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**The Diffusion of Chloride Ion
in Cement Paste**

by

Kevin M^acDonald

A Thesis

Submitted to the Faculty of Graduate Studies and Research Through
the Department of Mechanical Engineering (Engineering Materials
Group) in Partial Fulfillment of the Requirements for the Degree
of Master of Applied Science at The University of Windsor

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Abstract

The corrosion of embedded reinforcing steel in concrete and the associated premature deterioration of the reinforced concrete itself is a problem of worldwide proportion.

Utilizing a modified two compartment non-perturbative diffusion cell, the effect of the composition of the cement paste with respect to the water:cement ratio and mineral pozzolan content on the effective chloride ion diffusivity is investigated. The diffusivity is found to increase as the water:cement ratio increases. The effectiveness of pyrolized sheet moulding compound in preventing the diffusion of chloride ion is discussed. Pyrolized sheet moulding compound is found to be effective in decreasing the chloride ion diffusivity, and that the diffusivity decreased as the PSMC content of the paste is increased.

In addition, the effect of experimental parameters such as sample thickness and concentration gradient, and of modifications to the standard diffusion cell are investigated, and the results discussed. A change in the chloride ion concentration in cell 1 of the diffusion cell is found to have no significant effect on the measured chloride ion diffusivity. The sample thickness was found to effect the measured chloride ion diffusivity, and that an increase in sample thickkness by one millimeter decreases the mesured diffusivity by approximately 6 %.

The lithologic factor is utilized to relate the changes in

effective chloride ion diffusivity with cement paste composition to changes in the pore structure of the paste.

Recommendations for further work are included.

Acknowledgements

The author would like to thank Dr. D.O. Northwood for his assistance and patience with the performance of the present work and the preparation of this manuscript.

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Contents

Abstract	iv
Acnowledgements	vi
Contents	vii
Figures	x
Tables	xii
Nomenclature	xiii
1.0 INTRODUCTION	1
2.0 LITERATURE REVIEW	4
2.1 Chloride Induced Corrosion of Steel in Concrete-A Macroscopic View	4
2.2 Chloride Induced Corrosion of Steel in Concrete-Mechanism	8
2.2.1 The Concrete Environment	8
2.2.2 The Role of pH	9
2.2.3 The Role of Chloride Ion	9
2.2.4 Summary	14
2.3 Properties of Portland Cement	15
2.3.1 Chemical Aspects	15
2.3.2 Hydration Reactions	16
2.3.3 Microstructure	17
2.3.4 Paste in Concrete	20
2.3.5 Pozzolans	21
2.3.6 Pyrolized Sheet Moulding Compound	25
2.4 Nature of Chloride Ion in Cement Paste and Concrete	27

2.5	Diffusion and Diffusivity	30
2.5.1	Introduction to Diffusion	30
2.5.2	Diffusion in Porous Solids	32
2.6	Summary of Previous Work	36
3.0	EXPERIMENTAL DETAILS	44
3.1	Description of Diffusion Cell	44
3.2	Investigations	50
3.2.1	Sample Preparation	51
3.2.2	Measurement of Chloride Ion Concentration	52
3.2.3	Determination of Total Porosity of Cement Paste Disks	54
4.0	EXPERIMENTAL RESULTS	56
4.1	Variation of Water:Cement Ratio	56
4.2	Variation of PSMC Content	60
4.3	Variation of Chloride Ion Concentration in Cell 1	65
4.4	Variation of Sample Thickness	68
5.0	DISCUSSION	72
5.1	Methodology	72
5.1.1	Effect of Stirring Modification	72
5.2	Effect of Variation of the Apparatus	74
5.2.1	Sample Thickness	74
5.2.2	Cell 1 Concentration	75
5.3	Effect of Variation of Cement Paste Composition	76

5.3.1	Variation of Water:Cement Ratio	76
5.3.2	Variation of PSMC Content	79
5.4	Comparison of Present Results with those of Previous Researchers	85
6.0	CONCLUSIONS AND RECOMMENDATIONS	89
6.1	Conclusions	89
6.2	Recommendations	90
	References	93
Appendix A	One Solution of Fick's Second Law for One Dimensional Diffusion	102
Appendix B	Chloride Ion Selective Electrode Calibration	108
Appendix C	Chloride Ion Concentration in Cell 2 versus Time. Plots for variation of Water:Cement Ratio, PSMC Content Cell 1 Chloride Ion Concentration and Sample Thickness	112
Appendix D	Sample Calculation of D_{cleff}	137
Appendix E	Boundary Layer Solution for Diffusion 'Lag Time' using Unagitated Diffusion Cell	141
	Publications	146
	Vita Auctoris	147

Figures

2.1.1	Stages in Corrosion Induced Deterioration of Steel Reinforced Concrete	6
2.3.1	Relationship Between Water:Cement Ratio and Porosity	20
2.5.1	Flux of Species A through Non-Diffusing Species B	30
2.5.2	Definition of Tortuosity Coefficient	34
2.6.1	Plot of Effective Chloride Ion Diffusivity versus Water:Cement Ratio for Various Researchers	38
2.6.2	Generalized Diagram of Diffusion Cell as Utilized by Page et al.	40
2.6.3	Perturbative Diffusion Cell Used by Dhir et al.	42
3.1.1	Cross Section of Diffusion Cell showing Cell Identification and Stirring Modification	45
4.1.1	Plot of Concentration versus Time for Cell 1 for Variation of Water:Cement Ratio	58
4.1.2	Plot of Concentration versus Time for Cell 12 for Variation of Water:Cement Ratio	58
4.1.3	Plot of Effective Chloride Ion Diffusivity versus Water:Cement Ratio	59
4.2.1	Plot of Effective Chloride Ion Diffusivity versus PSMC Content for Cement Pastes of Water:Binder Ratio 0.5	62
4.2.2	Plot of Porosity versus PSMC Content of Cement Pastes of Water:Binder Ratio 0.5	65
4.3.1	Plot of Effective Chloride Ion Diffusivity	67

	versus Chloride Ion Concentration in Cell 1	
4.4.1	Plot of Effective Chloride Ion Diffusivity versus Sample Thickness	70
5.1.1	Cross Section of Page et al's Diffusion Cell	73
5.3.1	Plot of Lithologic Factor versus Water:Cement Ratio	78
5.3.2	Plot of Porosity versus Effective Chloride Ion Diffusivity for PSMC Modified Cement Pastes	80
5.3.3	Plot of Porosity versus Effective Chloride Ion Diffusivity for Cement Pastes of Varying Water:Cement Ratio	81
5.3.4	Plot of Lithologic Factor versus PSMC Content	84
5.4.1	Plot of Effective Chloride Ion Diffusivity versus Water:Cement Ratio for Various Studies including Results of Present Work	85
5.4.2	Plot of Effective Chloride Ion Diffusivity versus Pozzolan Content for Various Studies including Results of Present Work	87

Tables

2.3.1	Chemical Composition of PSMC	26
2.6.1	Typical Experimental Methods and Sample Details for Measuring Effective Diffusivity of Chloride Ion in Hardened Cement Paste	37
4.1.1	Experimental Results showing Variation of Effective Chloride Ion Diffusivity with Water:Cement Ratio	57
4.2.1	Experimental Results showing Variation of Effective Chloride Ion Diffusivity with PSMC Content	61
4.2.2	Total Porosity of PSMC Cement Pastes	64
4.3.1	Experimental Results showing Variation of Effective Chloride Ion Diffusivity with Chloride Ion Concentration in Cell 1	66
4.4.1	Experimental Results showing Effect of Sample Thickness on the Measured Effective Chloride Ion Diffusivity	69
5.3.1	Theoretical Total Porosity and Lithologic Factor for Hardened Cement Pastes of Various Water:Cement Ratios	77
5.3.2	Total Porosity and Lithologic Factor for Hardened Cement Pastes of Various PSMC Contents	83

Nomenclature

J_A	Diffusional flux per unit area of species A
D_{AB}	Diffusivity of species A in species B
$D_{Cl\text{eff}}$	Effective diffusivity of chloride ion in hardened cement paste
C	Concentration
z	Spatial direction
c_1, c_2	Concentration of chloride ion in cells one and two respectively of the diffusion cell
D_0	Bulk diffusivity
D_{eff}	Effective diffusivity
L	Lithologic factor
ϵ	Porosity
t	Time
V	Volume of cell two of the diffusion cell
A	Cross sectional area of cement paste disk available for diffusion
l	Thickness of cement paste disk
m	Slope of concentration versus time plot for diffusion cell
r	Ratio of explained variance to total variance

1.0 INTRODUCTION

In the past fifty years, reinforced concrete has become one of the most widely used building materials, predominantly due to the ease of forming the concrete into various architectural forms, the durability of the finished product and the relative abundance of raw materials on a world wide basis. Indeed, modern civilization is typically characterized by the skyscraper, which more often than not consists of reinforced concrete slabs and columns.

One type of structure in North America where concrete is utilized almost to the exclusion of other materials is in the construction of highway bridges. Advances in chemical admixtures for concrete and in aggregate testing have contributed to the increased durability and widespread use of concrete as a building material. However, concrete is still not a panacea to the construction trade, despite the advances of recent years.

The interaction between the structures service environment and the structure itself can lead to structural deterioration, in some cases rendering the structure unsuitable for its design purpose.

One of the more common modes of deterioration associated with reinforced concrete is the chloride ion induced corrosion of the embedded reinforcing steel. Although very few catastrophic failures have been reported, it is estimated that the cost to the United States interstate highway system alone ranges from 200 to 500 million (1983) dollars per year[1].

These costs, together with the large number of structures

which serve in marine environments or in areas where sodium or calcium chloride is used as a deicing chemical for roadways has led to a great scientific interest into the mechanism of, and means of protection from, corrosion of the embedded steel reinforcing bars in concrete.

It will be shown, in the pages to follow, that the chloride ion changes both the passive condition of the embedded reinforcing steel, and those aspects of the concrete environment which allowed the passive condition of the steel to develop in the first place. Indeed, although some structures are protected from corrosion by cathodic protection, by far the vast majority that are protected have systems which prevent chloride ion intrusion, thereby preventing corrosion.

The chemistry of concrete admixtures such as set accelerators and air entraining agents are rigidly controlled to prevent inclusion of chloride ion in the concrete at the time of mixing. The chloride content of aggregate sources in Ontario is monitored by the Ministry of Transportation Ontario. The risks of using chloride based deicing chemicals are perceived as being so high that highway authorities in North America seriously discuss the use of alternative deicing chemicals such as urea and calcium magnesium acetate, despite a cost increase of tenfold over that of salt to achieve approximately similar results in deicing ability[2].

The mode of exposure to chloride ion is remarkably similar in the majority of cases. A brine, whether seawater or formed by spreading deicing salts on snow or ice, sits on the horizontal

surfaces of the structure. The chloride ions are then able to penetrate into the concrete, either through cracks or by diffusion through the porous concrete. Once sufficient chloride ion has reached the reinforcing steel, corrosion of the steel takes place. The mechanism of the above phenomenon is detailed in sections 2.1 and 2.2.

Since the chloride ion is required to move from the surface of the concrete to the surface of the steel bar and to accumulate to sufficient quantity before corrosion induced deterioration of the reinforced concrete takes place, it is the rate of this mass transfer which controls the rate of deterioration, at least in the initial stages.

The mass transfer of a given material by virtue of a concentration gradient is defined as diffusion. The mass transfer coefficient, in this case known as diffusivity, is defined by Fick's first law as the ratio between the concentration gradient and the change in concentration with time[3].

It is the purpose of the present study to investigate the usefulness of a simple device for measuring the diffusivity of chloride ion in cementitious materials and to determine the effect of changes in experimental parameters on the measured diffusivity. To these ends, investigations were undertaken to determine the effect(s) of (i) changing the mix proportions and hence the pore distribution of the cement under study, and (ii) adding supplementary cementitious materials, on the diffusivity of the chloride ion in cement.

2.0 LITERATURE REVIEW

2.1 Chloride Induced Corrosion of Steel in Concrete -A

Macroscopic View

The performance of reinforced concrete in chloride environments has become a problem of astronomical proportions throughout the world. Although steel reinforcement embedded in concrete is normally found in the passivated state due to the alkalinity of the concrete matrix[4,5,6,7,8], this situation can rapidly change when the concrete is exposed to chloride ion or other sources of depassivation. The placement of sodium chloride on the structure, whether as a deicing chemical or in a salt spray, creates a solution of chloride ions which quickly penetrates the concrete through cracks and through the sound concrete. As these cracks are often located over the steel reinforcement, this penetration of chloride ion can be much faster than would be the case if the mass transfer was purely diffusional. Research has shown that the chloride ion an important catalyst in instigating corrosion of the embedded reinforcement[4,5,6,7,8]. The major problem associated with the corrosion of 'black' steel reinforced concrete structures is not due to the corrosion of the steel reinforcing rods, rather it is the failure of the concrete under the tensile stress exerted by the products of the corrosion

reaction. These corrosion products are not well known at this time, but are generally accepted to be ultimately hydrated ferrous oxides [6]. The deterioration of a reinforced concrete slab by corrosion of the embedded reinforcing rods can be broken down into four stages: i) contamination of the slab by chlorides, ii) localized corrosion at cracks or regions of permeable concrete, iii) delamination and iv) spalling.

In the first stage no corrosion is taking place, as the chloride ion content of the concrete is below the threshold level required to initiate corrosion of the embedded reinforcing steel. At this point all of the cracks present in the concrete are due to settlement, loading and shrinkage.

In the second stage, localized corrosion begins at those reinforcing bars located directly below the cracks. As mass transfer of chlorides continue, corrosion also begins at those areas of the reinforcing steel in contact with concrete where the chloride concentration is sufficiently high.

The third stage occurs when the corrosion products cause failures of the concrete to occur in tension. These failure planes are referred to as delaminations.

The ultimate stage of deterioration is the breaking loose of the delaminations due to impact or gravity. This defect is referred to as a spall. As the corroded steel was located at the base of the delamination, the spalling off of the concrete completely exposes a portion of the reinforcing bar. The

spall, being a low point, fills with debris and chloride laden water. This environment accelerates the corrosion of the exposed bar, especially those which are only partially exposed. The partially exposed bar sets up many macrocells which accelerate the process at the edges of the spall. The latter three of these stages are illustrated in figure 2.1.1.

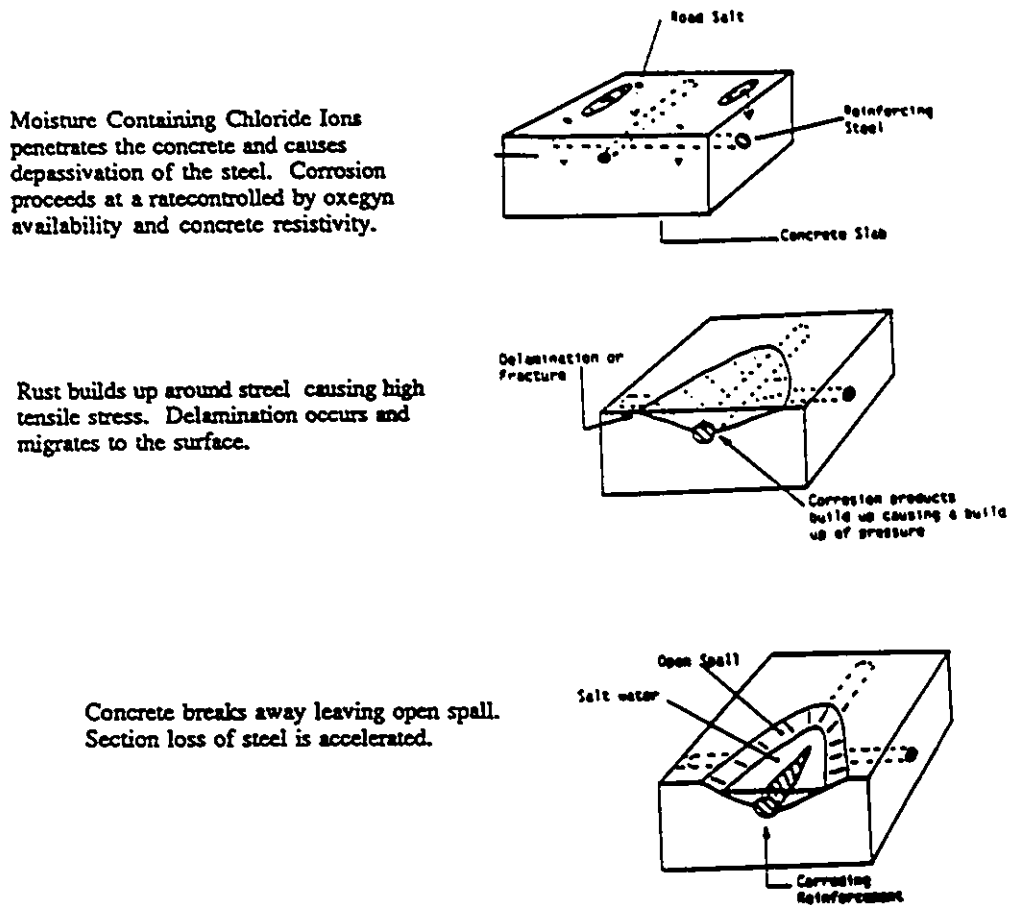


Figure 2.1.1 : Stages in Corrosion Induced Deterioration of Steel Reinforced Concrete.

Once a structure has reached this fourth stage of deterioration, rehabilitation is very expensive. For this reason the detection of chloride ion, active corrosion and delamination have received much study. It is also of great interest to be able to predict the risk of corrosion based on a combination of environment and structure information. In this regard, one of the more important parameters to measure is the diffusivity of chloride ion in the concrete.

2.2 Chloride Induced Corrosion of Steel in Concrete - Mechanism

The major differences between the corrosion of steel exposed to the environment and that of steel embedded in concrete are due to the properties of the concrete. Among these properties are the porous and heterogeneous nature of the concrete matrix, the high pH of the concrete environment and the ability of the concrete to store moisture. The microstructure of the concrete also slows the mass transfer of materials such as chloride ion and oxygen from the outside of the concrete.

2.2.1 The Concrete Environment

Normal concrete is a composite material made up of fine and coarse aggregates and hydrated portland cement. To this generic mix a number of admixtures are added at the time of mixing or placement to modify the properties of the finished concrete or the mix itself. Among these additives are air entraining agents, which, as the name implies entrain fine bubbles of air in the mix to prevent the breakup of the hardened concrete by freeze thaw weathering. The cement matrix, made up of hydrated cement and fine aggregate particles, is porous and permeable by its nature. It is through this pore system that chlorides, moisture and oxygen are able to reach the surface of the embedded steel, which ultimately leads to the deterioration of the reinforced concrete.

2.2.2 The Role of pH

The most interesting and useful consequence of embedding steel in concrete is the active to passive transition which the steel undergoes in the presence of the high pH of the concrete. This transition occurs due to the formation of a protective oxide film on the surface of the embedded steel bar by electrochemical processes. This oxide film is generally accepted to be $\gamma\text{-Fe}_2\text{O}_3$ [9], due to the extremely alkaline environment of the cementitious matrix, having a pH ranging from approximately 12.5 to approximately 14 [10].

2.2.3 The Role of the Chloride Ion.

The spreading of rock salt (NaCl) as a deicing chemical on highway bridges or other structures, or the exposure of a structure to salt water spray quickly affects the passivated condition of the embedded reinforcing steel. The chloride ions begin to penetrate through the concrete by diffusion or by other mechanisms working in conjunction with diffusion. These chloride ions react with the passivating layer on the embedded steel, and at the same time reduce the pH of the surrounding cementitious matrix. This destruction of both the passive layer, and the conditions which originally promoted passivation, leads to the corrosion of the reinforcing steel[7].

The process by which the chloride ions cause a passive to active transition is not well understood. At least three models have been proposed:[11]

1. The Oxide Film Model

In this model, the chloride ions are thought to penetrate through the oxide film, through either defects or through pores in the passivating film. The chloride ion then facilitates the movement of ferrous ions away from the anodic sites.

2. The Adsorption Model

This model suggests that the chloride ions are preferentially adsorbed by the passivating layer found on the steel surface in the pristine condition. Once adsorbed, the chlorides react with the steel substrate to form a soluble material which diffuses away from the anodic sites.

3. The Complex Model

This model states that the chloride ion forms a complex with the ferrous ions. This complex ion is able to diffuse away from

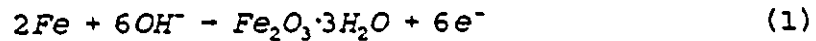
the anodic sites. At some point away from the steel, the complex breaks up, thereby freeing the chloride to return to the concrete metal interface and continue the process. The ferrous ions are then free to react with oxygen to form various oxides of iron depending on the external conditions.

A common element in all three models is that the chloride ion has to move within the pore system of the concrete. It is important therefore, to understand the manner in which the chloride ion can interact with the pore system, and the structure of the pore system in cement paste.

It is generally accepted that the chloride ion content at the level, or horizon, of the embedded steel rods must exceed a certain value to initiate corrosion of these rods, and that for chloride contents below this level, termed the threshold level, no corrosion of the embedded steel likely to take place. As a result there is a period early in the service life of a structure when no active corrosion is taking place, due to the fact that the chloride ion content is below the threshold value and therefore the steel is still passivated. This concept is still used by highway authorities and others concerned with assessing the corrosion risk to embedded steel, where it is difficult or too costly to determine other properties of the concrete[12].

