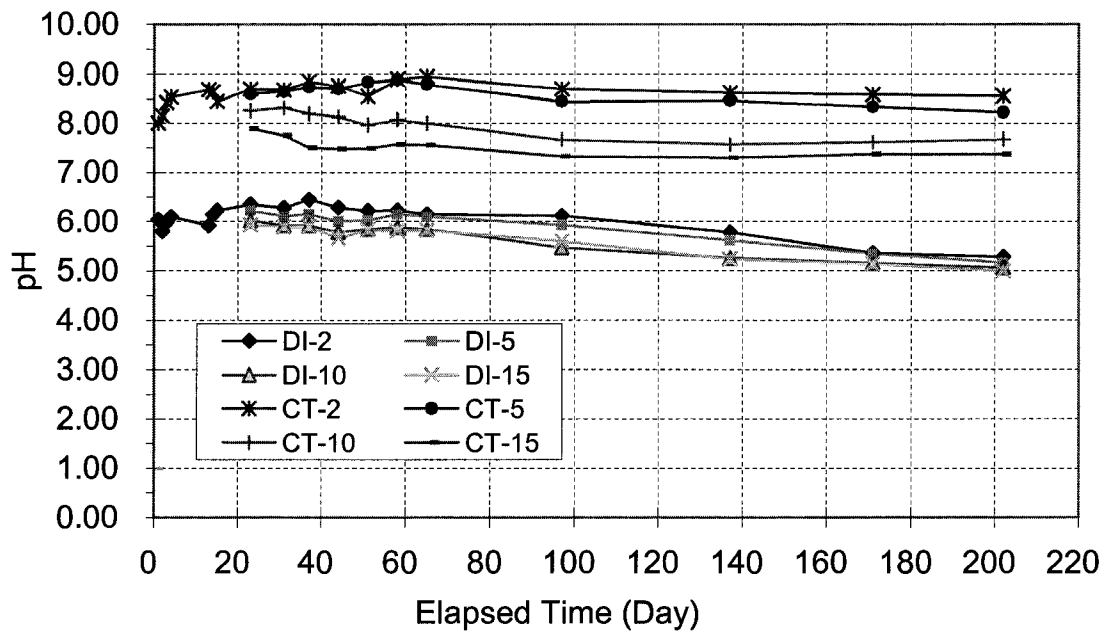


Fig. B2.17 pH - Time (A-24.9-DI-N-2, A-24.9-CT-N-2)

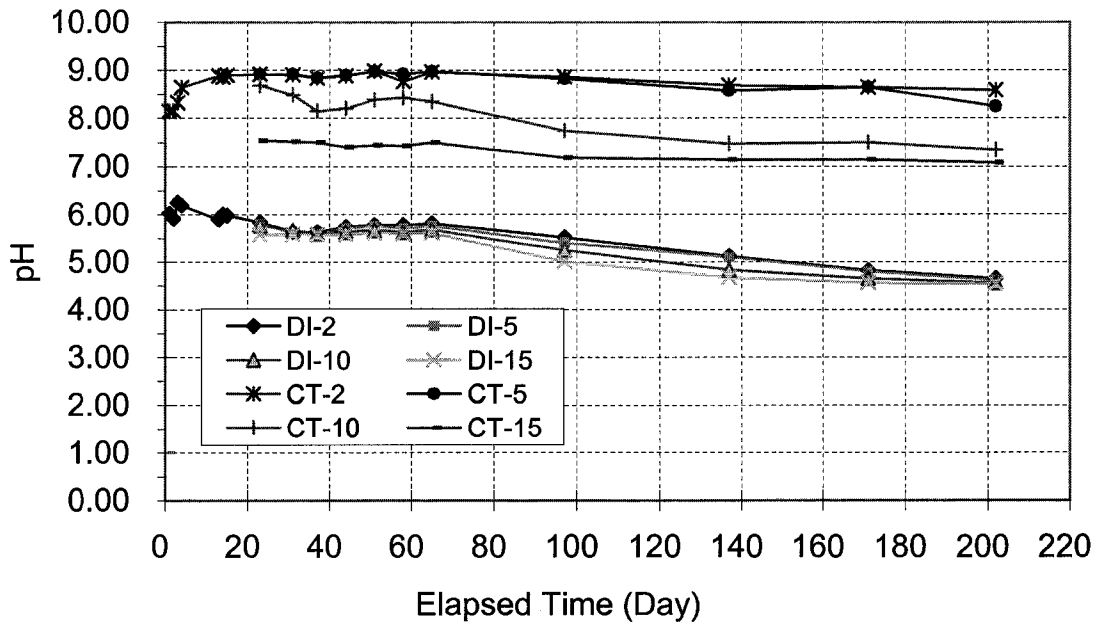


Fig.B2.18 pH - Time (A-24.9-DI-C-1, A-24.9-CT-C-1)

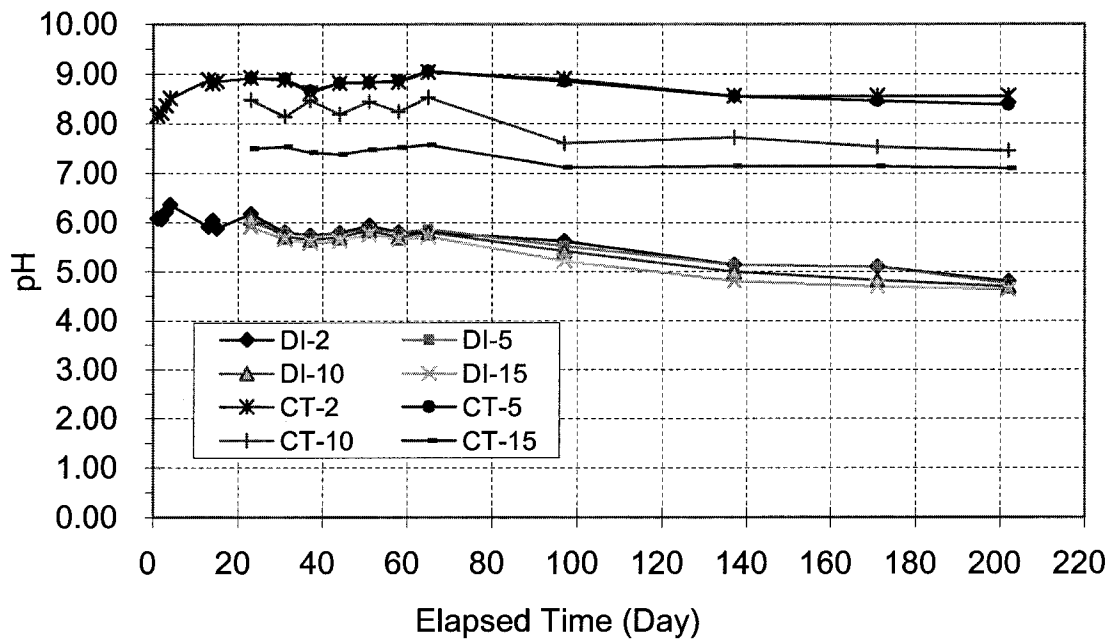


Fig. B2.19 pH - Time (A-24.9-DI-C-2, A-30.7-CT-C-2)

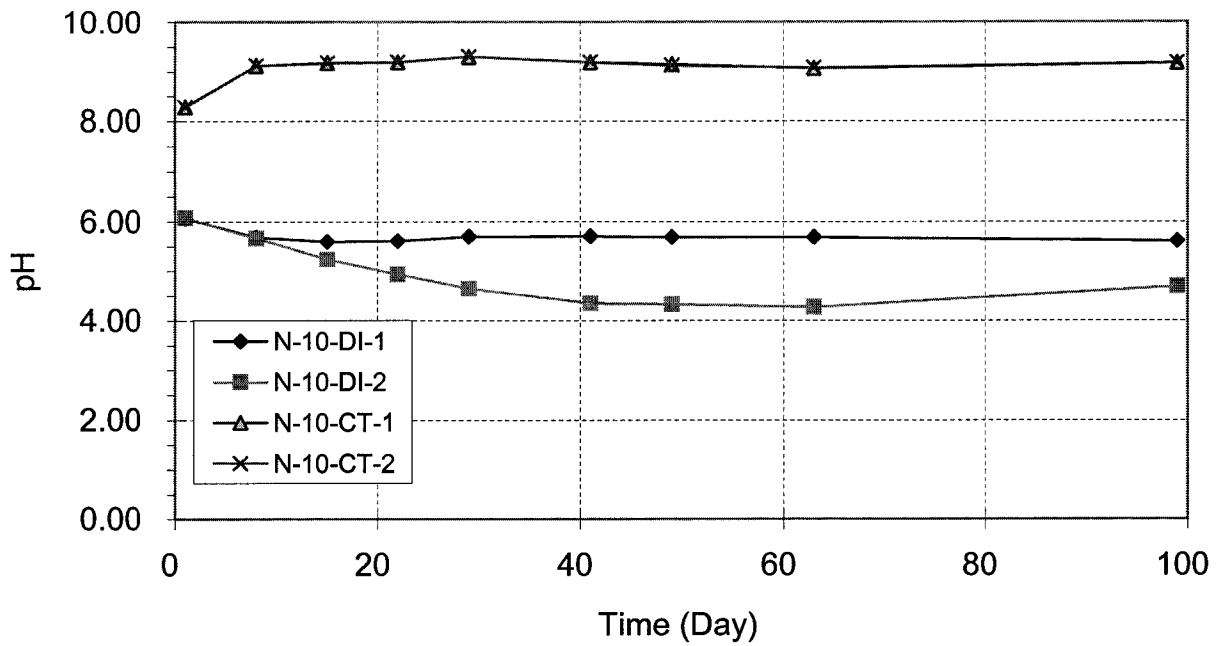


Fig. B2.20 pH -Time (10% Salt)

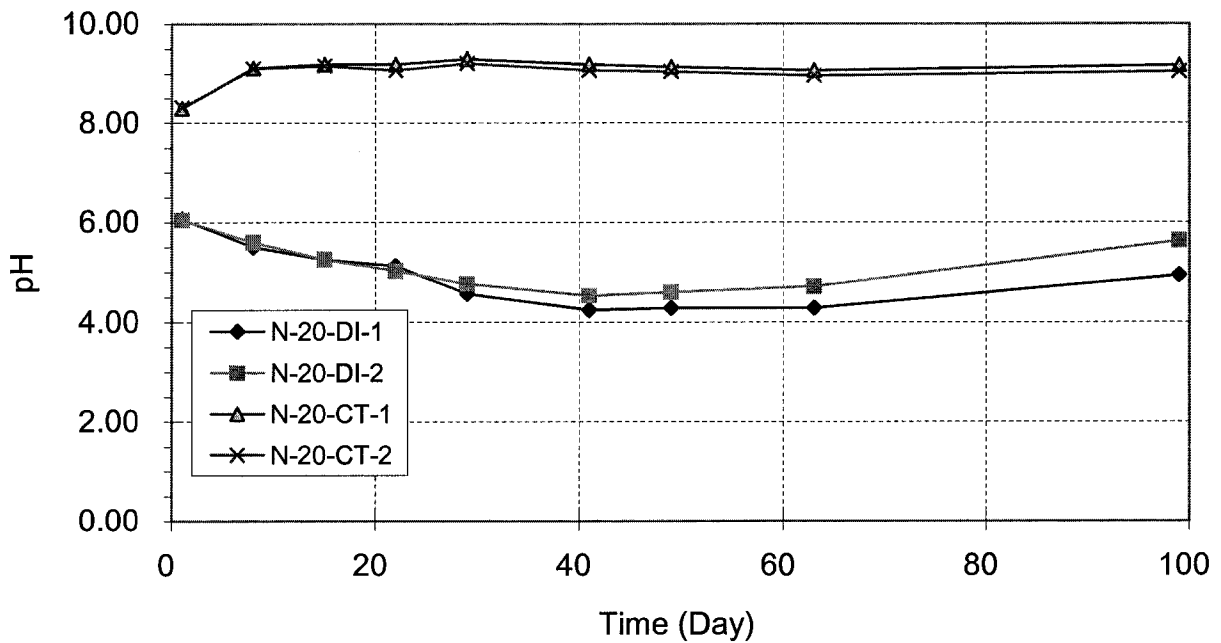


Fig. B2.21 pH -Time (20% Salt)

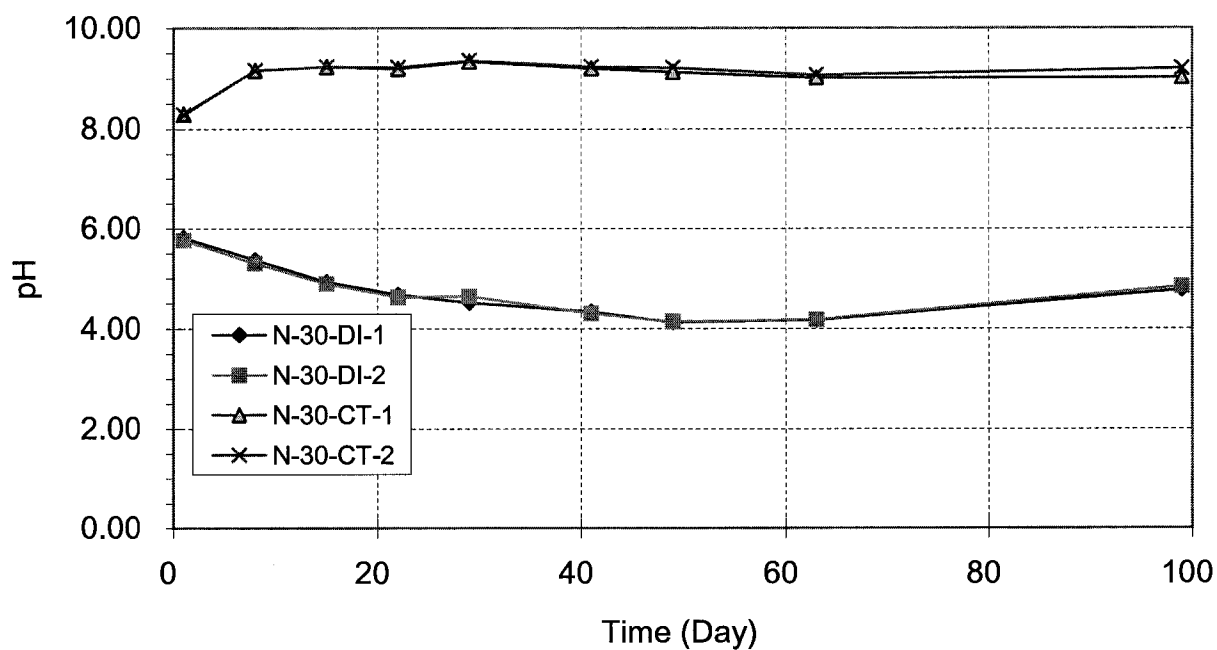


Fig. B2.22 EC -Time (30% Salt)

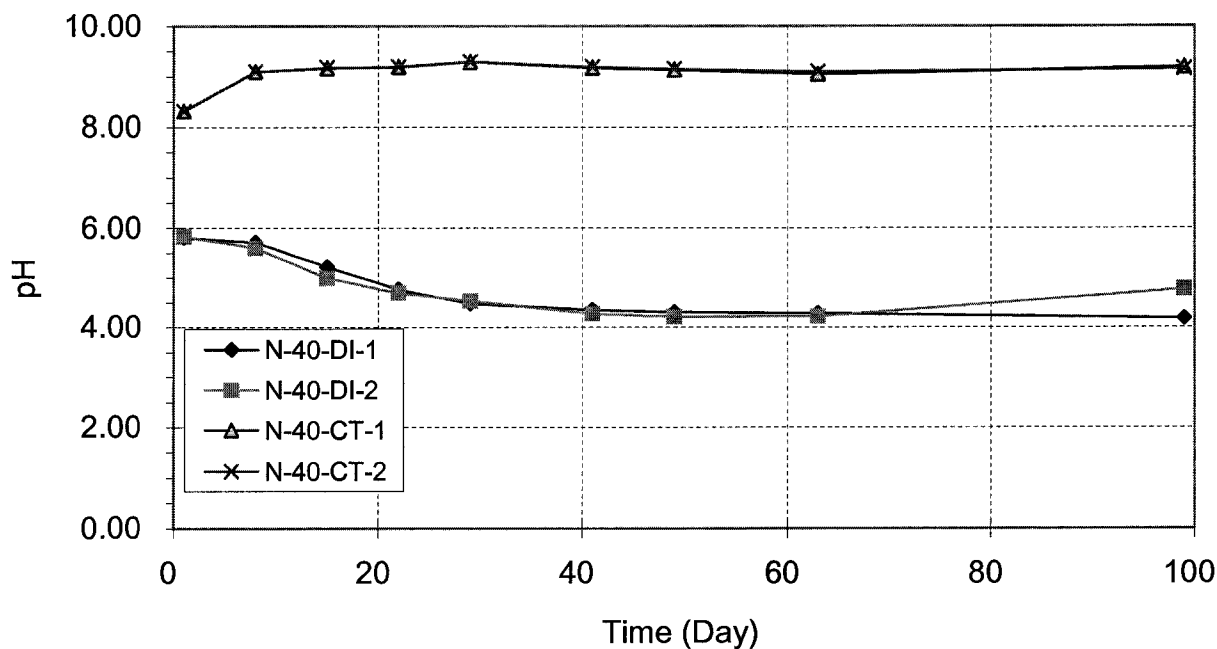


Fig. B2.23 pH-Time (40% Salt)

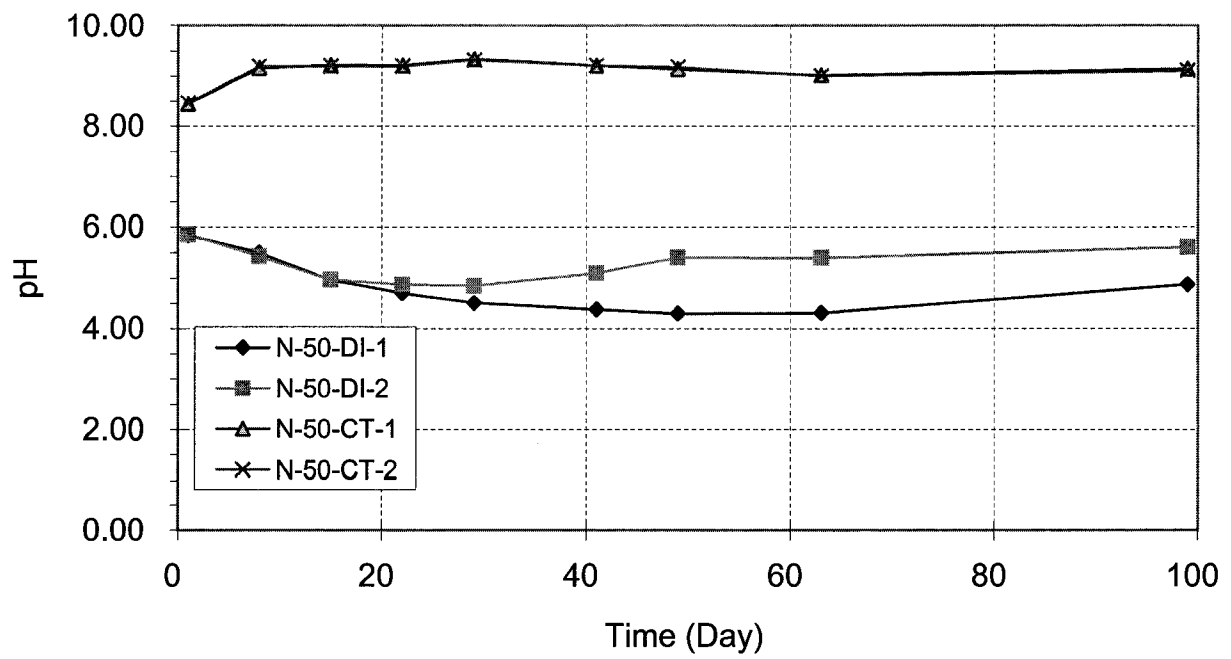


Fig. B2.24 pH -Time (50% Salt)

Table B3.1 DO (mg/L) vs. Time (day)

Sample#	Depth(cm)	6/26/03	6/27/03	6/28/03	7/7/03	7/8/03	7/9/03	7/22/03	8/1/03	8/8/03	8/15/03	8/22/03	8/28/03	9/30/03	11/9/03	12/12/03
		1	2	3	12	13	14	27	37	44	51	58	64	97	137	170
A-0-DI-1	DI-2	4.53		4.80	5.55	4.84	4.98	6.16	7.00	7.40	7.25	7.25	7.25			
	DI-5							5.89	6.90	7.35	7.20	7.20	7.20	7.80	8.30	8.20
	DI-10							5.99	7.10	7.35	7.30	7.35	7.20	7.70	8.20	8.20
	DI-15							6.14	7.10	7.40	7.20	7.60	7.60	7.50	8.20	8.20
A-0-DI-2	DI-2	4.78		4.92	5.36	5.26	5.11	6.27	7.10	7.40	7.00	7.35	7.25			
	DI-5							6.01	7.00	7.25	7.00	7.25	7.15	7.70	8.20	8.30
	DI-10							6.08	7.20	7.25	7.05	7.60	7.20	7.60	8.20	8.30
	DI-15							5.90	7.40	7.40	7.00	7.60	7.50	7.50	8.20	8.30
A-0-DI-3	DI-2								6.10	7.00	7.10	7.35	7.20			
	DI-5								5.90	7.00	7.10	7.30	7.20	7.80	8.20	8.30
	DI-10								5.90	7.00	7.10	7.40	7.40	7.70	8.10	8.20
	DI-15								6.00	7.00	7.10	7.50	7.60	7.50	8.00	8.20
A-0-CT-1	CT-2	2.31		2.14	2.78	2.87	2.96	4.58	5.60	5.70	6.00	5.80	6.00			
	CT-5							4.47	5.30	5.65	5.70	5.80	6.00	6.10	7.00	7.20
	CT-10							4.40	5.30	5.65	5.90	5.75	5.95	6.10	7.00	7.10
	CT-15							4.28	5.40	5.70	5.90	5.80	6.00	6.00	7.00	7.10
A-0-CT-2	CT-2	2.14		2.08	2.71	3.25	3.45	5.02	5.90	5.85	6.00	5.80	5.95			
	CT-5							4.71	5.80	5.80	5.80	5.70	5.80	6.30	7.00	7.20
	CT-10							4.40	5.70	5.70	5.90	5.70	5.80	6.10	7.00	7.10
	CT-15							4.53	5.60	5.70	6.10	5.90	5.80	5.90	7.00	7.00
A-0-CT-3	CT-2								1.60	0.60	3.90	3.90	4.20			
	CT-5								1.50	0.50	3.70	3.80	4.10	6.30	7.00	7.20
	CT-10								1.50	0.50	3.85	3.80	4.10	6.30	7.00	7.10
	CT-15								1.60	0.60	3.90	3.80	4.30	6.20	6.90	7.10

Table B3.1 DO (mg/L) vs. Time (day) (continued)

Sample#	Depth(cm)	6/26/03	6/27/03	6/28/03	7/7/03	7/8/03	7/9/03	7/22/03	8/1/03	8/8/03	8/15/03	8/22/03	8/29/03	9/30/03	11/9/03	12/13/03
		1	2	3	12	13	14	27	37	44	51	58	65	97	137	171
A-3.6-DI-N-1	DI-2								5.90	7.00	6.70	7.30	7.20			
	DI-5								5.90	7.00	6.80	7.00	7.10	7.50	8.00	7.40
	DI-10								6.00	6.90	6.40	5.55	5.00	6.20	7.00	6.60
	DI-15								6.10	6.00	3.10	2.10	2.50	4.60	4.70	4.10
A-3.6-DI-N-2	DI-2	4.59	4.74		4.79	4.9	4.64	5.95	7.10	7.00	7.00	6.80	7.30			
	DI-5							5.40	7.00	6.95	6.70	6.60	7.25	7.70	8.10	7.50
	DI-10							3.42	4.50	5.60	5.90	6.80	7.25	7.60	7.20	6.90
	DI-15							1.31	2.80	3.80	5.00	5.80	7.15	6.60	5.20	3.70
A-3.6-DI-C-1	DI-2								6.00	7.15	7.05	7.30	7.10			
	DI-5								5.90	7.10	6.90	7.10	7.10	7.70	8.20	7.80
	DI-10								5.90	7.15	7.15	7.20	7.20	7.40	7.80	7.00
	DI-15								6.00	7.20	7.10	7.45	7.30	6.30	6.70	5.80
A-3.6-DI-C-2	DI-2	4.19	4.68	5.06	5.2	5.13	4.82	5.83	7.30	7.25	7.20	7.35	7.45			
	DI-5							5.49	7.20	7.30	7.00	7.20	7.30	7.70	8.10	7.80
	DI-10							5.86	6.90	7.35	7.10	7.30	7.30	7.50	8.00	6.80
	DI-15							5.84	7.00	7.45	7.35	7.60	7.45	6.40	6.70	5.40
A-3.6-CT-N-1	CT-2								2.10	0.95	5.80	5.50	5.20			
	CT-5								1.80	0.85	5.70	4.30	4.05	4.50	4.20	2.50
	CT-10								1.30	0.35	0.30	0.30	0.30	0.00	2.50	1.70
	CT-15								0.80	0.15	0.20	0.20	0.20	0.00	0.00	1.60
A-3.6-CT-N-2	CT-2	3.01	3.39		3.92	3.08	3.67	4.36	4.60	4.20	6.00	0.90	2.20			
	CT-5							4.31	4.60	3.75	5.60	0.80	2.10	2.40	4.00	2.30
	CT-10							0.55	0.80	0.40	0.40	0.30	1.50	0.80	3.00	1.10
	CT-15							0.22	0.20	0.15	0.20	0.02	0.10	0.00	0.00	0.30
A-3.6-CT-C-1	CT-2								1.40	0.60	2.40	3.10	3.40			
	CT-5								1.40	0.55	2.30	3.00	3.40	6.40	6.50	6.10
	CT-10								1.40	0.55	2.30	3.00	3.35	5.90	5.70	4.90
	CT-15								1.40	0.20	2.40	3.10	3.40	1.80	3.00	4.60
A-3.6-CT-C-2	CT-2	3.06	3.50	3.00	3.05	2.82	3.4	4.21	5.50	5.85	4.80	5.00	5.80			
	CT-5							4.41	5.40	5.70	4.60	4.90	5.60	3.60	3.90	3.90
	CT-10							4.43	1.00	0.35	0.80	0.40	0.30	0.20	2.50	1.80
	CT-15							0.67	0.20	0.20	0.20	0.25	0.15	0.00	0.20	0.00

Table B3.1 DO (mg/L) vs. Time (day) (continued)

Sample#	Depth(cm)	6/26/03	6/27/03	6/28/03	7/7/03	7/8/03	7/9/03	7/22/03	8/1/03	8/8/03	8/15/03	8/22/03	8/29/03	9/30/03	11/9/03	12/13/03
		1	2	3	12	13	14	27	37	44	51	58	65	97	137	171
A-6.3-DI-N-1	DI-2								6.20	7.20	7.00	7.35	7.20			
	DI-5								6.05	7.00	7.00	7.20	6.90	6.90	7.60	7.40
	DI-10								6.15	7.10	6.70	5.40	4.70	5.20	5.50	6.40
	DI-15								6.30	5.70	2.00	0.90	0.90	3.00	2.70	3.50
A-6.3-DI-N-2	DI-2	4.44	4.42		4.65	4.3	4.4	4.98	7.30	7.40	6.70	7.30	7.20			
	DI-5							4.51	6.40	6.90	6.40	7.10	7.10	7.00	7.30	7.20
	DI-10							3.07	4.40	4.35	3.80	4.20	4.50	4.80	5.30	4.80
	DI-15							1.50	1.65	1.10	0.80	1.65	2.00	1.80	2.00	2.30
A-6.3-DI-C-1	DI-2								6.00	7.10	7.20	7.30	7.20			
	DI-5								6.00	6.95	7.00	7.30	7.10	7.60	8.30	7.80
	DI-10								6.00	7.10	7.05	7.30	7.30	7.40	7.70	7.60
	DI-15								6.30	7.15	7.30	7.60	7.40	7.00	6.70	6.60
A-6.3-DI-C-2	DI-2	4.79	4.55	4.51	4.95	4.69	5.12	5.64	7.40	7.35	7.20	7.20	7.30			
	DI-5							5.52	7.00	7.20	7.10	7.10	7.15	7.60	7.90	7.70
	DI-10							5.33	6.90	7.10	6.90	6.85	6.85	7.10	6.70	7.30
	DI-15							4.73	6.60	6.35	5.60	5.45	5.20	4.30	4.50	4.70
A-6.3-CT-N-1	CT-2								1.60	0.70	5.50	6.50	6.65			
	CT-5								1.55	0.65	5.50	5.70	6.40	3.00	3.70	3.80
	CT-10								1.55	0.25	0.60	0.50	0.30	0.60	0.60	1.80
	CT-15								0.80	0.15	0.20	0.20	0.15	0.00	0.00	0.00
A-6.3-CT-N-2	CT-2	3.00	3.21		3.33	3.76	3.70	4.58	6.60	6.00	3.10	4.30	5.30			
	CT-5							1.84	2.70	3.70	2.90	4.00	4.90	2.70	1.90	2.80
	CT-10							0.40	0.25	0.20	0.40	0.40	0.20	0.90	0.10	0.50
	CT-15							0.20	0.10	0.10	0.20	0.20	0.10	0.00	0.00	0.00
A-6.3-CT-C-1	CT-2								2.00	0.90	5.20	5.50	6.00			
	CT-5								1.60	0.75	4.80	5.50	6.00	5.90	3.40	2.70
	CT-10								1.60	0.80	3.00	5.40	5.90	1.78	1.00	0.20
	CT-15								1.15	0.10	0.25	0.20	0.30	0.00	0.00	0.00
A-6.3-CT-C-2	CT-2	2.82	2.82		2.79	2.92	3.04	4.10	5.30	4.30	5.00	4.10	4.05			
	CT-5							3.85	5.30	4.25	4.30	4.00	4.00	4.80	4.70	3.90
	CT-10							3.63	1.00	4.05	0.30	4.00	3.90	0.20	0.00	0.00
	CT-15							0.49	0.20	0.10	0.10	0.10	0.10	0.00	0.00	0.00

Table B3.1 DO (mg/L) vs. Time (day) (continued)

Sample#	Depth(cm)	6/26/03	6/27/03	6/28/03	7/7/03	7/8/03	7/9/03	7/22/03	7/31/03	8/7/03	8/14/03	8/21/03	8/28/03	9/30/03	11/9/03	12/12/03
		1	2	3	12	13	14	27	36	43	50	57	64	97	137	170
A-9.1-DI-N-1	DI-2								6.90	7.15	7.00	7.10	7.30			
	DI-5								6.80	7.15	7.00	7.10	7.30	7.50	7.50	7.40
	DI-10								6.80	7.30	6.70	6.30	5.60	6.00	5.50	5.50
	DI-15								6.90	6.75	5.20	2.60	3.00	2.70	2.20	2.80
A-9.1-DI-N-2	DI-2	4.55	4.66	4.80	4.44	4.14	4.81	4.66	7.20	7.15	7.15	7.00	7.20			
	DI-5							4.94	6.80	7.10	7.10	7.00	7.10	7.40	7.30	7.10
	DI-10							3.75	6.00	5.90	5.50	5.40	5.20	5.00	4.70	5.20
	DI-15							2.58	3.00	3.65	3.20	2.10	1.80	1.20	1.90	1.70
A-9.1-DI-C-1	DI-2								6.15	6.80	6.70	7.10	7.15			
	DI-5								6.00	6.80	6.60	7.10	7.20	7.50	8.20	8.10
	DI-10								6.00	6.95	6.80	7.20	7.35	7.40	8.20	7.00
	DI-15								6.20	6.80	7.00	7.60	7.80	7.10	7.50	6.00
A-9.1-DI-C-2	DI-2	4.83	4.96	4.72	4.55	4.56	4.92	5.46	7.30	7.35	7.20	7.10	7.20			
	DI-5							5.44	7.20	7.30	7.00	7.00	7.15	7.10	7.40	7.40
	DI-10							4.69	6.20	6.05	6.00	5.40	6.10	4.90	5.70	4.80
	DI-15							3.55	4.40	3.95	3.50	3.30	3.20	1.70	2.00	1.90
A-9.1-CT-N-1	CT-2								2.00	0.90	5.30	5.60	6.80			
	CT-5								1.80	0.80	5.30	5.05	5.15	3.40	2.70	2.10
	CT-10								0.80	0.80	0.30	0.20	0.20	0.00	0.00	0.10
	CT-15								0.80	0.10	0.10	0.20	0.10	0.00	0.00	0.00
A-9.1-CT-N-2	CT-2	3.19	3.31	3.63	4.56	3.5	3.99	5.11	5.30	4.90	6.00	2.25	5.40			
	CT-5							2.00	1.00	1.75	5.00	2.20	5.35	2.40	3.80	1.50
	CT-10							0.43	0.15	0.15	0.20	0.15	0.20	0.00	0.00	0.10
	CT-15							0.19	0.10	0.07	0.07	0.10	0.10	0.00	0.00	0.00
A-9.1-CT-C-1	CT-2								1.50	0.50	4.00	5.60	5.95			
	CT-5								1.35	0.40	3.90	5.40	5.85	6.80	3.30	3.30
	CT-10								1.35	0.30	4.00	2.15	6.00	4.40	2.40	2.80
	CT-15								1.25	0.10	0.30	0.02	3.10	0.10	0.00	0.20
A-9.1-CT-C-2	CT-2	2.91	3.02	3.02	3.7	3.62	2.92	3.64	5.70	6.00	5.40	5.90	5.20			
	CT-5							3.54	5.50	6.00	5.15	5.80	5.10	4.60	2.90	3.70
	CT-10							3.53	5.50	5.95	5.00	0.30	4.50	1.20	2.40	1.80
	CT-15							2.30	0.50	0.20	0.20	0.20	0.15	0.00	0.00	0.70