In general, however, the concept of a single threshold

chloride ion content which is independent of the concrete under study has been replaced by the concept of a critical chloride to hydroxide ratio. This theory was first proposed in 1967, and is based upon the assumption that the critical chloride to hydroxide ratio is defined as the conditions which exist when the rate of passive film production (equation 1) is equal to the rate of corrosion of the anode (equation 2).[11]



This critical chloride to hydroxide ratio has been determined experimentally utilizing two steel bars in saturated $CaOH_2$ solution, with a pH ranging from 11.6 to 12.4. Under these experimental conditions the critical chloride to hydroxide ratio was determined to be approximately 0.6[11]. A further study undertaken in 1982, used steel samples embedded in concrete to take into account the higher pH potentially found in concrete due to the presence of KOH and NaOH in the pore solution, the chloride binding properties of the cement matrix and the diffusive nature of the concrete. This work determined that the critical chloride hydroxide ratio is approximately 3 for chloride contamination from an outside source.[13]

The rate of diffusion, described by the diffusivity, of chloride ions through the concrete controls the time required for initiation of corrosion of the embedded reinforcing steel. Indeed an increase in the chloride ion diffusivity by four orders of magnitude can reduce the theoretical time required for depassivation from approximately 10 years to approximately 15 days, assuming that diffusion is the only mass transport mechanism[14]. The chloride ion diffusivity has been shown to be a function of the water:cement ratio of the cement paste, and that an increase in the water:cement ratio leads to an increase in the chloride ion diffusivity[15,16,17,18]. Another factor which affects the depassivation time is the length of path through which the chloride ion must travel. The clear cover to the reinforcing steel is therefore an important variable in determining the depassivation time[4,5,6,7,8]. Once the chloride ion content of the concrete at the surface of the embedded steel has exceeded the threshold value and corrosion of the embedded reinforcing steel has begun, other factors such as the resistivity, moisture content and oxygen supply become the important factors affecting the rate of the deterioration. This phase of the deterioration process is beyond the scope of the present work.

2.2.4 Summary

It follows from the above discussion that it is the movement of the chloride ions through concrete which is ultimately responsible for the deterioration of steel reinforced concrete exposed to chloride environments. The chloride ion achieves this deterioration by destroying the passivating properties of the concrete matrix and causing an active to passive transition of the steel to take place. In order to better appreciate how the chloride ion penetrates through the concrete to the reinforcing steel, it is necessary to develop a knowledge of the following:

- 1.) The chemical and physical nature of portland cement and supplementary cementing materials,
- 2.) The interaction between the cement paste and the chloride ion and,
- 3.) The nature of diffusion and diffusive processes.

2.3 Properties of Portland Cement

2.3.1 Chemical Aspects

Portland cement is a manufactured compound consisting of a finely divided mineral in powder form which is grey in appearance. It typically consists of a number of silicates, aluminates and oxides. The term portland cement is used to describe a family of closely related cements having similar properties[19].

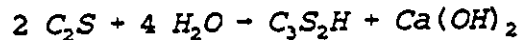
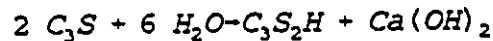
The major constituents of the cement powder are tricalcium silicate ($3\text{CaO}\cdot\text{SiO}_2$, abbreviated as C_3S), dicalcium silicate ($2\text{CaO}\cdot\text{SiO}_2$, abbreviated as C_2S), tricalcium aluminate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3$, abbreviated as C_3A), and tetracalcium aluminoferrite ($4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$, abbreviated as C_4AF). Of these major constituents, the first two are the chemical species responsible for the majority of the strength of the hydrated paste. The C_3A contributes little or nothing to the strength of the hydrated paste in the early stages[20]. The presence of the hydration products of the C_3A can lead to problems in sulphate containing environments, as reaction with the sulphates leads to the formation of gypsum (calcium sulphate hydrate) ettringite (calcium sulfoaluminate hydrate) or other similar materials, and to breakup of the paste[19]. The presence of C_4AF in the kiln at the time of manufacture of the cement allows the reactions forming the cement

clinker to take place at lower temperature. There is very little C_4AF present in the cement, and this material has little effect on the performance of the cement.

In addition to the C_2S , C_3S , C_3A and C_4AF , there are also a number of minor constituents in portland cement. Among these are the oxides of magnesium, titanium, potassium and sodium.

2.3.2 Hydration Reactions

The reaction between the various components of the portland cement and water, referred to as the hydration of the cement, leads to the formation of the cementitious paste, consisting mainly of tobermorite gel, $(3CaO \cdot 2SiO_2 \cdot H_2O)$, abbreviated as C_3S_2H or CSH). The hydration reactions for C_3S and C_2S are as listed below[20]:



In order to prevent the flash set of cement due to the hydration of the C_3A , an amount of calcium sulphate, or gypsum, is added to the cement[20].

The first reaction is relatively faster than the second. Note that one of the reaction products is calcium hydroxide, a strong

base. The presence of this material contributes to the basic nature of the pore water in concrete. The other reaction product, C_3S_2H , or CSH, is a microcrystalline hydrate. The calcium hydroxide also exists in its crystalline form.

2.3.3 Microstructure

Fresh cement paste is a plastic network of flocculated cement particles in water. Once the cement paste has achieved a final set, the volume of the material is approximately constant. The paste, as noted above, consists mainly of the various hydrates and calcium hydroxide particles. This combination of materials is referred to as the cement gel. The other major component of the green paste is water. It is the various forms which water takes on in the paste that is responsible for the porous microstructure of the hardened paste[20].

The water portion of the hydrated cement is found in three different forms. The combined water is that water held physically or chemically in the hydration products. This is also known as the 'non-evaporable water content'. Water is also found adsorbed to the surface of the cement gel, and is referred to as the gel water. This water forms the small pore system running through the agglomerations of gel, known as the gel pores. These pores are typically very small, in the range of 2 nm. The pore

water is that water found between large particles of hydrated cement. These spaces are the capillary pores and are much larger than the gel pores, typically in the range of 1 μm [20].

For a cement which contains only enough water to hydrate the cement powder, these capillary pores account for approximately 18.5 percent of the total volume of the hardened cement paste[20]. A mix of this type has a water cement ratio of 0.35. If the mix contained more water than was necessary for hydration of the cement, that is, if the water cement ratio was in excess of 0.35, then the proportion of capillary pores would be greater than 18.5 percent[19]. As the hydration of the slower reacting materials proceeds, new gel blocks the gel pores and the smaller capillary pores, segmenting them into closed void spaces. It is the expansive property of the hydration reaction where the gel occupies approximately twice the volume of the reactants which allows this blocking to take place once the cement has achieved an initial set.

A number of measured parameters have been defined to quantitatively assess the nature of the pore system in cement paste. Among them are the porosity and the pore size distribution. Porosity is the fraction of the cement volume which consists of voids and pores of all sizes. The pore size distribution is more useful than the porosity as it classifies the pore spaces as to their size, giving a more complete description of the pore system in concrete[16].

The permeability of the cement paste is one of the more

important properties relating to the durability of the cement paste and is related to the diffusivity of chloride ion. Permeability is defined as the ease with which a fluid can pass through a given material under a pressure gradient. The permeability of a porous material like hardened cement paste is directly related to the porosity and pore size distribution of the material[16,20]. Recall from the previous discussion that there are two types of pores in hardened cement paste, and that the smaller pores become segmented during the continued hydration of the cement. One of the more important aspects of the pore system is the threshold pore diameter, defined as the minimum pore diameter which is continuous and unsegmented. Any pore with a diameter larger than the threshold is assumed to be continuous. It is these pores through which water and any dissolved materials will travel, and through which the diffusion of chloride ion will take place[16].

The pore size distribution has been found to be effected by the water:cement ratio of the mix and the manner in which the cement was cured. As the water:cement ratio increases the maximum pore size also increases[21]. A similar result is found for the effect of the water cement ratio on porosity. This relationship is shown below in figure 2.3.1.

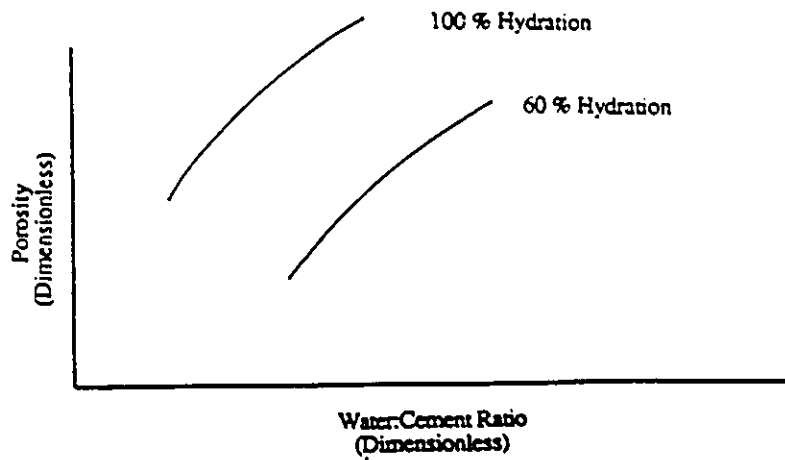


Figure 2.3.1 : Relationship Between Water Cement Ratio and Porosity [20].

2.3.4 Paste in Concrete

A recent study was undertaken to examine the difference between the microstructure of cement paste in mortar, concrete and cement paste alone[22]. It was determined that cement paste alone has a microstructure which is different to that found in the cement paste components of mortar and concrete. The major difference is manifested in the porosity of the matrix. The paste found in concrete has a much higher porosity than that found in mortar and cement paste, and mortar has a higher porosity than ordinary cement paste.

The bulk of the additional pore spaces (i.e. in concrete) were determined to be above the threshold pore diameter. An increase in the number of pore spaces above the threshold diameter would cause an increase in the permeability of the matrix and an increase in the diffusivity of ions through the paste. This would suggest that tests done on cement pastes alone may not be as good indicators of

the performance of that paste in concrete as tests on mortars would be. However, the fact that determination of the diffusion coefficient is much more rapid in cement pastes as compared with mortars, and that the uniformity of cement is easier to control than that of mortar and concrete, are among the reasons why the majority of diffusion determinations are made using hardened cementitious paste alone.

2.3.5 Pozzolans

A pozzolan is defined as a siliceous or siliceous and aluminous material, which by itself possesses little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties[20]. The use of this type of material as a replacement for ordinary portland cement in concrete has greatly increased in the last ten years.

Some examples of pozzolans which are in use today are pulverized fly ash (PFA), blast furnace slag (BFS) and condensed silica fume (CSF). All of these materials are byproducts of industrial processes such as the smelting of iron ore or the combustion of coal.

These pozzolans are used extensively in Canada and elsewhere as cement replacements, serving to dispose of these waste

materials, to reduce the consumption of the energy intensive cement, and to improve the durability or other properties of the concrete. Extremely high strength concrete (greater than 95 MPa) can now be produced on a regular basis utilizing pozzolans and superplasticizing admixtures[23]. The use of these pozzolans improves the durability of concrete in sulphate environments[10]. It has been shown to reduce the diffusivity of chloride ion in cement pastes[15,18,24,25,26]. The permeability of concrete manufactured with pozzolan is significantly reduced as compared with similar concretes which did not contain supplementary cementitious materials[9].

In Canada nearly one half of all of the CSF produced in 1984 found its way into concrete[10]. The use of PFA in concrete accounts for approximately ten percent of the 45 million tons of PFA produced annually in the United States.[27]

The chemical constituents of these pozzolans vary from source to source and with time. In general however, the main constituent compounds are silicon dioxide, (SiO_2), aluminum oxide (Al_2O_3), iron oxide (Fe_2O_3), calcium oxide (CaO) and the minor constituents are magnesium oxide (MgO), sodium oxide (Na_2O), and potassium oxide (K_2O).

The major reaction which leads to the formation of the pozzolanic cementitious gels is the combination of the oxides with calcium hydroxides and water to form CSH or similar gels. Because these reactions involve the products from the hydration of the

cement, their products do not form until after the immature pore structure of the cement has been established[20].

In general the curing of the concrete is extremely important as the reactions leading to the gel formation take place after the normal curing period of a few days. As water is a major component in this reaction, it is important that the concrete be kept moist for longer than is necessary with ordinary concrete. As these gels form they begin to block the gel and capillary pores[25], thereby reducing the gel to space ratio. This directly contributes to the increased strength of the resulting matrix. The complete blocking of a vast number of the pores by these gels also prevents the passage of fluids, hence lowering the permeability of the resulting matrix. As well, a reduction in the number of unblocked fluid filled pores leads to a corresponding reduction in the diffusivity of chloride ion through the matrix.

Much recent work has shown that there is a significant decrease in the chloride ion diffusivity with an increase in the pozzolan content of the mix. [15,18,24,25,26,28] There are a number of explanations put forth as to why this reduction in diffusivity takes place, among them the increased binding of chloride ion, the changes to the pore structure of the matrix and the increase in competitive ions within the pore solutions.

Some researchers have shown that there is an increase in the ratio of bound to free chloride ion with an increase in pozzolan content[24]. This tendency to remove the chloride ion from the

pore solution acts as a sink for chloride ion and would significantly increase the mass transfer coefficients such as diffusivity. In addition to blocking the smaller pores and decreasing the diameter of the larger pores, a reportedly marked increase in the tortuosity of the remaining pores has been noted[28]. The concentration of certain ions change with the addition of the pozzolan. The concentration of those cations which inhibit the progress of chloride ions such as calcium(Ca^{2+}) and aluminum(Al^{4+}) have been reported to increase by up to two and one half times, while those cations which have been shown to aid in the progress of the chloride ion such as potassium(K^+) have been reported to decrease by a similar amount[28]. These cations are found both in the bulk pore solution and in the layer around the pore surfaces. It is likely that a combination of these factors leads to the observed reduction in chloride diffusivity achieved by using these cement replacements.

One negative side effect of the use of pozzolanic supplementary cementitious materials is the consumption of hydroxyl ions in the pozzolanic reaction. Many researchers have investigated the effect that this reduction in hydroxyl ion has on the pH of the pore solution in the cement matrix. In general, it is agreed that while there is a lowering of the pH with the inclusion of pozzolanic materials, the magnitude of the decrease is not great enough to affect the passivity of the embedded steel [10,15,29,30,31]. The reduction in pH does, however, reduce the

amount of chloride ion required to reach the critical chloride to hydroxide ratio, and therefore also reduces the initiation time[14,32,33]. However, the same study asserted that the general lowering of the chloride ion mobility more than offsets any reduction in hydroxyl ion concentration[32].

Researchers do agree, however, that the inclusion of pozzolans in the cementitious component of concrete can increase the rate of carbonation of the concrete[10,29]. Carbonation is defined as the process by which calcium hydroxide in the cementitious matrix reacts with carbon dioxide in the atmosphere to form calcium carbonate. This process reduces the pH of the matrix. Carbonation can thereby cause a passive to active transition of the embedded reinforcement. However, for high compressive strength (> 40 MPa), good quality concrete, carbonation is not generally regarded as a threat to the embedded reinforcing steel[10].

2.3.6 Pyrolized Sheet Moulding Compound

Sheet moulding compound(SMC) is a mineral and glass fibre reinforced polyester, and is currently used by essentially all of the major international automobile manufacturers[34].

One of the major problems which is associated with the use of this material is that due to its thermosetting properties it cannot be readily or effectively recycled. In order to improve the cost effectiveness of this material, a cheap disposal method is

required[35].

The SMC Automotive Alliance has developed an environmentally sound method of pyrolyzing the polymer, the products of the pyrolysis being energy, an oil product and ash. It has been suggested that the ash be utilized as an additive to concrete to economically dispose of the ash and modify the properties of the concrete itself. A chemical analysis of the ash component of the pyrolyzed sheet moulding compound, or PSMC, is found in Table 2.3.1.

Table 2.3.1 : Chemical Composition of PSMC[33].

Component	Component Composition.%
CaCO ₃	55
C	12
E-glass	33
Consisting of:	
SiO ₂	54
Al ₂ O ₃	14
CaO	20
Boric Acid	8
Oxides of K,Na,Mg,Ti and Fe	Trace

It is clear from the above chemical composition that the finely divided components of the E-glass will have pozzolanic properties. As well, the mineral fines portion of the PSMC will act to block or reduce in size the pore spaces of the cement matrix. Addition of PSMC to concretes and mortars has been shown to increase the compressive strength of these materials and to increase their resistance to alkali-aggregate reactions [35].

2.4 Nature of Chloride Ion in Cement Paste and Concrete

In general, the chloride ion can exist in four different forms in the concrete matrix[11]. These forms are as follows:

1) As a chemical constituent of the fine and/or coarse aggregate used to make up the aggregate. In the province of Ontario the chloride content of aggregates from various sources is documented by the Ministry of Transportation[36].

2) Chemically bound with the Tricalcium Aluminate and the Tetracalcium Aluminoferrite in the cementitious paste.

3) Physically bound by sorption on the interior pore surfaces

4) As free chloride ions in aqueous solution located in the pore spaces of the cementitious matrix.

Due to the bound nature of the first three chloride forms, it is generally accepted that only the free chloride ion is available for initiating the corrosion of embedded reinforcing steel.

It is due to these various forms of chloride ion that the chloride content of any concrete is always discussed in terms of a

'total' chloride ion content, a 'background' chloride content, and an 'available' chloride content. These three chloride contents can readily be interpreted in terms of the above chloride ion forms.

The 'total' chloride ion content is the sum total of all the chloride ions in the four types listed above.

The 'background' chloride content is that chloride ion in the concrete which is considered to be immobile and therefore unable to depassivate the embedded steel. In terms of the above forms of chloride, this is made up of the chloride ion which is chemically bound in the aggregate particles and the chemical constituents of the hydrated cement. As these materials are chemically bound, they are inherently unable to move within the concrete pore structure and are therefore unable to participate in the depassivation of the steel.

The 'available' chloride ion content is a term used to describe the risk of reinforcing steel corrosion in a particular concrete. The 'available' chloride ion content is defined as the difference between the 'total' and 'background' chloride ion contents. In terms of our four chloride forms the 'available' chloride content is that chloride ion which is physically bound on the pore surfaces or exists as free ions in the pore solution. One accepted interpretation of this risk, based on the threshold concept, is that if the available chloride ion content is greater than the 'threshold' content, normally accepted to be 0.020 percent

by mass of concrete, then there is a risk of corrosion of embedded steel. The corollary to this is that if the 'available' chloride content is below the threshold value, there is no risk of corrosion of embedded steel. Again in terms of our four chloride ion forms, the threshold value can be interpreted as the amount of chloride ion required to completely fill all of the active adsorption sites found in the pore system of the concrete.

2.5 Diffusion and Diffusivity

2.5.1 Introduction to Diffusion

Diffusion is the motion of molecules from a point of higher concentration to a point of lower concentration by virtue of a concentration gradient[3]. By this process a solution in which a difference in concentration exists will, with time, become homogeneous. The rate at which the diffusing species moves is dependent on the temperature, the magnitude of the concentration gradient, the diffusing species itself and the material through which the diffusion takes place[37].

In order to describe the rate of movement due to diffusional processes, consider the flux of species A through non diffusing species B, as shown in figure 2.5.1 below.

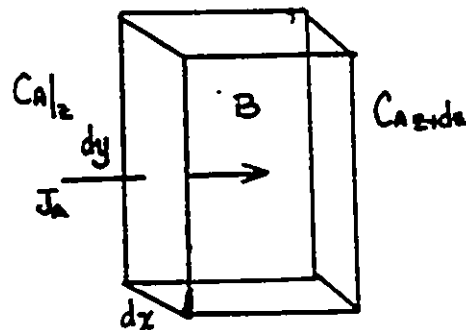


Figure 2.5.1 : Flux of Species A Through Non-Diffusing Species B.

If the diffusional flux per unit area, J_A , is defined as the flux of a given constituent A relative to the bulk motion of the solution, then the diffusivity of species A in species B, D_{AB} , is defined by Fick as the ratio between the diffusional flux and the concentration gradient ∇C . The defining equation found below is Fick's first law, and was derived by observing the similarity between diffusive mass transfer and Fourier's observations of heat transfer[3].

$$J_A = -D_{AB} \nabla C \quad (1)$$

Written in the z direction only, that is where the concentration gradients in the x and y directions are zero the one dimensional form of Fick's first law becomes

$$J_A = -D_{AB} \frac{dC}{dz} \quad (2)$$

The negative sign indicates that the flux is positive in the

direction of decreasing concentration gradient, that is that the net movement of species A is in the direction of decreasing chloride ion concentration, (down the concentration gradient). The diffusivity is a thermodynamic variable and is a function of temperature, pressure and composition. For strong electrolytes in aqueous solution, where disassociation is essentially complete, the diffusion coefficient is expressed for each of the constituent ions which are able to move freely[37]. Both anions and cations are forced to diffuse at the same rate due to the tendency for the solution to remain electrically neutral.

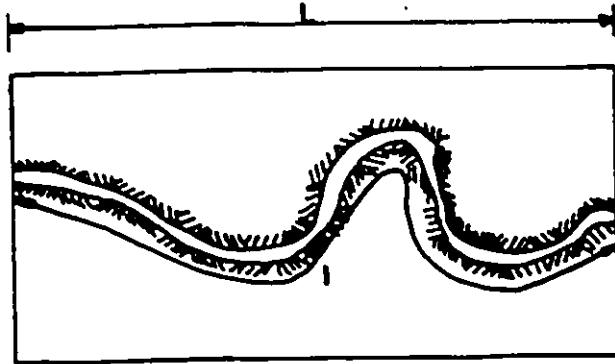
2.5.2 Diffusion in Porous Solids

The structure of a solid material and the nature of the diffusing materials can have a pronounced effect on the nature of the diffusion occurring within the solid. Solid materials can be affected by other materials diffusing into the solid. One good example of this phenomena is the hydrogen embrittlement of steel where the properties of the steel are altered as a result of hydrogen diffusing into the steel. Solid diffusional processes are extremely slow relative to diffusion in liquids and solids. In porous materials the diffusion usually takes place in the fluid filled pores as opposed to in the solid. The diffusional movement can also occur along the pore surfaces by adsorbed species, where the molecules move from one adsorption site to another.

Due to the nature of the pores in most materials such as hardened cement paste, where the pores are tortuous and do not exhibit a constant diameter, and where there is significant interconnectivity of the pores, it is inconvenient to define the flux based upon the cross sectional area of the pores themselves. In the case of hardened cement paste the adsorption of chloride ion also makes the traditional expression of diffusivity difficult.

For this reason the diffusional flux is often based upon an easily measured parameter of the solid. For example, the diffusive flux of a species A into a porous spherical particle can easily be expressed with respect to the diameter of the sphere as opposed to the actual surface area of the fluid filled pores available for diffusion. The diffusivities computed from these artificial fluxes are referred to as effective diffusivities, or D_{eff} . This value must be obtained experimentally.

Other methods have been proposed to describe the effect of the pore structure on the measured effective diffusivity, using the properties of the porous material. One family of methods involves the use of the porosity and a tortuosity coefficient[38]. The tortuosity is defined as the ratio of the average of the true path length within the sample of the porous material to the thickness of the sample[38]. This is illustrated in Figure 2.5.2.



For a Total of n Pores of length l_i ,
the Tortuosity is defined as:

$$\text{Tortuosity} = \frac{1}{n} \sum_{i=1}^n l_i$$

Figure 2.5.2 : Definition of Tortuosity Coefficient.

Another variable used to describe the pore system is the constrictivity, which is related to the variable diameter of the pores. This factor is sometimes used in conjunction with the tortuosity to describe the pore system of porous solids[39]. In general, the effective diffusivity can be expressed as a function any combination of the bulk diffusivity, porosity, tortuosity and

the constrictivity.

A more empirical approach was developed by Klinkenburg[40] based on an approach by Garrels[41], based on studies of ionic diffusion in porous rock and consolidated soils. The lithological factor, L , was used as a grouped parameter to describe the characteristics of the pore system other than the void fraction. The lithological factor is defined as follows [40,41]:

$$L = \frac{D_o \epsilon}{D_{eff}} \quad (3)$$

Where D_o is the diffusivity in bulk solution in the absence of the porous material, D_{eff} is the measured effective diffusivity, and ϵ is the porosity of the porous substrate. In this study the total porosity has been utilized to calculate the lithologic factor.

The magnitude of the lithological factor can be used to interpret the nature of the pore structure of the material under study. In general, a higher lithologic factor is indicative of higher tortuosity, greater constrictivity and the presence of more ink bottle type and closed pores than in a material with a lower lithologic factor[38,40,41].

2.6 Summary of Previous Work

A number of other researchers have measured the effective diffusivity of chloride ion in cement pastes and mortars. The majority of this research is concentrated on measuring the effect of the replacement of some of the portland cement by various pozzolans or supplementary cementitious material on the chloride ion diffusivity. A representative summary of typical test methods and samples investigated is given in Table 2.6.1. In addition to this, a plot of effective diffusivities for ordinary portland cement samples with various water:cement ratios has been constructed from the references in Table 2.6.1 and is found in Figure 2.6.1.

Table 2.6.1 : Typical Experimental Methods and Sample Details for Measuring Effective Diffusivity of Chloride Ion.

SAMPLE DETAILS	APPARATUS	YEAR OF PUBLICATION	RESULTS for Dcl*	REFERENCE
OPC ⁽¹⁾ PFA ⁽²⁾ , BFS ⁽³⁾ , T ⁽⁴⁾ , w/c ⁽⁵⁾ .	Diffusion Cell	1981	Yes	18
OPC w/c	Uncracked Cylinders in Cl Bath	1984	No	42
OPC, w/c	Diffusion Cell	1986	Yes	31
OPC, CSF ⁽⁶⁾ , PFA, sp ⁽⁷⁾ .	Diffusion Cell	1987	Yes	15
OPC and mortars with polymer ⁽⁸⁾ .	Diffusion Cell	1988	Yes	43
OPC and PFA concretes	Perturbative Diffusion Cell	1990	Yes	44

- (1) Ordinary Portland Cement * Chloride Ion Diffusivity
(2) Pulverized Fly Ash
(3) Blast Furnace Slag
(4) Effects of Temperature
(5) Water:Cement Ratio
(6) Condensed Silica Fume
(8) In Situ Polymer used to block pores.

The first study was the initial foray into the use of diffusion cells to measure the effective diffusivity. Page et al [18] computed the Arrhenius relationship between effective diffusivity and temperature. The other studies concentrated on the effect of differing cement composition and curing on the measured effective chloride ion diffusivity. The final study introduced a new type of diffusion cell.

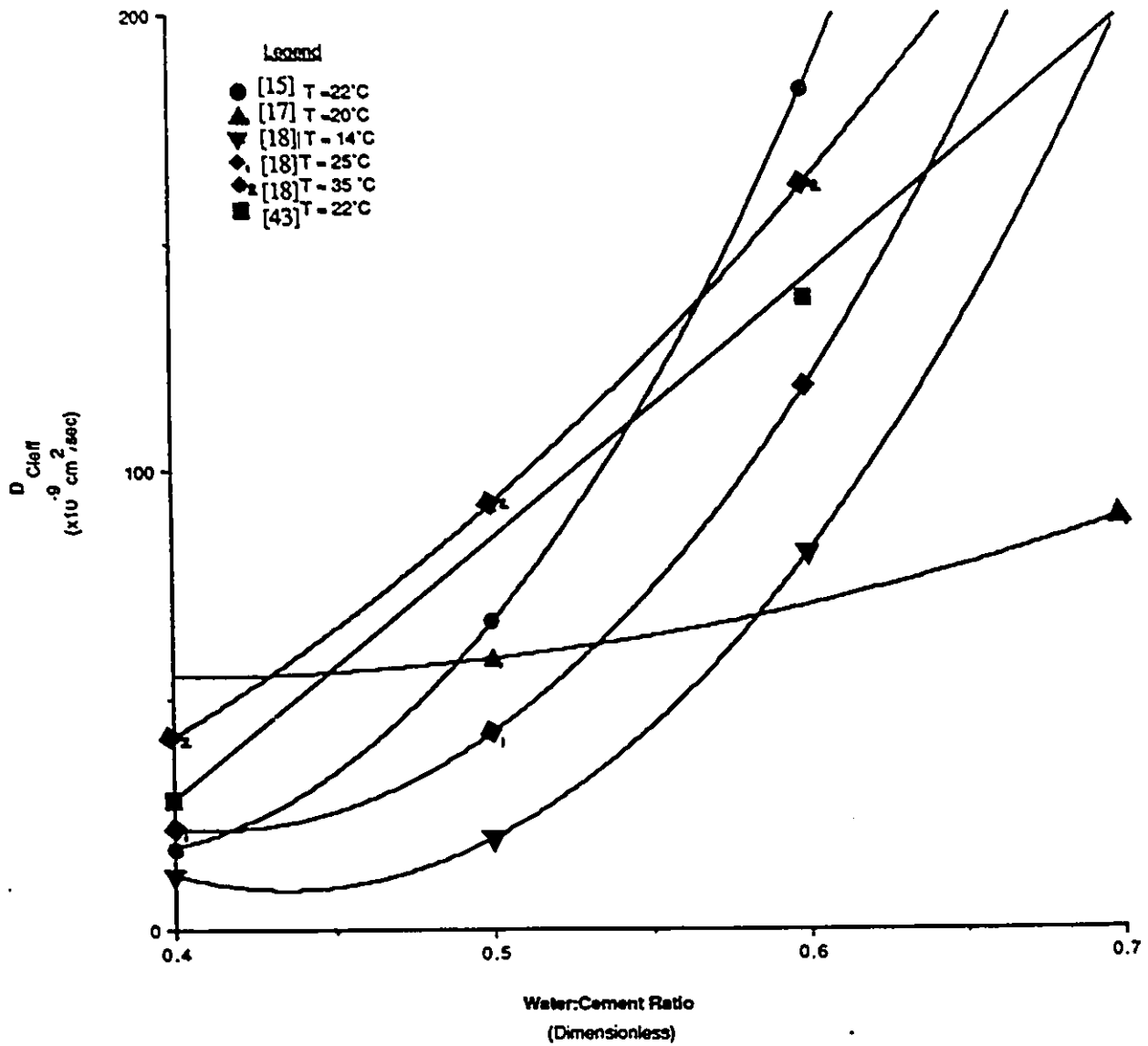


Figure 2.6.1 : Plot of Effective Chloride Ion Diffusivity versus Water:cement Ratio for Various Researchers. Curves Through Individual Points by Second Order Polynomial Regression.

As can be seen from Figure 2.6.1 there is an obvious trend of increasing effective diffusivities with increasing water:cement ratio.

A number of other researchers have published results of their experimental determination of chloride ion diffusivities in concrete and cement pastes[24,25,26,28,45,46,47,48,49]. The effect of a vast array of mix parameters have been studied, as well as the effects of various curing regimes and the use of supplementary cementing materials. In general again there is a similar evident in the quoted diffusivities in the various published results with changes in pozzolan content, water:cement ratio and curing.

Various experimental techniques have been utilized to measure chloride ion diffusivity. The apparatus used by many researchers and utilized in the experimental phase of this work was developed by C. L. Page, N.R. Short and A. El Tarras at the University of Aston in Birmingham, U.K[18]. The apparatus consists of two identical cells, which are open at one end and closed at the other. They have, in general, an opening at the top of the cell so that fluids can be added or removed from each compartment. These two cells are clamped together with a disk of the material under study between them. One cell is then filled with water saturated with calcium hydroxide, the other cell is filled with 1 molar solution of sodium chloride and saturated calcium hydroxide. A diagram of this apparatus is found in Figure 2.6.2.

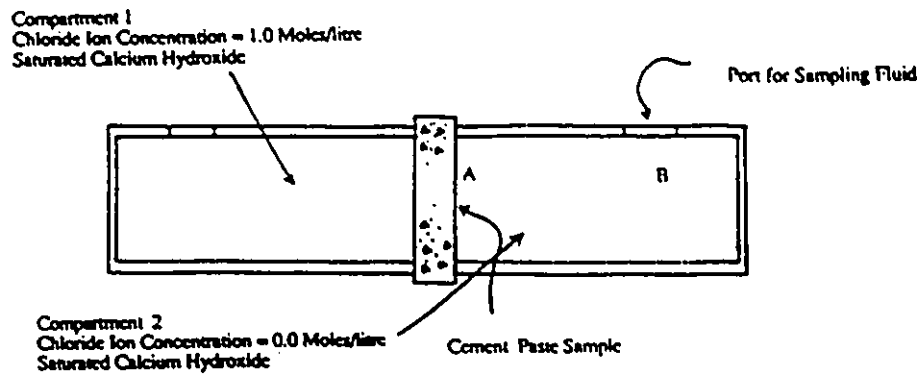


Figure 2.6.2 : Generalized Diagram of Diffusion Cell as Utilized by Page et al. [18]

Other researchers have utilized simpler techniques, among them the ponding of prisms or the exposure of prisms to seawater [42,49,50]. These researchers are normally not attempting to directly measure the diffusivity of chloride, rather they are attempting to make quantitative comparisons between various cementitious mixes, surface treatments or curing methods. Diffusivity coefficients can be determined in this fashion however, by utilizing Fick's second law of diffusion [25,26]. One solution for one dimensional diffusion into a semi-infinite slab with the concentration gradient in the z direction is found in Appendix A, which yields the following relationship:

$$C(z, t) = C_0 \left(1 - \operatorname{erf} \left(\frac{z}{\sqrt{2D_{eff}t}} \right) \right) \quad (1)$$

where, for a prism of concrete or cement with only one face exposed to a solution of chloride ion, the chloride content of the concrete at $z = 0$ is C_0 , the chloride content $C(z,t)$ at a distance z from the exposed face after exposure time t is given by the above equation. The error function is a well known special function. Both C_0 and $D_{Cl\text{eff}}$ are determined by iteration.[24,25,26].

This ability to solve the above equation for C_0 and $D_{Cl\text{eff}}$ allows the results of ponding experiments to be used to compute the effective chloride ion diffusivity in the material under study.[24]

This method is not normally used due to the difficulty in measuring the chloride ion content of small paste samples, the destructive nature of the test method, the possible variability of chloride content within the mix, and the difficulty in interpreting the physical implications of C_0 .

A third experimental technique for measuring the chloride diffusivity was developed by R.K Dhir et al. at the University of Dundee[44]. This technique was used to measure the effective diffusivity of chloride ion in concrete and significantly reduced the time required to make these measurements relative to the normal two compartment cell. The apparatus consisted of one half of a normal diffusion cell with a graphite anode inserted into one end

opposite the sample of material under study. Thus modified, the cell was then placed into a chloride ion bath of known concentration. A stainless steel anode in the bath was connected to a voltage source, the other end of which was connected to the graphite anode. The apparatus is illustrated in Figure 2.6.3 below.

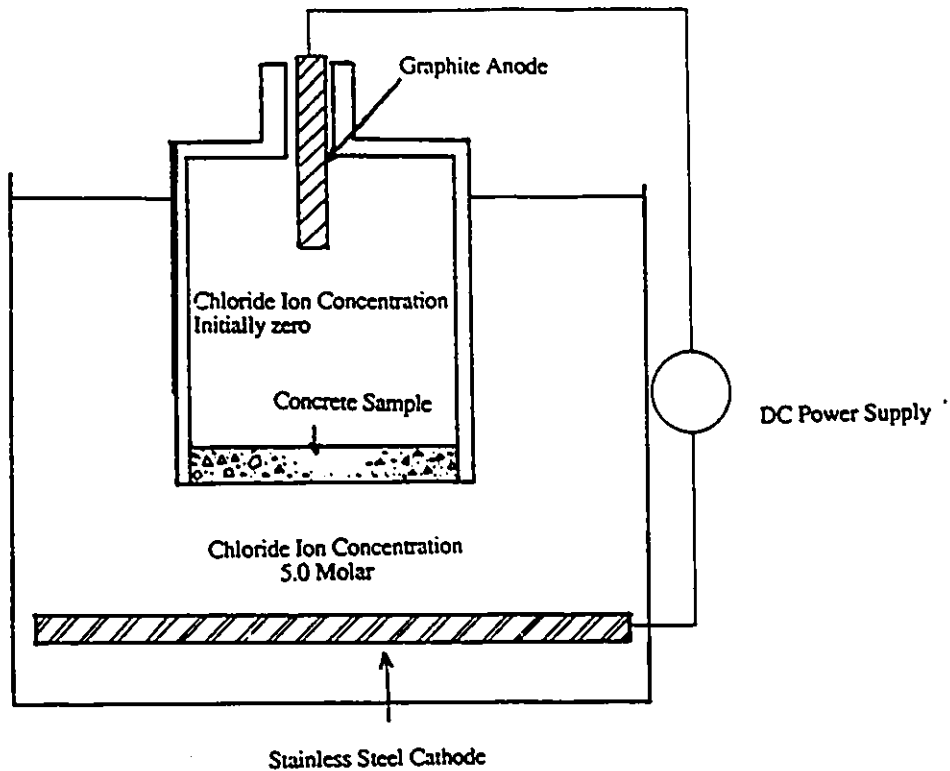


Figure 2.6.3 : Perturbative Diffusion Cell Used by Dhir et al.[44].

This method holds great promise for utilization in determining diffusivities in concretes, which are more directly applicable to assessing corrosion risk.

A very recent study by Tang and Nilsson[48] has presented a similarly rapid method of determining the effective chloride ion diffusivity in concrete. This method utilized an electric field to increase the rate of mass transfer. If the driving potential of the electric field is known, the diffusivity can be computed from the chloride ion profiles. These profiles were determined both by traditional total chloride ion analysis and by colorimetric means. This method seems to hold some promise for measuring effective chloride ion diffusivities in concretes.

3.0 EXPERIMENTAL DETAILS

3.1 Description of Diffusion Cell

The effective diffusivity of chloride ion in cement paste was determined using a modified version of the two compartment diffusion cell first utilized in 1981 by Page et al. at the University of Aston [18].

The apparatus, illustrated in Figure 3.1.1, consists primarily of two identical cylindrical cells which are open at one end. Each of the cells has an opening in the top so that the fluid inside could easily be accessed. A small hole was drilled into the top of each of the cylindrical cells approximately 15mm from the sealed end. A flexible polystyrene rod was then inserted into these holes. The other end of these rods was attached to 0.5 amp variable voltage direct current electric motors. These motors are used to stir continuously the solution in each cell for the duration of the experiment. The solution was not stirred when the chloride ion concentration in cell 2 was measured, since the stirring would interfere with the cell operation [51].

At the open end of the cell there is a flange which allows the two cells to be bolted together. These flanges contain a bevel for sandwiching a thin disk of the cement paste under study between them. Each flange also contains a rubber 'O' ring set into a second bevel so that when the cells are bolted together with a

cement paste disk between them, a waterproof seal is effected.

One cell, referred to as cell 1, is filled with a sodium chloride solution of known concentration. The other cell, referred to as cell 2, is filled with distilled water. The concentration of the solution in cell 2 was monitored using a chloride ion selective electrode as described in section 3.2.2. The measured chloride ion concentration in cell 2 is recorded with respect to time.

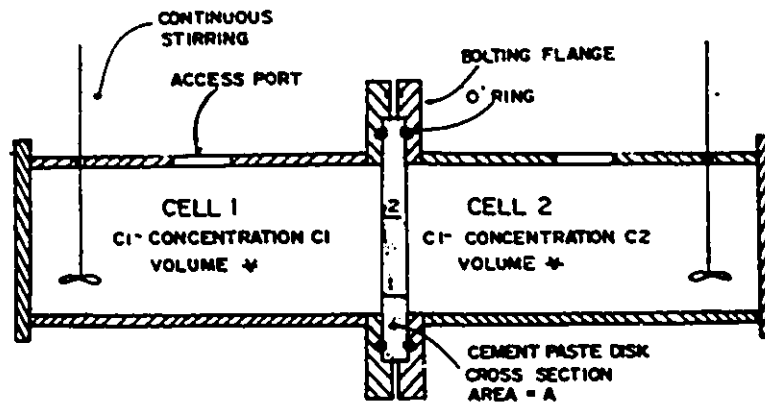


Figure 3.1.1 : Cross Section of Diffusion Cell Showing Cell Identification and Stirring Modification.

Based on these measurements, the effective diffusivity of chloride ion in cement paste can be calculated, based on Fick's first law[18].

As stated previously, Ficks first law of diffusion states that, with diffusion in the z direction

$$J_{Cl} = -D_{Cl\text{eff}} \frac{dC}{dz} \quad (1)$$

where J is the flux of the chloride ion in the diffusion layer, $D_{Cl\text{eff}}$ is the chloride diffusivity and dC/dz is the chloride ion concentration gradient in the z direction.

In addition, the following boundary conditions and assumptions are used:

Boundary Conditions :

$$c_2 = 0 \quad \text{at time}(t) = 0$$

Assumptions:

$$dc_1/dt = 0 \quad \text{for all } t$$

$$dC/dz = 0 \quad \text{except in the interval } 0 < z < 1$$

The boundary condition implies that diffusion starts at time = 0. The first assumption implies that, at all times, $c_1 \gg c_2$. The second assumption implies that there exists a concentration gradient only in the z direction within the cement disk sandwiched between the cells, and that the concentration is constant at all

points within a given fluid in the cells.

Using equation (1), and realizing that the flux out of cell 1 is equal to the flux into cell 2, the flux can be expressed as

$$J_{c1} = \frac{V}{A} \frac{dc_2}{dt} \quad (2)$$

Where V is the volume of cell 2, A is the area of the diffusing layer, and dc_2/dt is the rate of change of the concentration in cell 2 .

Substituting equation (2) for J in equation (1), Ficks Law becomes

$$\frac{V}{A} \frac{dc_2}{dt} = -D_{c1eff} \frac{dC}{dz} \quad (3)$$

To simplify the solution of this equation, the concentration gradient of chloride ion across a disk of thickness l is approximated by

$$\frac{dC}{dz} = \frac{(c_1 - c_2)}{l} \quad (4)$$

Substitution of equation (4) into equation (3) yields

$$\frac{V}{A} \frac{dc_2}{dt} = -D_{\text{cleff}} \frac{(c_1 - c_2)}{l} \quad (5)$$

Rearranging equation (4), then integrating both sides and applying the boundary condition and the assumptions

$$\int_0^{c_1} \frac{dc_2}{(c_1 - c_2)} = - \int_0^t \frac{D_{\text{cleff}} A}{V l} dt \quad (6)$$

Integrating both sides yields

$$\ln(c_1 - c_2) - \ln(c_1) = \frac{D_{\text{cleff}} A t}{V l} \quad (7)$$

rearranging yields

$$\ln\left(\frac{c_1 - c_2}{c_1}\right) = \ln\left(1 - \frac{c_2}{c_1}\right) = \frac{D_{\text{cl}^-} A t}{V_1} \quad (8)$$

Recalling that

$$\ln(1-x) = -x \quad (9)$$

when x is close to zero, and substituting this into equation (8), the final result is

$$c_2 = \frac{D_{\text{cl}^-} A c_1}{V_1} t \quad (10)$$

A rectilinear plot of c_2 versus time yields a straight line. The effective diffusivity of chloride ion can be easily determined from the slope of this straight line as the cell volume (V), the concentration of chloride in cell 1 (c_1), the area and thickness of the disk are easily measured, and all of the other variables are known. This model is based on the previously stated boundary conditions and assumptions, as well as the implicit assumption that the chloride ion concentration in cell 2 is much less than that in cell 1.

3.2 Investigations

The experiments performed as a part of this work were designed with two purposes. The first was to measure the effect of changes in the physical and chemical structure of the cementitious material on the diffusivity of chloride ion. To this end two experiments were carried out, namely:

A) to investigate the effect of the water:cement ratio on the effective diffusivity of the chloride ion in hardened cement paste. Cement disks were prepared as outlined below with water:cement ratios of 0.4, 0.5, 0.6 and 0.7.

B) to investigate the effect of replacing a portion of the type 10 portland cement with pulverized PSMC on the effective diffusivity of chloride ions in hardened cement paste. Cement disks were prepared with 5, 10, 20 and 30 percent of the portland cement replaced by PSMC. All samples were prepared with a water:binder ratio of 0.5, where binder refers to the total of the portland cement and the pozzolanic components of the PSMC.

Another set of experiments were designed both to investigate the effect of changes in the experimental conditions used by the majority of other researchers (e.g. 1 Molar chloride concentration and 3 mm sample thickness) on the measured chloride diffusivity, and investigate the dependence of the effective chloride ion diffusivity on the magnitude of the chloride ion concentration

gradient.

These experiments were conducted as outlined below. The cement disks used in this experiment had a water cement ratio of 0.45 and consisted only of ordinary portland cement.