Table B3.1 DO (mg/L) vs. Time (day) (continued)

Sample#	Depth(cm)	6/26/03	6/27/03	6/28/03	7/7/03	7/8/03	7/9/03	7/22/03	7/31/03	8/7/03	8/14/03	8/21/03	8/28/03	9/29/03	11/8/03	12/12/03
		1	2	3	12	13	14	27	36	43	50	57	64	96	136	170
A-24.9-DI-N-1	DI-2	4.78	4.44	4.80	4.54	3.27	3.55	5.65	7.20	7.00	6.25	7.15	6.90			
	DI-5							4.04	5.80	5.90	6.20	5.75	5.55	4.40	5.90	5.70
	DI-10							2.37	3.00	2.85	2.65	2.45	2.60	1.60	1.90	2.50
	DI-15							0.43	0.30	0.20	0.20	0.15	0.15	0.00	0.10	0.70
A-24.9-DI-N-2	DI-2	4.21	4.54	4.51	4.29	4.35	3.23	4.41	6.60	6.70	6.60	6.65	6.60			
	DI-5							3.35	5.00	4.90	5.40	4.90	5.40	4.50	7.00	7.30
	DI-10							1.80	2.65	1.90	1.65	1.60	1.60	1.20	2.20	3.60
	DI-15							0.43	0.25	0.20	0.08	0.10	0.10	0.00	0.20	0.60
A-24.9-DI-C-1	DI-2	4.62	4.76	4.63	4.53	4.46	4.31	6.08	7.20	7.30	7.50	7.35	7.25			
	DI-5							5.98	7.00	7.10	7.50	7.25	7.25	7.00	7.60	7.50
	DI-10							4.99	6.60	6.80	6.65	6.75	6.60	5.20	5.60	6.70
	DI-15							4.19	5.80	5.90	5.60	5.45	5.20	2.30	2.70	2.40
A-24.9-DI-C-2	DI-2	4.81	4.64	4.78	4.54	4.6	4.56	6.01	7.30	7.50	7.40	7.35	7.30			
	DI-5							5.64	7.20	7.40	7.40	7.25	7.30	7.00	7.80	7.20
	DI-10							5.00	6.80	7.10	6.90	7.15	7.00	6.20	6.20	6.20
	DI-15							4.17	6.10	6.05	6.30	5.80	5.85	3.90	3.80	3.40
A-24.9-CT-N-1	CT-2	3.14	3.80	3.61	3.91	3.2	2.9	4.74	6.40	7.05	6.30	6.25	5.80			
	CT-5							3.80	4.50	3.90	3.20	1.70	3.90	1.70	3.00	2.80
	CT-10							0.63	0.15	0.15	0.15	0.20	0.15	0.20	0.20	0.00
	CT-15							0.23	0.10	0.10	0.10	0.10	0.10	0.00	0.10	0.00
A-24.9-CT-N-2	CT-2	3.13	3.36	3.81	3.45	3.96	1.83	4.81	6.80	6.75	5.90	6.20	6.00			
	CT-5							3.47	4.30	3.90	5.10	2.20	3.20	1.40	3.90	2.80
	CT-10							0.60	0.15	0.15	0.20	0.15	0.20	0.00	0.20	0.00
	CT-15							0.23	0.10	0.10	0.10	0.10	0.10	0.00	0.10	0.00
A-24.9-CT-C-1	CT-2	3.00	2.95	3.08	4.4	4.09	4.06	4.78	4.70	4.80	5.55	2.20	6.00			
	CT-5							4.56	4.70	4.70	5.40	2.20	5.90	5.30	3.20	2.70
	CT-10							0.43	0.30	0.20	0.20	0.80	0.25	0.40	0.40	2.00
	CT-15							0.23	0.20	0.10	0.10	0.10	0.10	0.00	0.10	0.00
A-30.7-CT-C-2	CT-2	2.94	3.05	3.04	4.35	4.03	4.02	4.40	4.40	5.20	5.75	5.45	6.45			
	CT-5							3.99	4.40	5.20	6.10	5.20	6.35	5.10	2.00	3.40
	CT-10							0.60	0.30	0.25	1.28	0.25	0.25	0.20	0.20	0.20
	CT-15							0.31	0.15	0.10	0.10	0.10	0.12	0.00	0.10	0.00

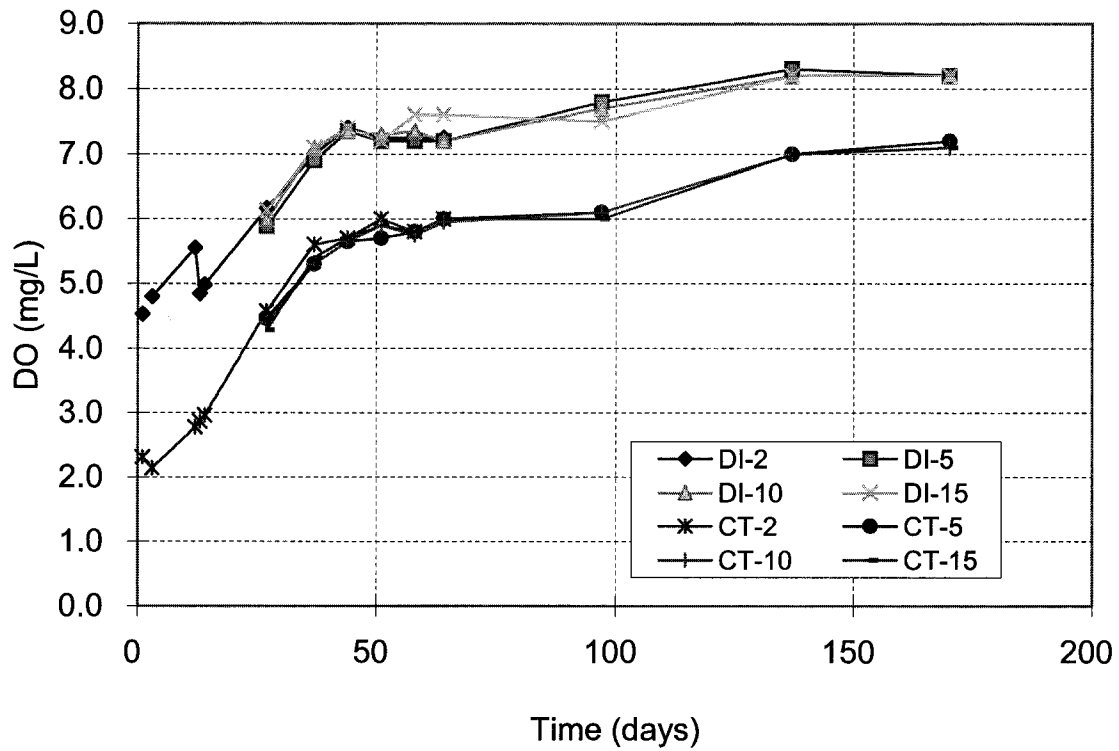


Fig. B3.1 DO-Time (A-0-DI-1, A-0-CT-1)

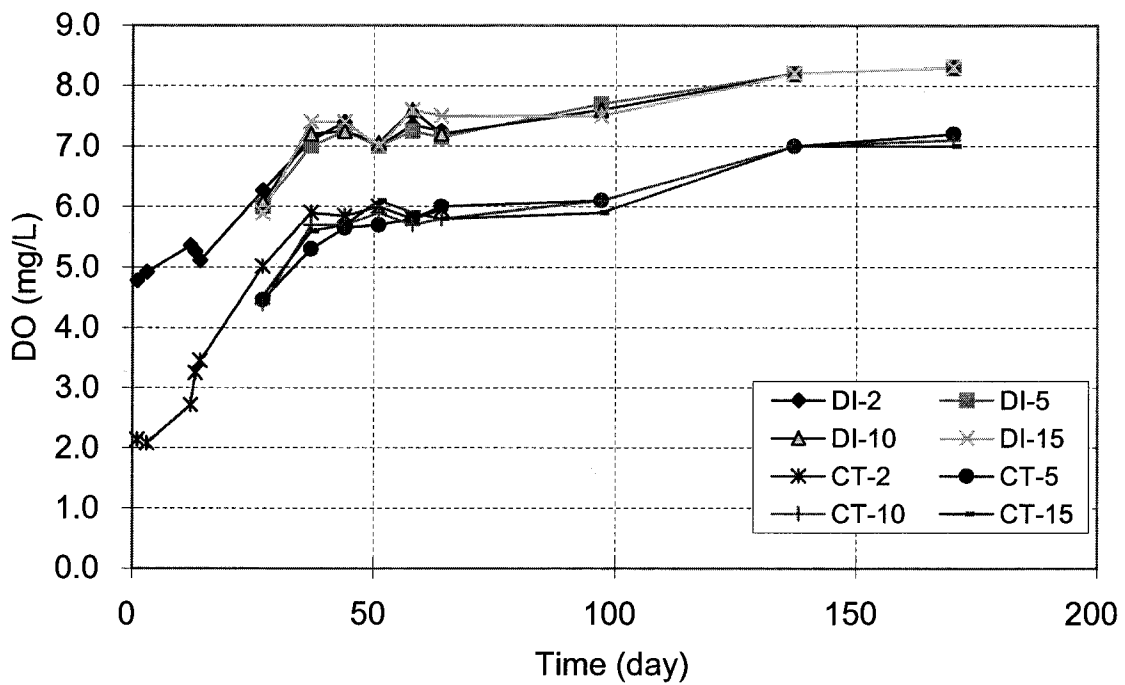


Fig. B3.2 DO-Time (A-0-DI-2, A-0-CT-2)

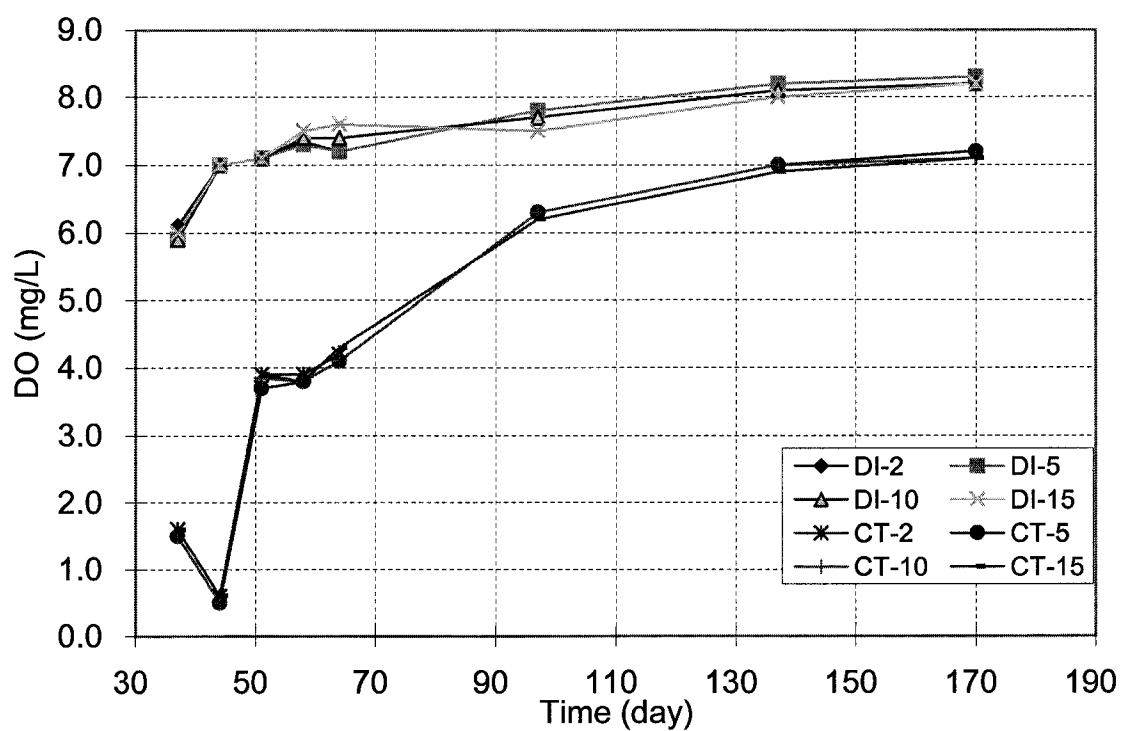


Fig. B3.3 DO-Time (A-0-DI-3, A-0-CT-3)

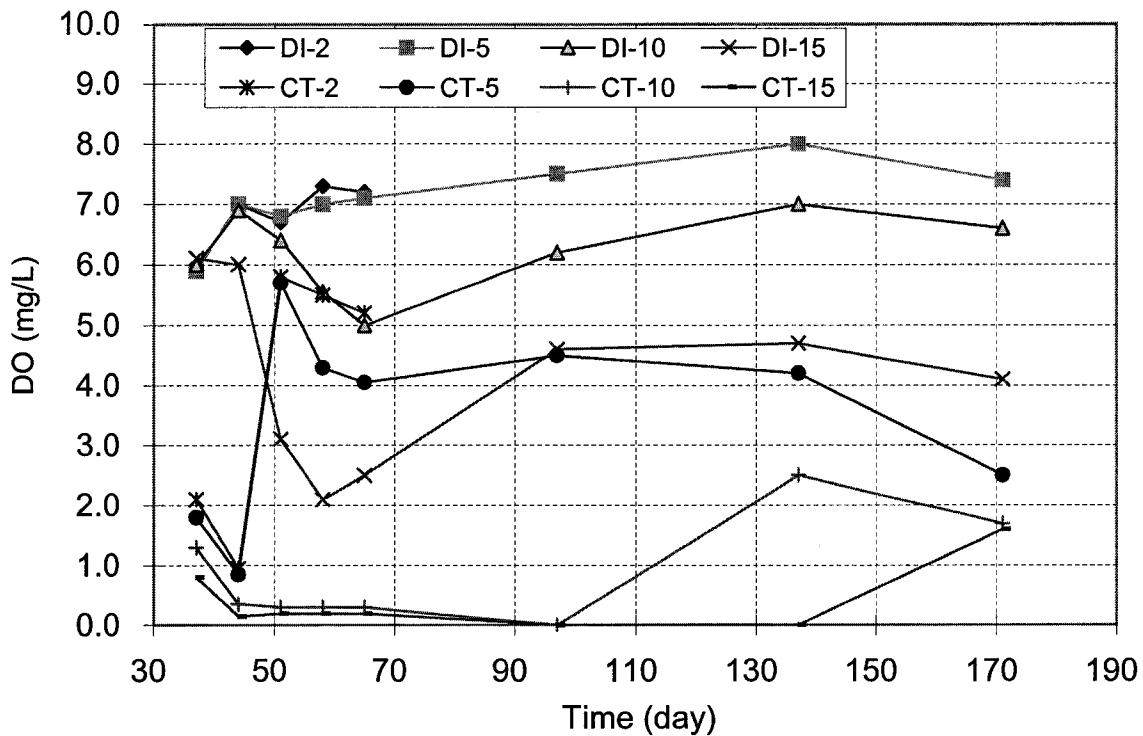


Fig. B3.4 DO - Time (A-3.6-DI-N-1, A-3.6-CT-N-1)

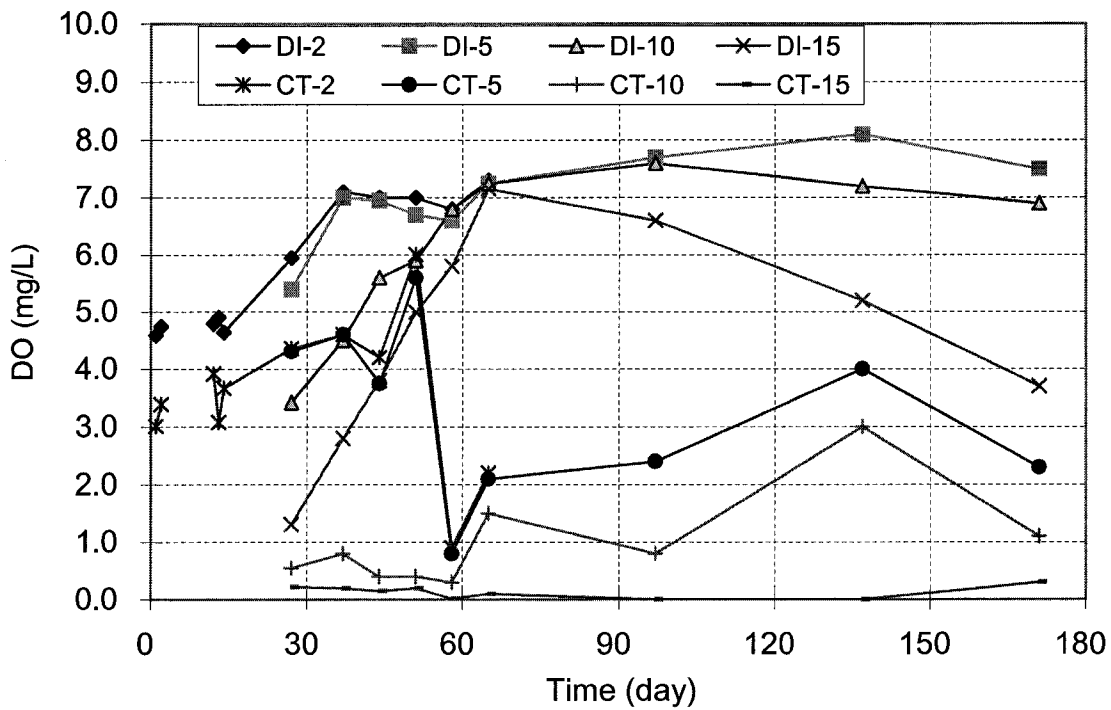


Fig. B3.5 DO - Time (A-3.6-DI-N-2, A-3.6-CT-N-2)

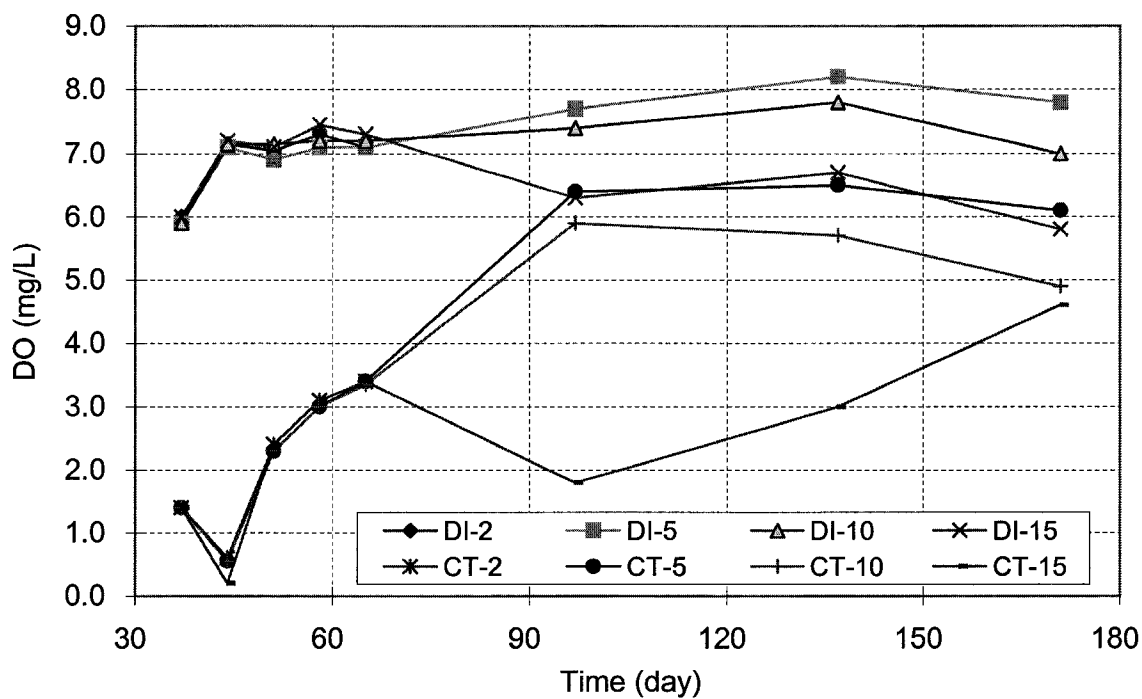


Fig. B3.6 DO - Time (A-3.6-DI-C-1, A-3.6-CT-C-1)

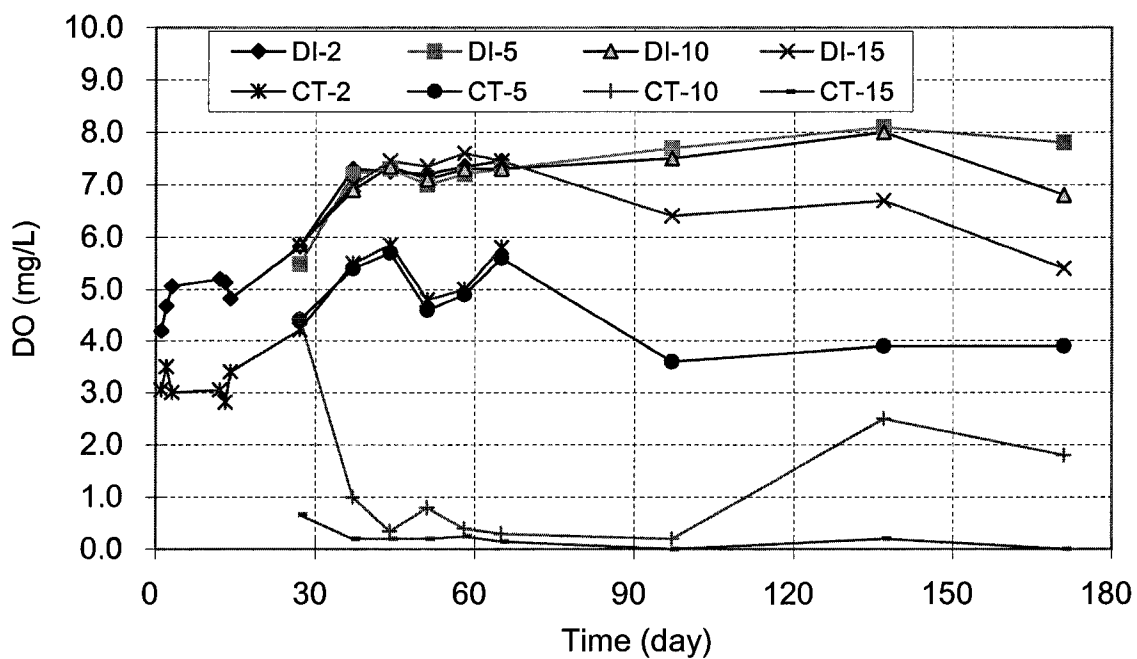


Fig. B3.7 DO - Time (A-3.6-DI-C-2, A-3.6-CT-C-2)

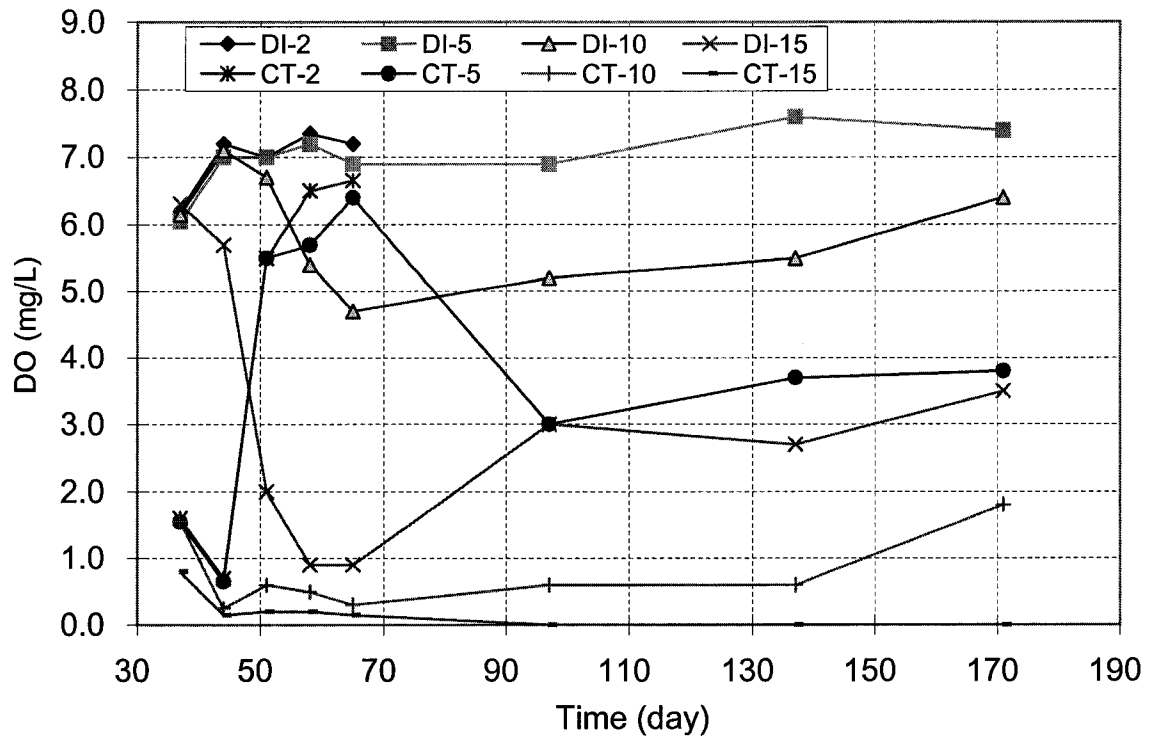


Fig. B3.8 DO - Time (A-6.3-DI-N-1, A-6.3-CT-N-1)

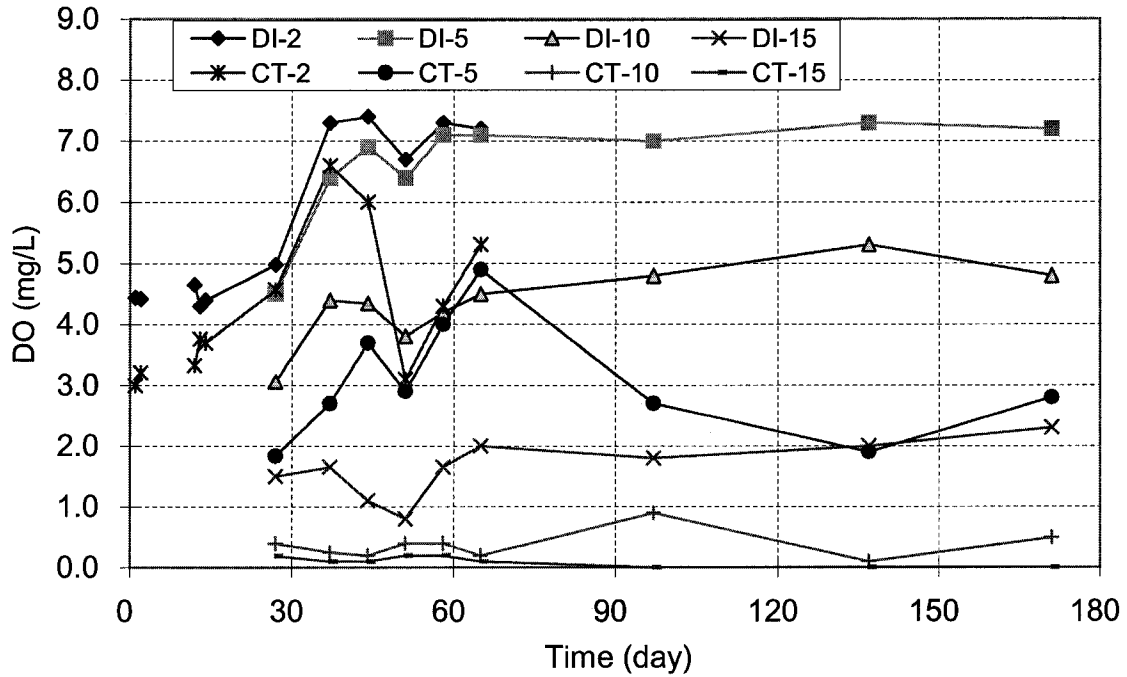


Fig. B3.9 DO - Time (A-6.3-DI-N-2, A-6.3-CT-N-2)

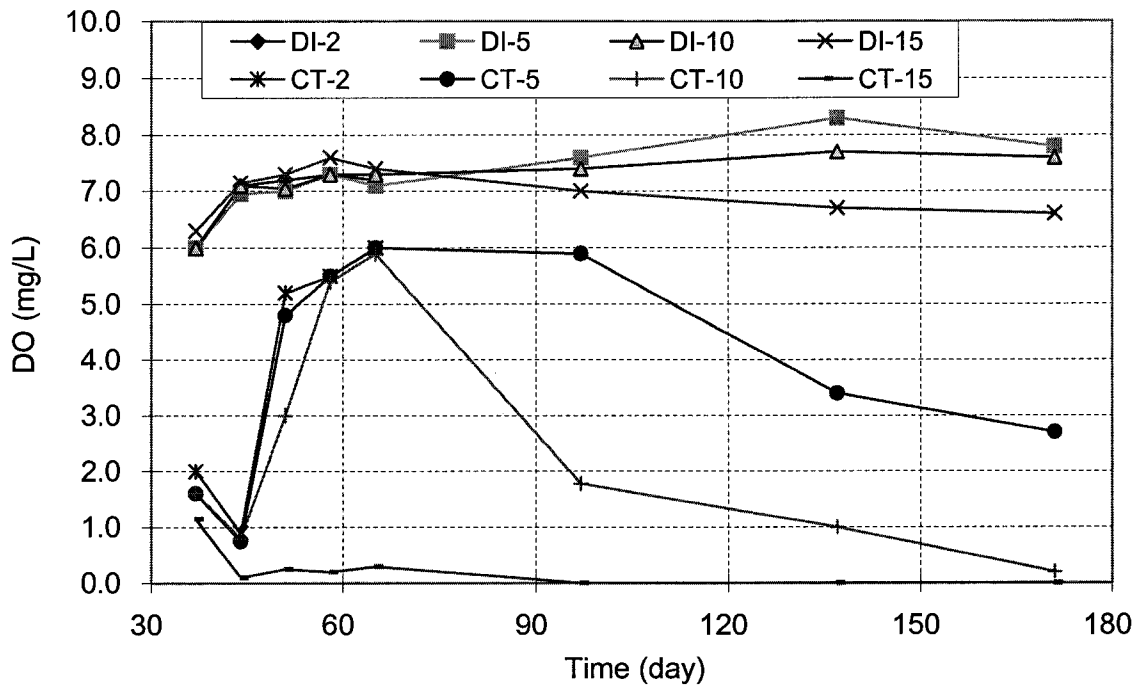


Fig. B3.10 DO - Time (A-6.3-DI-C-1, A-6.3-CT-C-1)

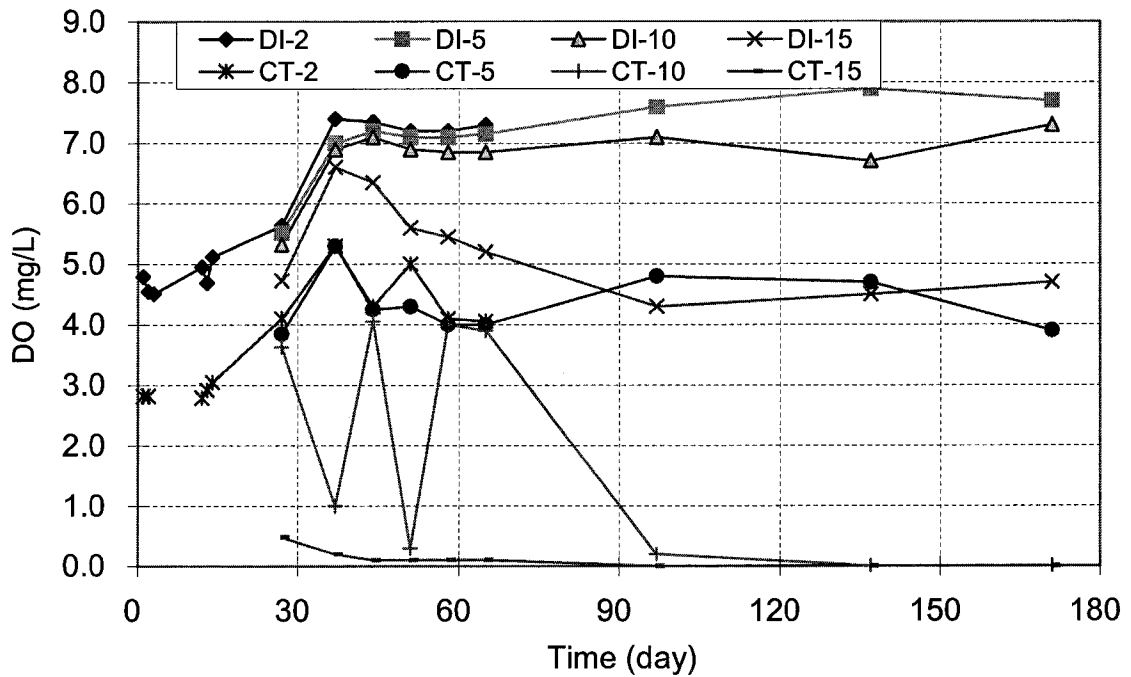


Fig. B3.11 DO - Time (A-6.3-DI-C-2, A-6.3-CT-C-2)

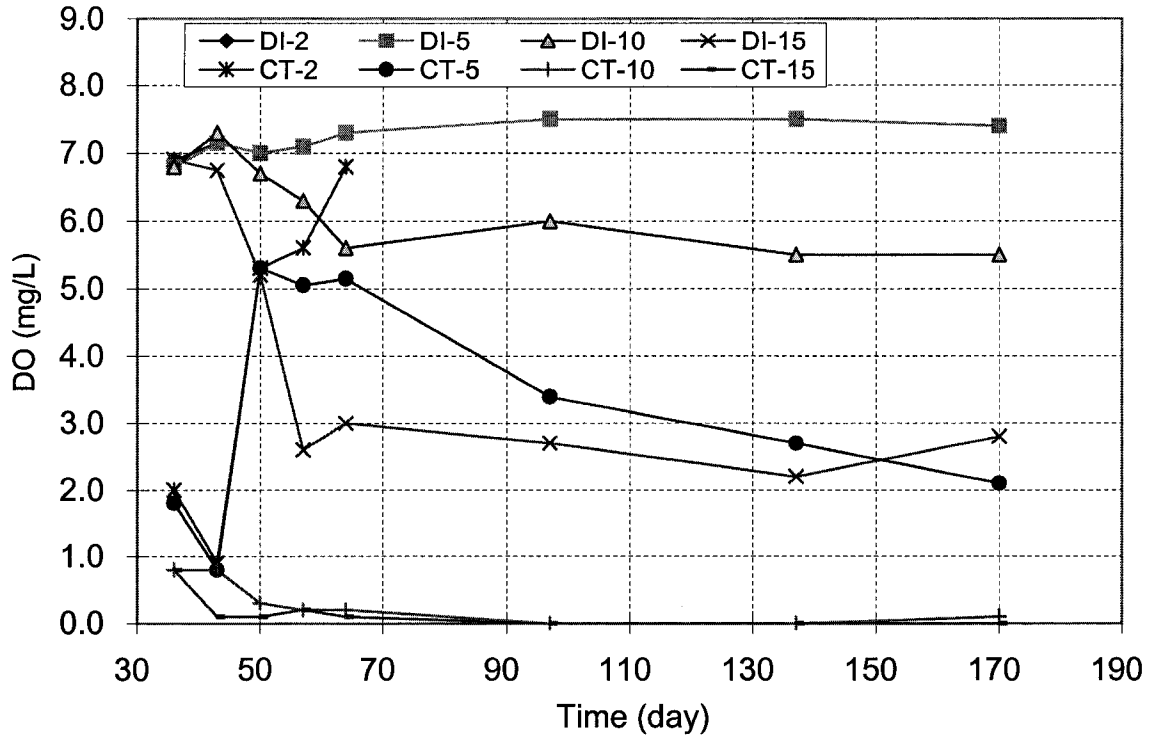


Fig. B3.12 DO - Time (A- 9.1-DI-N-1, A-9.1-CT-N-1)

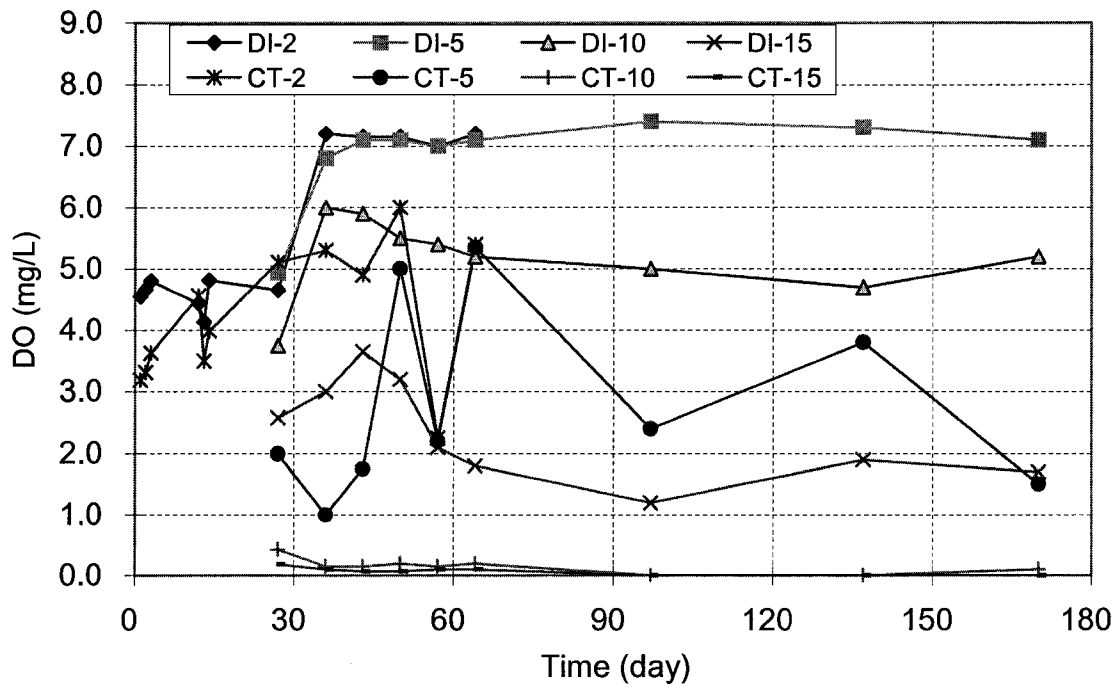


Fig. B3.13 DO - Time (A-9.1-DI-N-2, A-9.1-CT-N-2)

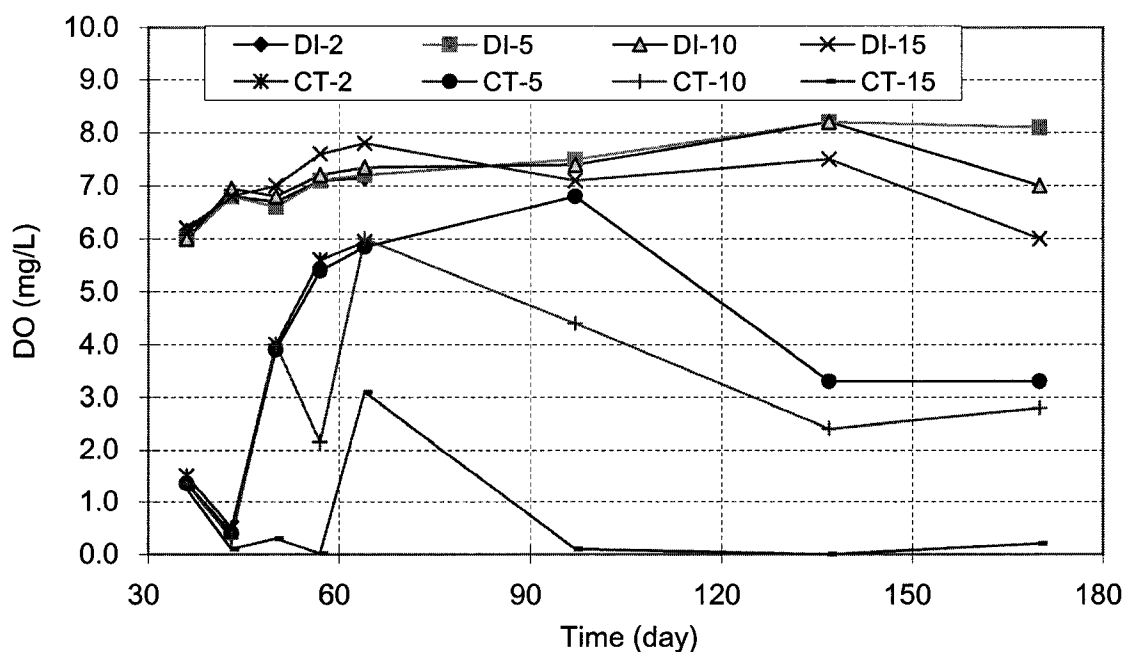


Fig. B3.14 DO - Time (A-9.1-DI-C-1, A-9.1-CT-C-1)

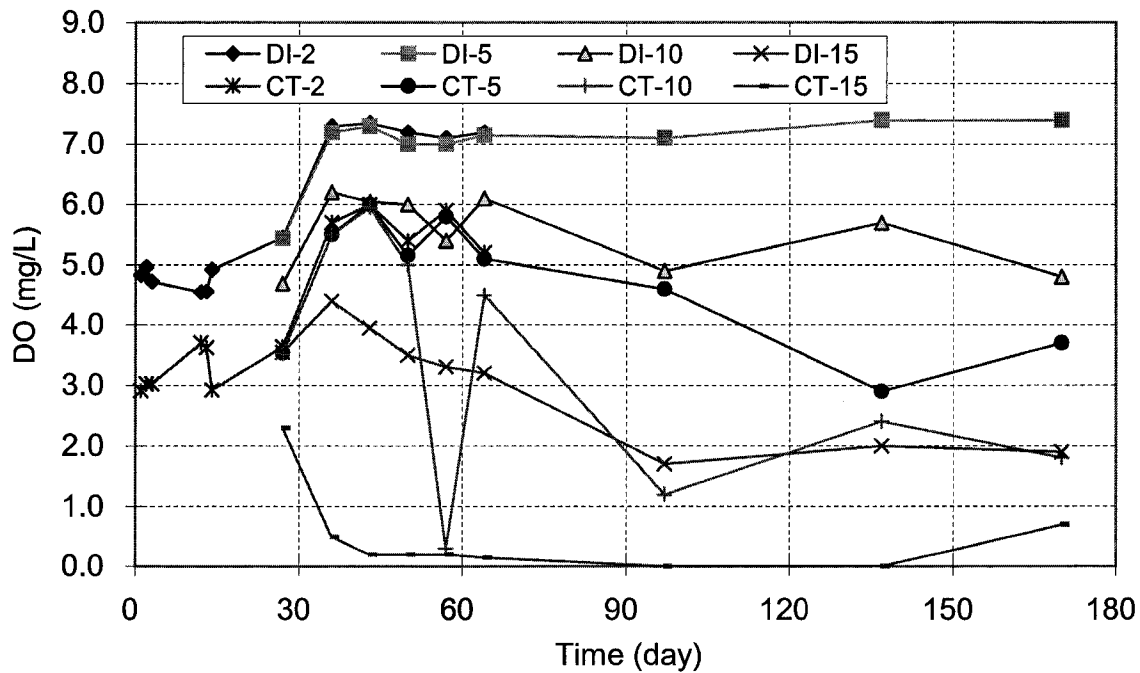


Fig. B3.15 DO - Time (A-9.1-DI-C-2, A-9.1-CT-C-2)

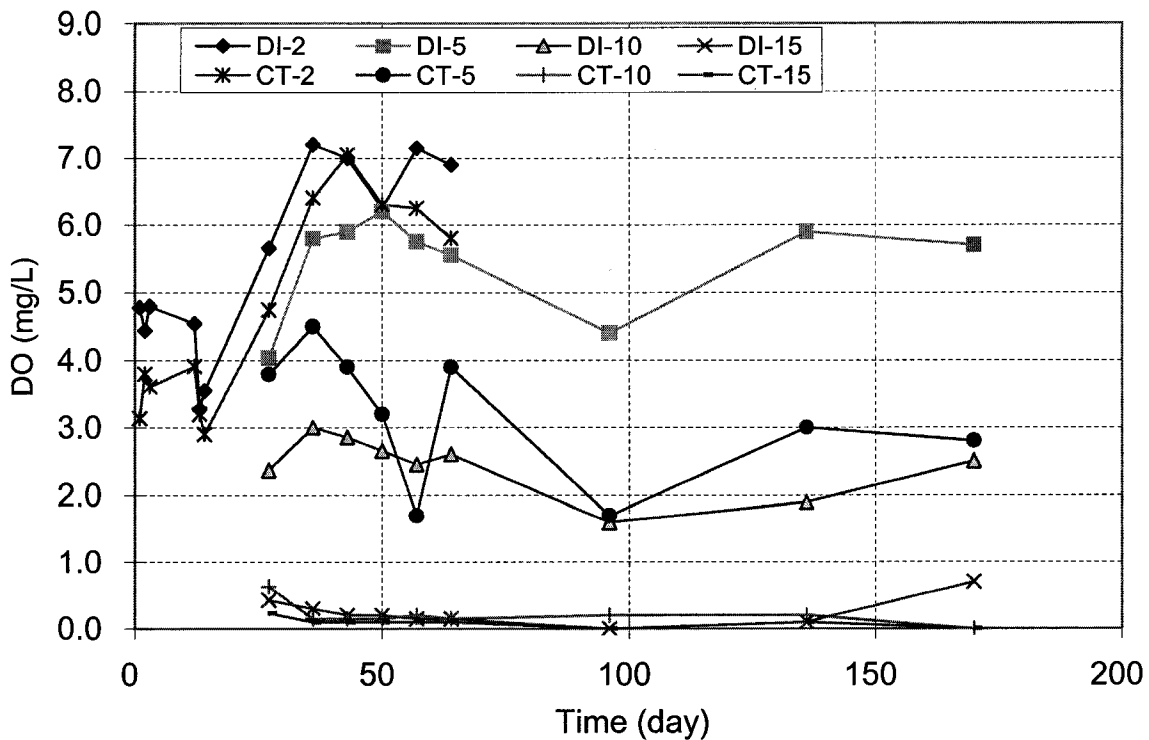


Fig.B3.16 DO - Time (A-24.9-DI-N-1, A-24.9-CT-N-1)

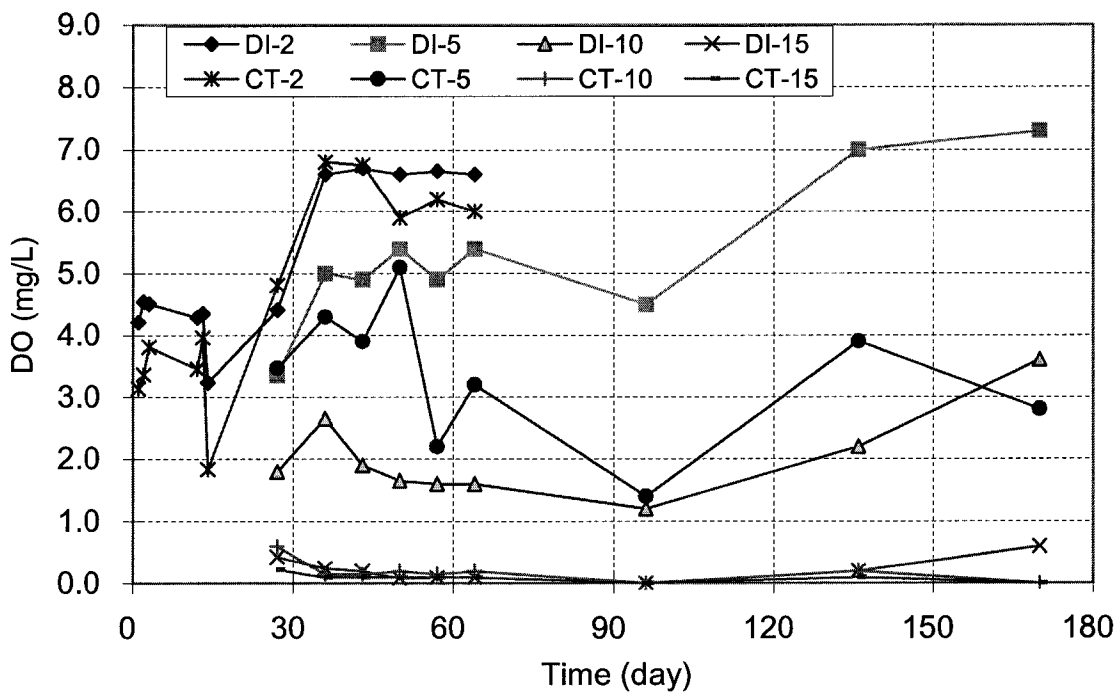


Fig. B3.17 DO - Time (A-24.9-DI-N-2, A-24.9-CT-N-2)

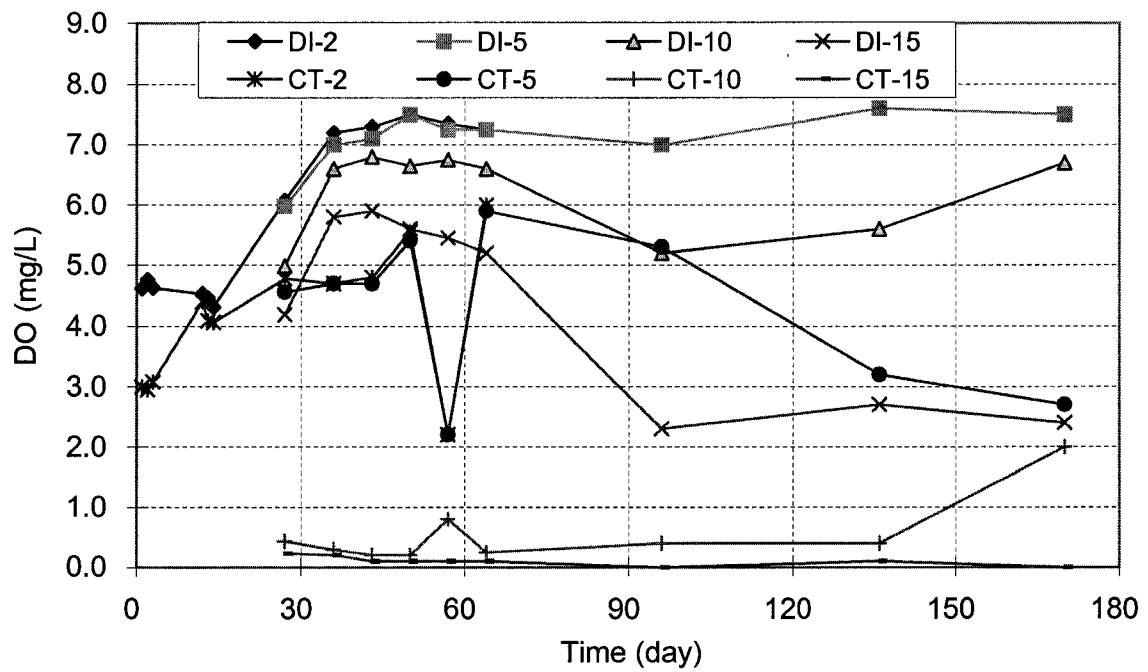


Fig. B3.18 DO - Time (A- 24.9-DI-C-1, A-24.9-CT-C-1)

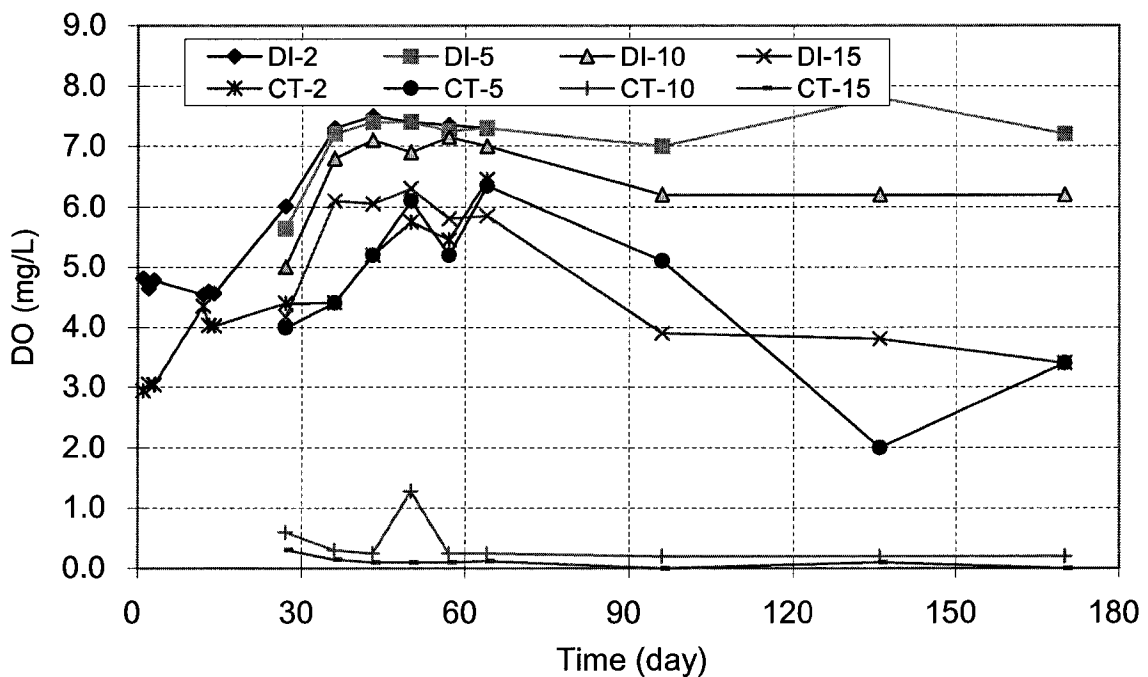


Fig. B3.19 DO - Time (A-24.9-DI-C-2, A-30.7-CT-C-2)

Table B4.1 Total Alkalinity (mg/L) vs. Time

Days at Sampling*			7	30	121	180
Times of Sampling	0	1	2	3	5	7
Date of Sampling	24/06/2003	08/07/2003	23/07/2003	15/08/2003	14/11/2003	12/01/2004
Days at Sampling**	0	14	29	52	143	202
A-24.9-DI-N-1						
A-24.9-DI-N-2						
A-24.9-DI-C-1						
A-24.9-DI-C-2						
A-24.9-CT-N-1	663.6	734.4	752.5	681.8	589.1	565.8
A-24.9-CT-N-2	663.6	755.0	714.0	704.5	600.0	572.7
A-24.9-CT-C-1	663.6	712.5	705.3	705.9	560.0	450.0
A-30.7-CT-C-2	663.6	682.5	681.4	651.4	462.2	402.3
A-9.1-DI-N-1						
A-9.1-DI-N-2						
A-9.1-DI-C-1						
A-9.1-DI-C-2						
A-9.1-CT-N-1			663.6	671.4	553.3	450.0
A-9.1-CT-N-2	663.6	700.0	700.0	646.5	479.5	431.8
A-9.1-CT-C-1			663.6	678.6	413.3	327.3
A-9.1-CT-C-2	663.6	709.0	680.0	666.0	568.2	507.1
A-6.3-DI-N-1						
A-6.3-DI-N-2						
A-6.3-DI-C-1						
A-6.3-DI-C-2						
A-6.3-CT-N-1			663.6	654.5	562.8	482.5
A-6.3-CT-N-2	663.6	690.5	681.0	660.0	452.3	416.7
A-6.3-CT-C-1			663.6	685.7	434.9	425.0
A-6.3-CT-C-2	663.6	700.0	720.0	688.0	540.9	483.7
A-3.6-DI-N-1						
A-3.6-DI-N-2						
A-3.6-DI-C-1						
A-3.6-DI-C-2						
A-3.6-CT-N-1			663.6	655.8	478.0	425.0
A-3.6-CT-N-2	663.6	714.3	711.9	650.0	409.1	333.3
A-3.6-CT-C-1			663.6	700.0	400.0	325.0
A-3.6-CT-C-2	663.6	711.8	700.0	660.0	485.7	461.9
A-0-DI-1						
A-0-DI-2						
A-0-DI-3						
A-0-CT-1	663.6	694.1	681.0	640.0	434.3	392.9
A-0-CT-2	663.6	712.5	670.0	635.0	437.2	376.2
A-0-CT-3			663.6	676.7	461.9	397.6

* Measurement of the samples started from July, 16, 2003

** Measurement of the samples started from June 24, 2003

Table B4.1 Total Alkalinity (mg/L) vs. Time (continued)

Sampling Date	25/11/2003	23/12/2003	13/01/2004	02/03/2004
Interval Days	0	28	49	98
N-10-DI-1				
N-10-DI-2				
N-10-CT-1	663.6	650.0	638	590.7
N-10-CT-2	663.6	648.8	631	604.7
N-20-DI-1				
N-20-DI-2				
N-20-CT-1	663.6	683.3	660	614.0
N-20-CT-2	663.6	611.6	587	500.0
N-30-DI-1				
N-30-DI-2				
N-30-CT-1	663.6	684.1	661	631.0
N-30-CT-2	663.6	672.7	631	541.9
N-40-DI-1				
N-40-DI-2				
N-40-CT-1	663.6	677.6	635	547.6
N-40-CT-2	663.6	630.4	618	581.0
N-50-DI-1				
N-50-DI-2				
N-50-CT-1	663.6	666.7	646	595.2
N-50-CT-2	663.6	631.0	627	621.4