C) This experiment investigated the effect of different chloride ion concentrations in cell number one on the time required to measure the effective chloride ion diffusivity. In addition, this experiment investigated the dependence of the effective diffusivity of chloride ion on the magnitude of the concentration gradient.

D) This experiment investigated the effect of the sample thickness on the measured effective chloride ion diffusivity in cement paste. Twelve disks of varying thickness were studied during this experiment.

3.2.1 Sample Preparation

The cement paste disks were cast in 50mm diameter cylindrical moulds approximately 300mm in length. The samples were filled in thirds and each layer was rodded a total of 25 times. The second and third layers were rodded with care to ensure that the rod did not penetrate into the underlying layers. The addition of PSMC to the cement mix decreased the workability of the paste, and the decrease became more pronounced for PSMC contents greater than 10 percent. After allowing 24 hours for the cylinder to set the

specimens were demoulded and placed in an automatically controlled curing room at 23 ± 2 °C and 100 percent relative humidity. The samples were allowed to cure under these conditions for approximately 5 to 6 weeks. Those samples containing PSMC were allowed to cure under the above conditions for 8 weeks.

The samples were then cut to the desired thickness using a rock saw with a diamond blade. The edges were turned to ensure a good fit into the diffusion cells. Each side of the disk was then abraded using 60 grit silicon carbide abrasive powder. The specimens were then bolted into the diffusion cells, the seal leak tested with pressurized air and the respective compartments were filled with solution. The charged cell was then placed into the holder, the stirring apparatus was put into place and the experiment was allowed to proceed. The chloride ion concentration in cell 2 was then measured at different times and the slope of the concentration versus time plot was used to compute the effective chloride ion diffusivity.

3.2.2 Measurement of Chloride Ion Concentration

The ability to measure easily and accurately the chloride ion concentration of the solution in cell 2 was essential to the successful completion of this experiment. In the present work a chloride ion selective electrode (Orion Research Inc. model 96-17B combination chloride electrode) was utilized to measure the

chloride ion concentration in cell 2 of the diffusion cell.

A chloride ion selective electrode is an electrochemical cell which develops a potential when placed into a solution of chloride ions. When the other terminal of a voltmeter is connected to a reference electrode, the potential difference, or voltage, can be measured. In the case of a combination electrode like the one used in this study, there exists within the electrode a reference electrode and no second electrode is required. The measurements were made using the direct calibration technique, which is a simple procedure for making a large number of measurements as was required during the course of this study. In this procedure, the electrode is calibrated using two or more standard samples which bracket the expected range of chloride concentrations. A plot is then made of the voltage developed by the electrode versus the chloride ion concentration. The electrode requires several seconds to several minutes to achieve a stable voltage, depending on the concentration of the solution being studied.

The reproducibility of the measurements made using this electrode is independent of the concentration of the sample under study, and the manufacturer states that following the manufacturer's recommendation of calibration on an hourly basis the direct electrode measurements are reproducible to within 2%[51]. The electrode as configured for this experiment is capable of measuring chloride ion concentrations in the range of 1 Molar to 10^{-5} Molar. A typical calibration curve for the electrode is

found in Appendix B.

3.2.3 Determination of Total Porosity of Cement Paste Disks

The porosity of the cement paste disks made up with various PSMC contents was determined in order to allow calculation of the lithologic factor. The procedure followed to determine the porosity is as follows.

The disks were immersed in water for at least six weeks to ensure that the paste was in the saturated condition. In all cases, the samples were never allowed to dry following casting. After the saturation period the disks were removed from the water bath and the height and diameter of each sample was measured in order to compute its total volume. Once the samples had reached the saturated, surface dry condition the samples were weighed. The samples were then placed in an oven at 100 °C for 48 hours. This was done to drive off all of the evaporable water contained in the pore volumes of the cement paste. After drying, each sample was again weighed. The difference between the initial and final weights was assumed to be accounted for by the evaporable water content. Using the well established density of water, the volume of the void and pore spaces could be calculated. Combining this quantity and the computed total volume of the cement paste samples,

the porosity of the sample is easily computed as follows.

$$\epsilon = \frac{V_p}{V_t} \quad (11)$$

Where ϵ is the total porosity, V_p is the pore and void volume and V_t is the total sample volume.

4.0 EXPERIMENTAL RESULTS

The results for the four experiments using the diffusion cells are given in sections 4.1 to 4.4. The sample details and the effective chloride diffusivity are reported, as are the slopes of the chloride concentration versus time plot which were obtained by linear regression of the experimental data, and the correlation coefficient, which is a measure of how close the plot of the experimental data was to a perfect straight line.

In addition to these tables, selected plots of the experimental data are presented. As well, plots of the effective chloride ion diffusivity versus water:cement ratio, sample thickness, chloride concentration in cell 1 and PSMC content are presented. Finally, the total porosity measurements are presented for the PSMC pastes.

A plot of chloride ion concentration versus time for each determination is given in Appendix C. A sample calculation for D_{cleff} is given in Appendix D.

4.1 Variation of Water:Cement Ratio

Cement paste disks were made up with water:cement ratios of 0.4, 0.5, 0.6 and 0.7 and the effective diffusivity was measured in triplicate for each set of samples. Two plots of the individual cell concentration versus time are presented in Figures 4.1.1 and

4.1.2, and the data calculated from all twelve cells is given in Table 4.1.1.

Table 4.1.1: Experimental Results showing Variation of Effective Chloride Ion Diffusivity with Water: Cement Ratio.

Sample No.	Water Cement Ratio	Sample Thickness (mm)	Slope of C vs t plot moles/l hr	$D_{cleff}^{(1)}$ $\times 10^{-9} \text{cm}^2/\text{sec}$	$r^{(2)}$
A1	0.4	4.28	2.49 E -5	29.3	0.99
A2	0.4	4.10	2.10 E -5	23.6	.99
A3	0.4	4.12	2.55 E -5	28.9	.99
Mean	0.4	--	--	27.3	--
A4	0.5	4.18	5.99 E -5	68.8	1.0
A5	0.5	3.77	7.09 E -5	73.4	1.0
A6	0.5	4.30	5.66 E -5	66.9	1.0
Mean	0.5	--	--	69.7	--
A7	0.6	4.38	11.7 E -5	140	1.0
A8	0.6	4.10	11.0 E -5	124	1.0
A9	0.6	4.42	10.4 E -5	126	1.0
Mean	0.6	--	--	130	--
A10	0.7	4.18	18.8 E -5	216	1.0
A11	0.7	3.99	17.3 E -5	189	1.0
A12	0.7	4.11	19.2 E -5	217	1.0
Mean	0.7	--	--	207	--

(1) $D_{cleff} = l(\text{cm}) \times m(\text{moles/lhr}) \times 0.00275$

(2) $r = \text{correlation coefficient} = \text{explained}/\text{total variance}$

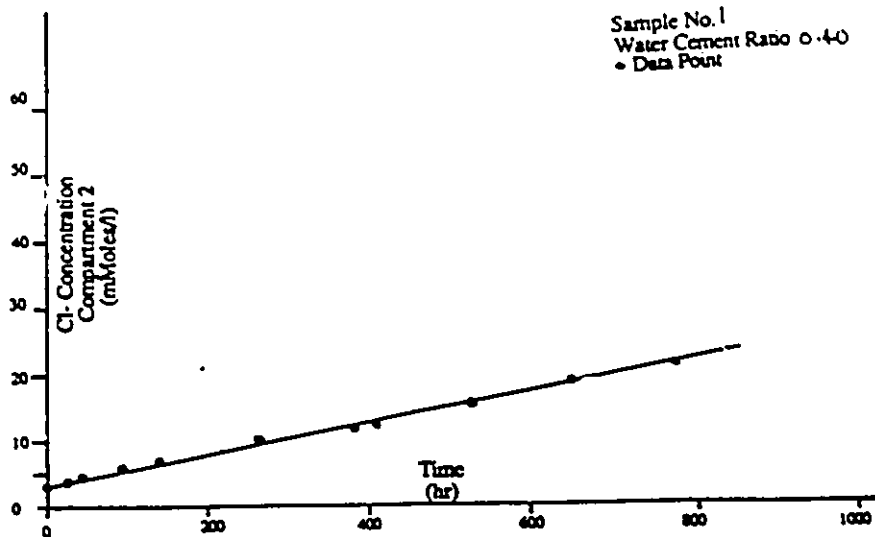


Figure 4.1.1 : Plot of Concentration versus Time for Cell 1 for Variation of Water:Cement Ratio.

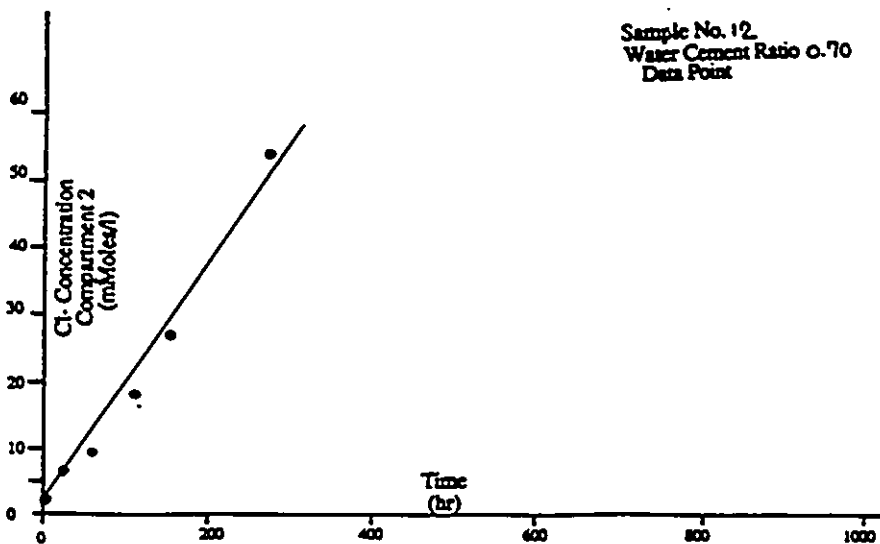


Figure 4.1.2 : Plot of Concentration versus Time for Cell 12 for Variation of Water:Cement Ratio.

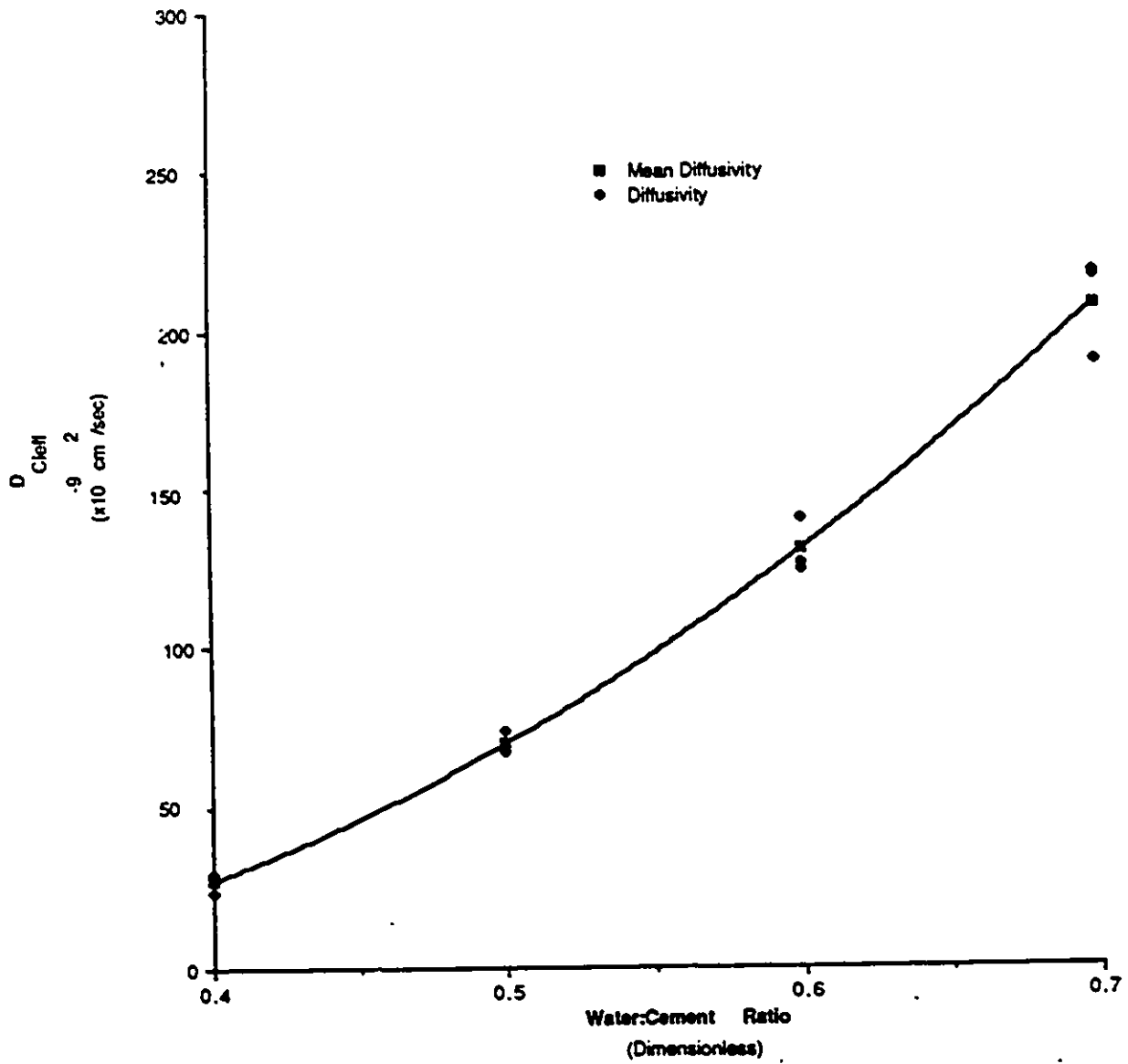


Figure 4.1.3: Plot of Effective Chloride Ion Diffusivity versus Water:Cement Ratio.

In Figures 4.1.1 and 4.1.2, the difference from c_2 at time zero from zero is due to contamination of the cell from previous runs and of the distilled water used in the experiment. This source of error was accounted for by measuring c_2 at time zero.

It is clear from Figure 4.1.3 that there is a very strong relation between the water cement ratio and the effective diffusivity, and that for an increase in water cement ratio there is an increase in the effective diffusivity of chloride ion.

4.2 Variation of PSMC Content

Cement paste disks of water cement ratio 0.5 were made up with PSMC contents of 5, 10, 20 and 30 % respectively. Each sample was tested in triplicate to determine the effective chloride ion diffusivity through the material. The measured effective diffusivities, sample data and linear regression data are given in Table 4.2.1.

Table 4.2.1 : Experimental Results showing Variation of Effective Chloride Ion Diffusivity with PSMC Content.

Sample No.	PSMC ⁽³⁾ Content (%)	Sample Thickness (mm)	Slope of C vs t plot moles/l hr	$D_{c,eff}^{(1)}$ $\times 10^{-9} \text{cm}^2/\text{sec}$	$r^{(2)}$
B1	5	1.59	12.8E-5	55.9	1.0
B2	5	1.67	14.6E-5	67.0	1.0
B3	5	1.51	13.3E-5	55.3	0.99
Mean	5	--	--	59.4	--
B4	10	1.71	8.65E-5	40.7	.98
B5	10	1.63	9.69E-5	43.4	.99
B6	10	1.63	8.17E-5	36.6	.95
Mean	10	--	--	40.2	--
B7	20	2.12	4.09E-5	23.8	.99
B8	20	3.98	1.68E-5	18.4	.97
B9	20	2.23	3.62E-5	22.2	.99
Mean	20	--	--	21.5	--
B10	30	1.49	4.29E-5	17.6	.99
B11	30	2.46	2.91E-5	19.7	.99
B12	30	2.33	2.33E-5	15.7	.99
Mean	30	--	--	17.7	--

(1) $D_{c,eff} = l(\text{cm}) \times m(\text{moles/lhr}) \times 0.00275 / c_1$

(2) $r = \text{correlation coefficient} = \text{explained}/\text{total variance}$

(3) Water Binder Ratio of 0.50 CSA Type 10 Portland Cement

The effective diffusivity of the chloride ion is plotted versus PSMC content in Figure 4.2.1 for the four PSMC contents studied as well as that for a water cement ratio of 0.5 and no

added PSMC given in section 4.1.

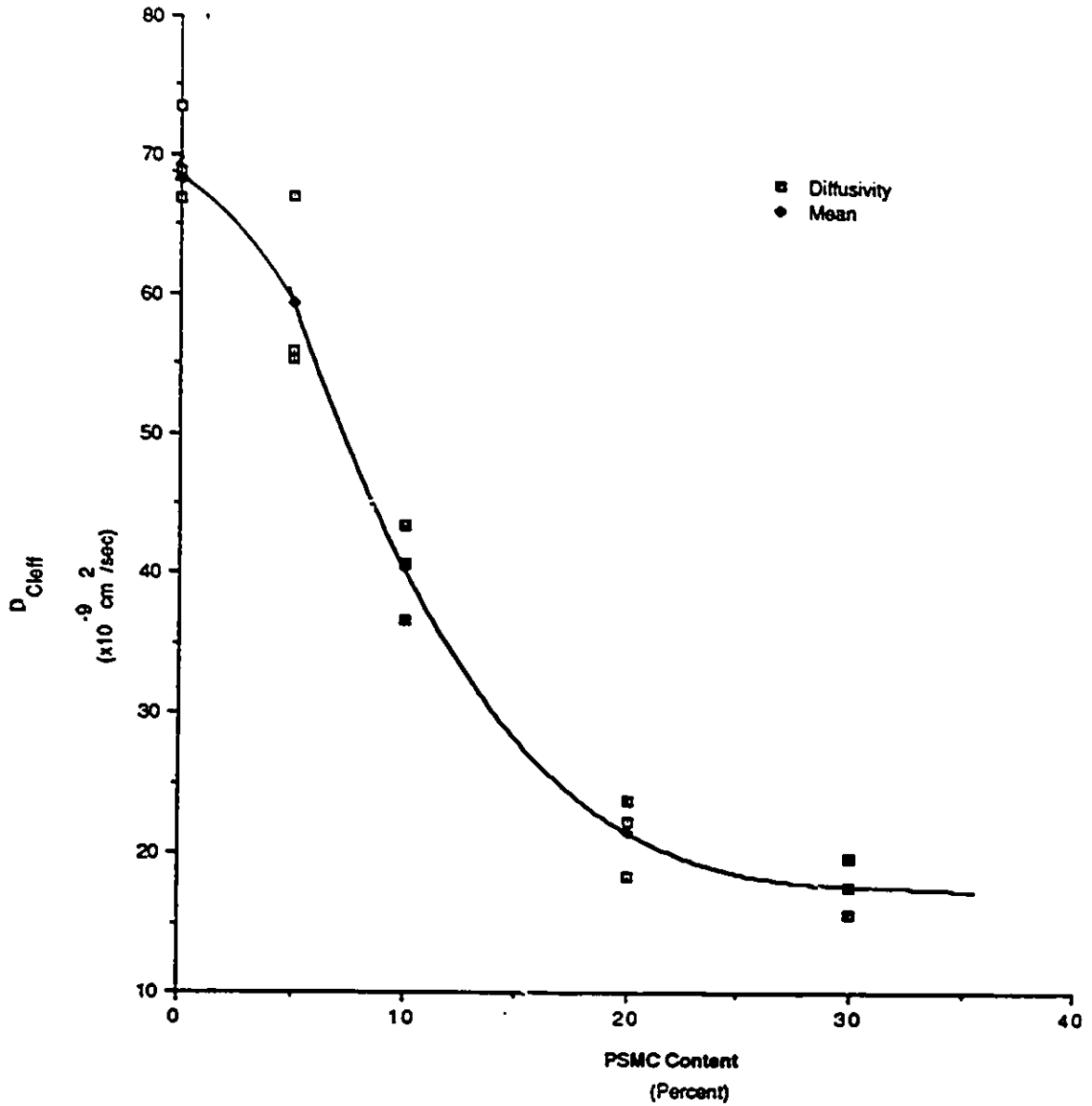


Figure 4.2.1 : Plot of Effective Chloride Ion Diffusivity versus PSMC Content for Cement Pastes of Water: Binder Ratio 0.5.

It is clear from Figure 4.2.1 that the addition of PSMC to the mix

has a marked effect on the effective chloride ion diffusivity. An increase in the PSMC content of the cement paste causes a reduction in the effective diffusivity.

The total porosity of the PSMC cement pastes was determined, and the results are given in Table 4.2.2

Table 4.2.2 : Total Porosity of PSMC Cement Pastes

Sample No. (1)	PSMC Content %	$V_p^{(2)}$ cm ³	$V_t^{(3)}$ cm ³	Porosity
1	5	2.315	4.268	0.5424
2	5	2.289	4.364	.5245
3	5	2.590	4.747	.5456
Mean	5	--	--	.5375
4	10	2.534	4.893	.5179
5	10	2.700	5.184	.5208
6	10	2.565	4.975	.5156
Mean	10	--	--	.5181
7	20	5.004	11.42	.4382
8	20	2.887	6.359	.4540
9	20	2.429	5.392	.4505
Mean	20	--	--	.4476
10	30	1.243	2.848	.4366
11	30	2.002	4.507	.4442
12	30	2.191	4.975	.4404
Mean	30	--	--	.4404

- (1) Not the same samples as used for effective chloride ion diffusivity determination. Water to Binder Ratio 0.5. CSA Type 10 portland cement.
- (2) The total volume of pore and void spaces filled with evaporable water.
- (3) The total volume of the disk based upon its height and diameter.

The porosity of the PSMC pastes is plotted against PSMC content in Figure 4.2.2.