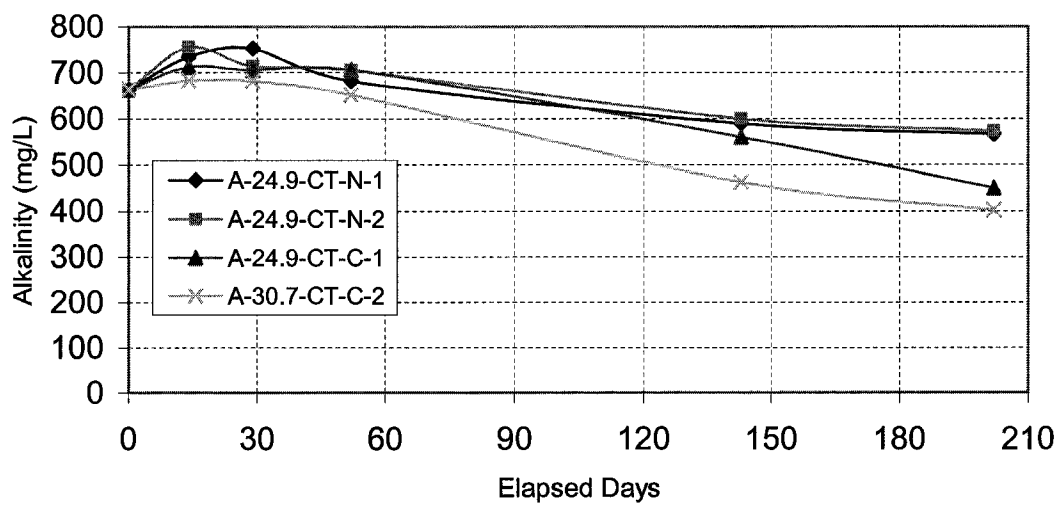


Fig. B4.1 Alkalinity vs. Time

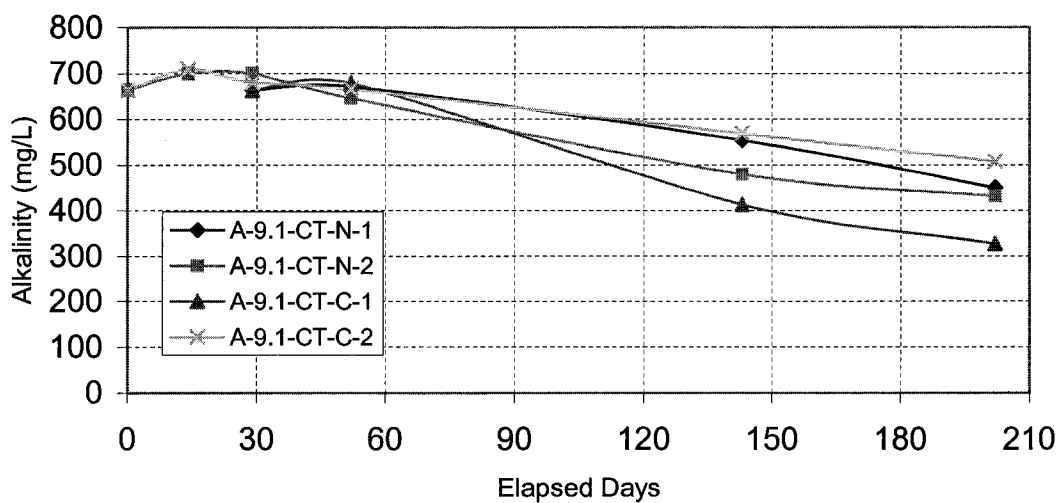


Fig. B4.2 Alkalinity vs. Time

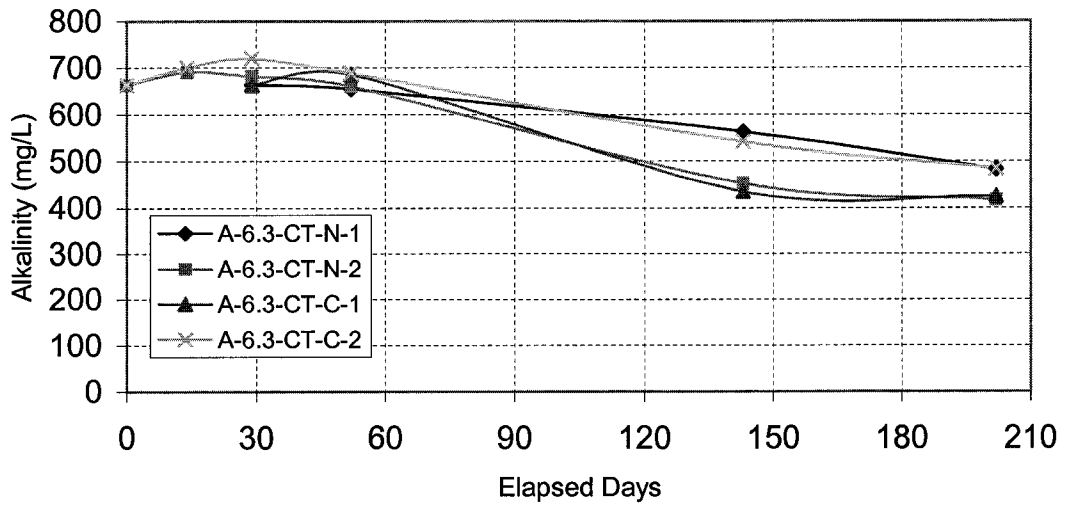


Fig.B4.3 Alkalinity vs. Time

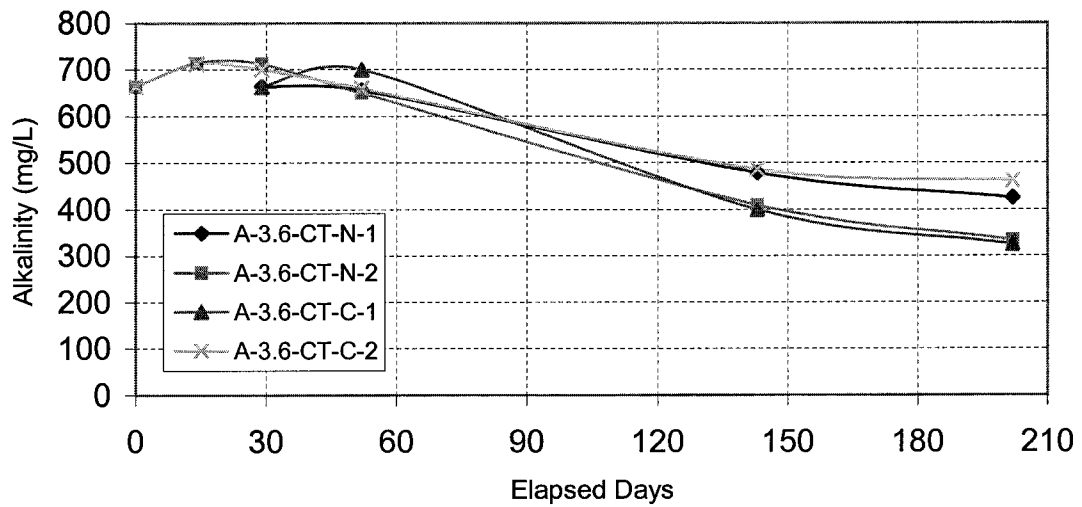


Fig.B4.4 Alkalinity vs. Time

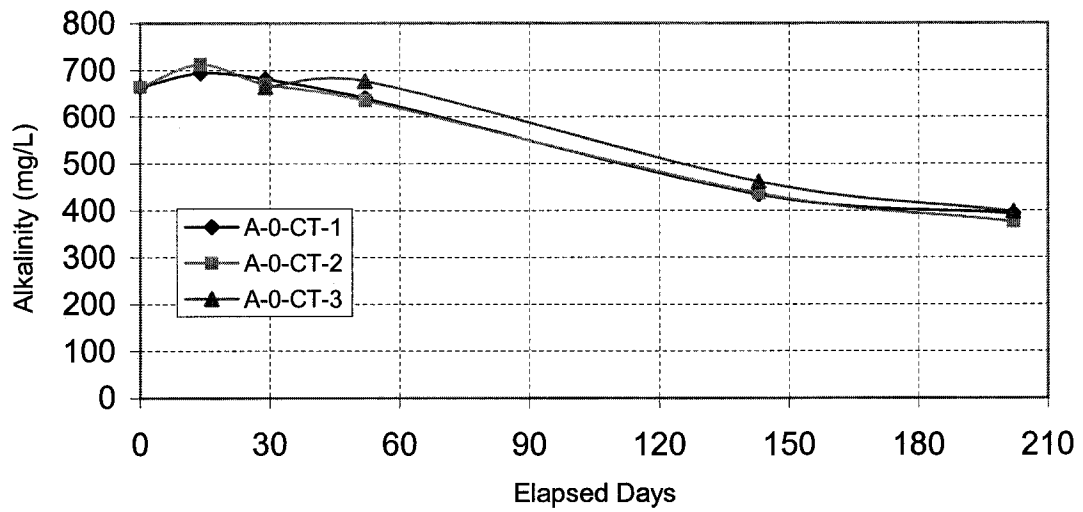


Fig. B4.5 Alkalinity vs. Time

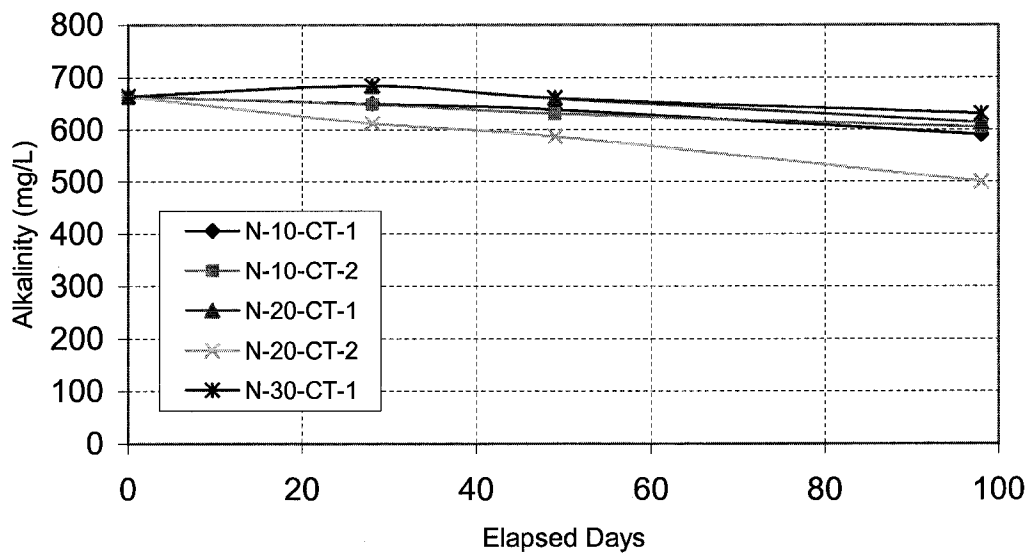


Fig. B4.6 Alkalinity vs. Time

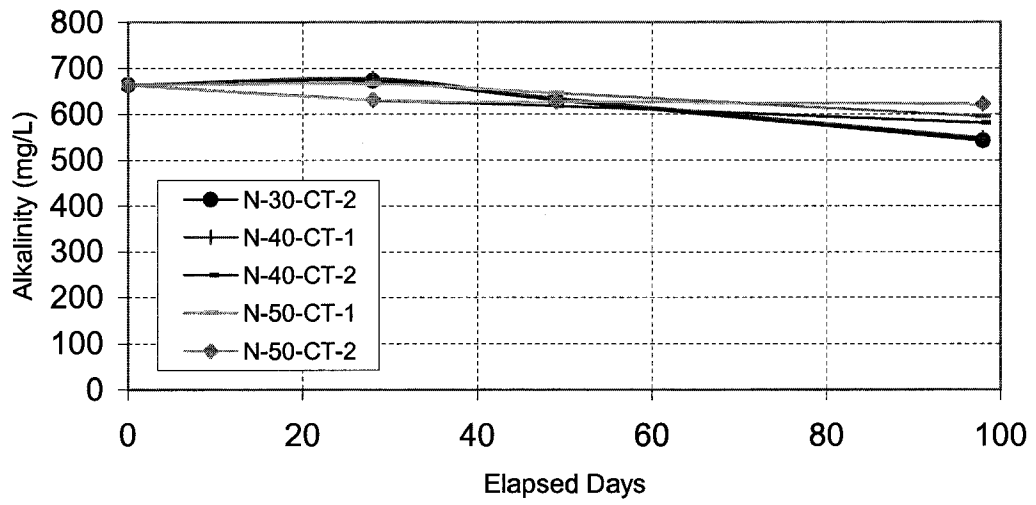


Fig. B4.7 Alkalinity vs. Time

Table B5.1 Ion Concentration (mg/L) vs. Time

	Sampling Times	0	1	2	3	5	7
	Sampling Date	24/06/2003	08/07/2003	23/07/2003	15/08/2003	14/11/2003	12/01/2004
Sample #	Sampling Days	0	14	29	52	143	202
A-24.9-DI-N-1	SO ₄ ²⁻		1263.23	1830.76	2526.77	5750.92	7473.76
	Cl ⁻		3344.43	4619.99	6267.11	12042.64	15624.36
	F ⁻		2.53	2.36	3.58	5.42	5.61
	Br ⁻		1.63		0.03		
	HCO ₃ ⁻						
	NO ₃ ⁻						
	NO ₂ ⁻						
	Na ⁺	0.83	2862.13	3901.42	4988.07	9419.44	11745.39
	K ⁺		76.92	91.91	146.48	267.26	294.63
	Ca ²⁺	0.345	34.76	33.25	49.29	112.69	129.76
Mg ²⁺		44.15	39.13	15.19	55.00	98.82	
Li ⁺		0.72	0.72	1.17	2.26	2.51	
SA1	NH ₄ ⁺						
	SUM	1.175	7630.48	10519.54	13997.69	27655.63	35374.85
	CBE (%)		4.44	2.48	-1.07	-3.66	-5.57

	Sampling Times	0	1	2	3	5	7
	Sampling Date	24/06/2003	08/07/2003	23/07/2003	15/08/2003	14/11/2003	12/01/2004
Sample #	Sampling Days	0	14	29	52	143	202
A-24.9-DI-N-2	SO ₄ ²⁻		1665.68	2666.86	3756.35	6677.88	7867.01
	Cl ⁻		4078.71	5846.66	8193.60	13367.39	15785.29
	F ⁻		2.19	3.21	3.52	5.72	6.12
	Br ⁻		2.55				
	HCO ₃ ⁻						
	NO ₃ ⁻						
	NO ₂ ⁻						
	Na ⁺	0.83	3045.24	4981.94	6208.81	10159.86	11850.33
	K ⁺		90.44	115.29	180.70	285.62	315.40
	Ca ²⁺	0.345	36.21	44.46	68.92	119.58	137.80
Mg ²⁺		55.45	51.11	24.37	68.66	113.78	
Li ⁺		0.82	1.44	1.56	2.31	2.50	
SA2	NH ₄ ⁺						
	SUM	1.175	8977.30	13710.97	18437.81	30687.02	36078.22
	CBE (%)		-2.93	1.29	-4.92	-5.63	-6.00

Table B5.2 Ion Concentration (mg/L) vs. Time

Sample #	Sampling Times	0	1	2	3	5	7
	Sampling Date	24/06/2003	08/07/2003	23/07/2003	15/08/2003	14/11/2003	12/01/2004
	Sampling Days	0	14	29	52	143	202
A-24.9-DI-C-1	SO ₄ ²⁻		70.79	117.22	165.06	617.26	991.75
	Cl ⁻		264.81	496.43	700.55	2357.48	3439.23
	F ⁻		0.11	0.19			0.00
	Br ⁻					4.02	5.47
	HCO ₃ ⁻						
	NO ₃ ⁻						
	NO ₂ ⁻						
SA3	Na ⁺	0.83	192.90	333.38	481.79	1522.44	2222.73
	K ⁺		8.22	17.28	28.24	97.02	143.20
	Ca ²⁺	0.345	1.95	2.71	3.59	8.64	10.87
	Mg ²⁺		2.07	1.96	0.00	13.29	29.93
	Li ⁺		0.05	0.09	0.00	0.58	0.81
	NH ₄ ⁺						
	SUM	1.175	540.90	969.26	1379.23	4620.74	6843.99
CBE (%)		-0.38	-3.76	-2.94	-6.04	-6.42	

Sample #	Sampling Times	0	1	2	3	5	7
	Sampling Date	24/06/2003	08/07/2003	23/07/2003	15/08/2003	14/11/2003	12/01/2004
	Sampling Days	0	14	29	52	143	202
A-24.9-DI-C-2	SO ₄ ²⁻		51.57	82.72	164.99	546.60	873.85
	Cl ⁻		215.60	377.02	701.98	2181.34	3168.90
	F ⁻		0.07		0.21		
	Br ⁻					3.78	4.62
	HCO ₃ ⁻						
	NO ₃ ⁻						
	NO ₂ ⁻						
SA4	Na ⁺	0.83	168.19	251.55	461.12	1391.12	2012.16
	K ⁺		8.36	14.89	30.30	97.17	141.20
	Ca ²⁺	0.345	1.43	1.82	2.77	6.01	7.40
	Mg ²⁺		1.33	3.23	1.84	13.82	31.55
	Li ⁺		0.05	0.08	0.16	0.48	0.81
	NH ₄ ⁺						
	SUM	1.175	446.60	731.32	1363.36	4240.33	6240.49
CBE (%)		3.78	-2.74	-4.70	-6.12	-6.62	

Table B5.3 Ion Concentration (mg/L) vs. Time

Sample #	Sampling Times	0	1	2	3	5	7
	Sampling Date	24/06/2003	08/07/2003	23/07/2003	15/08/2003	14/11/2003	12/01/2004
	Sampling Days	0	14	29	52	143	202
A-24.9-CT-N-1	SO ₄ ²⁻	288.73	1569.89	2015.09	3200.59	6127.50	7208.31
	Cl ⁻	1108.08	5007.92	6189.96	7567.12	13287.30	16765.68
	F ⁻	2.98	4.62	5.89	5.94	8.24	7.96
	Br ⁻		2.58		0.04		
	HCO ₃ ⁻	663.6	600.00	752.50	681.82	589.13	565.79
	NO ₃ ⁻	25					
	NO ₂ ⁻	15.47					
	Na ⁺	1005.87	3800.78	5009.06	6031.34	10219.34	12493.79
	K ⁺	14.31	91.98	111.93	161.08	279.86	301.83
	Ca ²⁺	16.09	50.97	52.58	60.04	92.92	104.83
SB1	Mg ²⁺	16.28	44.12	59.36	24.70	103.46	136.17
	Li ⁺	0.12	0.92	0.95	1.40	2.41	2.62
	NH ₄ ⁺		105.66	113.31			
	SUM	3156.53	11279.44	14310.66	17734.07	30710.15	37586.97
	CBE (%)	-2.88	-1.03	1.29	-3.51	-4.82	-5.37

Sample #	Sampling Times	0	1	2	3	5	7
	Sampling Date	24/06/2003	08/07/2003	23/07/2003	15/08/2003	14/11/2003	12/01/2004
	Sampling Days	0	14	29	52	143	202
A-24.9-CT-N-2	SO ₄ ²⁻	288.73	2192.15	2827.06	3752.79	6750.24	7875.66
	Cl ⁻	1108.08	5423.32	6456.98	7994.97	12926.40	15881.20
	F ⁻	2.98	5.45	6.66	6.66	7.99	9.70
	Br ⁻		2.53				
	HCO ₃ ⁻	663.6	755.00	714.00	704.55	600.00	572.73
	NO ₃ ⁻	25					
	NO ₂ ⁻	15.47					
	Na ⁺	1005.87	4660.04	5518.74	6271.82	10230.50	11830.95
	K ⁺	14.31	107.63	130.59	170.48	276.35	311.39
	Ca ²⁺	16.09	58.00	67.18	76.91	106.69	119.89
SB2	Mg ²⁺	16.28	71.13	0.00	31.02	99.26	146.88
	Li ⁺	0.12	1.11	1.24	1.58	2.44	2.57
	NH ₄ ⁺			123.26			
	SUM	3156.53	13276.36	15845.71	19010.77	30999.87	36750.96
	CBE (%)	-2.88	0.74	0.24	-5.28	-5.03	-6.93

Table B5.4 Ion Concentration (mg/L) vs. Time

Sample #	Sampling Times	0	1	2	3	5	7
	Sampling Date	24/06/2003	08/07/2003	23/07/2003	15/08/2003	14/11/2003	12/01/2004
	Sampling Days	0	14	29	52	143	202
A-24.9-CT-C-1	SO ₄ ²⁻	288.73	276.93	382.46	554.33	1319.47	1804.37
	Cl ⁻	1108.08	1338.58	1415.41	1674.70	3388.56	4706.40
	F ⁻	2.98	3.10	3.35	3.18	3.88	3.92
	Br ⁻		0.00	0.00	0.00	4.43	6.68
	HCO ₃ ⁻	663.6	712.50	705.26	705.88	560.00	450.00
	NO ₃ ⁻	25	1.90	0.00	0.00	0.00	0.00
	NO ₂ ⁻	15.47	0	0	0	0	0
SB3	Na ⁺	1005.87	1106.64	1307.00	1467.69	2518.70	3404.44
	K ⁺	14.31	19.04	25.10	37.69	113.94	174.40
	Ca ²⁺	16.09	17.59	15.00	14.63	20.56	24.92
	Mg ²⁺	16.28	11.49			26.61	52.44
	Li ⁺	0.12		0.32	0.35	0.74	1.08
	NH ₄ ⁺		55.86	60.50	56.05		
	SUM	3156.53	3543.63	3914.41	4514.50	7956.89	10628.65
CBE (%)	-2.88	-1.50	1.85	-1.15	-6.70	-5.84	

Sample #	Sampling Times	0	1	2	3	5	7
	Sampling Date	24/06/2003	08/07/2003	23/07/2003	15/08/2003	14/11/2003	12/01/2004
	Sampling Days	0	14	29	52	143	202
A-30.7-CT-C-2	SO ₄ ²⁻	288.73	400.00	412.65	574.69	1423.19	1870.51
	Cl ⁻	1108.08	1343.52	1577.02	1777.01	3802.99	5155.81
	F ⁻	2.98	2.69	3.13	3.13	3.77	3.89
	Br ⁻					5.10	6.15
	HCO ₃ ⁻	663.6	682.50	681.40	651.43	462.22	402.27
	NO ₃ ⁻	25					
	NO ₂ ⁻	15.47					
SB4	Na ⁺	1005.87	1116.15	1339.57	1545.56	2831.87	3700.68
	K ⁺	14.31	18.82	33.81	48.31	136.73	187.80
	Ca ²⁺	16.09	15.59	15.57	16.82	21.85	24.43
	Mg ²⁺	16.28	11.27			33.41	48.47
	Li ⁺	0.12	0.25	0.43	0.40	0.89	1.18
	NH ₄ ⁺		55.15	71.63	64.62		
	SUM	3156.53	3645.94	4135.21	4681.96	8722.03	11401.20
CBE (%)	-2.88	-3.15	-0.15	0.18	-5.10	-5.52	

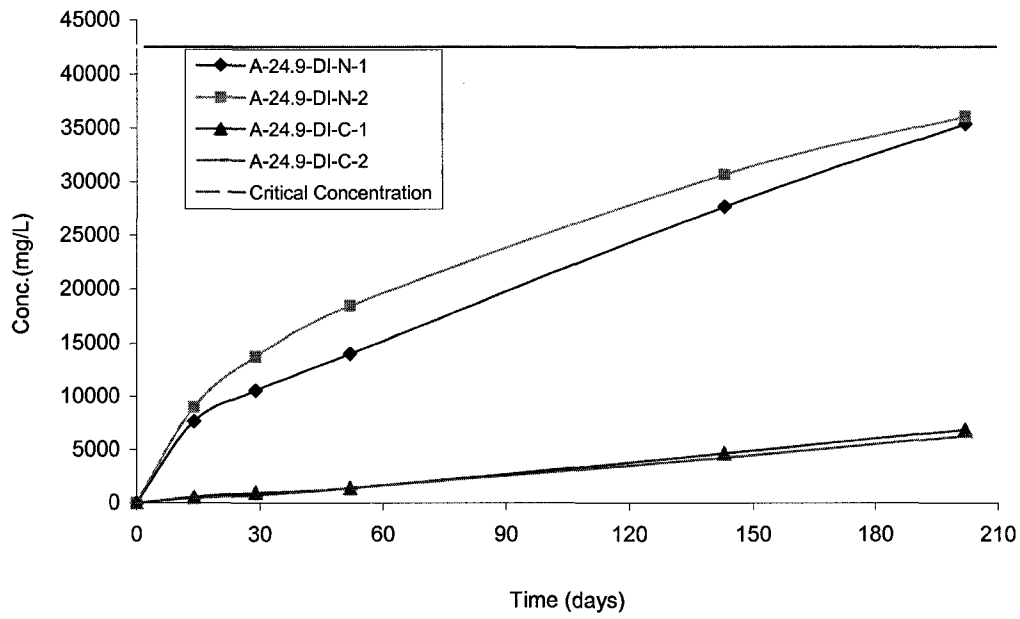


Fig. B5.1 Total Concentration-Time

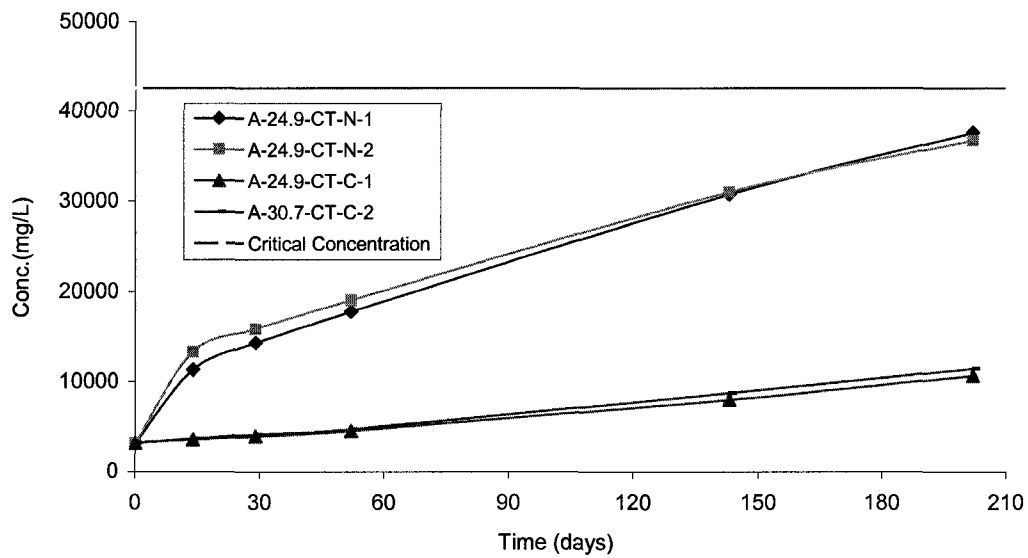


Fig. B5.2 Total Concentration-Time

Table B5.5 Ion Concentration (mg/L) vs. Time

Sample #	Sampling Times	0	1	2	3	5	7
	Sampling Date	24/06/2003	08/07/2003	23/07/2003	15/08/2003	14/11/2003	12/01/2004
	Sampling Days	0		0	30	121	180
A-9.1-DI-N-1	SO ₄ ²⁻				152.85	593.03	873.97
	Cl ⁻				439.16	2190.11	3257.05
	F ⁻						
	Br ⁻					2.50	3.51
	HCO ₃ ⁻						
	NO ₃ ⁻						
	NO ₂ ⁻						
	Na ⁺			0.83	299.23	1416.08	2187.13
	K ⁺				12.02	91.44	144.87
	Ca ²⁺			0.35	2.80	12.55	16.19
	Mg ²⁺				1.20	15.41	41.59
	Li ⁺				0.07	0.46	0.82
	NH ₄ ⁺						
SUM			1.18	907.34	4321.58	6525.13	
CBE (%)				-6.83	-5.87	-3.21	

Sample #	Sampling Times	0	1	2	3	5	7
	Sampling Date	24/06/2003	08/07/2003	23/07/2003	15/08/2003	14/11/2003	12/01/2004
	Sampling Days	0	14	29	52	143	202
A-9.1-DI-N-2	SO ₄ ²⁻		139.60	443.96	544.50	1002.75	1257.86
	Cl ⁻		672.10	1169.30	1543.77	2968.12	3653.01
	F ⁻		0.26	0.60	0.68	0.75	1.69
	Br ⁻				1.40	5.08	6.31
	HCO ₃ ⁻						
	NO ₃ ⁻						
	NO ₂ ⁻						
	Na ⁺	0.83	456.55	877.77	1149.39	2078.18	2600.15
	K ⁺		16.81	29.62	40.47	129.45	170.97
	Ca ²⁺	0.345	3.24	10.15	13.05	21.74	24.24
	Mg ²⁺		3.95		4.94	28.67	47.32
	Li ⁺		0.10	0.24	0.30	0.75	0.98
	NH ₄ ⁺						
UA2	SUM	1.175	1292.62	2531.65	3298.50	6235.50	7762.53
	CBE (%)		-2.52	-3.37	-2.59	-3.66	-2.62

Table B5.6 Ion Concentration (mg/L) vs. Time

Sample #	Sampling Times	0	1	2	3	5	7
	Sampling Date	24/06/2003	08/07/2003	23/07/2003	15/08/2003	14/11/2003	12/01/2004
	Sampling Days			0	30	121	180
A-9.1-DI-C-1	SO ₄ ²⁻				16.06	61.65	122.01
	Cl ⁻				35.21	223.21	396.35
	F ⁻						
	Br ⁻						
	HCO ₃ ⁻						
	NO ₃ ⁻						
	NO ₂ ⁻						
	Na ⁺			0.83	30.14	148.22	289.68
	K ⁺				0.97	9.51	15.74
	Ca ²⁺			0.35	0.47	1.85	2.64
Mg ²⁺						8.15	
Li ⁺							
UA3	NH ₄ ⁺						
	SUM			1.18	82.85	444.45	834.58
	CBE (%)				1.19	-5.51	0.34

Sample #	Sampling Times	0	1	2	3	5	7
	Sampling Date	24/06/2003	08/07/2003	23/07/2003	15/08/2003	14/11/2003	12/01/2004
	Sampling Days	0	14	29	52	143	202
A-9.1-DI-C-2	SO ₄ ²⁻		28.92	139.71	214.18	770.53	1117.77
	Cl ⁻		171.35	596.99	1065.35	2612.98	3453.32
	F ⁻		0.08	0.23			
	Br ⁻		0.27	0.90	0.02	3.10	6.68
	HCO ₃ ⁻						
	NO ₃ ⁻						
	NO ₂ ⁻						
	Na ⁺	0.83	112.64	409.28	718.86	1851.10	2499.99
	K ⁺		7.63	25.30	38.80	118.85	162.67
	Ca ²⁺	0.345	1.02	2.61	3.86	10.75	14.83
Mg ²⁺		0.82		2.79	19.07		
Li ⁺			0.15	0.20	0.60	0.90	
UA4	NH ₄ ⁺						
	SUM	1.175	322.74	1175.17	2044.07	5386.99	7256.16
	CBE (%)		-2.12	-3.02	-2.64	-2.27	-2.95

Table B5.7 Ion Concentration (mg/L) vs. Time

Sample #	Sampling Times	0	1	2	3	5	7
	Sampling Date	24/06/2003	08/07/2003	23/07/2003	15/08/2003	14/11/2003	12/01/2004
	Sampling Days	0	14	29	52	143	202
A-9.1-CT-N-1	SO ₄ ²⁻	288.73	504.77	927.48	1141.67	1574.34	1874.34
	Cl ⁻	1108.08	2001.65	2400.04	2709.22	3780.22	4315.98
	F ⁻	2.98	3.47	4.14	4.49	3.37	4.79
	Br ⁻						
	HCO ₃ ⁻	663.60	700.00	700.00	646.51	479.55	431.82
	NO ₃ ⁻	25					
	NO ₂ ⁻	15.47					
	Na ⁺	1005.87	1728.82	2142.88	2309.89	2773.65	3024.11
	K ⁺	14.31	35.77	45.42	52.56	117.34	163.89
	Ca ²⁺	16.09	24.50	29.32	29.97	33.21	38.95
	Mg ²⁺	16.28	16.90		12.12	31.36	52.34
	Li ⁺	0.12	0.37	0.50	0.42	0.79	1.04
	UB1	NH ₄ ⁺		74.38	84.20	77.08	76.49
	SUM	3156.53	5090.64	6333.97	6983.92	8870.31	9907.25
	CBE (%)	-2.88	2.82	1.10	-0.94	-5.32	-8.35

Table B5.8 Ion Concentration (mg/L) vs. Time

Sample #	Sampling Times	0	1	2	3	5	7
	Sampling Date	24/06/2003	08/07/2003	23/07/2003	15/08/2003	14/11/2003	12/01/2004
	Sampling Days	0	14	29	52	143	202
A-9.1-CT-C-1	SO ₄ ²⁻			288.73	323.45	627.77	1009.94
	Cl ⁻			1108.08	1355.62	1871.58	2250.00
	F ⁻			2.98	3.21	3.02	3.50
	Br ⁻						
	HCO ₃ ⁻			663.60	678.57	413.33	327.27
	NO ₃ ⁻			25.00			
	NO ₂ ⁻			15.47	50.36		
	Na ⁺			1005.87	1224.58	1542.97	2010.88
	K ⁺			14.31	16.66	48.90	86.84
	Ca ²⁺			16.09	19.87	14.22	18.90
	Mg ²⁺			16.28	5.76	15.79	29.58
	Li ⁺			0.12	0.22	0.35	0.56
	UB3	NH ₄ ⁺					
	SUM			3156.53	3678.30	4537.93	5737.47
	CBE (%)			-2.88	-1.91	-1.63	1.72
A-9.1-CT-C-2	SO ₄ ²⁻	288.73	330.33	415.58	521.70	1054.53	1347.53
	Cl ⁻	1108.08	1251.70	1321.38	1523.52	2384.57	3158.67
	F ⁻	2.98	2.94	3.09	2.95	3.39	3.76
	Br ⁻					3.00	3.73
	HCO ₃ ⁻	663.60	709.00	680.00	666.00	568.18	507.14
	NO ₃ ⁻	25					
	NO ₂ ⁻	15.47					
	Na ⁺	1005.87	1042.12	1089.68	1213.99	1921.02	2390.38
	K ⁺	14.31	16.89	17.88	23.14	78.89	115.32
	Ca ²⁺	16.09	20.24	18.87	15.10	18.06	20.67
	Mg ²⁺	16.28	12.74		6.30	21.38	35.13
	Li ⁺	0.12	0.25	0.27	0.27	0.52	0.71
	UB4	NH ₄ ⁺		59.75	61.00	61.17	60.44
	SUM	3156.53	3445.96	3607.75	4034.12	6113.99	7649.60
	CBE (%)	-2.88	-2.44	-4.37	-5.34	-3.59	-4.49

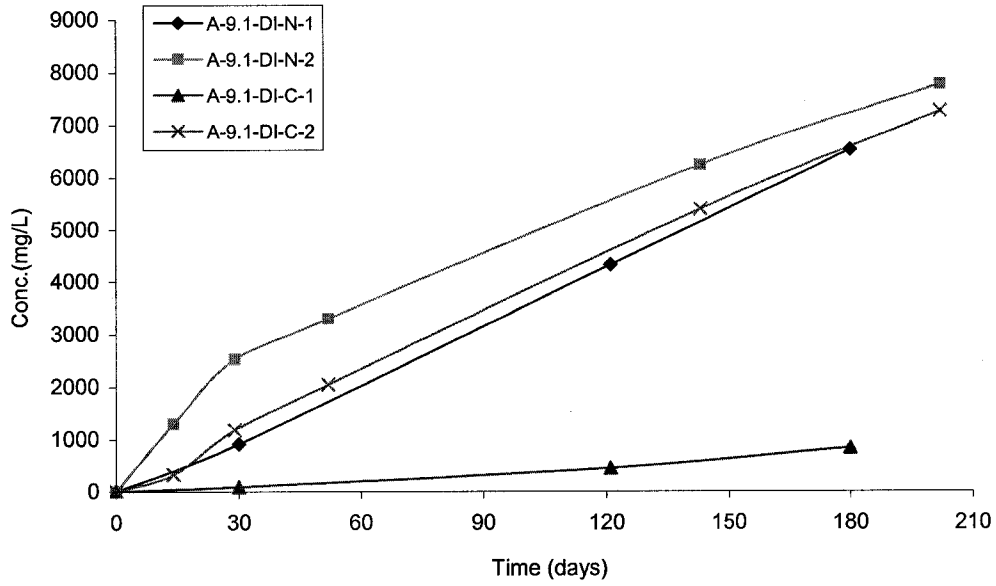


Fig. B5.3 Total Concentration-Time

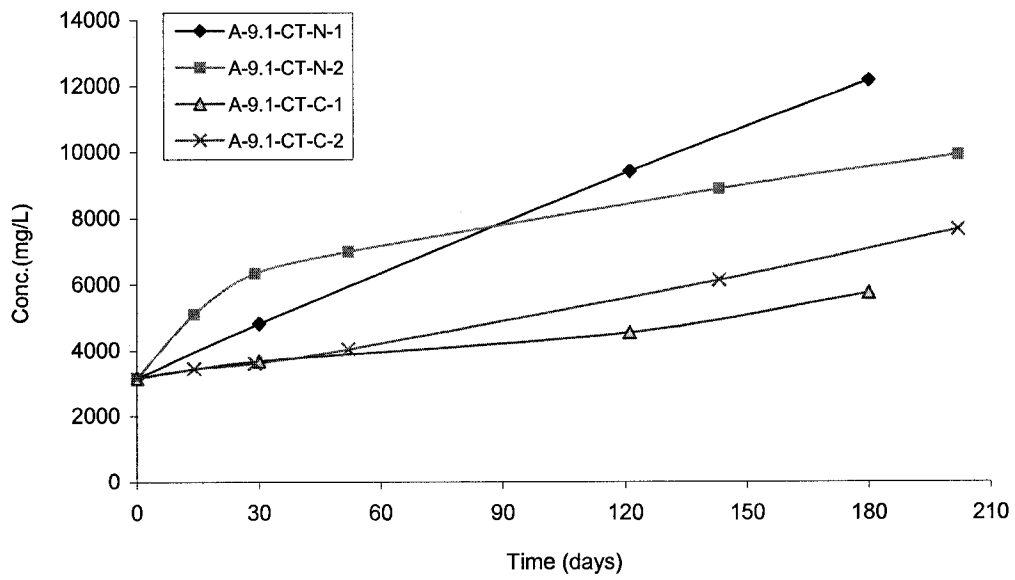


Fig. B5.4 Total Concentration-Time

Table B5.9 Ion Concentration (mg/L) vs. Time

	Sampling Times	0	1	2	3	5	7
	Sampling Date	24/06/2003	08/07/2003	23/07/2003	15/08/2003	14/11/2003	12/01/2004
Sample #	Sampling Days	0		0	30	121	180
A-6.3-DI-N-1	SO ₄ ²⁻				287.79	798.35	1118.94
	Cl ⁻				987.21	2387.12	3192.38
	F ⁻				0.59	1.51	1.64
	Br ⁻					3.30	4.79
	HCO ₃ ⁻						
	NO ₃ ⁻						
	NO ₂ ⁻						
	Na ⁺			0.83	668.35	1716.65	2319.99
	K ⁺				21.31	88.43	146.50
	Ca ²⁺			0.35	6.66	24.80	29.24
	Mg ²⁺				2.82	20.96	39.27
	Li ⁺					0.48	0.82
	LA1	NH ₄ ⁺					
	SUM			1.18	1974.73	5041.59	6853.58
	CBE (%)				-5.73	-2.48	-1.78

	Sampling Times	0	1	2	3	5	7
	Sampling Date	24/06/2003	08/07/2003	23/07/2003	15/08/2003	14/11/2003	12/01/2004
Sample #	Sampling Days	0	14	29	52	143	202
A-6.3-DI-N-2	SO ₄ ²⁻		240.03	607.72	739.37	1169.09	1364.99
	Cl ⁻		1056.77	1579.28	1928.69	3310.82	4240.72
	F ⁻		0.63	1.45	1.32	1.67	2.15
	Br ⁻					4.25	5.90
	HCO ₃ ⁻						
	NO ₃ ⁻						
	NO ₂ ⁻						
	Na ⁺	0.83	709.07	1123.62	1385.26	2237.96	2831.84
	K ⁺		22.19	32.47	45.10	132.80	171.89
	Ca ²⁺	0.345	7.01	16.74	21.70	28.85	30.98
	Mg ²⁺		5.62	2.85	7.52	31.68	50.36
	Li ⁺		0.17	0.30		0.74	0.96
	LA2	NH ₄ ⁺					
	SUM	1.175	2041.47	3364.42	4128.98	6917.87	8699.78
	CBE (%)		-3.83	-5.95	-5.05	-5.80	-5.23