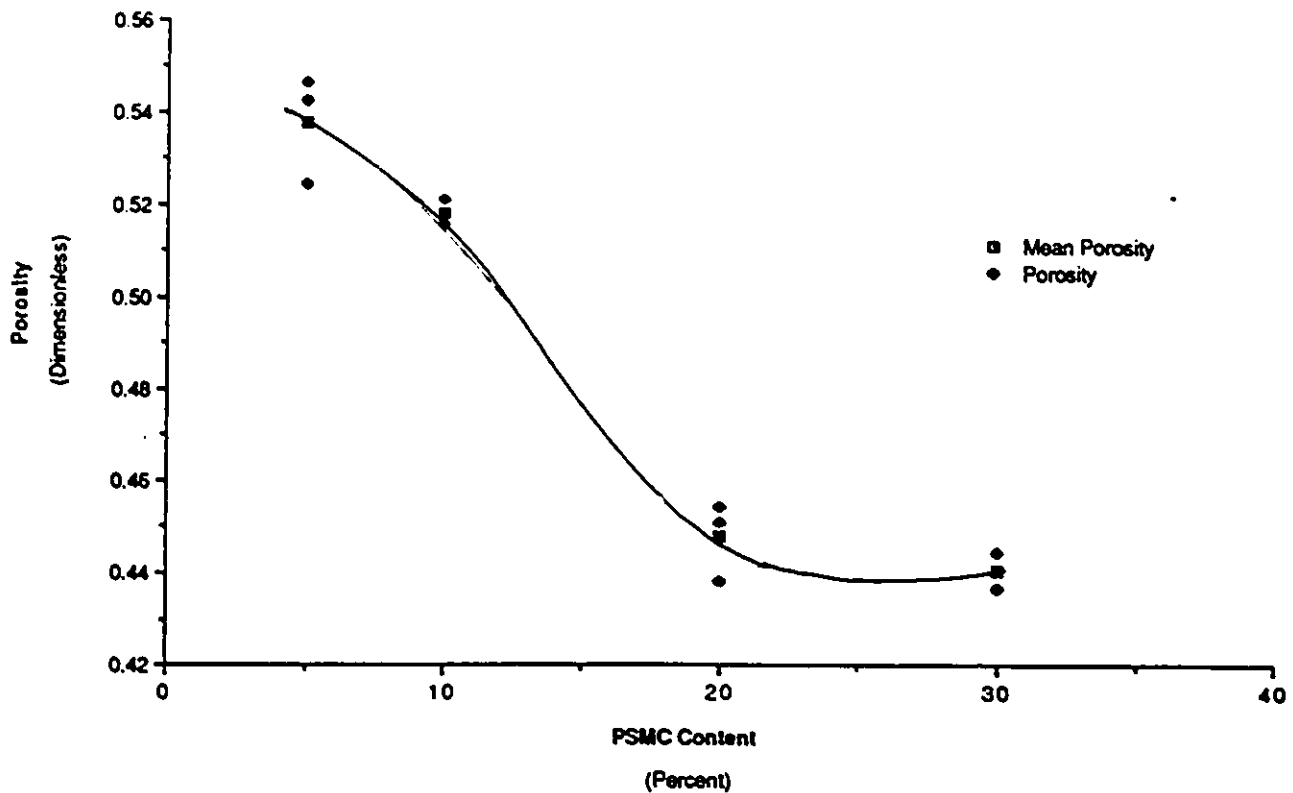


Figure 4.2.2 : Plot of Porosity versus PSMC Content of Cement Paste of Water:Binder Ratio 0.5.

4.3 Variation of Chloride Ion Concentration in Cell 1.

The first two experiments were carried out with the aim of ascertaining the effect of changes in the hardened cement paste on the effective chloride ion diffusivity. The second pair of experiments concentrated on determining the effect of varying the parameters of the experimental setup on the measured effective chloride ion diffusivity.

The chloride ion concentration in cell 1 of the diffusion cell was varied from the normally used value of 1 molar. Using cement

paste disks of a water cement ratio of 0.45, the cell 1 concentration was varied from 0.5 to 2.0 to 3.0 to 4.0 molar.

The calculated effective chloride ion diffusivity results from the above study are presented in Table 4.3.1.

Table 4.3.1 : Experimental Results showing Variation of Effective Chloride Ion Diffusivity with Chloride Ion Concentration in Cell 1.

Sample No.	Cell 1 Chloride (moles/l)	Sample ⁽³⁾ Thickness (mm)	Slope of C vs t plot moles/l hr	$D_{cl\text{eff}}^{(1)}$ $\times 10^{-9} \text{cm}^2/\text{sec}$	$r^{(2)}$
C1	0.5	4.06	3.27 E -5	73.0	0.99
C2	0.5	4.51	2.39 E -5	52.5	.95
C3	0.5	4.27	2.68 E -5	58.1	.99
Mean	0.5	--	--	61.1	--
C4	2.0	4.21	10.0 E -5	58.1	1.0
C5	2.0	4.02	12.1 E -5	66.7	0.99
C6	2.0	3.94	9.53 E -5	54.6	1.0
Mean	2.0	--	--	59.8	--
C7	3.0	5.01	12.6 E -5	62.9	0.99
C8	3.0	4.24	17.9 E -5	69.4	1.0
C9	3.0	5.03	11.83 E -5	54.6	1.0
Mean	3.0	--	--	62.3	--
C10	4.0	3.99	24.7 E -5	67.7	1.0
C11	4.0	4.02	27.6 E -5	76.3	1.0
C12	4.0	3.89	20.51	54.8	1.0
Mean	4.0	--	--	66.3	--

(1) $D_{cl\text{eff}} = l(\text{cm}) \times m(\text{moles/lhr}) \times 0.00275 / c_1$

(2) r = correlation coefficient = explained/total variance

(3) Water Cement Ratio of 0.45 CSA Type 10 Portland Cement

The effective chloride ion diffusivities determined during this experiment are plotted against the chloride ion concentration in cell 1 in Figure 4.3.1.

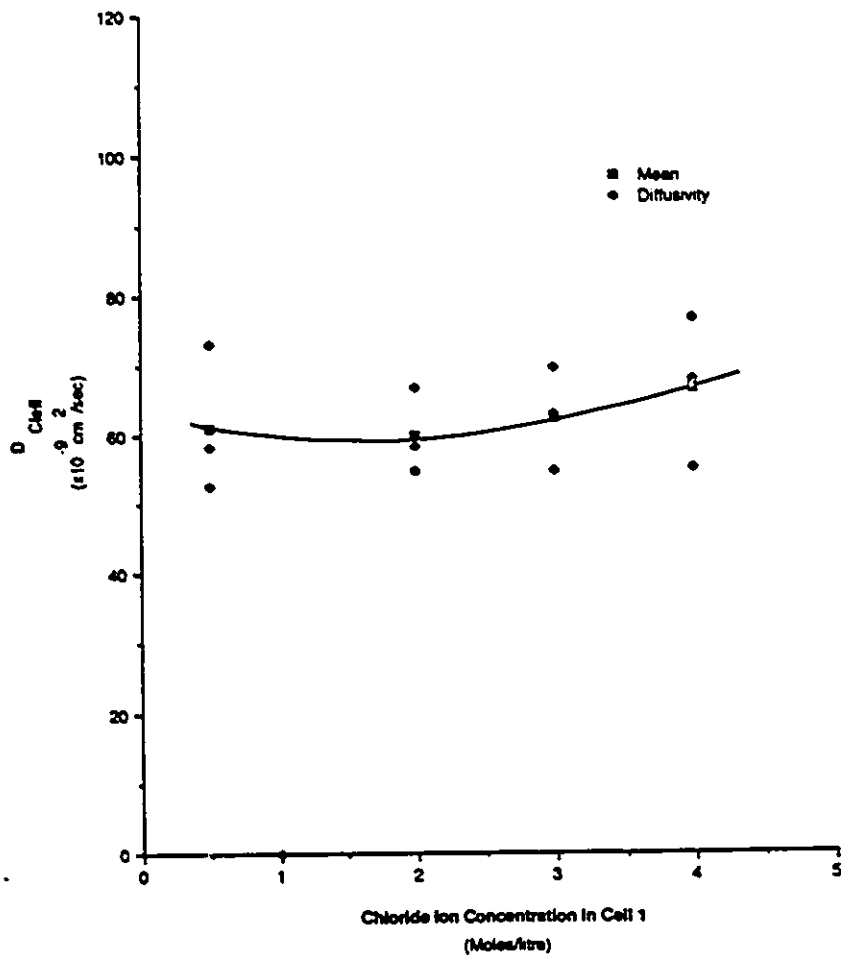


Figure 4.3.1 : Plot of Effective Chloride Ion Diffusivity versus Chloride Ion Concentration in Cell 1.

It is apparent from Figure 4.3.1 that there is little dependence of the measured effective chloride ion diffusivity on the concentration of the chloride ion in cell 1.

4.4 Variation of Sample Thickness

The final experiment involved the use of cement paste disks of varying thicknesses ranging from 1.78 to 5.22 mm. These disks were prepared using a water cement ratio of 0.45. The calculated effective chloride ion diffusivity results from this study are given in Table 4.4.1.

Table 4.4.1 : Experimental Results Showing Effect of Sample Thickness on the Measured Effective Chloride Ion Diffusivity, CSA Type 10 Portland Cement.

Sample No.	Sample ⁽³⁾ Thickness (mm)	Slope of C vs t plot moles/l hr	D _{cleff} ⁽¹⁾ x10 ⁻⁹ cm ² /sec	r ⁽²⁾
D1	4.32	2.04 E -5	24.3	0.97
D2	2.80	8.12 E -5	62.5	1.0
D3	4.87	3.69 E -5	49.5	0.99
D4	4.21	4.38 E -5	50.7	.99
D5	1.79	11.5 E -5	56.3	.99
D6	5.22	3.37 E -5	48.3	.95
D7	1.87	12.2 E -5	62.5	1.0
D8	2.27	10.2 E -5	63.5	1.0
D9	2.48	10.9 E -5	74.3	1.0
D10	3.10	6.70 E -5	57.1	.99
D11	4.33	4.50 E -5	53.5	.98
D12	1.78	28.0 E -5	137	.99

(1) $D_{cleff} = l(\text{cm}) \times m(\text{moles/lhr}) \times 0.00275 / c_1$

(2) $r = \text{correlation coefficient} = \text{explained/total variance}$

(3) Water Cement Ratio of 0.45

The measured effective chloride ion diffusivity is plotted against the sample thickness in Figure 4.4.1.

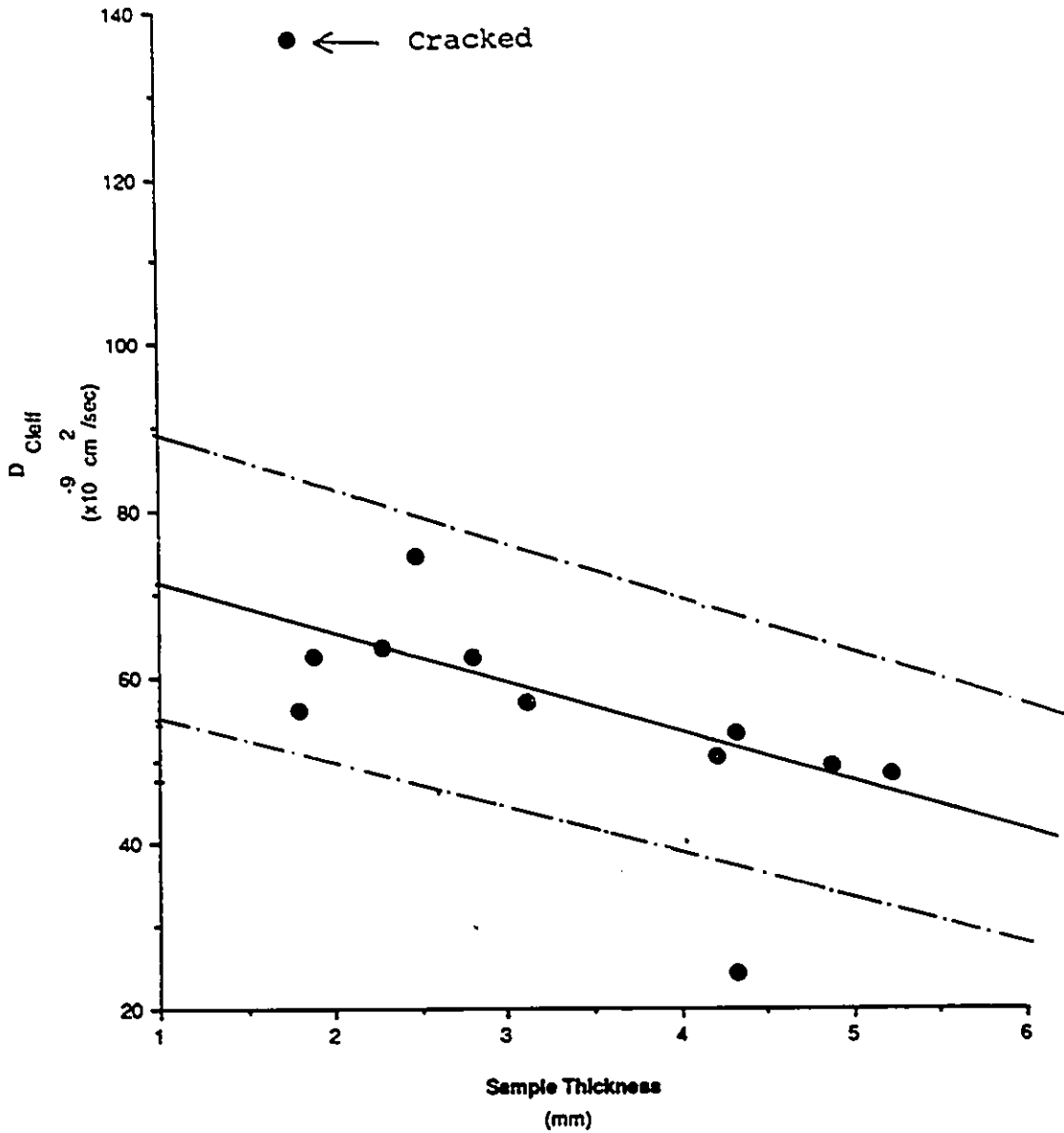


Figure 4.4.1 : Plot of Effective Chloride Ion Diffusivity versus Sample Thickness.

It would appear, based on Figure 4.4.1 that there is a relationship between the thickness of the sample under study and the measured chloride ion diffusivity. An increase in the sample thickness causes a decrease in the measured effective chloride ion diffusivity. A best fit straight line has been constructed using linear regression, and a 95% confidence interval has been computed. The two outlying results have not been included in these calculations. All of the individual measurements, with the exception of the outlying results, fall within the confidence interval. The equation of the best fit line is :

$$D_{Cl_{eff}} = -4.74 \times 10^{-9} \frac{cm^2}{mmsec} l(mm) + 73.4 \frac{cm^2}{sec} \times 10^{-9} \quad (1)$$

The results from cell C12 are of interest, as the high diffusivity is a result of the sample having cracked during its installation into the cell. It is clear from this result that the diffusivity is much greater through cracked paste than through uncracked paste.

5.0 DISCUSSION

5.1 Methodology

5.1.1 Effect of Stirring Modification

The results obtained as a part of this present study differ in part from those presented by Page et al.[18] and others, in that no delay in the increase of chloride ion concentration in cell 2 was noted. In at least Pages initial study a time lag was reported before the chloride ion concentration in cell 2 differed from zero[18]. This observed time lag was attributed to the time required to fill the active chloride ion adsorption sites in the pore structure of the hardened cement paste[18]. Another possible explanation of this observed time lag is the time required for the chloride ion to diffuse from the cell 2 side surface of the cement paste disk (Marked as A in Figure 5.1.1) to the location of the port for removal of the solution for analysis (Marked as B in Figure 5.1.1).

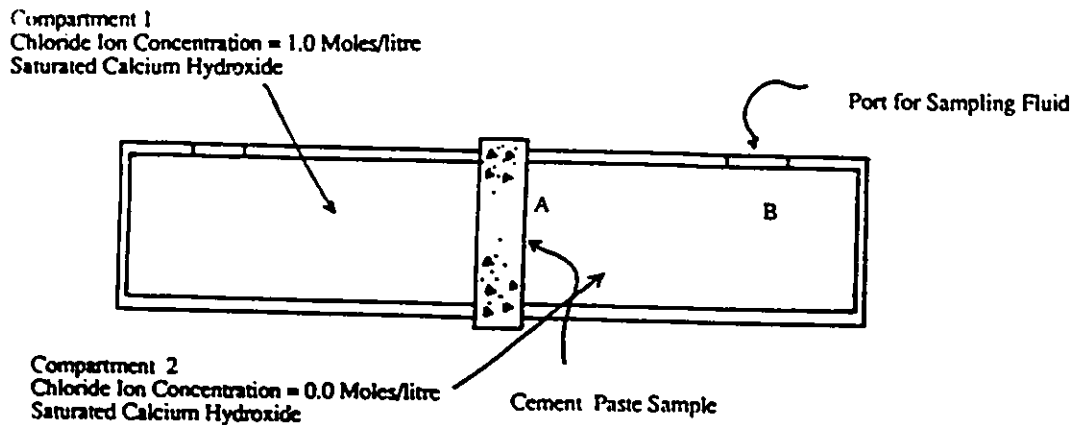


Figure 5.1.1 : Cross Section of Page et al.'s Diffusion Cell[18].

A calculation to estimate the time for chloride ion to diffuse 40 mm in aqueous solution based on boundary layer theory is found in Appendix E. This calculation has shown that this lag may be typically in the range of 60 hours. Page reports a time lag in one of his determinations of 74 hours[18]. It is therefore plausible to assume that this time lag may be at least partially accounted for by this intracell diffusion.

In this study, the effect of this type of error is reduced by providing continuous stirring to both cells of the diffusion cell. This validates the implicit assumption in the development of the model of the diffusion cell that the chloride ion concentration in each cell is uniform. The lack of external agitation in Page's apparatus does not seem to have affected the measured chloride ion diffusivity, with the exception of this reported time lag, as the

diffusivity of chloride ion in the bulk solution in cells one and two is many hundreds of times greater than the effective diffusivity in the cement paste. Some mixing in Page's unstirred apparatus would have occurred due to convection.

5.2 Effect of Variation of the Apparatus

5.2.1 Sample Thickness

The linear regression performed on the data showed that an increase in sample thickness of 1 mm leads to a decrease in the measured diffusivity of 4.74×10^{-9} cm²/sec for the sample thickness range tested. This represents a decrease of approximately 6 percent of the mean diffusivity. The experimental scatter in other experiments in this study are in the range of 10 to 30 percent of the mean diffusivity. However, changes in diffusivity that would arise from a small change (up to ± 1.5 mm) in sample thickness are typically of the same order as changes in diffusivity resulting from experimental variations. Changes in sample thickness greater than this can lead to problems with the comparison of the different results, as the error due to sample thickness would approach the magnitude of the experimental error.

A decrease in diffusivity with increasing sample thickness at relatively small thicknesses is expected as the number of pores which are below the threshold diameter yet still penetrate the total width of the specimen decreases as the sample thickness

increases.

Two measured values for $D_{Cl_{eff}}$ fall outside of the 95 % confidence interval. Sample D12 has a much larger diffusivity than would be expected for its sample thickness or composition. This particular sample was cracked when mounted in the diffusion cell, and therefore the cross sectional area available for diffusion was greatly increased. Sample D1 has an abnormally low diffusivity. A reduction in chloride ion diffusivity could result from either a partial blocking of the pore system or by adsorption of the chloride ions by the cement paste.

5.2.2 Cell 1 Concentration

The plot of measured effective chloride ion diffusivity in hardened cement paste, found in Figure 4.3.1, clearly demonstrates that there is no significant dependence of the effective chloride ion diffusivity as measured using the diffusion cell on the chloride ion concentration of the solution contained in cell 1 of the diffusion cell, within the range studied in this present work. The time required to reach a chloride ion concentration in cell 2 of the diffusion cell of 100 mmolar is decreased from approximately 3000 hours for a cell 1 concentration of 0.5 molar to approximately 400 hours for a cell 1 concentration of 4.0 molar. This is indicative of the time required to measure the effective chloride ion diffusivity. Thus the use of a relatively high chloride ion

concentration in cell 1 can be used to reduce the time time required to perform the chloride ion diffusivity determinations.

5.3 Effect of Variation of Cement Paste Composition

5.3.1 Variation of Water:Cement Ratio

The experimental data presented in section 4.1 clearly show that there is a relationship between the water:cement ratio of the cement paste and the measured effective diffusivity of chloride ion in that paste. An increase in the water:cement ratio results in an increase in the effective chloride ion diffusivity. The same relationship can also be observed between the water cement ratio and the total porosity of the paste. The relative magnitude of these relationships is not equal, and therefore it is likely that there are changes to the nature of the pore structure itself, and not simply in the amount of the sample made up by the pore and void volume. In order to attempt to quantify these changes, the lithologic factor, L , [40,41] has been calculated for each of the mean results reported in section 4.1. This calculation is based on the total theoretical porosity of the paste at 100 % hydration as reported by Neville[20]. These theoretical porosities and the calculated lithologic factors are presented in Table 5.3.1.

Table 5.3.1 : Theoretical Total Porosity and Lithologic Factor for Hardened Cement Pastes of Various Water:Cement Ratios.

Water:cement Ratio	$D_{cleff}^{(1)}$ ($\times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$)	Porosity ⁽²⁾	Lithologic Factor ⁽³⁾
0.4	27.3	0.31	140
0.5	69.7	0.45	80
0.6	130	0.48	46
0.7	207	0.53	32

(1) Average of three results presented in Table 4.1.1.

(2) Theoretical total porosity at 100% hydration[20].

(3) $D_{clo} = 1.24 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ [37].

The calculated lithologic factor has been plotted against the water:cement ratio in Figure 5.3.1.