Table B5.10 Ion Concentration (mg/L) vs. Time

Sample #	Sampling Times	0	1	2	3	5	7
	Sampling Date	24/06/2003	08/07/2003	23/07/2003	15/08/2003	14/11/2003	12/01/2004
	Sampling Days	0		0	30	121	180
A-6.3-DI-C-1	SO ₄ ²⁻				16.53	85.24	149.67
	Cl ⁻				33.43	432.73	593.71
	F ⁻						
	Br ⁻						
	HCO ₃ ⁻						
	NO ₃ ⁻						
	NO ₂ ⁻						
	Na ⁺			0.83	25.63	293.22	395.51
	K ⁺				0.75	15.38	41.02
	Ca ²⁺			0.35	2.17	1.60	2.91
	Mg ²⁺					2.36	9.77
	Li ⁺					0.11	0.21
	LA3	NH ₄ ⁺					
	SUM			1.18	78.50	830.64	1192.80
	CBE (%)				-1.76	-1.95	-1.58

Sample #	Sampling Times	0	1	2	3	5	7
	Sampling Date	24/06/2003	08/07/2003	23/07/2003	15/08/2003	14/11/2003	12/01/2004
	Sampling Days	0	14	29	52	143	202
A-6.3-DI-C-2	SO ₄ ²⁻		29.52	37.73	65.49	370.60	521.58
	Cl ⁻		89.87	225.05	479.92	1646.74	2408.83
	F ⁻		0.06	0.09			
	Br ⁻				0.53	2.63	3.61
	HCO ₃ ⁻						
	NO ₃ ⁻						
	NO ₂ ⁻						
	Na ⁺	0.83	65.89	146.72	284.63	994.91	1500.59
	K ⁺		4.22	7.34	15.99	78.63	119.77
	Ca ²⁺	0.345	0.91	1.08	2.37	4.22	5.87
	Mg ²⁺		0.86			14.96	29.70
	Li ⁺		0.00	0.04		0.37	0.60
	LA4	NH ₄ ⁺		1.01			
	SUM	1.175	192.35	418.05	848.93	3113.07	4590.54
	CBE (%)		-0.03	-3.66	-7.15	-7.31	-5.09

Table B5.11 Ion Concentration (mg/L) vs. Time

Sample #	Sampling Times	0	1	2	3	5	7
	Sampling Date	24/06/2003	08/07/2003	23/07/2003	15/08/2003	14/11/2003	12/01/2004
	Sampling Days	0		0	30	121	180
A-6.3-CT-N-1	SO ₄ ²⁻			288.73	524.38	1533.65	1861.11
	Cl ⁻			1108.08	2192.76	4267.30	5202.49
	F ⁻			2.98	3.51	4.53	2.80
	Br ⁻					5.16	5.24
	HCO ₃ ⁻			663.60	654.55	562.79	482.50
	NO ₃ ⁻			25.00			
	NO ₂ ⁻			15.47	43.65		
	Na ⁺			1005.87	1607.36	2907.25	3665.76
	K ⁺			14.31	34.18	128.81	184.59
	Ca ²⁺			16.09	23.86	32.88	41.59
	Mg ²⁺			16.28	7.77	41.63	43.44
	Li ⁺			0.12	0.33	0.86	1.03
	LB1	NH ₄ ⁺					
	SUM			3156.53	5092.34	9484.87	11490.54
	CBE (%)			-2.88	-7.58	-9.03	-6.48

Sample #	Sampling Times	0	1	2	3	5	7
	Sampling Date	24/06/2003	08/07/2003	23/07/2003	15/08/2003	14/11/2003	12/01/2004
	Sampling Days	0	14	29	52	143	202
A-6.3-CT-N-2	SO ₄ ²⁻	288.73	350.63	844.83	1074.96	1447.36	1691.44
	Cl ⁻	1108.08	1778.54	2602.86	2903.45	4123.24	5056.06
	F ⁻	2.98	3.63	3.96	4.24	3.36	2.63
	Br ⁻					5.40	
	HCO ₃ ⁻	663.60	690.50	680.95	660.00	452.27	416.67
	NO ₃ ⁻	25					
	NO ₂ ⁻	15.47					
	Na ⁺	1005.87	1294.53	1944.91	2206.23	3015.97	3674.55
	K ⁺	14.31	22.34	44.21	52.32	136.79	174.65
	Ca ²⁺	16.09	22.71	28.03	26.60	36.07	38.20
	Mg ²⁺	16.28	17.74		12.39	25.03	46.79
	Li ⁺	0.12		0.48	0.48	0.80	0.98
	LB2	NH ₄ ⁺		72.22	79.75	75.34	68.33
	SUM	3156.53	4252.83	6229.98	7016.01	9314.63	11101.97
	CBE (%)	-2.88	-3.93	-5.38	-5.07	-3.82	-4.09

Table B5.12 Ion Concentration (mg/L) vs. Time

Sample #	Sampling Times	0	1	2	3	5	7
	Sampling Date	24/06/2003	08/07/2003	23/07/2003	15/08/2003	14/11/2003	12/01/2004
	Sampling Days	0		0	30	121	180
A-6.3-CT-C-1	SO ₄ ²⁻			288.73	337.29	638.15	842.58
	Cl ⁻			1108.08	1309.81	2507.89	2856.20
	F ⁻			2.98	3.11	2.74	2.34
	Br ⁻						
	HCO ₃ ⁻			663.60	685.71	434.88	425.00
	NO ₃ ⁻			25.00			
	NO ₂ ⁻			15.47	54.55		
	Na ⁺			1005.87	1086.34	1818.06	2508.34
	K ⁺			14.31	17.26	66.59	124.03
	Ca ²⁺			16.09	20.39	15.57	20.45
Mg ²⁺			16.28	6.95	13.51	34.15	
Li ⁺			0.12	0.25	0.41	0.73	
LB3	NH ₄ ⁺						
	SUM			3156.53	3521.67	5497.79	6813.81
	CBE (%)			-2.88	-6.82	-4.90	5.00

Sample #	Sampling Times	0	1	2	3	5	7
	Sampling Date	24/06/2003	08/07/2003	23/07/2003	15/08/2003	14/11/2003	12/01/2004
	Sampling Days	0	14	29	52	143	202
A-6.3-CT-C-2	SO ₄ ²⁻	288.73	319.89	377.27	559.38	1116.25	1238.14
	Cl ⁻	1108.08	1122.22	1301.50	1754.69	3138.54	3857.11
	F ⁻	2.98	3.41	3.47	3.10	5.77	2.92
	Br ⁻		1.16		0.02	4.08	3.39
	HCO ₃ ⁻	663.60	700.00	720.00	688.00	540.91	483.72
	NO ₃ ⁻	25					
	NO ₂ ⁻	15.47					
	Na ⁺	1005.87	1047.05	1137.44	1315.19	2156.73	2808.33
	K ⁺	14.31	19.02	21.44	34.57	109.35	156.80
	Ca ²⁺	16.09	19.88	17.14	15.66	18.63	21.37
Mg ²⁺	16.28	15.97		8.12	22.83	42.76	
Li ⁺	0.12	0.26	0.27	0.31	0.65	0.88	
LB4	NH ₄ ⁺		60.75	56.22	64.90	69.94	78.73
	SUM	3156.53	3309.62	3634.75	4443.94	7183.69	8694.16
	CBE (%)	-2.88	1.95	-2.08	-6.73	-7.71	-2.56

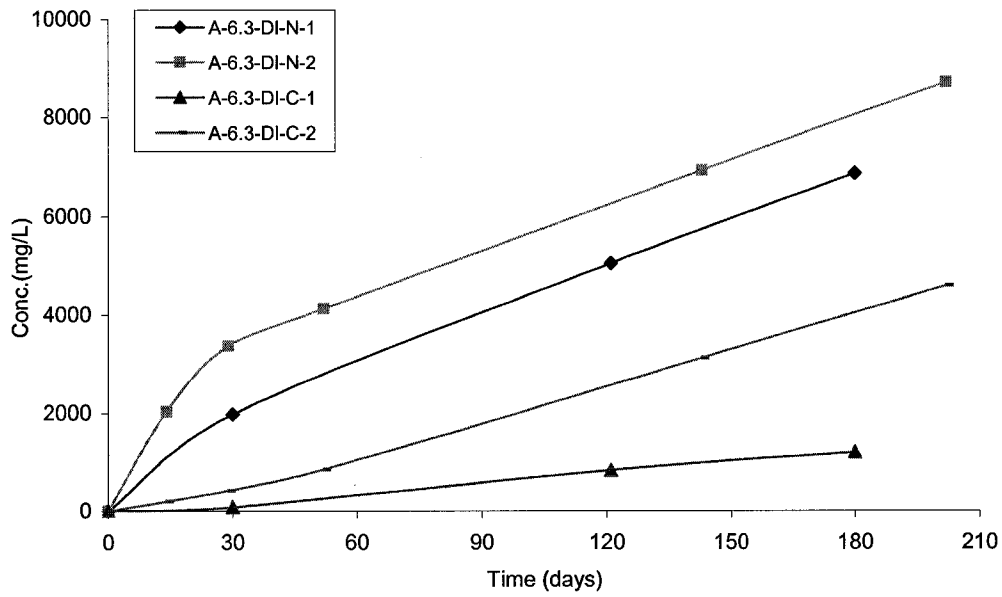


Fig. B5.5 Total Concentration-Time

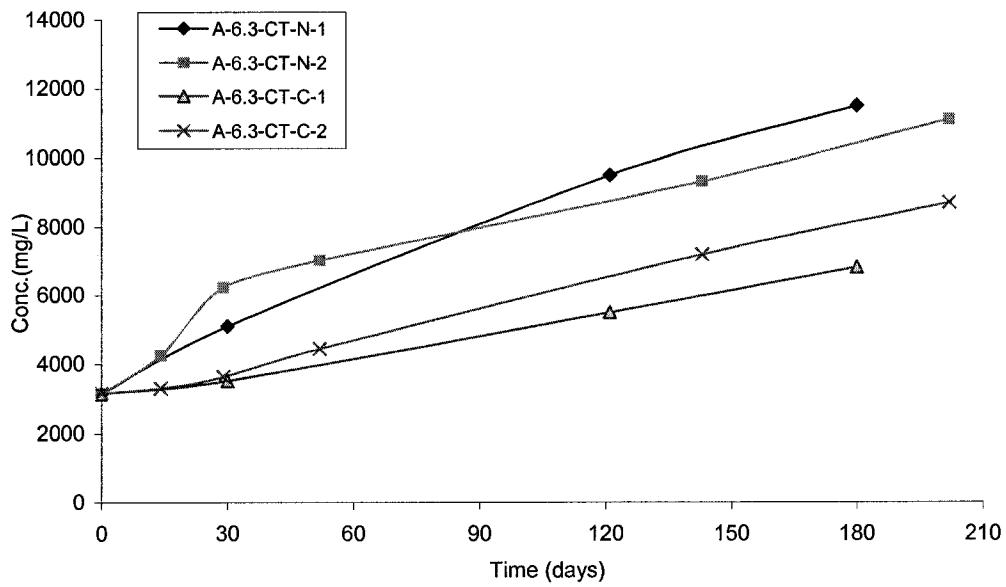


Fig. B5.6 Total Concentration-Time

Table B5.13 Ion Concentration (mg/L) vs. Time

	Sampling Times	0	1	2	3	5	7
	Sampling Date	24/06/2003	08/07/2003	23/07/2003	15/08/2003	14/11/2003	12/01/2004
Sample #	Sampling Days	0		0	30	121	180
A-3.6-DI-N-1	SO ₄ ²⁻				238.40	743.27	883.05
	Cl ⁻				985.02	2215.19	2916.05
	F ⁻				0.53	1.18	1.55
	Br ⁻						
	HCO ₃ ⁻						
	NO ₃ ⁻					4.63	
	NO ₂ ⁻				1.22		
	Na ⁺			0.83	659.37	1528.47	1937.28
	K ⁺				17.74	66.61	109.27
	Ca ²⁺			0.35	4.55	21.50	22.73
Mg ²⁺				2.74	17.34	38.34	
Li ⁺				0.13	0.38	0.62	
FA1	NH ₄ ⁺						
	SUM			1.18	1909.70	4598.57	5908.88
	CBE (%)				-5.09	-4.91	-4.80

	Sampling Times	0	1	2	3	5	7
	Sampling Date	24/06/2003	08/07/2003	23/07/2003	15/08/2003	14/11/2003	12/01/2004
Sample #	Sampling Days	0	14	29	52	143	202
A-3.6-DI-N-2	SO ₄ ²⁻		404.02	522.98	636.80	750.31	774.61
	Cl ⁻		1188.61	1399.34	1555.54	1837.24	2068.37
	F ⁻		1.05	1.48	1.87	1.74	1.51
	Br ⁻						
	HCO ₃ ⁻						
	NO ₃ ⁻						
	NO ₂ ⁻						
	Na ⁺	0.83	824.68	1022.89	1142.38	1358.21	1458.23
	K ⁺		27.62	23.82	25.06	48.90	86.95
	Ca ²⁺	0.345	13.00	16.73	21.21	24.35	25.49
Mg ²⁺		10.76		7.33	15.87	35.99	
Li ⁺		0.18	0.23	0.23			
FA2	NH ₄ ⁺						
	SUM	1.175	2469.91	2987.47	3390.43	4036.63	4451.15
	CBE (%)		-4.79	-4.61	-4.74	-3.57	-3.20

Table B5.14 Ion Concentration (mg/L) vs. Time

Sample #	Sampling Times	0	1	2	3	5	7
	Sampling Date	24/06/2003	08/07/2003	23/07/2003	15/08/2003	14/11/2003	12/01/2004
	Sampling Days	0		0	30	121	180
A-3.6-DI-C-1	SO ₄ ²⁻				11.49	135.82	231.43
	Cl ⁻				47.29	562.19	908.31
	F ⁻						
	Br ⁻						
	HCO ₃ ⁻						
	NO ₃ ⁻						
	NO ₂ ⁻						
	Na ⁺			0.83	34.29	382.84	586.62
	K ⁺				0.64	22.42	48.04
	Ca ²⁺			0.35	0.48	1.51	2.22
Mg ²⁺					5.37	14.14	
Li ⁺					0.12	0.25	
FA3	NH ₄ ⁺						
	SUM			1.18	94.18	1110.26	1791.01
	CBE (%)				-1.30	-2.51	-4.04
A-3.6-DI-C-2	SO ₄ ²⁻		11.19	16.07	29.55	183.27	282.64
	Cl ⁻		24.29	47.78	116.11	630.89	872.74
	F ⁻						
	Br ⁻					0.48	1.71
	HCO ₃ ⁻						
	NO ₃ ⁻						
	NO ₂ ⁻						
	Na ⁺	0.83	20.95	33.74	76.61	399.21	633.93
	K ⁺		0.76	1.46	3.24	22.11	46.21
	Ca ²⁺	0.345	0.53	0.73	0.91	2.35	4.04
Mg ²⁺					5.30	15.14	
Li ⁺					0.12	0.24	
FA4	NH ₄ ⁺						
	SUM	1.175	57.72	99.78	226.42	1243.75	1856.66
	CBE (%)		2.10	-4.35	-5.82	-7.74	-0.44

Table B5.15 Ion Concentration (mg/L) vs. Time

Sample #	Sampling Times	0	1	2	3	5	7
	Sampling Date	24/06/2003	08/07/2003	23/07/2003	15/08/2003	14/11/2003	12/01/2004
	Sampling Days	0		0	30	121	180
A-3.6-CT-N-1	SO ₄ ²⁻			288.73	495.91	1352.89	1548.02
	Cl ⁻			1108.08	1938.90	3069.20	3706.24
	F ⁻			2.98	3.84	4.67	4.28
	Br ⁻					2.38	
	HCO ₃ ⁻			663.60	655.81	478.00	425.00
	NO ₃ ⁻			25.00			
	NO ₂ ⁻			15.47	45.81		
	Na ⁺			1005.87	1533.15	2350.15	2888.21
	K ⁺			14.31	32.71	56.90	69.71
	Ca ²⁺			16.09	24.32	40.40	42.38
	Mg ²⁺			16.28		18.01	44.59
Li ⁺			0.12		0.51	0.64	
FB1	NH ₄ ⁺						
	SUM			3156.53	4730.46	7373.11	8729.09
	CBE (%)			-2.88	-5.62	-6.76	-3.83

Sample #	Sampling Times	0	1	2	3	5	7
	Sampling Date	24/06/2003	08/07/2003	23/07/2003	15/08/2003	14/11/2003	12/01/2004
	Sampling Days	0	14	29	52	143	202
A-3.6-CT-N-2	SO ₄ ²⁻	288.73	729.01	828.27	1034.69	1640.48	1804.43
	Cl ⁻	1108.08	1868.50	2331.98	2667.75	3414.75	4060.78
	F ⁻	2.98	4.42	4.69	4.70	5.12	4.42
	Br ⁻					2.27	2.43
	HCO ₃ ⁻	663.60	714.30	711.90	650.00	409.09	333.33
	NO ₃ ⁻	25					
	NO ₂ ⁻	15.47					
	Na ⁺	1005.87	1569.54	1783.94	2023.92	2642.86	3121.32
	K ⁺	14.31	41.78	39.94	43.81	60.68	73.51
	Ca ²⁺	16.09	38.97	29.25	32.83	32.06	34.26
	Mg ²⁺	16.28	32.64		13.20	23.87	44.07
Li ⁺	0.12	0.49	0.44	0.46	0.59	0.70	
FB2	NH ₄ ⁺		81.38	74.27	72.23		
	SUM	3156.53	5081.04	5804.68	6543.60	8231.76	9479.26
	CBE (%)	-2.88	-0.61	-5.79	-5.62	-6.70	-4.88

Table B5.16 Ion Concentration (mg/L) vs. Time

Sample #	Sampling Times	0	1	2	3	5	7
	Sampling Date	24/06/2003	08/07/2003	23/07/2003	15/08/2003	14/11/2003	12/01/2004
	Sampling Days	0		0	30	121	180
A-3.6-CT-C-1	SO ₄ ²⁻			288.73	321.51	672.14	797.91
	Cl ⁻			1108.08	1203.37	1544.26	1763.64
	F ⁻			2.98	3.25	3.25	2.76
	Br ⁻						
	HCO ₃ ⁻			663.60	700.00	400.00	325.00
	NO ₃ ⁻			25.00			1.09
	NO ₂ ⁻			15.47	49.08	22.63	9.28
FB3	Na ⁺			1005.87	1007.20	1227.73	1547.72
	K ⁺			14.31	14.42	23.86	38.06
	Ca ²⁺			16.09	16.22	17.02	18.38
	Mg ²⁺			16.28	6.44	11.48	24.51
	Li ⁺			0.12	0.21	0.25	0.37
	NH ₄ ⁺						
	SUM			3156.53	3321.71	3922.61	4528.72
CBE (%)			-2.88	-7.87	-7.38	-0.52	

Sample #	Sampling Times	0	1	2	3	5	7
	Sampling Date	24/06/2003	08/07/2003	23/07/2003	15/08/2003	14/11/2003	12/01/2004
	Sampling Days	0	14	29	52	143	202
A-3.6-CT-C-2	SO ₄ ²⁻	288.73	311.29	378.74	538.68	1095.28	1354.62
	Cl ⁻	1108.08	1201.12	1393.82	1648.87	2516.90	3074.02
	F ⁻	2.98	3.05	3.41	3.05	3.51	2.88
	Br ⁻						
	HCO ₃ ⁻	663.60	711.80	700.00	660.00	485.71	461.90
	NO ₃ ⁻	25					
	NO ₂ ⁻	15.47					
FB4	Na ⁺	1005.87	1036.65	1118.37	1252.54	1898.13	2376.68
	K ⁺	14.31	17.36	20.87	25.60	59.86	82.75
	Ca ²⁺	16.09	19.86	14.60	13.74	17.46	20.89
	Mg ²⁺	16.28	9.93	2.94	8.96	18.49	44.86
	Li ⁺	0.12	0.22	0.26	0.26	0.45	0.62
	NH ₄ ⁺		55.03	62.33	61.24	60.61	58.68
	SUM	3156.53	3366.32	3695.34	4212.95	6156.41	7477.91
CBE (%)	-2.88	-1.51	-4.42	-6.58	-6.14	-3.73	

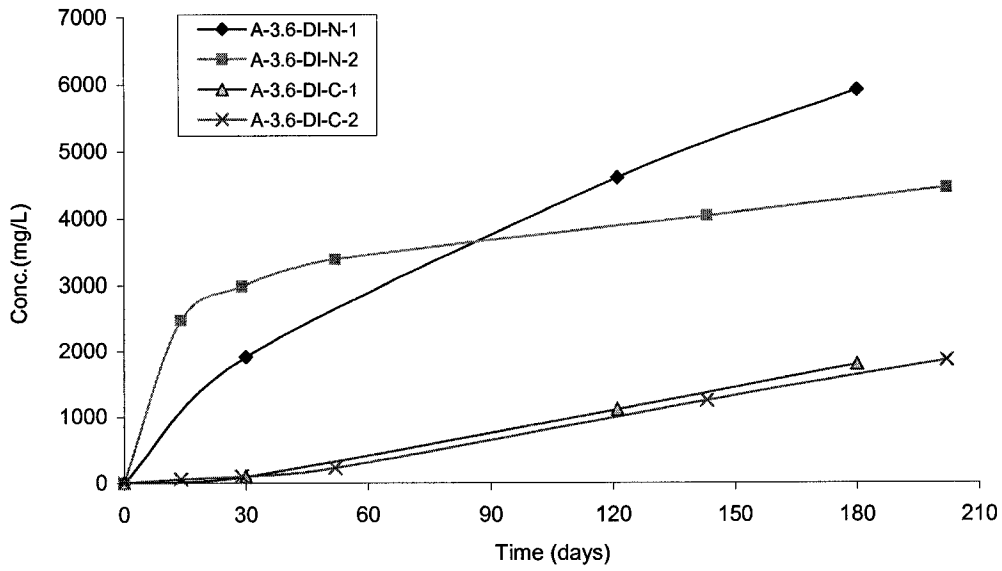


Fig. B5.7 Total Concentration-Time

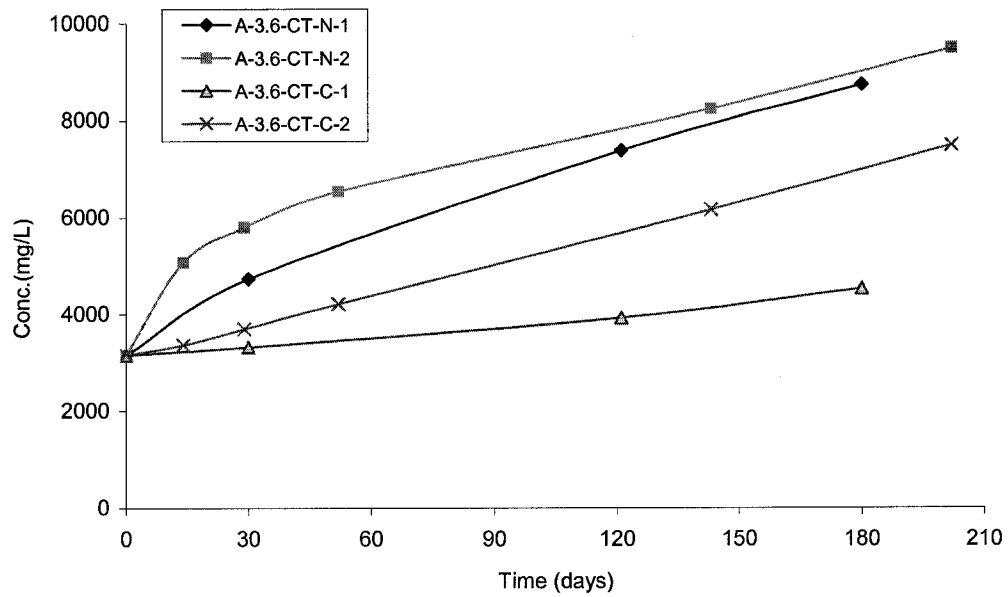


Fig. B5.8 Total Concentration-Time

Table B5.17 Ion Concentration (mg/L) vs. Time

Sample #	Sampling Times	0	1	2	3	5	7
	Sampling Date	24/06/2003	08/07/2003	23/07/2003	15/08/2003	14/11/2003	12/01/2004
	Sampling Days	0	14	29	52	143	202
A-0-DI-1	SO ₄ ²⁻		0.63	0.81	1.35	4.99	5.09
	Cl ⁻		0.78	0.89	1.26	1.24	2.05
	F ⁻						
	Br ⁻						
	HCO ₃ ⁻						
	NO ₃ ⁻						
	NO ₂ ⁻						
	Na ⁺	0.83	0.60	0.59	0.65	1.25	1.51
	K ⁺			0.18	0.31	0.67	0.67
	Ca ²⁺	0.345	0.14	0.18	0.28	0.39	0.37
Mg ²⁺							
Li ⁺							
RA1	NH ₄ ⁺						
	SUM	1.18	2.14	2.66	3.86	8.55	9.68
	CBE (%)		-3.12	-3.31	-11.69	-20.91	-23.57

Sample #	Sampling Times	0	1	2	3	5	7
	Sampling Date	24/06/2003	08/07/2003	23/07/2003	15/08/2003	14/11/2003	12/01/2004
	Sampling Days	0	14	29	52	143	202
A-0-DI-2	SO ₄ ²⁻		0.97	1.56	2.59	6.03	7.02
	Cl ⁻		0.70	0.75	0.67	0.83	1.47
	F ⁻						
	Br ⁻						
	HCO ₃ ⁻						
	NO ₃ ⁻						
	NO ₂ ⁻						
	Na ⁺	0.83	0.49	0.62	0.79	0.62	1.04
	K ⁺		0.27	0.22	0.21	0.25	0.35
	Ca ²⁺	0.345	0.44	0.19	0.15	0.25	0.38
Mg ²⁺							
Li ⁺							
RA2	NH ₄ ⁺						
	SUM	1.175	2.86	3.34	4.40	7.99	10.27
	CBE (%)		11.45	-11.88	-21.50	-52.99	-43.73

Table B5.18 Ion Concentration (mg/L) vs. Time

Sample #	Sampling Times	0	1	2	3	5	7
	Sampling Date	24/06/2003	08/07/2003	23/07/2003	15/08/2003	14/11/2003	12/01/2004
	Sampling Days	0		0	30	121	180
A-0-DI-3	SO ₄ ²⁻				0.30	2.85	3.73
	Cl ⁻				0.91	1.37	1.37
	F ⁻						
	Br ⁻						
	HCO ₃ ⁻						
	NO ₃ ⁻						
	NO ₂ ⁻						
	Na ⁺			0.83	0.40	0.56	0.91
	K ⁺				0.16	0.24	0.31
	Ca ²⁺			0.35	0.19	0.25	0.50
RA3	Mg ²⁺						
	Li ⁺						
	NH ₄ ⁺						
	SUM			1.18	1.96	5.26	6.83
	CBE (%)				-1.28	-38.88	-23.10

Sample #	Sampling Times	0	1	2	3	5	7
	Sampling Date	24/06/2003	08/07/2003	23/07/2003	15/08/2003	14/11/2003	12/01/2004
	Sampling Days	0	14	29	52	143	202
A-0-CT-1	SO ₄ ²⁻	288.73	273.13	388.88	486.72	679.10	687.50
	Cl ⁻	1108.08	1111.87	1136.45	1177.37	1190.15	1172.89
	F ⁻	2.98	2.82	3.25	3.16	3.25	2.64
	Br ⁻						
	HCO ₃ ⁻	663.60	694.10	680.95	640.00	434.29	392.86
	NO ₃ ⁻	25				1.56	28.29
	NO ₂ ⁻	15.47				43.81	16.63
	Na ⁺	1005.87	1040.75	1026.81	1058.72	1034.50	1093.83
	K ⁺	14.31	15.20	14.97	16.01	16.39	16.69
	Ca ²⁺	16.09	20.00	19.17	15.61	13.73	14.48
RB1	Mg ²⁺	16.28	12.32		8.08	12.73	20.97
	Li ⁺	0.12	0.21	0.23	0.23	0.23	0.22
	NH ₄ ⁺		56.01	55.43	58.18		
	SUM	3156.53	3226.41	3326.15	3464.07	3429.73	3447.00
	CBE (%)	-2.88	2.45	-2.15	-2.49	-8.51	-4.08

Table B5.19 Ion Concentration (mg/L) vs. Time

Sample #	Sampling Times	0	1	2	3	5	7
	Sampling Date	24/06/2003	08/07/2003	23/07/2003	15/08/2003	14/11/2003	12/01/2004
	Sampling Days	0	14	29	52	143	202
A-0-CT-2	SO ₄ ²⁻	288.73	314.81	381.27	477.58	674.98	684.79
	Cl ⁻	1108.08	1109.53	1117.99	1150.00	1186.71	1171.65
	F ⁻	2.98	2.88	3.09	3.04	3.08	0.00
	Br ⁻						
	HCO ₃ ⁻	663.60	712.50	670.00	635.00	437.21	376.19
	NO ₃ ⁻	25					
	NO ₂ ⁻	15.47				44.74	
	Na ⁺	1005.87	1001.61	1027.92	1054.47	1078.51	1075.13
	K ⁺	14.31	14.48	15.55	15.37	16.01	
	Ca ²⁺	16.09	19.05	19.13	14.48	12.98	0.57
	Mg ²⁺	16.28	12.08	3.18	8.33	12.73	
	Li ⁺	0.12	0.21	0.23	0.23	0.23	
	RB2	NH ₄ ⁺		56.94	59.80	58.73	
	SUM	3156.53	3244.09	3298.15	3417.22	3467.16	3308.34
	CBE (%)	-2.88	-0.40	-0.72	-1.71	-6.45	-6.65

Sample #	Sampling Times	0	1	2	3	5	7
	Sampling Date	24/06/2003	08/07/2003	23/07/2003	15/08/2003	14/11/2003	12/01/2004
	Sampling Days			0	30	121	180
A-0-CT-3	SO ₄ ²⁻			288.73	317.79	626.18	652.45
	Cl ⁻			1108.08	1084.89	1134.14	1152.44
	F ⁻			2.98	2.68	3.12	3.18
	Br ⁻						
	HCO ₃ ⁻			663.60	676.74	461.90	397.62
	NO ₃ ⁻			25.00			
	NO ₂ ⁻			15.47		51.82	
	Na ⁺			1005.87	1019.70	1050.46	1043.02
	K ⁺			14.31	15.68	14.93	15.22
	Ca ²⁺			16.09	18.71	13.27	14.56
	Mg ²⁺			16.28	13.81	12.83	13.65
	Li ⁺			0.12	0.19	0.21	0.16
	RB3	NH ₄ ⁺					
	SUM			3156.53	3150.19	3368.86	3292.30
	CBE (%)			-2.88	-1.66	-5.95	-5.11

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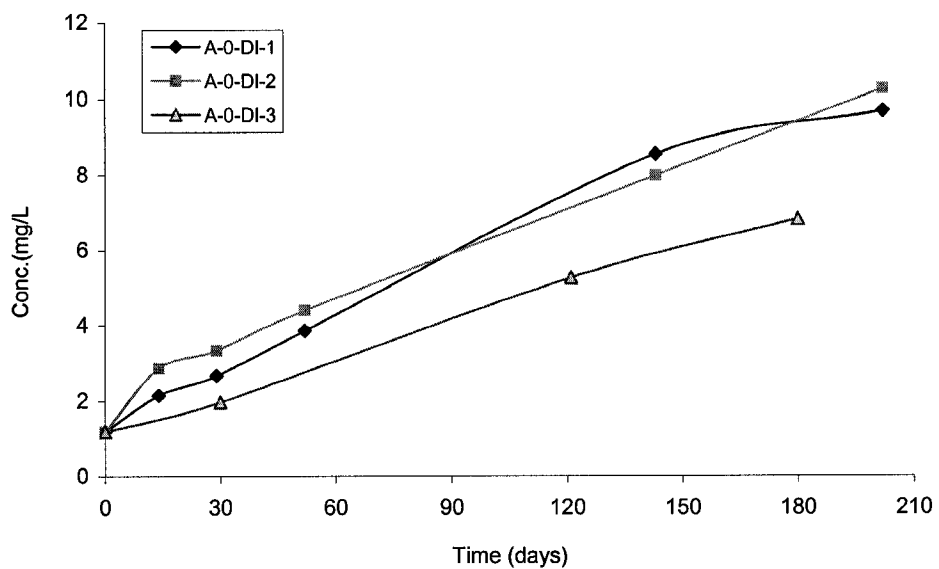