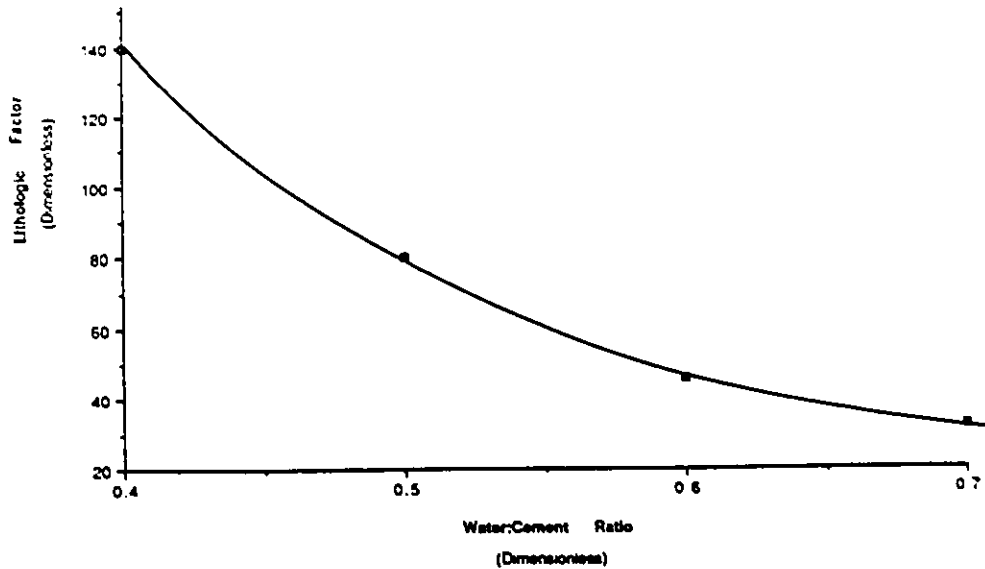


Figure 5.3.1 : Plot of Lithologic Factor versus Water:Cement Ratio.

It is clear from the above plot that there is a strong relationship between the lithologic factor and the water:cement ratio of the ordinary portland cement samples.

The interpretation of the lithologic factor is, as mentioned previously, a relative one, that samples with high lithologic factors have more complex pore structures than those samples with lower lithologic factors. This interpretation agrees with the results presented here in that it is well established that the pore system of portland cement paste becomes more complex as the water:cement ratio is reduced[19,20]. This lithologic factor will be utilized in our discussion of the variation of effective chloride ion diffusivity with PSMC content of the paste, where the changes in the pore system are not as well known as that in ordinary portland cement.

These results confirm that concretes which contain paste with high water:cement ratios are not as protective of the embedded

reinforcing steel from chloride ion induced corrosion as those with lower water:cement ratios, due to the increase in diffusivity which results from the higher water:cement ratio.

5.3.2 Variation of PSMC Content

There is also a distinct relation between the measured chloride ion diffusivity and the PSMC content of the cementitious paste. As shown previously in Figure 4.2.1, as the amount of ordinary cement paste replaced by PSMC in the mix increases, the effective chloride ion diffusivity through the hardened paste decreases. It is of interest to note that the rate of effective chloride ion diffusivity reduction is also dependent on the PSMC content of the paste.

The porosity of the PSMC pastes, as plotted in Figure 4.2.2, shows similar behaviour. This would suggest that there is some dependence of the effective chloride ion diffusivity and the porosity of the PSMC modified cement paste. Indeed, as shown in Figure 5.3.2, the effective chloride ion diffusivity is directly proportional to the porosity of the paste. It is likely that there is a pore blocking effect both due to the potential pozzolanic nature of the PSMC and due to the presence of mineral; fines in the PSMC, specifically the carbon and calcium carbonate components. These mineral fines behave in such a way as to block the pores in the cement matrix. These mineral fines also significantly reduced

the workability of the freshly mixed paste, which may have contributed to an increase in the porosity of the paste by inhibiting proper consolidation.

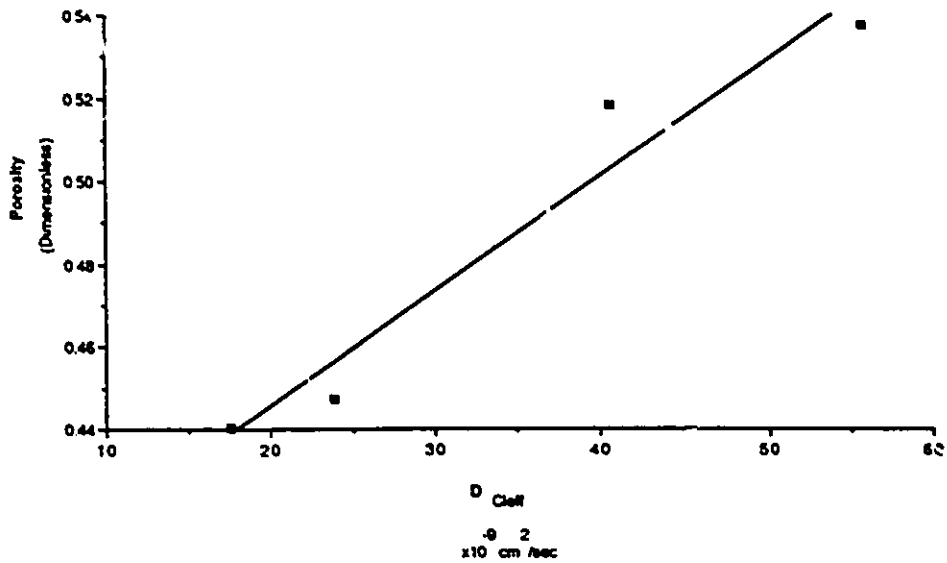


Figure 5.3.2 : Plot of Porosity versus Effective Chloride Ion Diffusivity for PSMC Modified Cement Pastes.

A similar direct proportionality between porosity and effective chloride ion diffusivity is also observed for samples of varying water:cement ratios greater than 0.5 as is seen in figure 5.3.3. Below a water:cement ratio of 0.5, the porosity drops off rapidly with decreasing water:cement ratio.

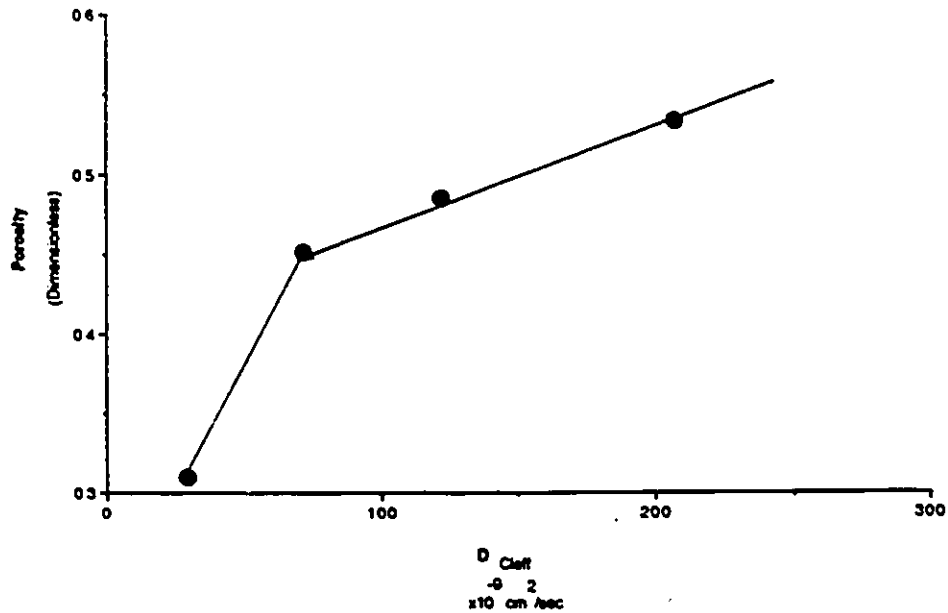


Figure 5.3.3 : Plot of Porosity versus Effective Chloride Ion Diffusivity for Cement Pastes of Varying Water:Cement Ratio.

It is interesting to observe this behaviour, and the two distinct lines suggest two controlling mechanisms for the observed increase in D_{cleff} . Below a water:cement ratio of 0.5, the controlling mechanism is likely the interconnecting of capillary pores. Above a water:cement ratio of 0.5, a second mechanism takes

over. This second mechanism is likely the increase in the number of capillary pores larger than the threshold diameter. The similarity in behaviour between the second domain and the manner in which the PSMC content affects porosity and diffusivity is likely due to the similarity in the manner in which the pore volume is changed when the water:cement ratio is increased and when the PSMC content is reduced. Both result in an increase in porosity, and in both cases that increase is due to the increase in the number of pores above the threshold diameter and hence the number of pores which are connected and unblocked. The resulting increase in the capillary porosity has the effect of increasing the cross sectional area of the pores above the threshold diameter, which is directly proportional with the effective diffusivity. The same is observed with an increase in the PSMC content of the cement paste. As the potential pozzolanic reaction takes place, and due to the presence of the mineral fines, some of the capillary pores above the threshold diameter become segmented. As these pores are no longer continuous, they no longer contribute to the cross sectional area of pores available for diffusion.

Again recalling Figure 4.2.2, which plotted porosity of cement paste versus PSMC content, it is apparent that there is an approximately linear relationship between paste porosity and PSMC content up to a PSMC content of approximately 15 percent. Beyond this PSMC content, the rate of change of porosity with respect to PSMC content decreases dramatically. The same relationship is

observed between effective chloride ion diffusivity and PSMC content. This behaviour could be explained by considering that as the PSMC content is increased, at some point the majority of the smaller diameter pores will be filled or almost filled with gel or mineral fines, or both. After this point, an increase in PSMC content would no longer be filling pores at the same rate, and hence there is decrease in the rate of change of porosity with PSMC content. This decrease in the rate of blocking pores would be mirrored by a decrease in the reduction of cross sectional pore area, and would be reflected by a decrease in the rate of decrease of the effective chloride ion diffusivity with increasing PSMC content of the cement.

It is of interest to compute the lithologic factor for the PSMC containing hardened cement pastes. The tabulated results of this calculation are found in Table 5.3.2.

Table 5.3.2 : Total Porosity and Lithologic Factor for Hardened Cement Pastes of Various PSMC Contents.

PSMC Content %	$D_{cl}^{eff(1)}$ ($\times 10^{-9} \text{ cm}^2 \text{ sec}^{-1}$)	Porosity ⁽²⁾	Lithologic Factor ⁽³⁾
5	59.4	0.5375	112
10	40.3	.5181	159
20	21.5	.4476	258
30	17.7	.4404	308

(1) Average of three results presented in Table 4.2.1.

(2) Computed Porosity presented in Table 4.2.2.

(3) $D_{cl0} = 1.24 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ [36].

Again it is clear that there is a marked dependence of the lithologic factor on the PSMC content, as shown in Figure 5.3.4.

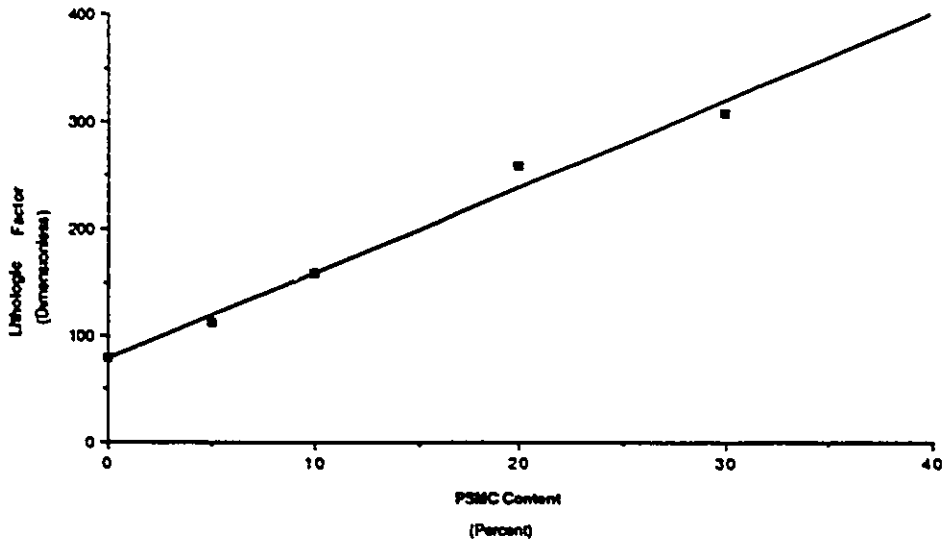


Figure 5.3.4 : Plot of Lithologic Factor versus PSMC Content.

It is of interest to note that the lithologic factor increases nearly linearly with the PSMC content of the hardened cement paste. In relative terms, it is clear that there is a decrease in interconnectivity between the pores increases with the an increase in the PSMC content of the paste, and that this increase is directly proportional to the PSMC content. As this differs markedly from the relationship between porosity and water:cement content of the paste, this would suggest that the diffusivity is much more sensitive to a decrease in the cross sectional area of pores above the threshold rather than in the increase in pore system complexity, and therefore diffusion path, which may

accompany an increase in PSMC content of the paste.

5.4 Comparison of Present Results with those of Previous Researchers

A number of researchers have investigated the effect of varying the water:cement ratio on the effective chloride ion diffusivity [15,17,18,42,43,44]. These results are presented graphically in Figure 5.4.1, along with the results determined in this study.

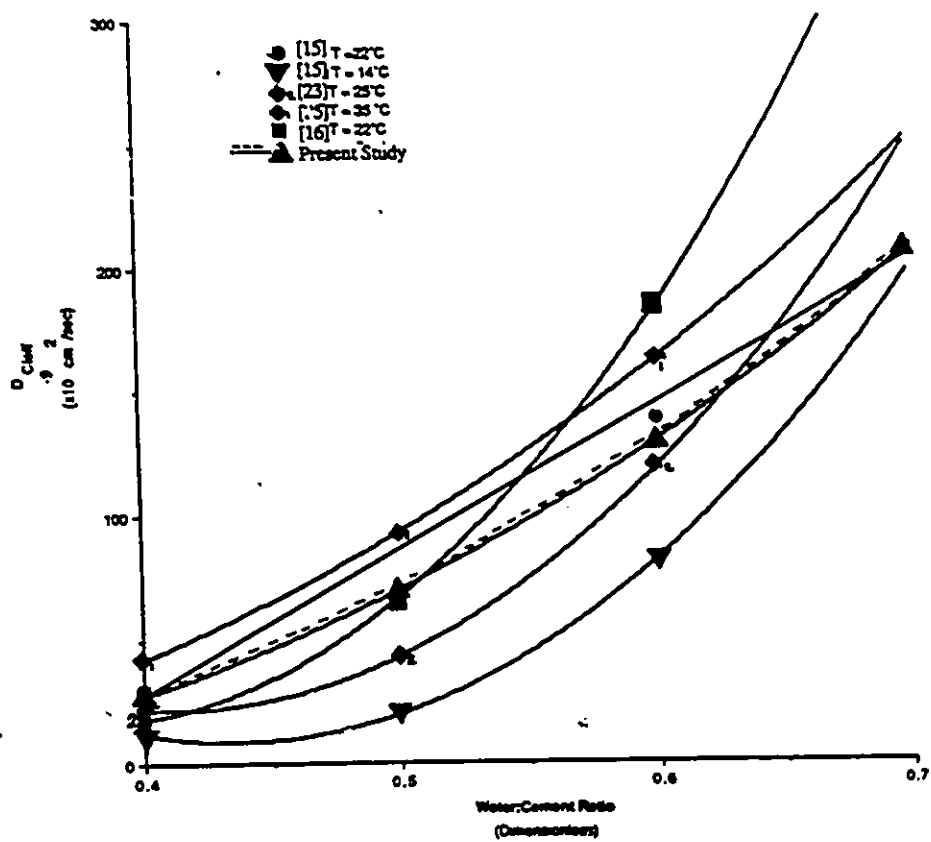


Figure 5.4.1 : Plot of Effective Chloride Ion Diffusivity versus Water:Cement Ratio for Various Studies, including Results of Present Work.

It is clear from figure 5.4.1 that the effective diffusivities measured with respect to water:cement ratios are in good agreement with previously published results. It is of interest to note the magnitude of the scatter of the diffusivities measured as a part of this study and by others, which is often up to 25% of the mean value at any given water:cement ratio. This may indicate that there are variations in the pore structures of the samples used in the various studies. These variations may be due to the different maturities or different curing regimes of the samples. It may, however, be indicative of the effect of using relatively thin cement paste disk samples. Samples of thickness less than 10 mm may be affected by the presence of small entrapped air voids. Presenting the parameters of the cement in terms of the lithologic factor or some other parameter which accounts for the porosity and other aspects of the pore distribution of the cement could reduce the effect of these local variations. Also, the use of samples of relatively large thickness (>10 mm) could minimize the effect of any local variations in the cement paste. The sides of these larger samples should be sealed with a chloride ion and water impermeable barrier to prevent evaporation and chloride loss from the sides of the sample not in contact with either cell fluid. This type of large sample is commonly used in the AASHTO test method for determination of rapid chloride ion permeability of concrete, where the cylindrical samples of the concrete under study

are 100 mm in length. This length is thought to be sufficient to reduce the effect of local variation in aggregate content, and therefore addresses the same type of problem as is faced with local variation of void content.

A similar plot has been constructed to compare the reduction of the effective chloride ion diffusivity by PSMC additions with the reduction in effective chloride ion diffusivity achieved with other common pozzolan materials, using data from a number of researchers [15,17,24,26]. This plot is presented as Figure 5.4.2.

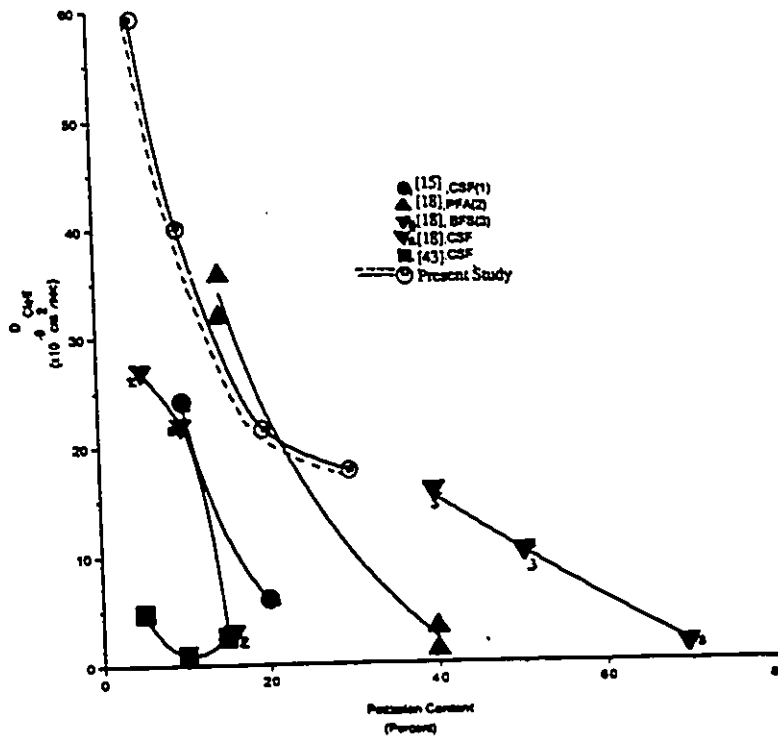


Figure 5.4.2 : Plot of Effective Chloride Ion Diffusivity versus Pozzolan Content for Various Studies Including Results of Present Work.

It is clear from Figure 5.4.2 that PSMC is as effective as other pozzolans in reducing the effective chloride ion diffusivity in cement paste above the 10 % level of replacement. Below the 10 % level of replacement, however, PSMC is not as effective as other pozzolans in reducing chloride ion diffusion in cement paste.

6.0 CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The main conclusions of the present study are as follows:

1.) The concentration of chloride ion in cell 1 of the diffusion cell, within the limits examined in this study, have no significant effect on the measured diffusivity of the chloride ion. There is an observed decrease in the effective chloride ion diffusivity in hardened cement paste with an increase in the sample thickness. As the thickness of the sample is increased by one millimeter, there is a decrease in the diffusivity of approximately 6 %.

2.) The diffusivity of chloride ion in cement paste is a function of the water:cement ratio of the cement mix. An increase in the water:cement ratio causes an increase in the effective chloride ion diffusivity.

3.) The effective diffusivity of chloride ion through cracks in the cement paste samples is many times greater than that through uncracked paste.

4.) The time lag in recording a chloride ion concentration in cell 2, observed by other researchers utilizing similar equipment

to that used in this study may be due to the lack of stirring in either of the cells of the diffusion cell and the resultant concentration gradients that exist in these cells.

5.) Pyrolysed sheet moulding compound utilized as an additive to cement in ordinary cement pastes is effective in reducing the effective diffusivity of chloride ion in concrete and that an increase in PSMC content causes a decrease in the measured effective chloride diffusivity. It is not clear whether this is due to a possible pozzolanic reaction which is taking place, or due to the presence of mineral fines, or both.

6.) The lithologic factor is useful in describing the nature of the pore structure of cement pastes, and it forms a good basis for comparing the effective diffusivities of hardened cementitious pastes of different cement compositions.

7.) An increase in the chloride ion concentration in cell 1 can be used to reduce the time required to make chloride ion diffusivity measurements with the apparatus used in this study.

6.2 Recommendations for Future Work

Based on the present findings, a number of new research areas have been identified. These include:

1.) That the E-Glass be separated from the inert components of the PSMC and utilized separately in finely divided form to eliminate the variance in fines content of the cement pastes under study, and to enable low water:cement ratio cementitious pastes with high PSMC contents to be investigated.

Cement pastes with 10, 20, 30, and 40 percent of the portland cement replaced with PSMC should be studied. Samples should be fabricated both with and without the use of superplasticizers. The study should include determination of the total porosity of the resulting pastes so that the lithologic factor can be calculated. Further, the effective chloride ion diffusivity should be determined in cement pastes of similar composition but using other pozzolans. This would allow comparison of both of these pozzolans based upon their lithologic factors.

2.) That the effective diffusivity of chloride through cementitious paste be related to the effective diffusivity of chloride ion in structural concrete, and that both be related to the Rapid Chloride Permeability test now extensively used in industry. Samples of concretes and cement pastes with similar cement compositions would have their effective chloride ion diffusivities measured, and comparisons between the effective diffusivity in cement paste and concrete can be made. Further, the rapid chloride permeability would be measured for each sample, and

the results compared with the measured effective chloride ion diffusivities.