Fig. B5.9 Total Concentration-Time

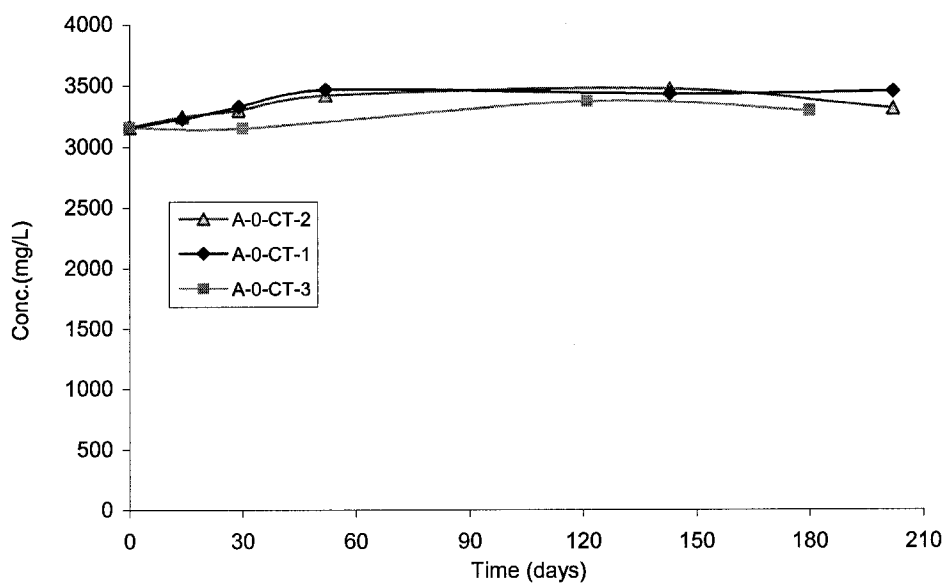


Fig. B5.10 Total Concentration-Time

Table B5.20 Ion Concentration (mg/L) vs. Time

Sample #	Sampling Times Sampling Date Sampling Days	0	1	2	3
		25/11/2003	23/12/2003	13/01/2004	02/03/2004
		0	28	49	98
N-10-DI-1	SO ₄ ²⁻		495.84	1983.32	2694.03
	Cl ⁻		1719.71	5519.60	7978.2002
	F ⁻				
	Br ⁻				
	HCO ₃ ⁻				
	NO ₃ ⁻				
	NO ₂ ⁻				
	Na ⁺	0.83	1093.41	3742.63	5650.0434
	K ⁺		41.67	137.61	230.35
	Ca ²⁺	0.345	5.27	16.66	27.11
	Mg ²⁺		23.55	66.45	86.83
	Li ⁺			0.85	1.66
	NA1 NH ₄ ⁺				
SUM	1.18	3379.43	11467.11	16668.22	
CBE (%)		-7.27	-6.53	-3.80	

Sample #	Sampling Times Sampling Date Sampling Days	0	1	2	3
		25/11/2003	23/12/2003	13/01/2004	02/03/2004
		0	28	49	98
N-10-DI-2	SO ₄ ²⁻		0.65	27.99	157.75
	Cl ⁻		2.20	85.34	492.04
	F ⁻				
	Br ⁻				
	HCO ₃ ⁻				
	NO ₃ ⁻				
	NO ₂ ⁻				
	Na ⁺	0.83	1.33	58.11	337.98
	K ⁺		0.17	1.98	13.30
	Ca ²⁺	0.345	0.20	0.35	1.08
	Mg ²⁺			1.08	5.25
	Li ⁺				
	NA2 NH ₄ ⁺				
SUM	1.18	4.54	174.85	1007.38	
CBE (%)		-2.33	-5.36	-4.98	

Table B5.21 Ion Concentration (mg/L) vs. Time

Sample #		Sampling Times	0	1	2	3
		Sampling Date	25/11/2003	23/12/2003	13/01/2004	02/03/2004
		Sampling Days	0	28	49	98
N-10-CT-1	SO ₄ ²⁻		288.73	378.23	728.59	903.41
	Cl ⁻		1108.08	1277.54	2144.21	2480.59
	F ⁻		2.98	2.88	3.80	3.32
	Br ⁻					
	HCO ₃ ⁻		663.6	650.0	638.0	590.70
	NO ₃ ⁻		25	45.84	46.16	2.31
	NO ₂ ⁻		15.47	8.82		
	Na ⁺		1005.87	1166.92	1636.99	2132.0563
	K ⁺		14.31	18.99	37.67	76.29
	Ca ²⁺		16.09	5.65	7.85	9.02
	Mg ²⁺		16.28	11.87	31.14	34.60
	Li ⁺		0.12			0.58
	NB1	NH ₄ ⁺				
		SUM		3156.53	3566.73	5274.40
	CBE (%)		-2.88	-2.89	-7.34	-0.29

Sample #		Sampling Times	0	1	2	3
		Sampling Date	25/11/2003	23/12/2003	13/01/2004	02/03/2004
		Sampling Days	0	28	49	98
N-10-CT-2	SO ₄ ²⁻		288.73	339.30	554.84	672.69
	Cl ⁻		1108.08	1194.69	1872.50	2300.3599
	F ⁻		2.98	2.88	3.80	3.62
	Br ⁻					
	HCO ₃ ⁻		663.6	648.84	631.0	604.65
	NO ₃ ⁻		25	46.31	49.75	2.49
	NO ₂ ⁻		15.47			
	Na ⁺		1005.87	1140.66	1452.92	1916.94
	K ⁺		14.31	17.77	34.00	69.54
	Ca ²⁺		16.09	7.04	6.97	8.37
	Mg ²⁺		16.28	12.59	27.52	26.71
	Li ⁺		0.12			0.48
	NB2	NH ₄ ⁺				
		SUM		3156.53	3410.07	4633.29
	CBE (%)		-2.88	-0.79	-6.32	-0.65

Table B5.22 Ion Concentration (mg/L) vs. Time

Sample #		Sampling Times	0	1	2	3
		Sampling Date	25/11/2003	23/12/2003	13/01/2004	02/03/2004
		Sampling Days	0	28	49	98
N-20-DI-1	SO ₄ ²⁻			0.56	67.90	243.54
	Cl ⁻			1.37	236.01	904.77
	F ⁻					
	Br ⁻					
	HCO ₃ ⁻					
	NO ₃ ⁻					
	NO ₂ ⁻					
	Na ⁺	0.83	0.78	160.85	636.88	
	K ⁺			4.73	28.88	
	Ca ²⁺	0.345	0.24	0.48	1.56	
	Mg ²⁺			2.95	9.99	
	Li ⁺					
	EA1 NH ₄ ⁺					
SUM	1.18	2.95	472.92	1825.62		
CBE (%)		-4.78	-4.42	-2.06		

Sample #		Sampling Times	0	1	2	3
		Sampling Date	25/11/2003	23/12/2003	13/01/2004	02/03/2004
		Sampling Days	0	28	49	98
N-20-DI-2	SO ₄ ²⁻			16.43	136.72	342.19
	Cl ⁻			66.69	746.30	1826.5599
	F ⁻					
	Br ⁻					
	HCO ₃ ⁻					
	NO ₃ ⁻					
	NO ₂ ⁻					
	Na ⁺	0.83	42.75	477.71	1179.83	
	K ⁺		2.15	21.01	69.22	
	Ca ²⁺	0.345	0.34		2.61	
	Mg ²⁺		0.78	7.99	15.63	
	Li ⁺					
	EA2 NH ₄ ⁺					
SUM	1.18	129.16	1389.72	3436.04		
CBE (%)		-5.35	-4.16	-3.62		

Table B5.23 Ion Concentration (mg/L) vs. Time

Sample #	Sampling Times Sampling Date Sampling Days	0	1	2	3
		25/11/2003	23/12/2003	13/01/2004	02/03/2004
		0	28	49	98
N-20-CT-1	SO ₄ ²⁻	288.73	347.31	614.20	769.94
	Cl ⁻	1108.08	1274.65	2294.08	2978.22
	F ⁻	2.98	2.91	3.48	3.54
	Br ⁻				
	HCO ₃ ⁻	663.6	683.3	660.0	614.0
	NO ₃ ⁻	25	45.41	50.84	29.90
	NO ₂ ⁻	15.47			
	Na ⁺	1005.87	1143.82	1642.43	2301.66
	K ⁺	14.31	19.86	48.69	99.73
	Ca ²⁺	16.09	6.09	7.92	9.71
	Mg ²⁺	16.28	20.02	19.14	32.69
	Li ⁺	0.12			0.63
	EB1	NH ₄ ⁺			
	SUM	3156.53	3543.40	5340.77	6839.98
	CBE (%)	-2.88	-2.83	-8.92	-2.21

Sample #	Sampling Times Sampling Date Sampling Days	0	1	2	3
		25/11/2003	23/12/2003	13/01/2004	02/03/2004
		0	28	49	98
N-20-CT-2	SO ₄ ²⁻	288.73	397.32	712.27	994.53
	Cl ⁻	1108.08	1135.70	2194.39	3438.36
	F ⁻	2.98	2.38	3.41	3.31
	Br ⁻				
	HCO ₃ ⁻	663.6	611.6	587.0	500
	NO ₃ ⁻	25	30.10	9.49	0.47
	NO ₂ ⁻	15.47	24.85		
	Na ⁺	1005.87	1069.07	1587.56	2588.21
	K ⁺	14.31	15.40	42.45	107.46
	Ca ²⁺	16.09	4.11	7.76	9.65
	Mg ²⁺	16.28	24.55	22.70	36.78
	Li ⁺	0.12			0.70
	EB2	NH ₄ ⁺			
	SUM	3156.53	3315.10	5167.02	7679.48
	CBE (%)	-2.88	-2.33	-8.96	-2.88

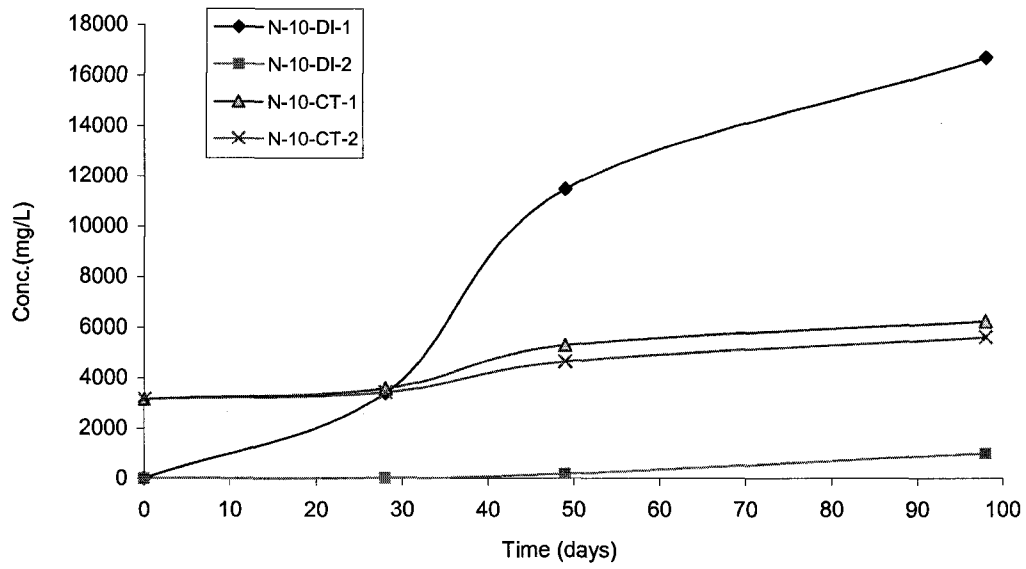


Fig. B5.11 Total Concentration-Time

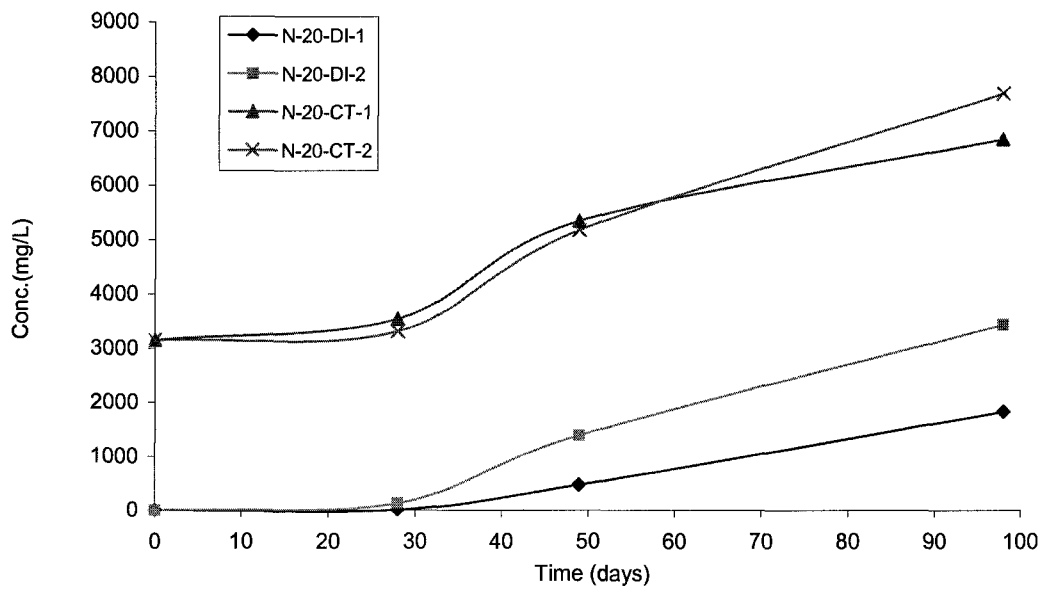


Fig. B5.12 Total Concentration-Time

Table B5.24 Ion Concentration (mg/L) vs. Time

Sample #	Sampling Times	0	1	2	3
	Sampling Date	25/11/2003	23/12/2003	13/01/2004	02/03/2004
	Sampling Days	0	28	49	98
N-30-DI-1	SO ₄ ²⁻		1.19	47.70	198.42
	Cl ⁻		3.05	192.11	807.24
	F ⁻				
	Br ⁻			0.28	
	HCO ₃ ⁻				
	NO ₃ ⁻				
	NO ₂ ⁻				
	Na ⁺	0.83	2.36	129.47	547.55
	K ⁺		0.20	6.21	39.19
	Ca ²⁺	0.345	0.19	0.38	1.30
Mg ²⁺			2.11	10.32	
WA1	Li ⁺				
	NH ₄ ⁺				
	SUM	1.18	6.99	378.26	1604.02
	CBE (%)		2.75	-3.46	-2.19

Sample #	Sampling Times	0	1	2	3
	Sampling Date	25/11/2003	23/12/2003	13/01/2004	02/03/2004
	Sampling Days	0	28	49	98
N-30-DI-2	SO ₄ ²⁻		0.80	36.59	153.25
	Cl ⁻		2.07	158.36	680.52
	F ⁻				
	Br ⁻				
	HCO ₃ ⁻				
	NO ₃ ⁻				
	NO ₂ ⁻				
	Na ⁺	0.83	1.49	100.98	461.81
	K ⁺			5.17	35.93
	Ca ²⁺	0.345	0.35	0.41	1.18
Mg ²⁺			1.79	8.67	
WA2	Li ⁺				
	NH ₄ ⁺				
	SUM	1.18	4.72	303.29	1341.36
	CBE (%)		4.76	-5.38	-1.34

Table B5.25 Ion Concentration (mg/L) vs. Time

Sample #	Sampling Times Sampling Date Sampling Days	0	1	2	3
		25/11/2003	23/12/2003	13/01/2004	02/03/2004
		0	28	49	98
N-30-CT-1	SO ₄ ²⁻	288.73	372.26	818.71	1227.85
	Cl ⁻	1108.08	1422.02	3816.02	6059.02
	F ⁻	2.98	2.94	3.52	4.03
	Br ⁻			4.52	8.17
	HCO ₃ ⁻	663.6	684.1	661.0	630.95
	NO ₃ ⁻	25	47.97	44.08	20.72
	NO ₂ ⁻	15.47	19.17		
WB1	Na ⁺	1005.87	1208.66	2424.29	4476.70
	K ⁺	14.31	28.34	122.46	294.76
	Ca ²⁺	16.09	6.10	8.66	11.67
	Mg ²⁺	16.28	27.03	55.28	76.97
	Li ⁺	0.12			1.58
	NH ₄ ⁺				
	SUM	3156.53	3818.57	7958.55	12812.42
CBE (%)	-2.88	-3.93	-9.13	0.50	

Sample #	Sampling Times Sampling Date Sampling Days	0	1	2	3
		25/11/2003	23/12/2003	13/01/2004	02/03/2004
		0	28	49	98
N-30-CT-2	SO ₄ ²⁻	288.73	328.35	499.35	586.08
	Cl ⁻	1108.08	1161.86	1823.18	2438.75
	F ⁻	2.98	2.97	3.31	3.18
	Br ⁻				
	HCO ₃ ⁻	663.60	672.73	631.00	541.86
	NO ₃ ⁻	25	46.13	51.76	2.59
	NO ₂ ⁻	15.47			
WB2	Na ⁺	1005.87	1072.64	1394.58	1913.65
	K ⁺	14.31	15.23	34.19	79.04
	Ca ²⁺	16.09	5.39	6.09	6.59
	Mg ²⁺	16.28	18.94	25.09	26.62
	Li ⁺	0.12			0.51
	NH ₄ ⁺				
	SUM	3156.53	3324.23	4468.55	5598.88
CBE (%)	-2.88	-2.63	-6.74	-1.23	

Table B5.26 Ion Concentration (mg/L) vs. Time

Sample #	Sampling Times Sampling Date Sampling Days	0	1	2	3
		25/11/2003 0	23/12/2003 28	13/01/2004 49	02/03/2004 98
N-40-DI-1	SO ₄ ²⁻		0.37	1.90	11.61
	Cl ⁻		1.44	4.27	36.37
	F ⁻				
	Br ⁻				
	HCO ₃ ⁻				
	NO ₃ ⁻				
	NO ₂ ⁻				
	Na ⁺	0.83	0.59	2.85	27.67
	K ⁺		0.20	0.33	1.86
	Ca ²⁺	0.345	0.23	0.24	0.29
	Mg ²⁺				
	Li ⁺				
	HA1 NH ₄ ⁺				
SUM	1.18	2.83	9.59	77.80	
CBE (%)		-6.78	-4.96	-0.06	

Sample #	Sampling Times Sampling Date Sampling Days	0	1	2	3
		25/11/2003 0	23/12/2003 28	13/01/2004 49	02/03/2004 98
N-40-DI-2	SO ₄ ²⁻		1.75	42.68	162.75
	Cl ⁻		3.52	200.62	815.68
	F ⁻				
	Br ⁻			0.31	0.02
	HCO ₃ ⁻				
	NO ₃ ⁻				
	NO ₂ ⁻				
	Na ⁺	0.83	2.49	123.56	534.50
	K ⁺		0.27	7.31	36.73
	Ca ²⁺	0.345	0.24	0.34	0.69
	Mg ²⁺			2.56	8.66
	Li ⁺				
	HA2 NH ₄ ⁺				
SUM	1.18	8.27	377.38	1559.03	
CBE (%)		-3.15	-6.14	-2.81	

Table B5.27 Ion Concentration (mg/L) vs. Time

Sample #	Sampling Times Sampling Date Sampling Days	0	1	2	3	
		25/11/2003	23/12/2003	13/01/2004	02/03/2004	
		0	28	49	98	
N-40-CT-1	SO ₄ ²⁻	288.73	328.73	480.77	500.70	
	Cl ⁻	1108.08	1121.38	1369.47	1716.30	
	F ⁻	2.98	2.47	3.30	3.36	
	Br ⁻					
	HCO ₃ ⁻	663.60	677.59	635.00	547.62	
	NO ₃ ⁻	25	45.15	51.85	2.59	
	NO ₂ ⁻	15.47				
	Na ⁺	1005.87	1036.46	1181.45	1508.90	
	K ⁺	14.31	13.95	18.06	45.12	
	Ca ²⁺	16.09	4.71	6.02	6.25	
	Mg ²⁺	16.28	24.48	24.42	19.10	
	Li ⁺	0.12				
	HB1	NH ₄ ⁺				
		SUM	3156.53	3254.90	3770.34	4349.94
	CBE (%)	-2.88	-2.79	-5.14	0.49	

Sample #	Sampling Times Sampling Date Sampling Days	0	1	2	3	
		25/11/2003	23/12/2003	13/01/2004	02/03/2004	
		0	28	49	98	
N-40-CT-2	SO ₄ ²⁻	288.73	333.11	467.85	565.95	
	Cl ⁻	1108.08	1159.11	1633.48	2406.45	
	F ⁻	2.98	2.69	3.34	3.07	
	Br ⁻					
	HCO ₃ ⁻	663.60	630.43	618.00	580.95	
	NO ₃ ⁻	25	45.26	51.11	2.56	
	NO ₂ ⁻	15.47				
	Na ⁺	1005.87	1067.67	1293.72	1893.97	
	K ⁺	14.31	14.62	24.13	65.71	
	Ca ²⁺	16.09	5.67	6.02	6.19	
	Mg ²⁺	16.28	24.08	25.00	23.33	
	Li ⁺	0.12			0.43	
	HB2	NH ₄ ⁺				
		SUM	3156.53	3282.64	4122.65	5548.60
	CBE (%)	-2.88	-1.74	-6.08	-1.70	

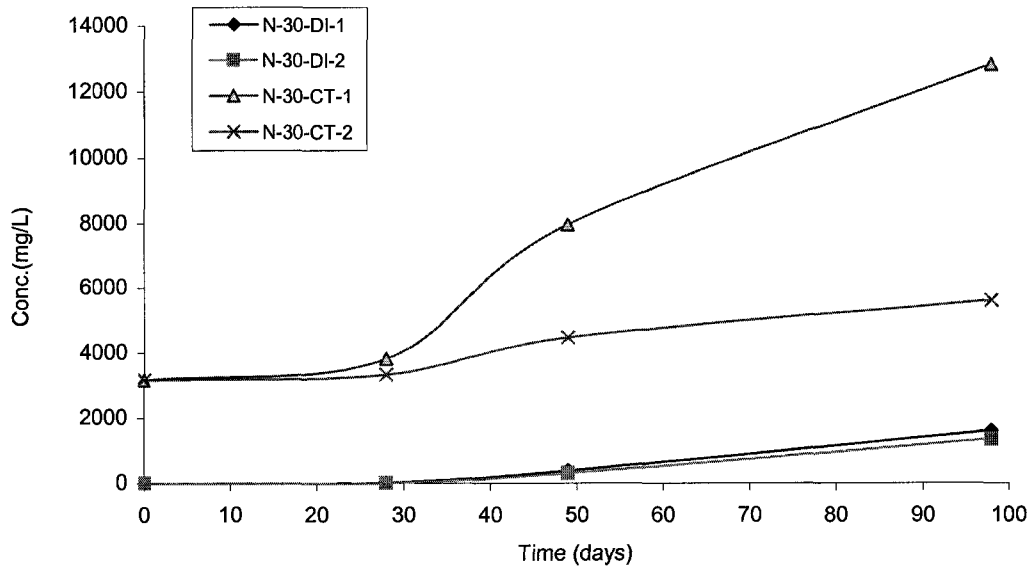


Fig. B5.13 Total Concentration-Time

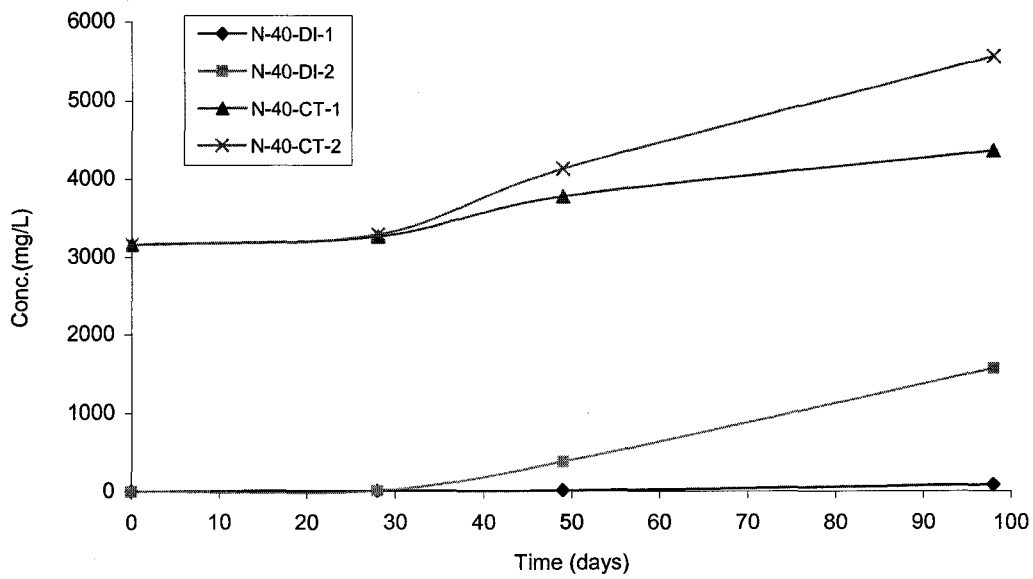


Fig. B5.14 Total Concentration-Time

Table B5.28 Ion Concentration (mg/L) vs. Time

	Sampling Times	0	1	2	3
	Sampling Date	25/11/2003	23/12/2003	13/01/2004	02/03/2004
Sample #	Sampling Days	0	28	49	98
N-50-DI-1	SO ₄ ²⁻		0.50	45.74	177.12
	Cl ⁻		1.32	148.73	719.15
	F ⁻				
	Br ⁻			0.25	0.01
	HCO ₃ ⁻				
	NO ₃ ⁻				
	NO ₂ ⁻				
	Na ⁺	0.83	0.64	101.03	488.04
	K ⁺	0	0.23	5.57	30.77
	Ca ²⁺	0.345	0.26	0.45	0.88
Mg ²⁺			1.39	8.316	
Li ⁺					
YA1	NH ₄ ⁺				
	SUM	1.18	2.95	303.15	1424.29
	CBE (%)		-0.98	-4.83	-2.60

	Sampling Times	0	1	2	3
	Sampling Date	25/11/2003	23/12/2003	13/01/2004	02/03/2004
Sample #	Sampling Days	0	28	49	98
N-50-DI-2	SO ₄ ²⁻		70.03	488.88	984.97
	Cl ⁻		219.97	1381.67	3289.70
	F ⁻				
	Br ⁻		0.24	2.68	4.32
	HCO ₃ ⁻				
	NO ₃ ⁻				
	NO ₂ ⁻				
	Na ⁺	0.83	143.31	952.75	2189.78
	K ⁺		8.09	59.67	151.75
	Ca ²⁺	0.345	0.60	2.09	3.26
Mg ²⁺		2.34	19.65	43.64	
Li ⁺		0.04		0.79	
YA2	NH ₄ ⁺				
	SUM	1.18	444.62	2907.38	6668.21
	CBE (%)		-6.92	-4.76	-4.76

Table B5.29 Ion Concentration (mg/L) vs. Time

		Sampling Times			
		0	1	2	3
		Sampling Date			
		25/11/2003	23/12/2003	13/01/2004	02/03/2004
Sample #	Sampling Days	0	28	49	98
N-50-CT-1	SO ₄ ²⁻	288.73	381.67	676.69	850.09
	Cl ⁻	1108.08	1478.47	2761.72	3901.80
	F ⁻	2.98	3.04	3.47	3.48
	Br ⁻			2.41	5.01
	HCO ₃ ⁻	663.60	666.67	646.00	595.24
	NO ₃ ⁻	25	48.23	48.76	30.93
	NO ₂ ⁻	15.47			
	Na ⁺	1005.87	1209.01	1922.79	2777.17
	K ⁺	14.31	27.45	75.10	149.30
	Ca ²⁺	16.09	7.49	8.30	8.40
	Mg ²⁺	16.28	18.14	29.18	40.76
	Li ⁺	0.12		0.41	0.79
YB1	NH ₄ ⁺				
	SUM	3156.53	3840.15	6174.82	8362.98
	CBE (%)	-2.88	-5.43	-7.86	-3.63

		Sampling Times			
		0	1	2	3
		Sampling Date			
		25/11/2003	23/12/2003	13/01/2004	02/03/2004
Sample #	Sampling Days	0	28	49	98
N-50-CT-2	SO ₄ ²⁻	288.73	430.39	815.97	987.63047
	Cl ⁻	1108.08	1755.39	3446.40	4638.67
	F ⁻	2.98	2.88	3.53	3.72
	Br ⁻			5.15	0.26
	HCO ₃ ⁻	663.60	630.95	627.00	621.43
	NO ₃ ⁻	25	47.37	45.09	22.62
	NO ₂ ⁻	15.47	18.39		
	Na ⁺	1005.87	1347.21	2328.07	3283.7977
	K ⁺	14.31	36.63	101.04	182.44
	Ca ²⁺	16.09	6.83	8.82	8.21
	Mg ²⁺	16.28	23.25	38.73	49.39
	Li ⁺	0.12		0.57	0.84
YB2	NH ₄ ⁺				
	SUM	3156.53	4299.29	7420.37	9799.0049
	CBE (%)	-2.88	-6.30	-7.65	-3.17

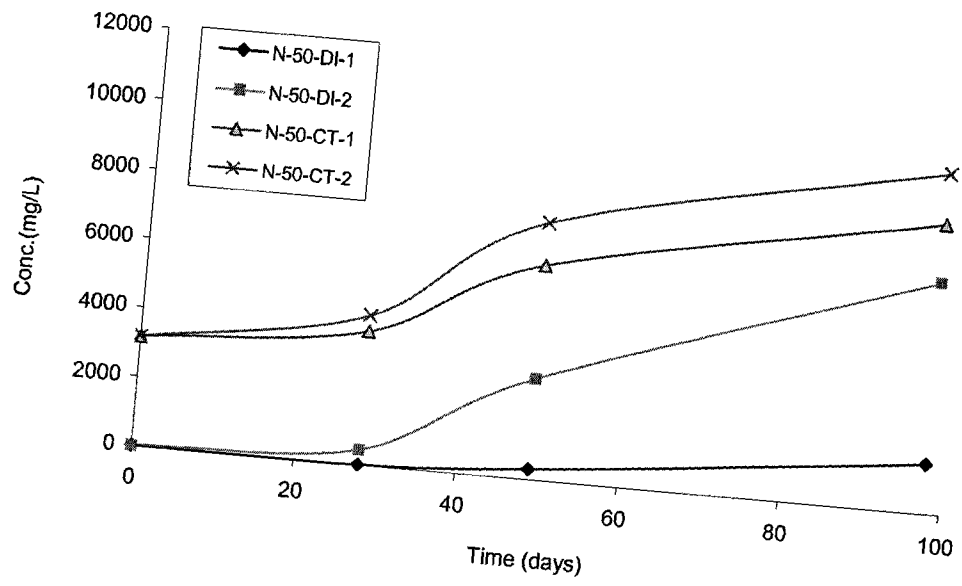


Fig. B5.15 Total Concentration-Time

Table B6.1 Salt Fluxes

Sampling Times	0	1	2	3	5	7
Sampling Date	24/06/2003	08/07/2003	23/07/2003	15/08/2003	14/11/2003	12/01/2004
Sampling Days	0	14	29	52	143	202
A-24.9-DI-N-1	1.18	7630.48	10519.54	13997.69	27655.63	35374.85
Flux (g/cm ² /s)	0.00E+00	5.68E-08	2.01E-08	1.58E-08	1.56E-08	1.36E-08
A-24.9-DI-N-2	1.18	8977.30	13710.97	18437.81	30687.02	36078.22
Flux (g/cm ² /s)	0.00E+00	6.68E-08	3.29E-08	2.14E-08	1.40E-08	9.52E-09
A-24.9-DI-C-1	1.18	540.90	969.26	1379.23	4620.74	6843.99
Flux (g/cm ² /s)	0.00E+00	4.02E-09	2.97E-09	1.86E-09	3.71E-09	3.93E-09
A-24.9-DI-C-2	1.18	446.60	731.32	1363.36	4240.33	6240.49
Flux (g/cm ² /s)	0.00E+00	3.31E-09	1.98E-09	2.86E-09	3.29E-09	3.53E-09
A-24.9-CT-N-1	3156.53	11279.44	14310.66	17734.07	30710.15	37586.97
Flux (g/cm ² /s)	0.00E+00	6.04E-08	2.11E-08	1.55E-08	1.49E-08	1.21E-08
A-24.9-CT-N-2	3156.53	13276.36	15845.71	19010.77	30999.87	36750.96
Flux (g/cm ² /s)	0.00E+00	7.53E-08	1.78E-08	1.43E-08	1.37E-08	1.02E-08
A-24.9-CT-C-1	3156.53	3543.63	3914.41	4514.50	7956.89	10628.65
Flux (g/cm ² /s)	0.00E+00	2.88E-09	2.57E-09	2.72E-09	3.94E-09	4.72E-09
A-30.7-CT-C-2	3156.53	3645.94	4135.21	4681.96	8722.03	11401.20
Flux (g/cm ² /s)	0.00E+00	3.64E-09	3.40E-09	2.48E-09	4.62E-09	4.73E-09