3.) That samples of cement paste with thicknesses much greater than that studied herein be utilized to reduce the effect of small entrapped air voids on the variance of the effective diffusivities measured by diffusion cell type apparatus. The initial decrease in the effective chloride ion diffusivity with an increase in the sample thickness observed in this study should be explored further, with samples up to 100 mm in thickness.

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Appendix A

One Solution of Fick's Second Law for One-Dimensional
Diffusion

Consider a homogeneous material in the shape of a semi infinite slab as depicted in Figure A.1 below.

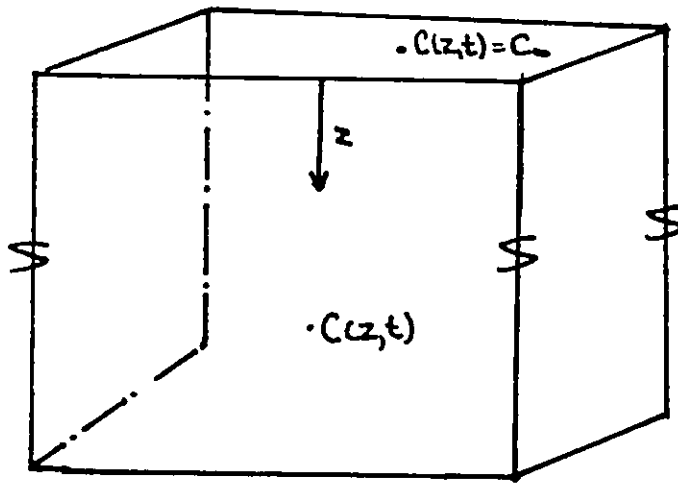


Figure A.1 : Illustration of Semi-Infinite Slab Subject to Diffusion From an Outside Source.

Assuming that the effective diffusivity, D_{eff} , is constant throughout the material, that the concentration of the diffusing species is C_0 at the surface of the material, and that the initial concentration of the diffusing species, $C(z,t)$ is zero at time zero

for all values of z greater than zero, a solution to Fick's second law of diffusion is as follows:

Fick's Law states that

$$\frac{\partial C}{\partial t} = D_{eff} \frac{\partial^2 C}{\partial z^2} \quad (1)$$

The boundary and initial conditions as outlined above are

boundary condition

$$C(0, t) = C_0 \quad (2)$$

initial conditions

$$C(z, 0) = 0 \quad z > 0, \quad (3)$$

Multiplying both sides of equation 1 by e^{-pt} and integrating with respect to t from zero to infinite (The Laplace transform)

$$\int_0^{\infty} e^{-pt} \frac{\partial C}{\partial t} dt = \int_0^{\infty} e^{-pt} D_{eff} \frac{\partial^2 C}{\partial z^2} dt \quad (4)$$

Rearrangement yields

$$\int_0^{\infty} e^{-pt} \frac{\partial C}{\partial t} dt - D_{eff} \int_0^{\infty} e^{-pt} \frac{\partial^2 C}{\partial z^2} dt = 0 \quad (5)$$

Integrating the first term one parts, and changing the order of integration and differentiation in the second term, equation (5) becomes

$$C e^{-pt} \Big|_0^{\infty} + p \int_0^{\infty} C e^{-pt} dt - D_{eff} \frac{\partial^2}{\partial z^2} \int_0^{\infty} e^{-pt} C dt = 0 \quad (6)$$

Noting that the first term is zero at the lower bound of zero due to the initial conditions and is zero at the upper bound due to the negative exponent on the exponential, and therefore this entire first term is zero. If we denote the Laplace transform of a function by placing a bar above it, then equation 6 becomes

$$p\bar{C} - D_{eff} \frac{\partial^2}{\partial x^2} \bar{C} = 0 \quad (7)$$

Transforming the boundary condition yeilds

$$C=C_0 \quad x=0 \quad (2)$$

$$\bar{C}=\int_0^{\infty} e^{-pt} C_0 dt \quad x=0 \quad (8)$$

$$\bar{C}=\frac{C_0}{p} \quad (9)$$

Thus the partial differential equation has been transformed to an ordinary differential equation. One general solution of equation 7, based on the requirement that c is finite as x approaches infinite, is

$$\bar{C}=Ae^{-\sqrt{\frac{p}{D}}x} \quad (10)$$

Based on the transformed initial condition,

$$A=\frac{C_0}{p} \quad (11)$$

and the specific solution of equation 7 is therefore

$$\bar{C} = \frac{C_0}{p} e^{-\sqrt{\frac{p}{D_{eff}}}} \quad (12)$$

Taking the inverse transform of equation 11 yields the desired solution

$$C = C_0 \left(1 - \operatorname{erf} \left(\frac{z}{2\sqrt{D_{eff}t}} \right) \right) \quad (13)$$

Appendix B
Chloride Ion Selective Electrode Calibration

Presented below are the calibration data for the chloride ion selective electrode used to measure the chloride ion concentration in water solutions during the course of the present work. The electrode is calibrated in the chloride ion concentration range 10^{-1} to 10^{-3} Moles per Litre. Included also are the time response curves for the calibration in the three test solutions (10^{-3} , 10^{-2} , and 10^{-1} Molar). This calibration data are used to generate a relationship between chloride ion concentration (expressed as pCl) and the electrode potential in mV, and to check that the electrode is in working order. This check of operation is carried out by determining the electrode response, which should be approximately 60 mV per decade.

Table B.1 : Calibration Data for Chloride Selective Electrode.

Chloride Ion Concentration (Molar)	pCl	Electrode Potential (mV)
10^{-1}	1	+50.1
10^{-2}	2	-14.3
10^{-3}	3	-71.1

In this case linear regression yields the following relation:

$$pCl = -\frac{1}{60.679} V + 1.806 \quad (B1)$$

Where V is the electrode potential in mV.

The electrode response, R , is calculated below:

$$R = \frac{(-71.7 - 50.1)}{2} \frac{mV}{decade} \quad (2)$$

$$|R| = 60.9 \frac{mV}{decade} \quad (3)$$

The magnitude of the response indicates that the cell is operating properly.

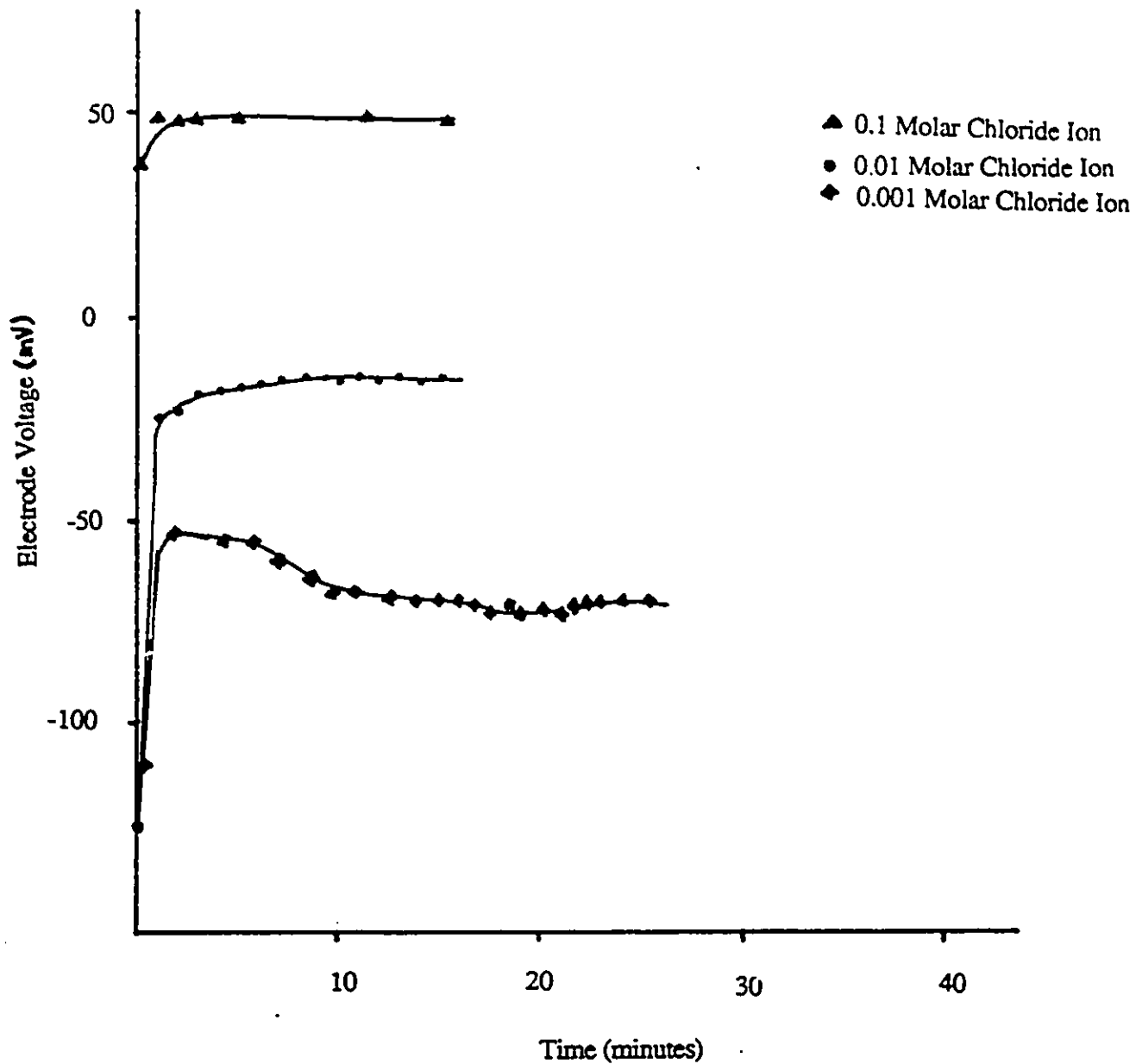
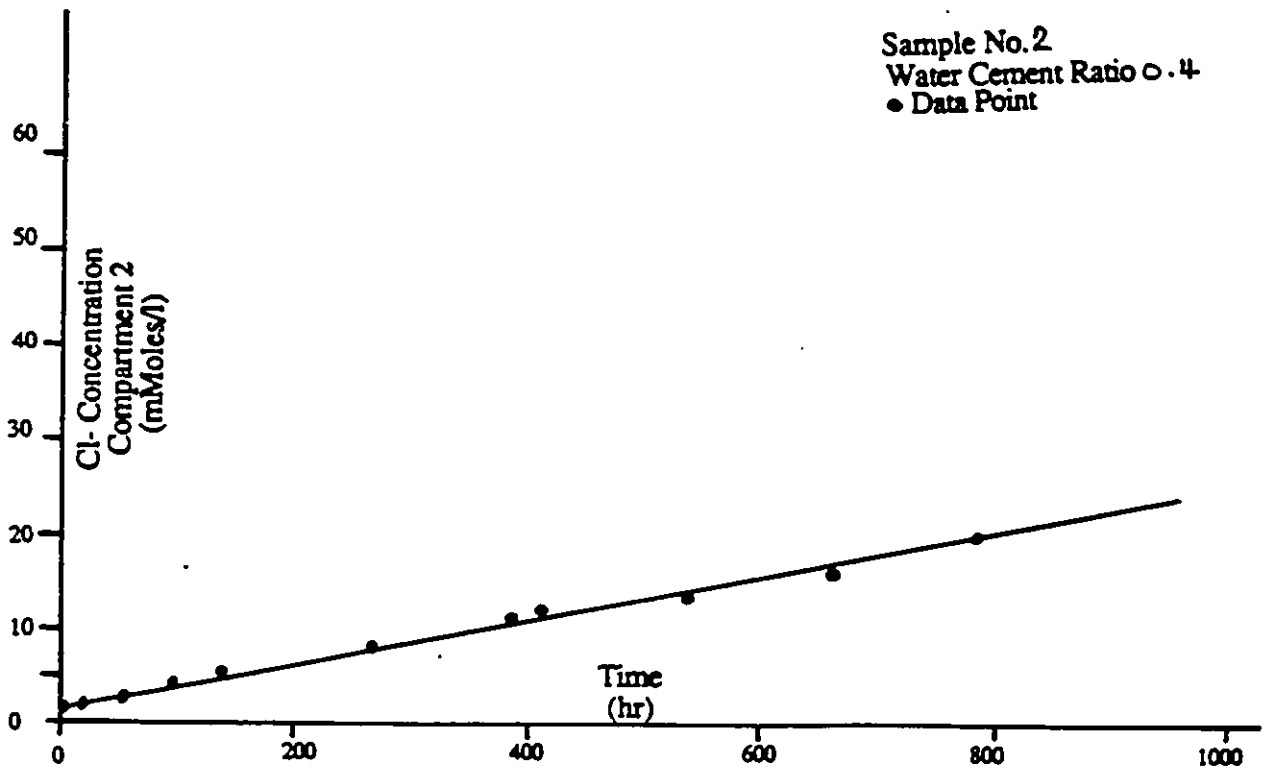
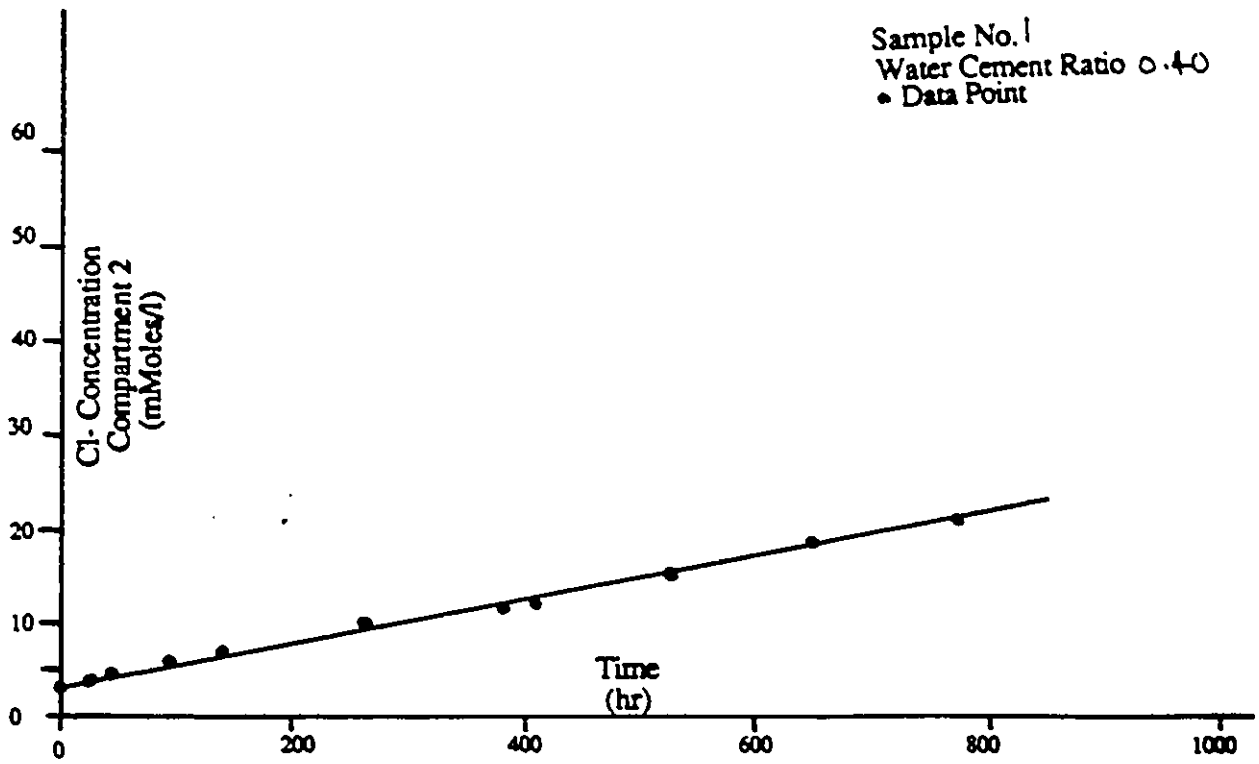
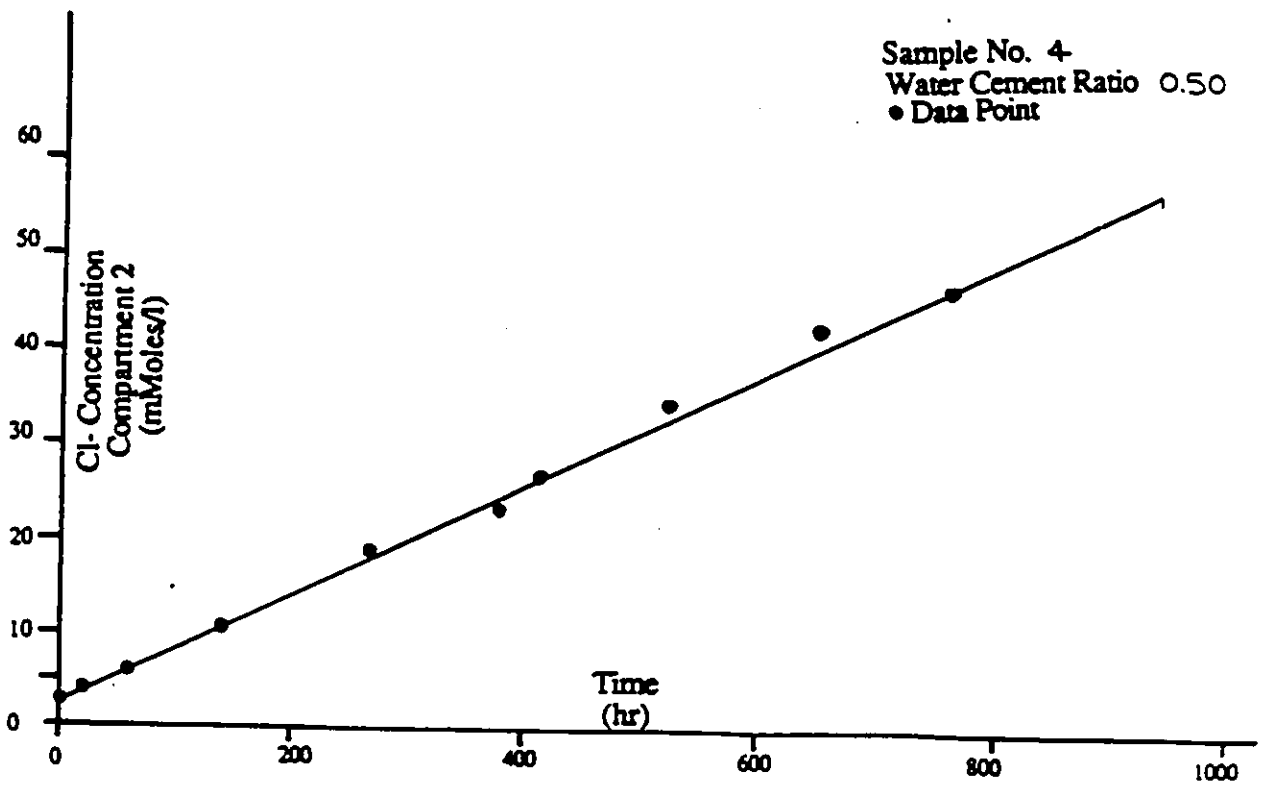
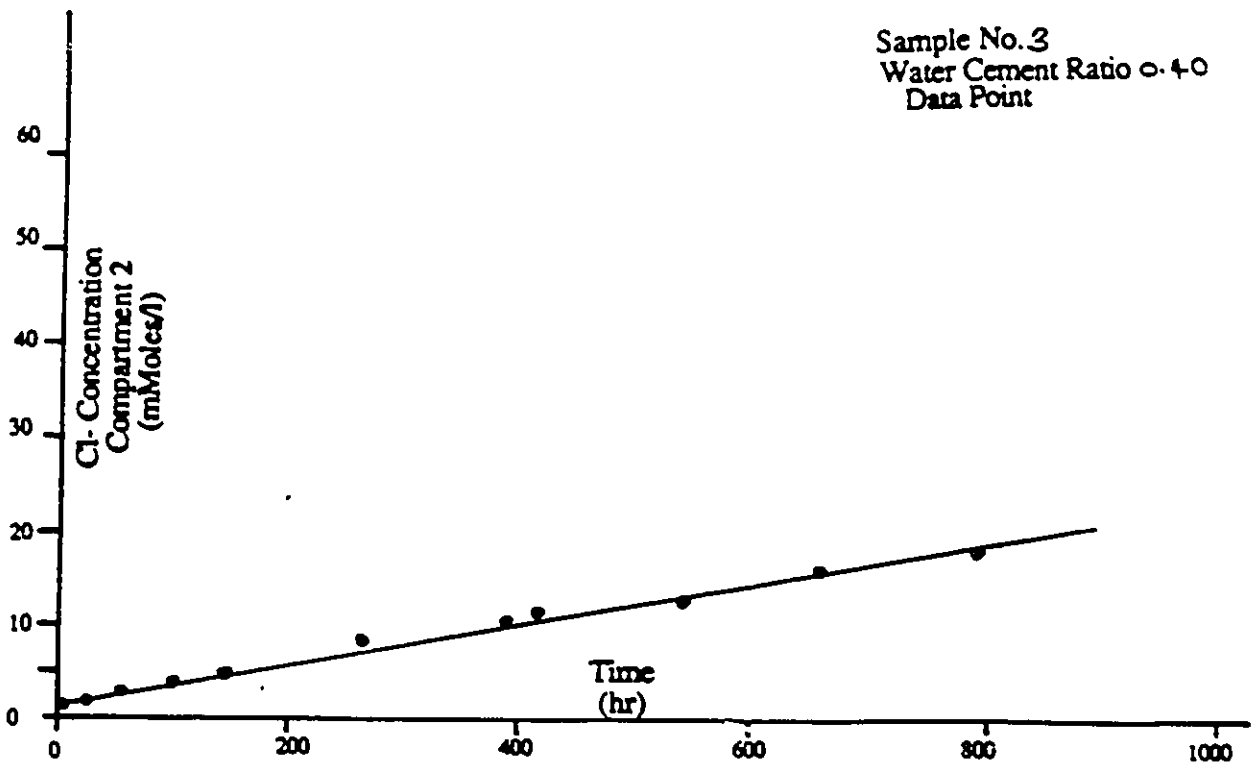