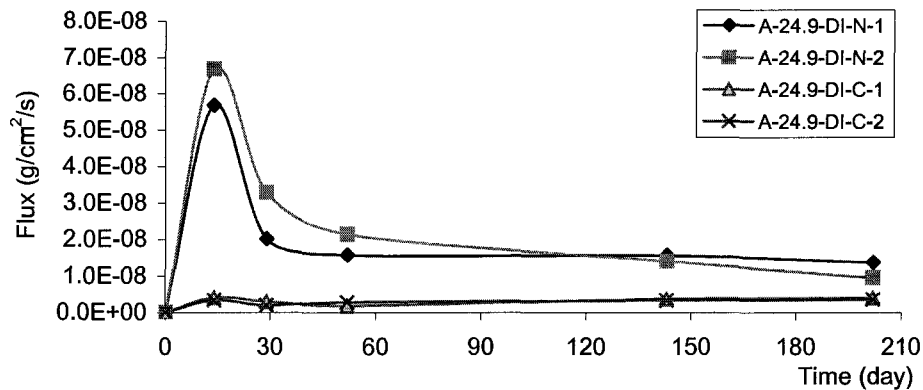


Fig. B6.1 Salt Flux

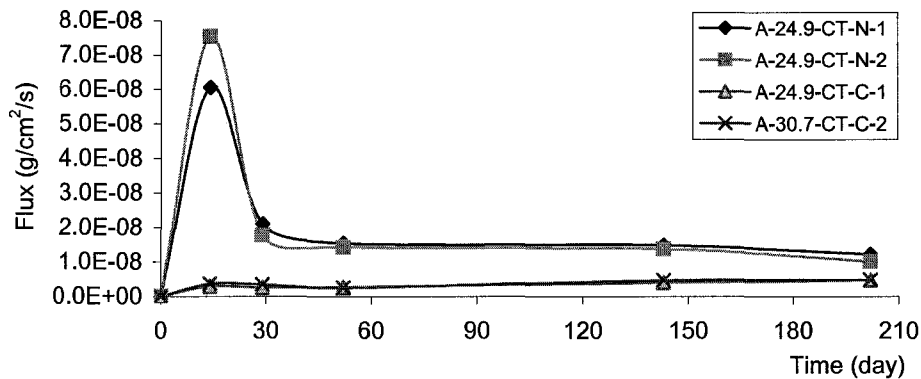


Fig. B6.2 Salt Flux

Table B6.2 Salt Fluxes

Sampling Days*	0	30	121	180		
Sampling Times	0	1	2	3	5	7
Sampling Date	24/06/2003	08/07/2003	23/07/2003	15/08/2003	14/11/2003	12/01/2004
Sampling Days**	0	14	29	52	143	202
A-9.1-DI-N-1			1.18	907.34	4321.58	6525.13
Flux (g/cm ² /s)			0.00E+00	3.15E-09	3.91E-09	3.89E-09
A-9.1-DI-N-2	1.18	1292.62	2531.65	3298.50	6235.50	7762.53
Flux (g/cm ² /s)	0.00E+00	9.61E-09	8.60E-09	3.47E-09	3.36E-09	2.70E-09
A-9.1-DI-C-1			1.18	82.85	444.45	834.58
Flux (g/cm ² /s)			0.00E+00	2.84E-10	4.14E-10	6.89E-10
A-9.1-DI-C-2	1.18	322.74	1175.17	2044.07	5386.99	7256.16
Flux (g/cm ² /s)	0.00E+00	2.39E-09	5.92E-09	3.94E-09	3.83E-09	3.30E-09
A-9.1-CT-N-1			3156.60	4813.26	9404.83	12153.72
Flux (g/cm ² /s)			0.00E+00	5.75E-09	5.26E-09	4.85E-09
A-9.1-CT-N-2	3156.53	5090.64	6333.97	6983.92	8870.31	9907.25
Flux (g/cm ² /s)	0.00E+00	1.44E-08	8.63E-09	2.94E-09	2.16E-09	1.83E-09
A-9.1-CT-C-1			3156.53	3678.30	4537.93	5737.47
Flux (g/cm ² /s)			0.00E+00	1.81E-09	9.84E-10	2.12E-09
A-9.1-CT-C-2	3156.53	3445.96	3607.75	4034.12	6113.99	7649.60
Flux (g/cm ² /s)	0.00E+00	2.15E-09	1.12E-09	1.93E-09	2.38E-09	2.71E-09

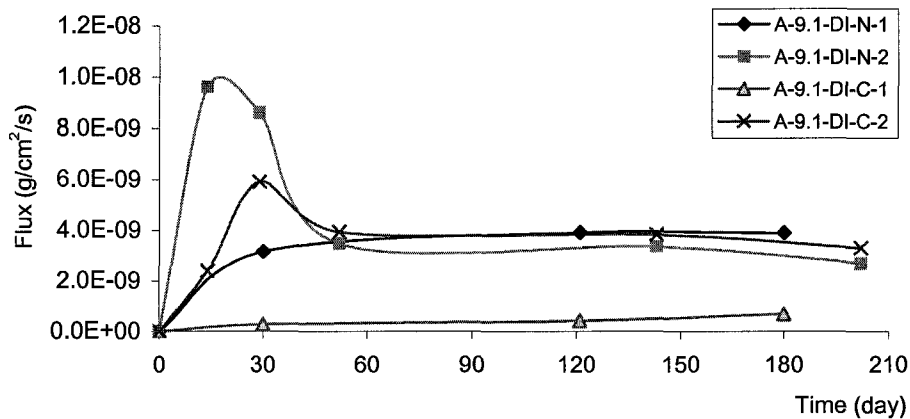


Fig.B6.3 Salt Flux

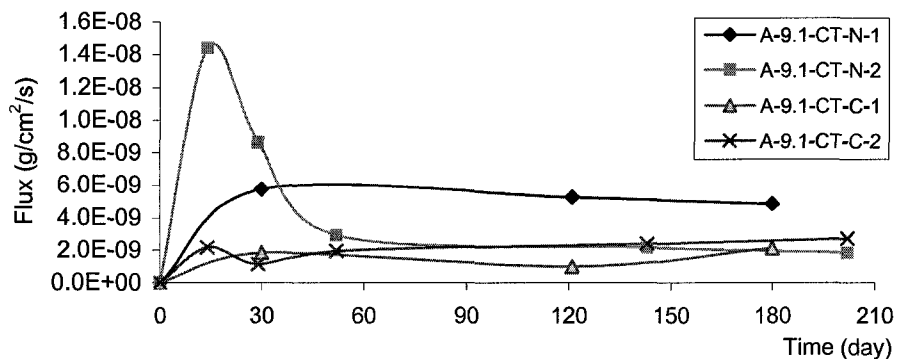


Fig. B6.4 Salt Flux

* Measurement of the samples started from July, 16, 2003

** Measurement of the samples started from June 24, 2003

Table B6.3 Salt Fluxes

Sampling Days*	0	30	121	180		
Sampling Times	0	1	2	3	5	7
Sampling Date	24/06/2003	08/07/2003	23/07/2003	15/08/2003	14/11/2003	12/01/2004
Sampling Days**	0	14	29	52	143	202
A-6.3-DI-N-1			1.18	1974.73	5041.59	6853.58
Flux (g/cm ² /s)			0.00E+00	6.85E-09	3.51E-09	3.20E-09
A-6.3-DI-N-2	1.18	2041.47	3364.42	4128.98	6917.87	8699.78
Flux (g/cm ² /s)	0.00E+00	1.52E-08	9.19E-09	3.46E-09	3.19E-09	3.15E-09
A-6.3-DI-C-1			1.18	78.50	830.64	1192.80
Flux (g/cm ² /s)			0.00E+00	2.68E-10	8.61E-10	6.39E-10
A-6.3-DI-C-2	1.18	192.35	418.05	848.93	3113.07	4590.54
Flux (g/cm ² /s)	0.00E+00	1.42E-09	1.57E-09	1.95E-09	2.59E-09	2.61E-09
A-6.3-CT-N-1			3156.53	5092.34	9484.87	11490.54
Flux (g/cm ² /s)			0.00E+00	6.72E-09	5.03E-09	3.54E-09
A-6.3-CT-N-2	3156.53	4252.83	6229.98	7016.01	9314.63	11101.97
Flux (g/cm ² /s)	0.00E+00	8.16E-09	1.37E-08	3.56E-09	2.63E-09	3.16E-09
A-6.3-CT-C-1			3156.53	3521.67	5497.79	6813.81
Flux (g/cm ² /s)			0.00E+00	1.27E-09	2.26E-09	2.32E-09
A-6.3-CT-C-2	3156.53	3309.62	3634.75	4443.94	7183.69	8694.16
Flux (g/cm ² /s)	0.00E+00	1.14E-09	2.26E-09	3.66E-09	3.14E-09	2.67E-09

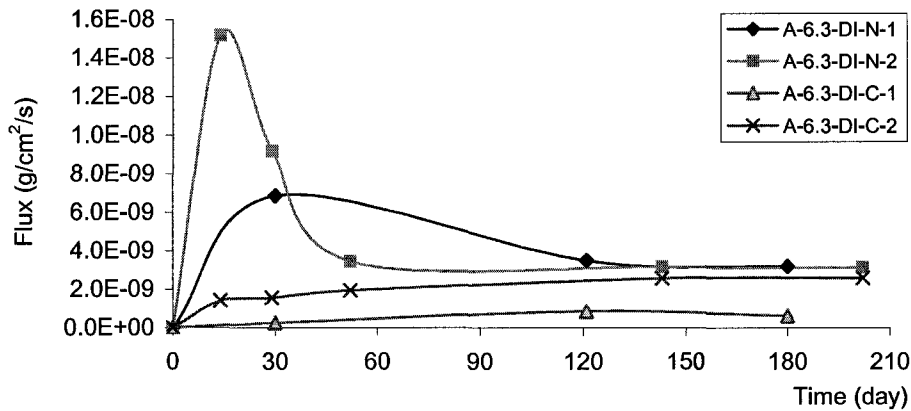


Fig. B6.5 Salt Flux

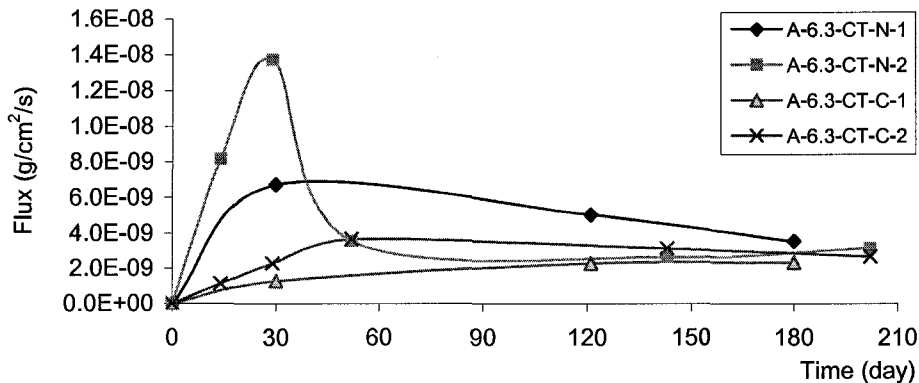


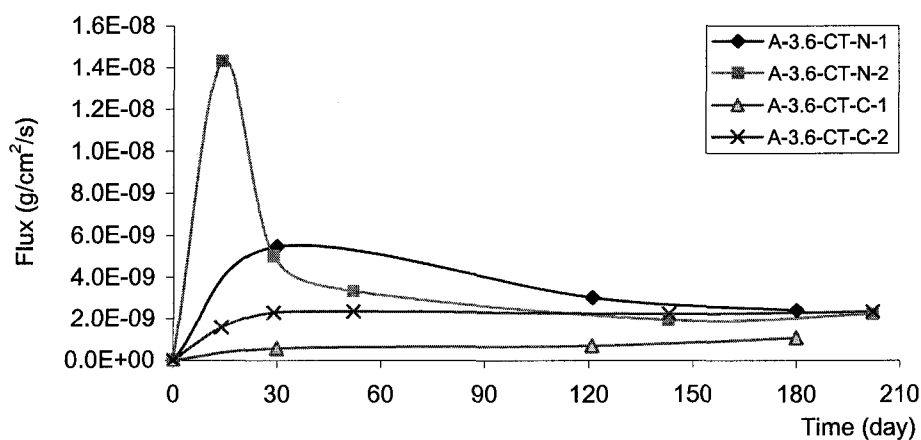
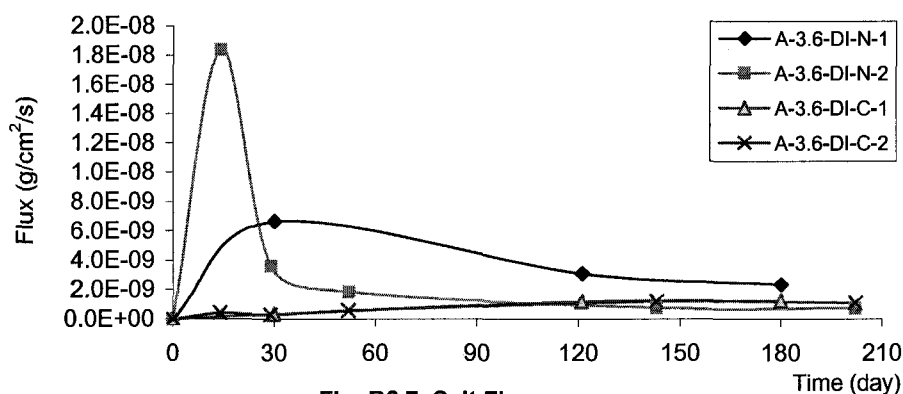
Fig. B6.6 Salt Flux

* Measurement of the samples started from July, 16, 2003

** Measurement of the samples started from June 24, 2003

Table B6.4 Salt Fluxes

Sampling Days*	0	30	121	180		
Sampling Times	0	1	2	3	5	7
Sampling Date	24/06/2003	08/07/2003	23/07/2003	15/08/2003	14/11/2003	12/01/2004
Sampling Days**	0	14	29	52	143	202
A-3.6-DI-N-1			1.18	1909.70	4598.57	5908.88
Flux (g/cm ² /s)			0.00E+00	6.63E-09	3.08E-09	2.31E-09
A-3.6-DI-N-2	1.18	2469.91	2987.47	3390.43	4036.63	4451.15
Flux (g/cm ² /s)	0.00E+00	1.84E-08	3.59E-09	1.82E-09	7.40E-10	7.32E-10
A-3.6-DI-C-1			1.18	94.18	1110.26	1791.01
Flux (g/cm ² /s)			0.00E+00	3.23E-10	1.16E-09	1.20E-09
A-3.6-DI-C-2	1.18	57.72	99.78	226.42	1243.75	1856.66
Flux (g/cm ² /s)	0.00E+00	4.21E-10	2.92E-10	5.74E-10	1.16E-09	1.08E-09
A-3.6-CT-N-1			3156.53	4730.46	7373.11	8729.09
Flux (g/cm ² /s)			0.00E+00	5.47E-09	3.03E-09	2.39E-09
A-3.6-CT-N-2	3156.53	5081.04	5804.68	6543.60	8231.76	9479.26
Flux (g/cm ² /s)	0.00E+00	1.43E-08	5.03E-09	3.35E-09	1.93E-09	2.20E-09
A-3.6-CT-C-1			3156.53	3321.71	3922.61	4528.72
Flux (g/cm ² /s)			0.00E+00	5.74E-10	6.88E-10	1.07E-09
A-3.6-CT-C-2	3156.53	3366.32	3695.34	4212.95	6156.41	7477.91
Flux (g/cm ² /s)	0.00E+00	1.56E-09	2.28E-09	2.34E-09	2.22E-09	2.33E-09



* Measurement of the samples started from July, 16, 2003

** Measurement of the samples started from June 24, 2003

Table B6.5 Salt Fluxes

Sampling Times	0	1	2	3
Sampling Date	25/11/2003	23/12/2003	13/01/2004	02/03/2004
Sampling Days	0	28	49	98
N-10-DI-1	1.18	3379.43	11467.11	16668.22
Flux (g/cm ² /s)	0	4.19E-09	1.34E-08	3.69E-09
N-10-DI-2	1.18	4.54	174.85	1007.38
Flux (g/cm ² /s)	0	4.17E-12	2.82E-10	5.90E-10
N-10-CT-1	3156.53	3566.73	5274.40	6232.87
Flux (g/cm ² /s)	0	5.09E-10	2.82E-09	6.79E-10
N-10-CT-2	3156.53	3410.07	4633.29	5605.85
Flux (g/cm ² /s)	0	3.14E-10	2.02E-09	6.89E-10
N-20-DI-1	1.18	2.95	472.92	1825.62
Flux (g/cm ² /s)	0	2.20E-12	7.77E-10	9.59E-10
N-20-DI-2	1.18	129.16	1389.72	3436.04
Flux (g/cm ² /s)	0	1.59E-10	2.08E-09	1.45E-09
N-20-CT-1	3156.53	3543.40	5340.77	6839.98
Flux (g/cm ² /s)	0	4.80E-10	2.97E-09	1.06E-09
N-20-CT-2	3156.53	3315.10	5167.02	7679.48
Flux (g/cm ² /s)	0	1.97E-10	3.06E-09	1.78E-09

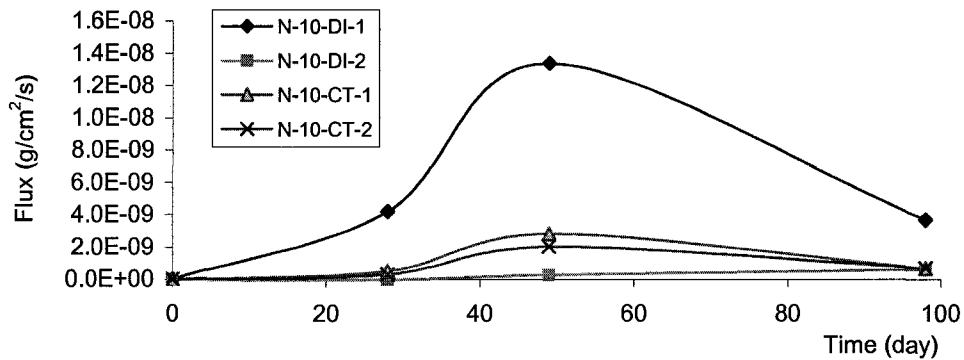


Fig. B6.9 Salt Flux

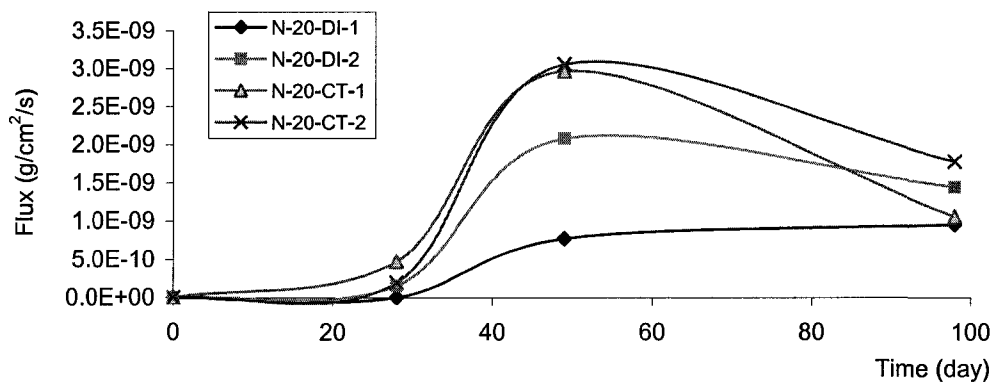


Fig. B6.10 Salt Flux

Table B6.6 Salt Fluxes

Sampling Times	0	1	2	3
Sampling Date	25/11/2003	23/12/2003	13/01/2004	02/03/2004
Sampling Days	0	28	49	98
N-30-DI-1	1.18	6.99	378.26	1604.02
Flux (g/cm ² /s)	0	7.21E-12	6.14E-10	8.69E-10
N-30-DI-2	1.18	4.72	303.29	1341.36
Flux (g/cm ² /s)	0	4.39E-12	4.94E-10	7.36E-10
N-30-CT-1	3156.53	3818.57	7958.55	12812.42
Flux (g/cm ² /s)	0	8.21E-10	6.85E-09	3.44E-09
N-30-CT-2	3156.53	3324.23	4468.55	5598.88
Flux (g/cm ² /s)	0	2.08E-10	1.89E-09	8.01E-10
N-40-DI-1	1.18	2.83	9.59	77.80
Flux (g/cm ² /s)	0	2.05E-12	1.12E-11	4.83E-11
N-40-DI-2	1.18	8.27	377.38	1559.03
Flux (g/cm ² /s)	0	8.80E-12	6.10E-10	8.37E-10
N-40-CT-1	3156.53	3254.90	3770.34	4349.94
Flux (g/cm ² /s)	0	1.22E-10	8.52E-10	4.11E-10
N-40-CT-2	3156.53	3282.64	4122.65	5548.60
Flux (g/cm ² /s)	0	1.56E-10	1.39E-09	1.01E-09

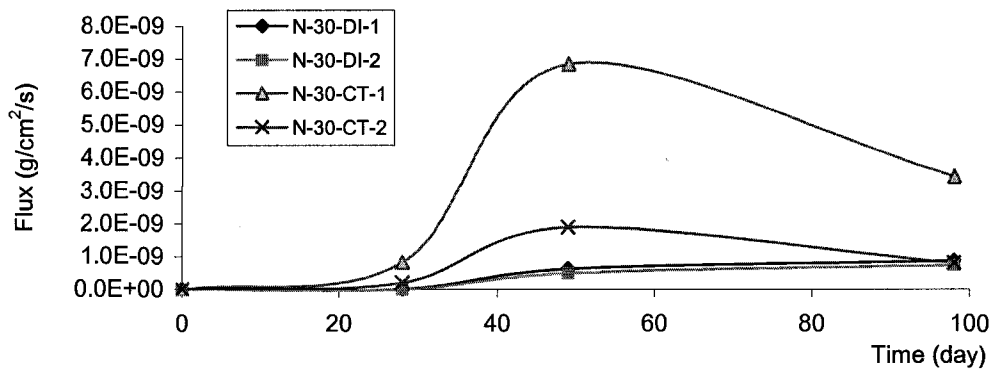


Fig. B6.11 Salt Flux

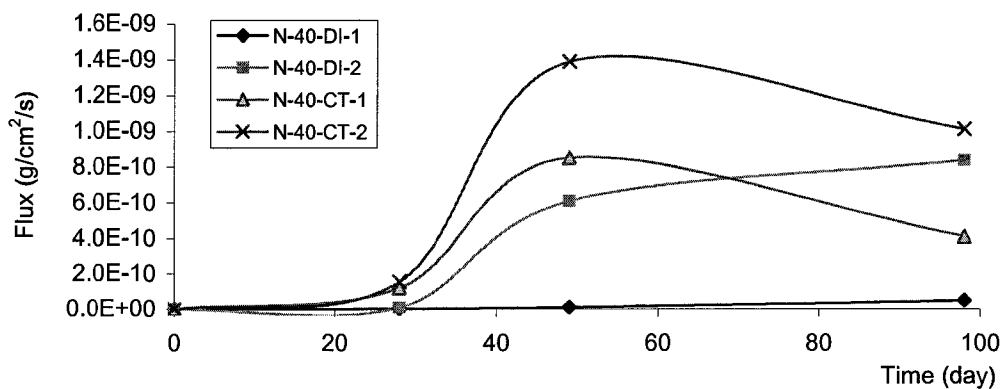
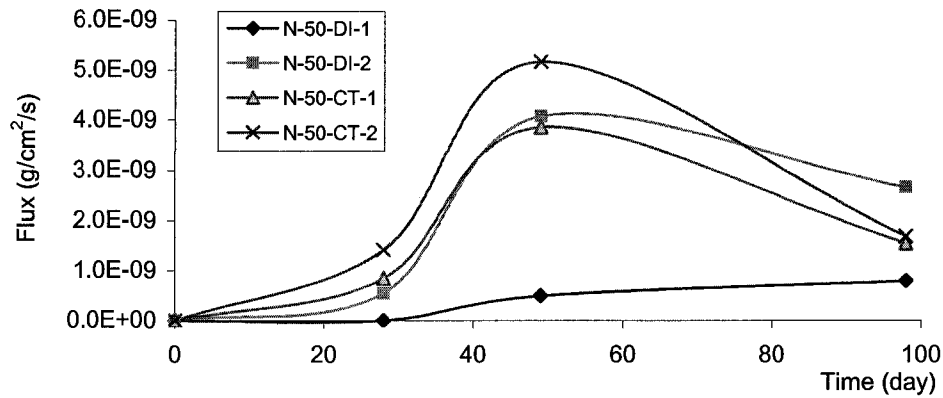


Fig. B6.12 Salt Flux

Table B6.7 Salt Fluxes

Sampling Times	0	1	2	3
Sampling Date	25/11/2003	23/12/2003	13/01/2004	02/03/2004
Sampling Days	0	28	49	98
N-50-DI-1	1.18	2.95	303.15	1424.29
Flux (g/cm ² /s)	0	2.20E-12	4.96E-10	7.94E-10
N-50-DI-2	1.18	444.62	2907.38	6668.21
Flux (g/cm ² /s)	0	5.50E-10	4.07E-09	2.66E-09
N-50-CT-1	3156.53	3840.15	6174.82	8362.98
Flux (g/cm ² /s)	0	8.48E-10	3.86E-09	1.55E-09
N-50-CT-2	3156.53	4299.29	7420.37	9799.00
Flux (g/cm ² /s)	0	1.42E-09	5.16E-09	1.69E-09

**Fig. B6.13 Salt Flux**



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SAMPLE No.: N-40-DI-1

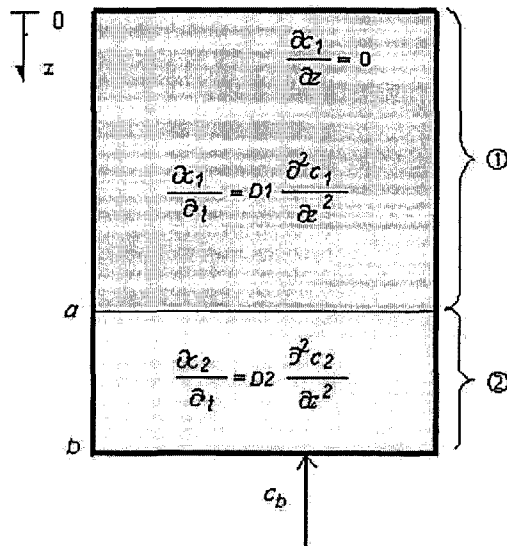
PROJECT Two-layer salt dissolution model
 (Sampling point flux profile and final concentration profile)

DESCRIPTION

Calculation of a flux profile of sampling point and final concentration profile from diffusion in a two-layer closed composite system

CALCULATION BY Yuhai (Winston) Ding

DATE May 18, 2004



**The Profile and the Settings
 of
 Salt Dissolution in a 2-Layer, 1-Dimensional, Closed System**

System parameters:

Diffusion coefficients, and layer locations as specified in the above diagram

$D_1 := 1.46 \cdot 10^{-5} \text{ cm}^2/\text{s}$	= Up layer diffusion coefficient
$D_2 := 0.66 \cdot 10^{-7} \text{ cm}^2/\text{s}$	= Bottom layer diffusion coefficient
$C_{\text{eq}} := 281 \cdot \frac{10^{-3}}{80} \text{ g/cm}^3$	= Saturated salt concentration
$C_1 := 0 \cdot 10^{-3} \text{ g/cm}^3$	= Initial salt concentration of top layer
$C_2 := 0 \cdot 10^{-3} \text{ g/cm}^3$	= Initial salt concentration of bottom later
$b := 7.0 \text{ cm}$	= Bottom layer data
$a := 5.4 \text{ cm}$	= Interface data
$sd := 3.0 \text{ cm}$	= Sampling depth
$C_b := C_{\text{eq}} \text{ g/cm}^3$	= Constant salt concentration at bottom

Simulation parameter:

$m := 1 \dots 83$	= array of time steps in which surface flux
$\text{time}_m := m \cdot 24 \cdot 3600 \text{ seconds}$	profile is calculated from

Initial concentration specification:

$$c0 := \begin{pmatrix} b & C_{eq} \\ a & C_2 \\ 0 & C_1 \end{pmatrix}$$

notes:

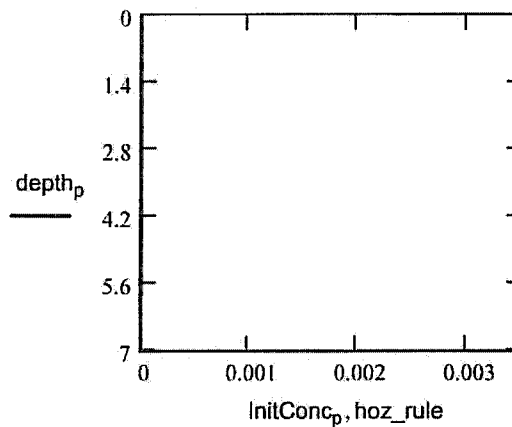
1. The 'c0' array should be in order of descending depth where the left entry is 'z' and the right is 'conc' of the layer directly below it.
2. Specify the interface position, 'a', explicitly in the array (as this simplifies the integration process).
3. Top entry must contain the value of 'b' in the 'z' position and the concentration of the surface zone in the 'conc' position.
4. This array is used to calculate the initialization integral.
5. Below is a plot which displays the initial concentration that has been specified by the 'c0' array.

```

plot_c0 := | x ← (c0_0,0 c0_0,1)
           | for i ∈ 0 .. (rows(c0) - 2)
           |   | y0,0 ← c0_i,0
           |   | y0,1 ← c0_{i+1},1
           |   | y1,0 ← c0_{i+1},0   p := 0 .. (rows(plot_c0) - 1)
           |   | y1,1 ← c0_{i+1},1   InitConc_p := plot_c0_p, 1
           |   | x ← stack(x, y)     depth_p := plot_c0_p, 0
           | x

```

the initial
concentration
profile



Calculate System Eigenvalues

System eigenvalues, β_n , are the roots of the following transcendental function, $R(\beta)$

$$C_3 := \frac{a}{\sqrt{D_1}} \quad * \quad C_4 := \frac{b-a}{\sqrt{D_2}} \quad * \quad C_5 := \sqrt{\frac{D_2}{D_1}} \quad *$$

$$R(\beta) := \tan(C_3 \cdot \beta) \cdot \tan(C_4 \cdot \beta) - C_5$$

Defining the range of significant eigenvalues, $\beta=[0, \beta_{\max}]$

$$\omega := 10$$

= adjustable parameter to define range of significance

$$\beta_{\max} := \frac{\omega \cdot \pi}{\min(|C_3|, |C_4|)} \quad *$$

= range of significance $\beta=[0, \beta_{\max}]$

$$\beta_{\max} = 0.0222$$

This subroutine calculates the roots of $R(\beta)$ within the range $\beta=[0, \beta_{\max}]$

notes:

1. The adjustable parameter ' ω ' is used to determine the range of significance $\beta=[0, \beta_{\max}]$ (i.e., the range in which the eigenvalues are calculated).
2. Choose an ' ω ' such that the final concentration profile has a high enough resolution frequency to yield an appropriate (smooth) curve. $\omega=20$ is a good initial estimate.
3. Usually 10-20 eigenvalues, i.e., ' β 's is a reasonable number for most 'time' variables.
4. Higher number of eigenvalues are required for short values of the 'time' variable (i.e., higher values of ' ω ').
5. The values of the eigenvalues are calculated by the rigorous bracketing-bisection algorithm.
6. Part of ' β -array' and $R(\beta)$, can be seen in the graph and the table on the following page.

```

β_array := | bnds0 ← 0
            | nb_sub ← 105
            | for j ∈ 1 .. nb_sub
            |   bnd_subj ←  $\frac{j \cdot \beta_{\max}}{nb\_sub}$ 
            | bnds ← stack(bnds, bnd_sub)
            | tol ← 10-8 · βmax
            | n ← 0
            | β0 ← 0
            | for i ∈ 2 .. (rows(bnds) - 1)
            |   if | bndsi-1 < bndsi
            |       | R(bndsi) ≠ 0
            |       | |R(bndsi-1) · R(bndsi)| ≤ 0
            |       | UB ← bndsi-1 if R(bndsi-1) = 0
            |       | UB ← bndsi otherwise
            |       | LB ← bndsi-1
            |       | while (UB - LB) ≥ tol
            |       |   | βn ← LB +  $\frac{UB - LB}{2}$ 
            |       |   | UB ← βn if R(UB) · R(βn) ≥ 0
            |       |   | LB ← βn if R(LB) · R(βn) ≥ 0
            |       |   | βn ← UB if |R(βn)| < 1
            |       |   | (continue) otherwise
            |       |   | n ← n + 1
            |   | β

```

Plot of the transcendental function and calculated roots, i.e., system eigenvalues

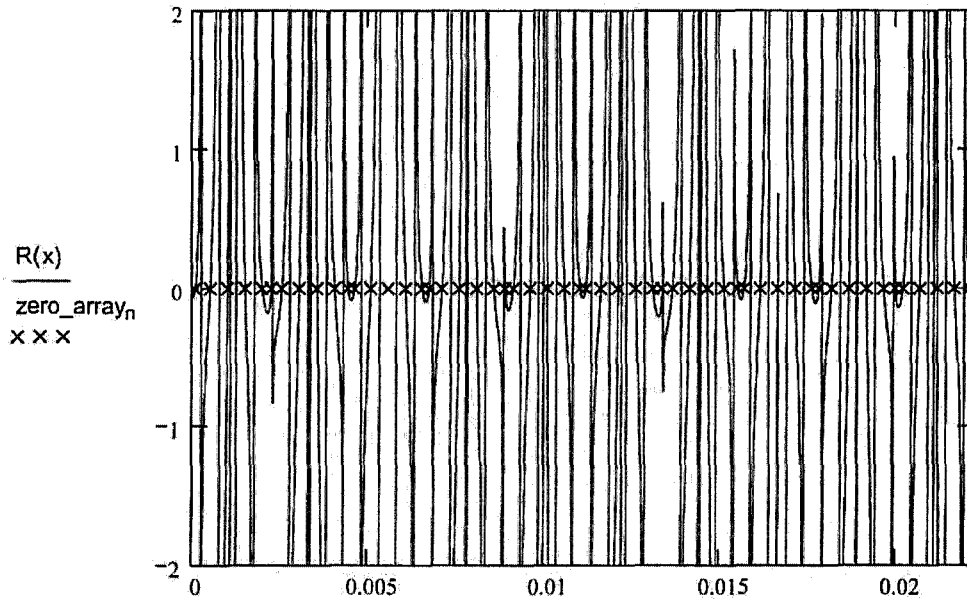
$n := 0 \dots (\text{rows}(\beta_array) - 1)$

$No_n := n$

$\beta := \beta_array$

$Nu := \max(No) \quad *$

$zero_array_n := 0$



$\beta_n =$	
0	$8.3137 \cdot 10^{-5}$
1	$5.1647 \cdot 10^{-4}$
2	$1.0104 \cdot 10^{-3}$
3	$1.5066 \cdot 10^{-3}$
4	$1.9869 \cdot 10^{-3}$
5	$2.2338 \cdot 10^{-3}$
6	$2.5441 \cdot 10^{-3}$
7	$3.0315 \cdot 10^{-3}$
8	$3.528 \cdot 10^{-3}$
9	$4.0198 \cdot 10^{-3}$
10	$4.4039 \cdot 10^{-3}$
11	$4.5903 \cdot 10^{-3}$
12	$5.0536 \cdot 10^{-3}$
13	$5.5489 \cdot 10^{-3}$
14	$6.0443 \cdot 10^{-3}$
15	$6.5113 \cdot 10^{-3}$

x, β_n	
0	$2.3978 \cdot 10^{-8}$
1	$4.1116 \cdot 10^{-7}$
2	$8.4535 \cdot 10^{-6}$
3	$-9.793 \cdot 10^{-7}$
4	$-4.5248 \cdot 10^{-8}$
5	$1.5702 \cdot 10^{-6}$
6	$6.1826 \cdot 10^{-7}$
7	$7.5664 \cdot 10^{-7}$
8	$-5.6788 \cdot 10^{-7}$
9	$-5.974 \cdot 10^{-7}$
10	$-3.8937 \cdot 10^{-7}$
11	$3.7886 \cdot 10^{-7}$
12	$2.4791 \cdot 10^{-7}$
13	$6.3612 \cdot 10^{-5}$
14	$-7.8763 \cdot 10^{-8}$
15	$-3.7162 \cdot 10^{-7}$

Calculate System Eigenfunctions

Define the eigenfunction coefficients, $X(i, \beta_n, z)$'s, $Y(i, \beta_n, z)$'s and $A(\beta_n)$'s

$i := 1..2$

$$X(i, \beta, z) := \begin{cases} \frac{\cos\left(\frac{\beta \cdot z}{\sqrt{D_1}}\right)}{\cos\left(\frac{\beta \cdot a}{\sqrt{D_1}}\right)} & \text{if } i = 1 \\ \frac{\sin\left[\frac{\beta \cdot (b - z)}{\sqrt{D_2}}\right]}{\sin\left[\frac{\beta \cdot (b - a)}{\sqrt{D_2}}\right]} & \text{otherwise} \end{cases}$$

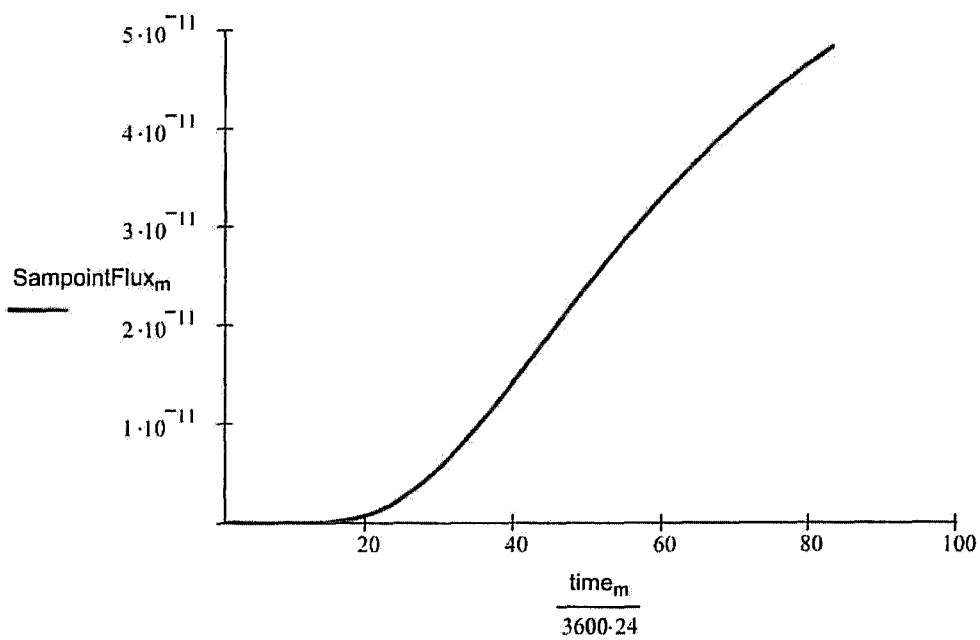
$$Y(i, \beta, z) := \begin{cases} \frac{-\sin\left(\frac{\beta \cdot z}{\sqrt{D_1}}\right) \cdot \frac{\beta}{\sqrt{D_1}}}{\cos\left(\frac{\beta \cdot a}{\sqrt{D_1}}\right)} & \text{if } i = 1 \\ \frac{\cos\left[\frac{\beta \cdot (b - z)}{\sqrt{D_2}}\right] \cdot \left(\frac{-\beta}{\sqrt{D_2}}\right)}{\sin\left[\frac{\beta \cdot (b - a)}{\sqrt{D_2}}\right]} & \text{otherwise} \end{cases}$$

$$A(\beta) := \frac{\int_0^a (C_1 - C_b) \cdot X(1, \beta, z) dz + \int_a^b (C_2 - C_b) \cdot X(2, \beta, z) dz}{\int_0^a X(1, \beta, z) \cdot X(1, \beta, z) dz + \int_a^b X(2, \beta, z) \cdot X(2, \beta, z) dz}$$

Calculate the flux profile of the sampling point

$$\text{time}_{\max} := \max(\text{time}) \quad \text{AY}_{m,n} := e^{-(\beta_n)^2 \cdot \text{time}_m} \cdot A(\beta_n) \cdot Y(1, \beta_n, \text{sd})$$

$$\text{SampointFlux}_m := D_1 \cdot \left(\sum_{n=0}^{\text{Nu}} \text{AY}_{m,n} \right)$$



Calculate the final concentration profile

$$\text{layer}(z) := \begin{cases} 2 & \text{if } a < z \leq b \\ 1 & \text{otherwise} \end{cases}$$

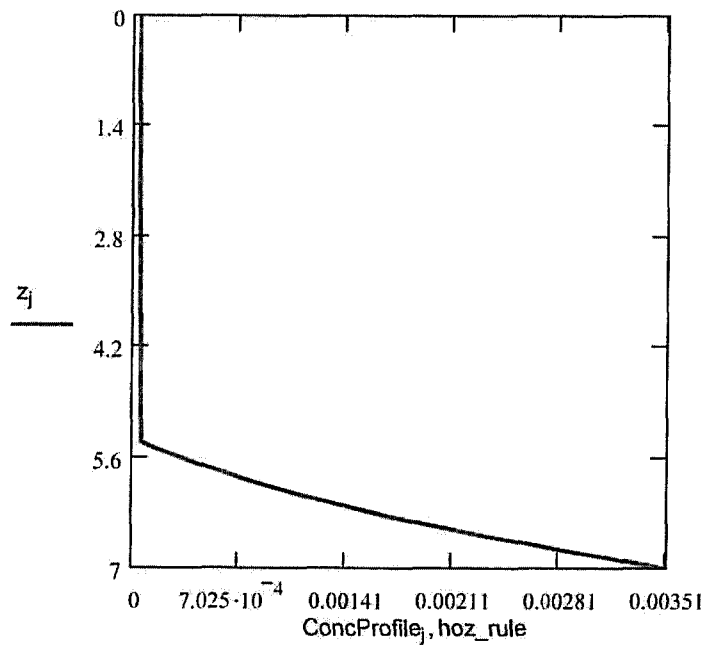
subroutine used to locate which layer a particular value of 'z' belongs to

$$z_{\text{max_div}} := 100 \quad j := 0..z_{\text{max_div}} \quad z_j := b \cdot \left(\frac{j}{z_{\text{max_div}}} \right)$$

The above line means that the depth of the sample is divided to calculate the concentration of each point.

$$\text{ConcCalc}(z) := \begin{cases} i \leftarrow \text{layer}(z) \\ \sum_{n=0}^{\text{Nu}} \left[e^{-\beta_n^2 \cdot \text{time}_{\text{max}}} \cdot X(i, \beta_n, z) \cdot A(\beta_n) \right] \end{cases}$$

$$\text{ConcProfile}_j := \text{ConcCalc}(z_j) + C_b$$





Geoenvironmental Engineering

University of Alberta, Edmonton AB, Canada

SAMPLE No.: N-20-DI-2

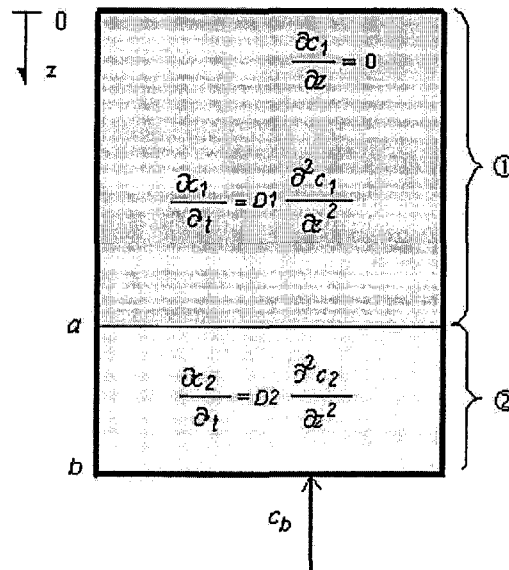
PROJECT Two-layer salt dissolution model
(Sampling point flux profile and final concentration profile)

DESCRIPTION

Calculation of a flux profile of sampling point and final concentration profile from diffusion in a two-layer closed composite system

CALCULATION BY Yuhai (Winston) Ding

DATE May 18, 2004



The Profile and the Settings
of
Salt Dissolution in a 2-Layer, 1-Dimensional, Closed System

System parameters:

Diffusion coefficients, and layer locations as specified in the above diagram

$D_1 := 1.46 \cdot 10^{-5} \text{ cm}^2/\text{s}$	= Up layer diffusion coefficient
$D_2 := 5.4 \cdot 10^{-7} \text{ cm}^2/\text{s}$	= Bottom layer diffusion coefficient
$C_{eq} := 146 \cdot \frac{10^{-3}}{10.6} \text{ g/cm}^3$	= Saturated salt concentration
$C_1 := 0 \cdot 10^{-3} \text{ g/cm}^3$	= Initial salt concentration of top layer
$C_2 := 0 \cdot 10^{-3} \text{ g/cm}^3$	= Initial salt concentration of bottom later
$b := 7.0 \text{ cm}$	= Bottom layer data
$a := 5.4 \text{ cm}$	= Interface data
$sd := 3.0 \text{ cm}$	= Sampling depth
$C_b := C_{eq} \text{ g/cm}^3$	= Constant salt concentration at bottom

Simulation parameter:

$m := 1 .. 73$	= array of time steps in which surface flux
$time_m := m \cdot 24 \cdot 3600 \text{ seconds}$	profile is calculated from

Initial concentration specification:

$$c0 := \begin{pmatrix} b & C_{eq} \\ a & C_2 \\ 0 & C_1 \end{pmatrix}$$

notes:

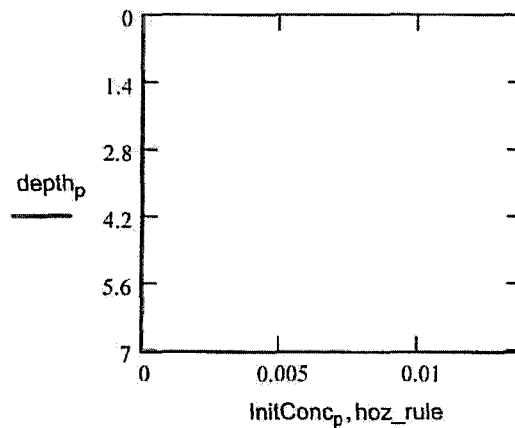
1. The 'c0' array should be in order of descending depth where the left entry is 'z' and the right is 'conc' of the layer directly below it.
2. Specify the interface position, 'a', explicitly in the array (as this simplifies the integration process).
3. Top entry must contain the value of 'b' in the 'z' position and the concentration of the surface zone in the 'conc' position.
4. This array is used to calculate the initialization integral.
5. Below is a plot which displays the initial concentration that has been specified by the 'c0' array.

```

plot_c0 := | x ← (c0_0,0 c0_0,1)
           | for i ∈ 0..(rows(c0) - 2)
           |   | y0,0 ← c0i,0
           |   | y0,1 ← c0i+1,1
           |   | y1,0 ← c0i+1,0   p := 0..(rows(plot_c0) - 1)
           |   | y1,1 ← c0i+1,1   InitConc_p := plot_c0_p,1
           |   | x ← stack(x,y)    depth_p := plot_c0_p,0
           | x

```

the initial
concentration
profile



Calculate System Eigenvalues

System eigenvalues, β_n , are the roots of the following transcendental function, $R(\beta)$

$$C_3 := \frac{a}{\sqrt{D_1}} * \quad C_4 := \frac{b-a}{\sqrt{D_2}} * \quad C_5 := \sqrt{\frac{D_2}{D_1}} *$$

$$R(\beta) := \tan(C_3 \cdot \beta) \cdot \tan(C_4 \cdot \beta) - C_5$$

Defining the range of significant eigenvalues, $\beta=[0, \beta_{\max}]$

$\omega := 15$ = adjustable parameter to define range of significance

$\beta_{\max} := \frac{\omega \cdot \pi}{\min(|C_3|, |C_4|)} *$ = range of significance $\beta=[0, \beta_{\max}]$

$$\beta_{\max} = 0.0333$$

This subroutine calculates the roots of $R(\beta)$ within the range $\beta=[0, \beta_{\max}]$

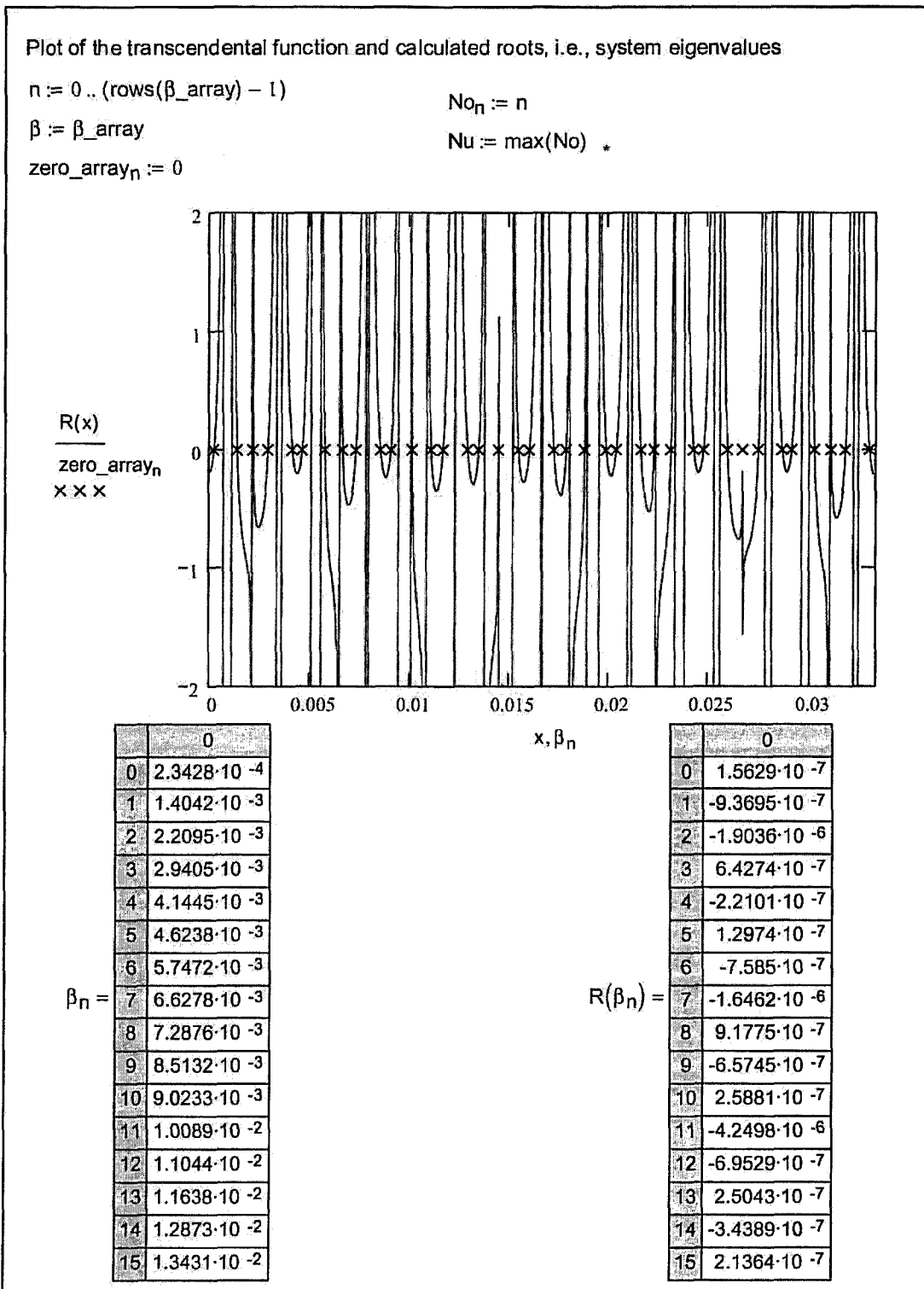
notes:

1. The adjustable parameter ' ω ' is used to determine the range of significance $\beta=[0, \beta_{\max}]$ (i.e., the range in which the eigenvalues are calculated).
2. Choose an ' ω ' such that the final concentration profile has a high enough resolution frequency to yield an appropriate (smooth) curve. $\omega=20$ is a good initial estimate.
3. Usually 10-20 eigenvalues, i.e., ' β 's is a reasonable number for most 'time' variables.
4. Higher number of eigenvalues are required for short values of the 'time' variable (i.e., higher values of ' ω ').
5. The values of the eigenvalues are calculated by the rigorous bracketing-bisection algorithm.
6. Part of ' β -array' and $R(\beta)$, can be seen in the graph and the table on the following page.

```

β_array := | bnds0 ← 0
            | nb_sub ← 105
            | for j ∈ 1 .. nb_sub
            |     bnd_subj ←  $\frac{j \cdot \beta_{\max}}{nb\_sub}$ 
            | bnds ← stack(bnds, bnd_sub)
            | tol ← 10-8 · βmax
            | n ← 0
            | β0 ← 0
            | for i ∈ 2 .. (rows(bnds) - 1)
            |     if | bndsi-1 < bndsi
            |         | R(bndsi) ≠ 0
            |         | (R(bndsi-1) · R(bndsi)) ≤ 0
            |         | UB ← bndsi-1 if R(bndsi-1) = 0
            |         | UB ← bndsi otherwise
            |         | LB ← bndsi-1
            |         | while (UB - LB) ≥ tol
            |         |     | βn ← LB +  $\frac{UB - LB}{2}$ 
            |         |     | UB ← βn if R(UB) · R(βn) ≥ 0
            |         |     | LB ← βn if R(LB) · R(βn) ≥ 0
            |         |     | βn ← UB if |R(βn)| < 1
            |         |     | (continue) otherwise
            |         |     | n ← n + 1
            |         |
            |         | β

```



Calculate System Eigenfunctions

Define the eigenfunction coefficients, $X(i, \beta_n, z)$'s, $Y(i, \beta_n, z)$'s and $A(\beta_n)$'s

$i := 1 \dots 2$

$$X(i, \beta, z) := \begin{cases} \frac{\cos\left(\frac{\beta \cdot z}{\sqrt{D_1}}\right)}{\cos\left(\frac{\beta \cdot a}{\sqrt{D_1}}\right)} & \text{if } i = 1 \\ \frac{\sin\left[\frac{\beta \cdot (b - z)}{\sqrt{D_2}}\right]}{\sin\left[\frac{\beta \cdot (b - a)}{\sqrt{D_2}}\right]} & \text{otherwise} \end{cases}$$

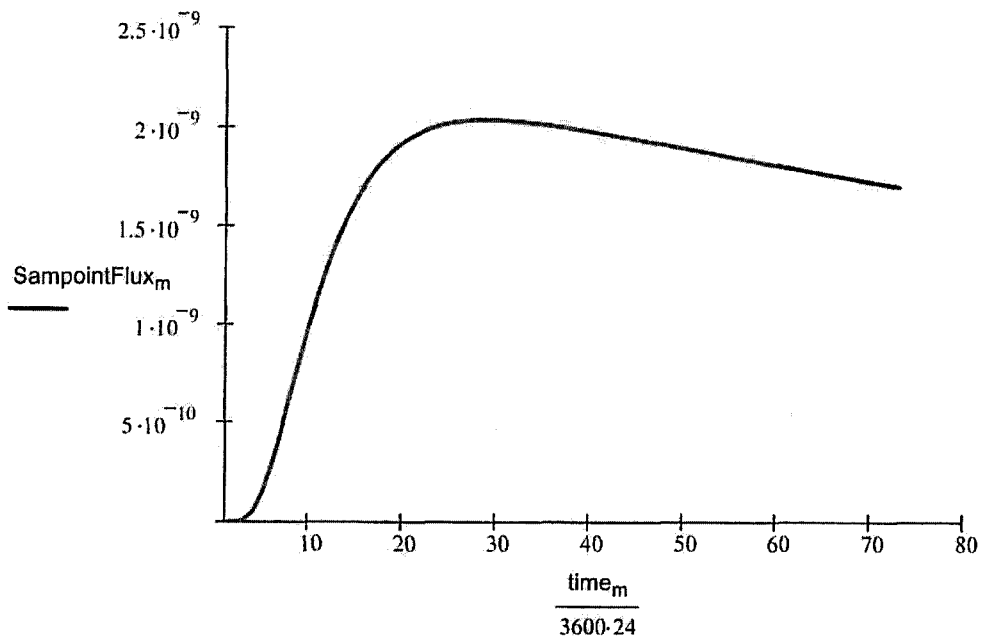
$$Y(i, \beta, z) := \begin{cases} \frac{-\sin\left(\frac{\beta \cdot z}{\sqrt{D_1}}\right) \cdot \frac{\beta}{\sqrt{D_1}}}{\cos\left(\frac{\beta \cdot a}{\sqrt{D_1}}\right)} & \text{if } i = 1 \\ \frac{\cos\left[\frac{\beta \cdot (b - z)}{\sqrt{D_2}}\right] \cdot \left(\frac{-\beta}{\sqrt{D_2}}\right)}{\sin\left[\frac{\beta \cdot (b - a)}{\sqrt{D_2}}\right]} & \text{otherwise} \end{cases}$$

$$A(\beta) := \frac{\int_0^a (C_1 - C_b) \cdot X(1, \beta, z) dz + \int_a^b (C_2 - C_b) \cdot X(2, \beta, z) dz}{\int_0^a X(1, \beta, z) \cdot X(1, \beta, z) dz + \int_a^b X(2, \beta, z) \cdot X(2, \beta, z) dz}$$

Calculate the flux profile of the sampling point

$$\text{time}_{\max} := \max(\text{time}) \quad * \quad \text{AY}_{m,n} := e^{-(\beta_n)^2 \cdot \text{time}_m} \cdot A(\beta_n) \cdot Y(1, \beta_n, \text{sd})$$

$$\text{SampointFlux}_m := D_1 \cdot \left(\sum_{n=0}^{\text{Nu}} \text{AY}_{m,n} \right)$$



Calculate the final concentration profile

$$\text{layer}(z) := \begin{cases} 2 & \text{if } a < z \leq b \\ 1 & \text{otherwise} \end{cases}$$

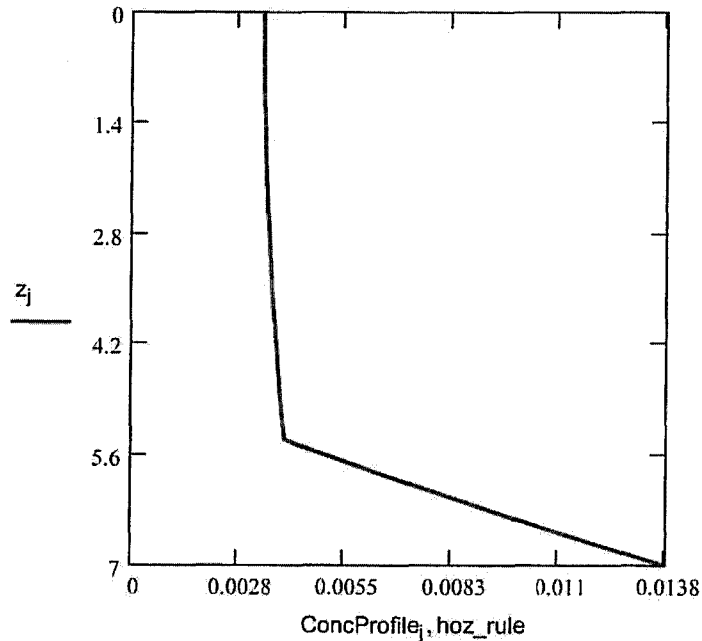
subroutine used to locate which layer a particular value of 'z' belongs to

$$z_max_div := 100 \quad j := 0..z_max_div \quad z_j := b \cdot \left(\frac{j}{z_max_div} \right)$$

The above line means that the depth of the sample is divided to calculate the concentration of each point.

$$\text{ConcCalc}(z) := \begin{cases} i \leftarrow \text{layer}(z) \\ \sum_{n=0}^{Nu} \left[e^{-(\beta_n)^2 \cdot \text{time}_{max}} \cdot X(i, \beta_n, z) \cdot A(\beta_n) \right] \end{cases}$$

$$\text{ConcProfile}_j := \text{ConcCalc}(z_j) + C_b$$



APPENDIX D

D1.0 Mathematical Solution to the Salt Dissolution and Diffusion in a 2-Layer, 1-Dimensional, Closed System

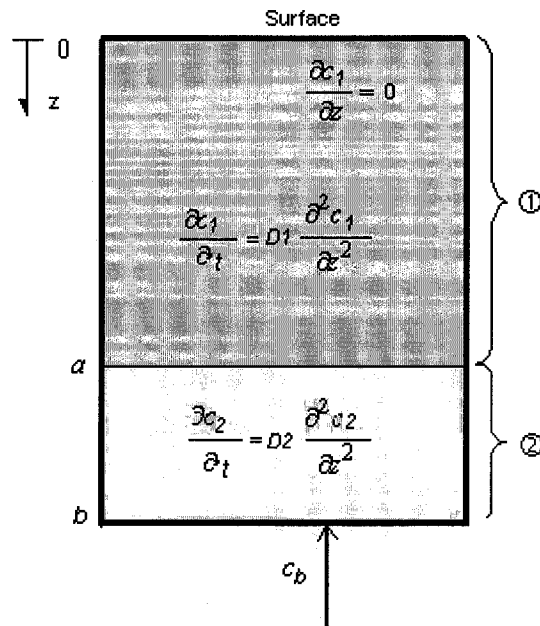


Fig. D-1 the Profile and the Settings of the Salt Dissolution and Diffusion in a Two-Layer, One-Dimension, Closed System

The one-dimensional diffusion equation is (see Section 2.1.1)

$$\frac{\partial c_1}{\partial t} = D_1 \frac{\partial^2 c_1}{\partial z^2} \quad (\text{D-1})$$

$$\frac{\partial c_2}{\partial t} = D_2 \frac{\partial^2 c_2}{\partial z^2} \quad (\text{D-2})$$

Mathematically, the boundary conditions are expressed as:

$$\frac{\partial c_1}{\partial z} = 0 \quad \text{at } z = 0, t > 0 \quad (\text{D-3})$$

$$D_1 \frac{\partial c_1}{\partial z} = D_2 \frac{\partial c_2}{\partial z} \quad \text{at } z = a, t > 0 \quad (\text{D-4})$$

$$c_1(z, t) = c_2(z, t) \quad \text{at } z = a, t > 0 \quad (\text{D-5})$$

$$c_b = c_{eq} \quad \text{at } z = b, t > 0 \quad (\text{D-6})$$

Equation (D-6) will be discussed in the following section.

The following equations specify initial conditions:

$$c_1(z,t) = c_1 \quad \text{at } t = 0, z \in [0, a] \quad (\text{D-7})$$

$$c_2(z,t) = c_2 \quad \text{at } t = 0, z \in [a, b] \quad (\text{D-8})$$

Liu and Brian (1999) give the general solution to the equation (D-1) to (D-8).

$$c(z,t) = c_b + \sum_{i=1}^N A_n \exp(-\beta_n^2 t) X_n(z) \quad (\text{D-9})$$

$$J(z) = D_{1,2} \sum_{i=1}^N A_n \exp(-\beta_n^2 t) Y_n(z) \quad (\text{D-10})$$

where

$$X_n(z) = \begin{cases} \frac{\cos \frac{\beta_n}{\sqrt{D_1}} z}{\cos \frac{\beta_n}{\sqrt{D_1}} a} & 0 < x < a \\ \frac{\sin \frac{\beta_n}{\sqrt{D_2}} (b-z)}{\sin \frac{\beta_n}{\sqrt{D_2}} (b-a)} & a \leq x \leq b \end{cases} \quad (\text{D-11})$$

$$Y_n(z) = \begin{cases} \frac{-\frac{\beta_n}{\sqrt{D_1}} \sin \frac{\beta_n}{\sqrt{D_1}} z}{\cos \frac{\beta_n}{\sqrt{D_1}} a} & 0 < x < a \\ \frac{-\frac{\beta_n}{\sqrt{D_2}} \cos \frac{\beta_n}{\sqrt{D_2}} (b-z)}{\sin \frac{\beta_n}{\sqrt{D_2}} (b-a)} & a \leq x \leq b \end{cases} \quad (\text{D-12})$$

where β_n is the root of the following solution:

$$\tan\left(\frac{\beta_n}{\sqrt{D_1}} a\right) \tan\left(\frac{\beta_n}{\sqrt{D_2}} (b-a)\right) = \sqrt{\frac{D_2}{D_1}} \quad (\text{D-13})$$

and A_n is expressed as,

$$A_n = \frac{\int_0^a (c_1 - c_b) X_n(z) dz + \int_a^b (c_2 - c_b) X_n(z) dz}{\int_0^a X_n(z) X_n(z) dz + \int_a^b X_n(z) X_n(z) dz} \quad (\text{D-14})$$

Using the analytical solutions by MathCAD to simulate the results of lab tests can be seen in the Appendix C: MathCAD Worksheet

Discussion on Equation (D-6)

Equation D-15 is the salt dissolution equation:

$$F = k_a(c_{eq} - c) \quad (D-15)$$

where F is the dissolution flux, k_a is the dissolution rate. At the bottom of our model, it is assumed that the diffusion flux: $J = D \frac{\partial c}{\partial z}$ is equal to the rate of salt dissolution, i.e. $F - J = 0$, which is Equation (D-16).

$$D_2 \frac{\partial c_2}{\partial z} + k_a \cdot c_2 = k_a \cdot c_s \quad \text{at } z = b, t > 0 \quad (D-16)$$

Integrating Equation D-16, it will be

$$- \int \frac{dc'}{c'} = \frac{k_a}{D_2} \int dz \quad (D-17)$$

where $c' = c_{eq} - c$

The limits of integration have to be determined to get a solution to Equation (D-17). However, no other point with known concentration in a closed model is found. In other words, the boundary input is not a constant. Nevertheless, to simplify the analysis, the boundary input is assumed to be a constant over certain time and certain area. If so, Equation (D-6) is the simplification of equation (D-16) and dissolution rate constant is wrapped in the assumption.