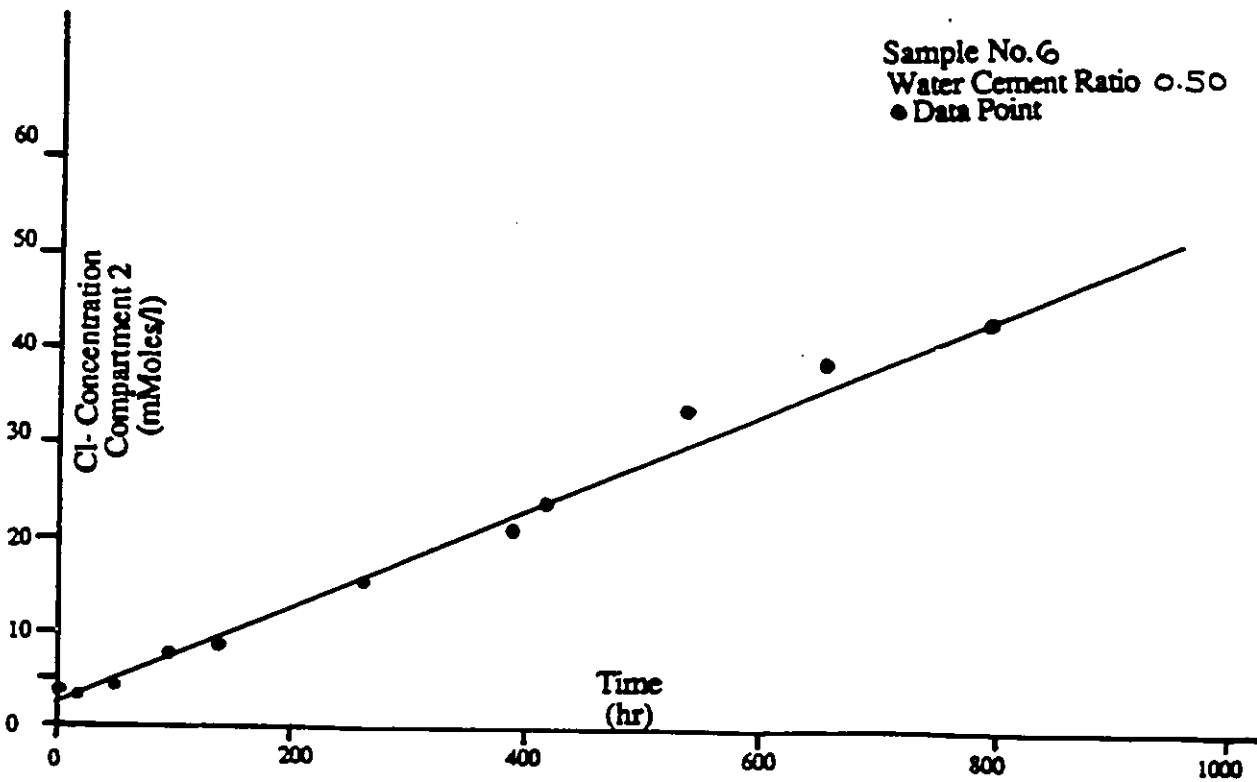
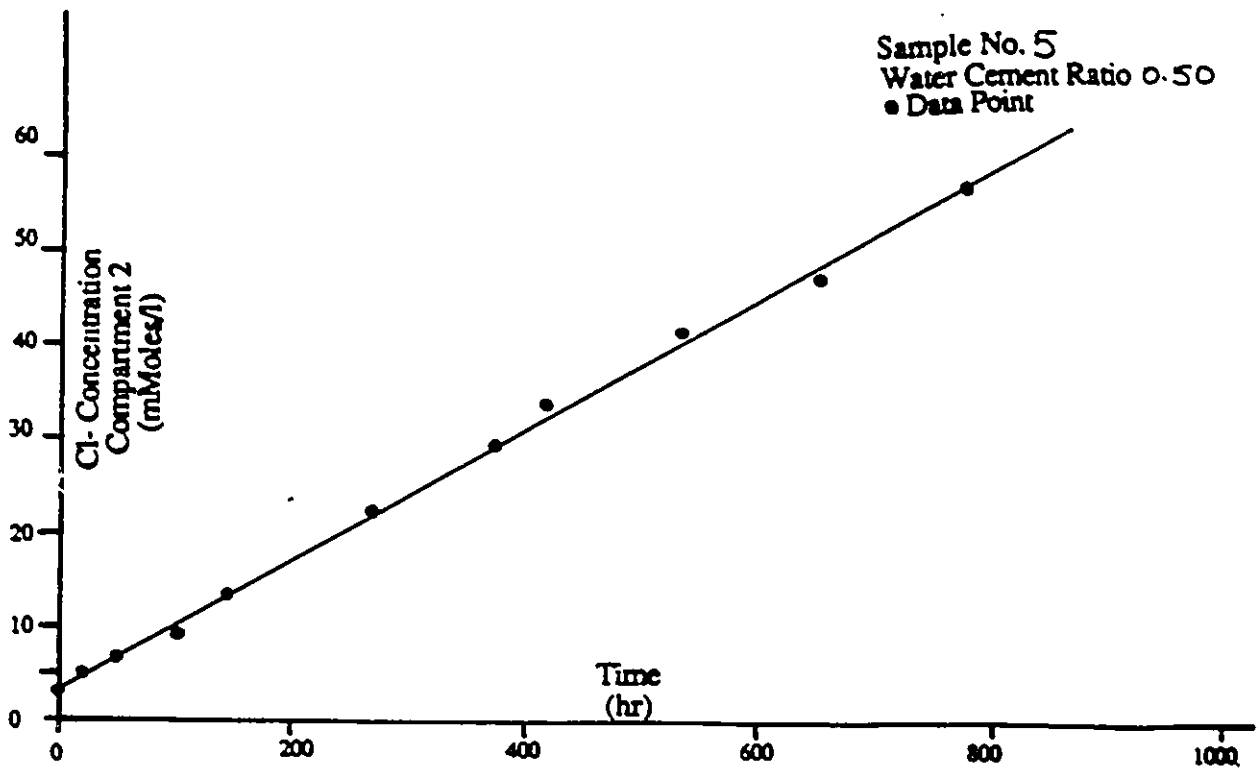
Figure B.1 : Time Response of Chloride Ion Selective Electrode For Various Chloride Ion Concentration Solutions.

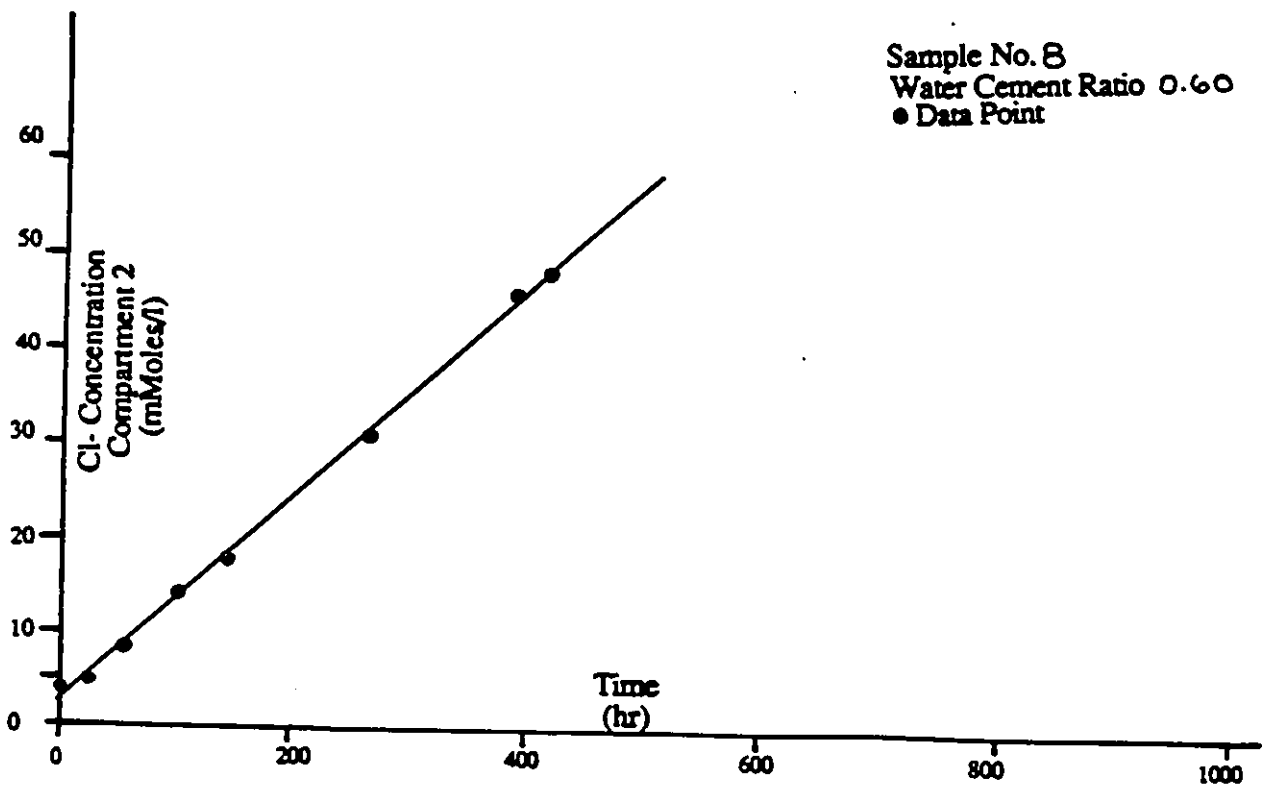
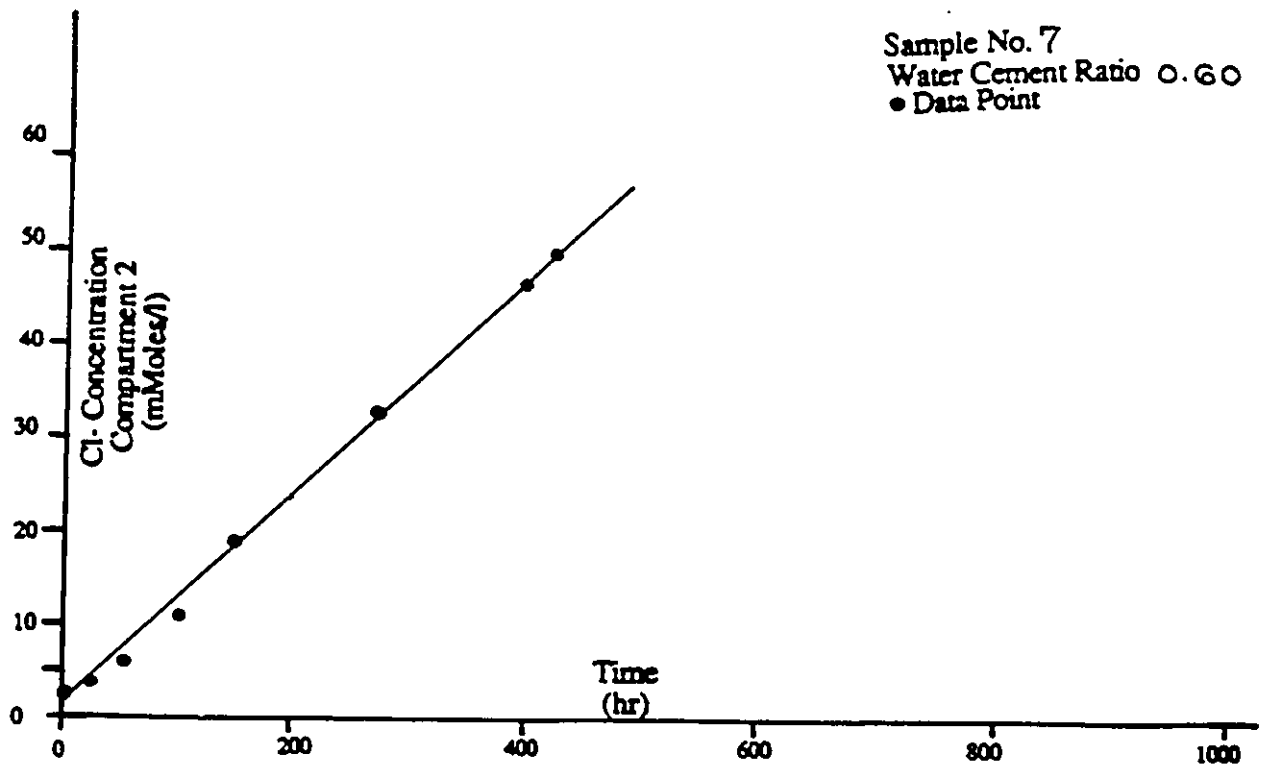
Appendix C

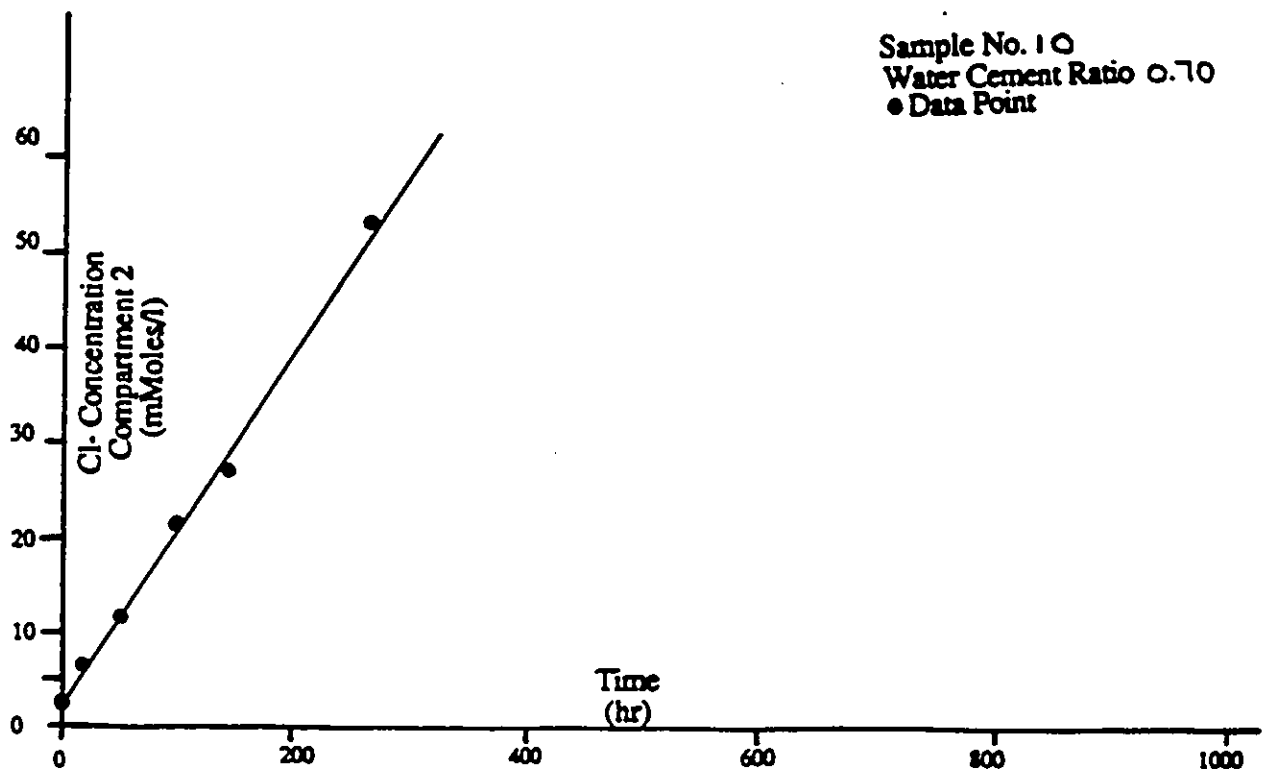
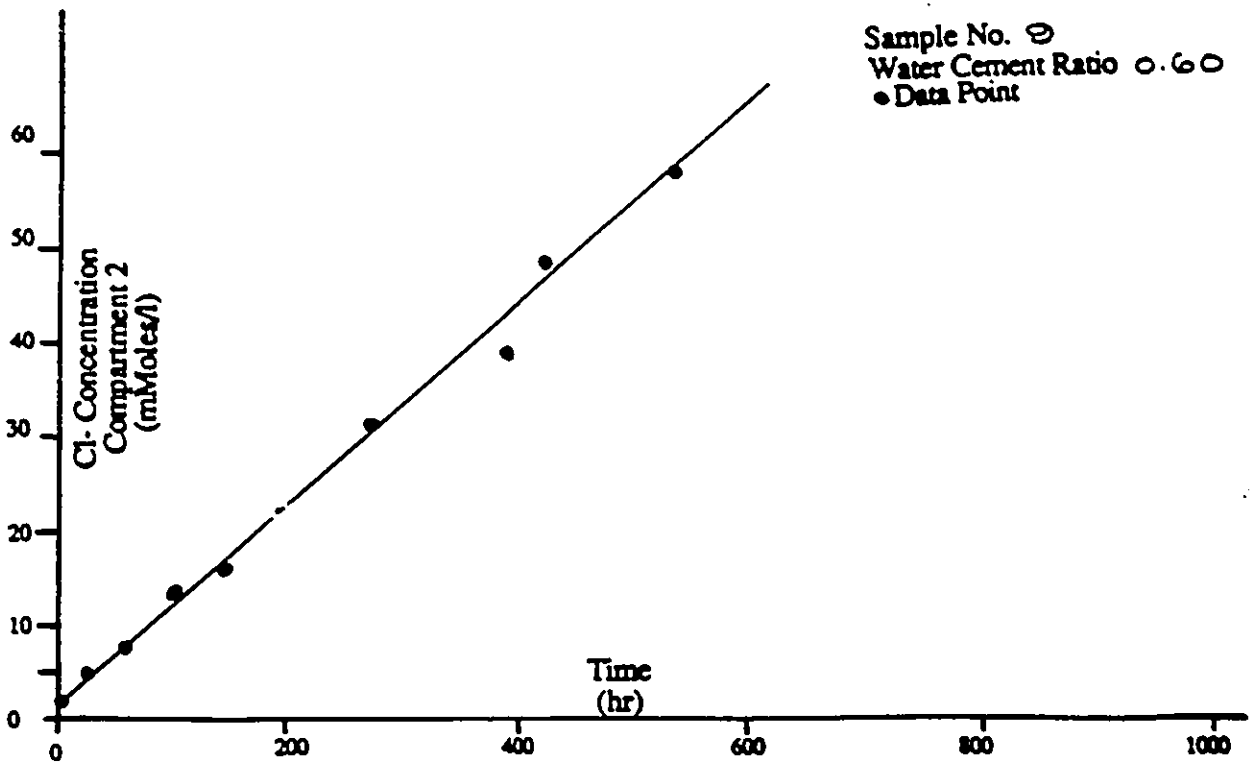
Chloride Ion Concentration in Cell 2 versus Time Plots
for Variation of Water:Cement Ratio, PSMC Content, Cell 1
Chloride Ion Concentration and Sample Thickness.



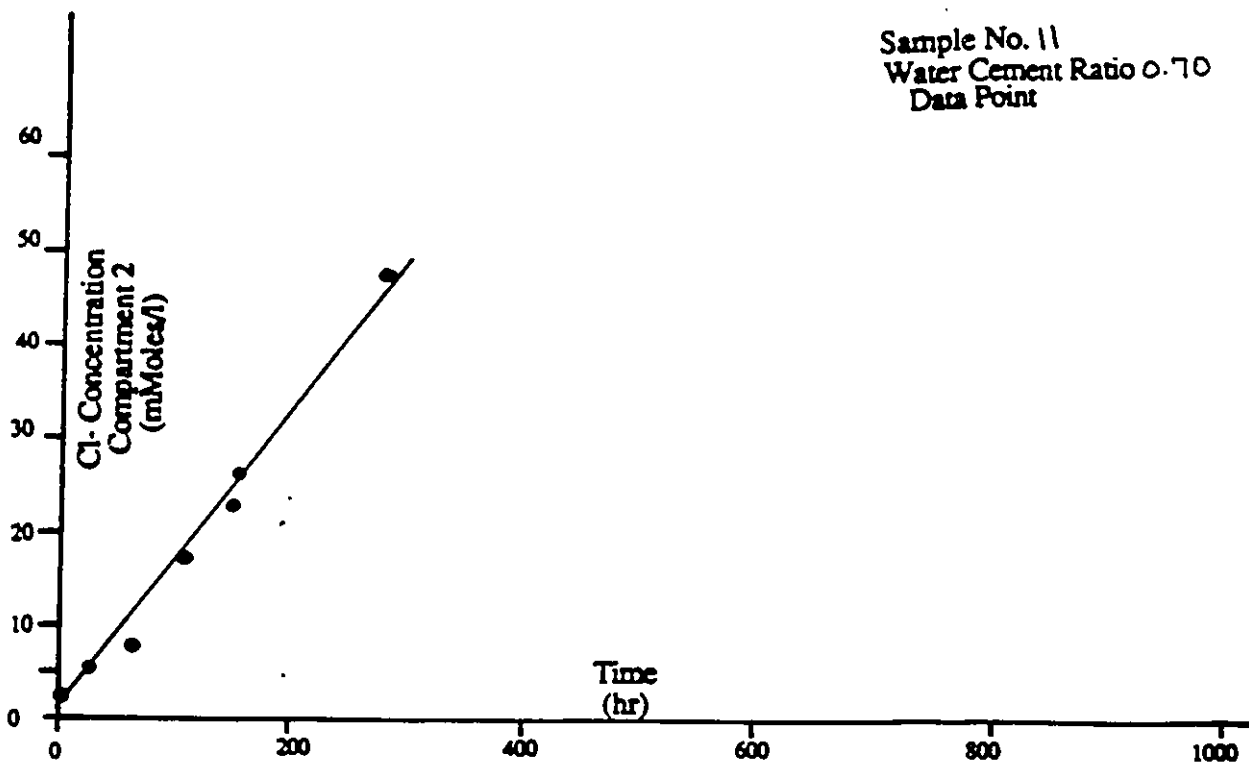




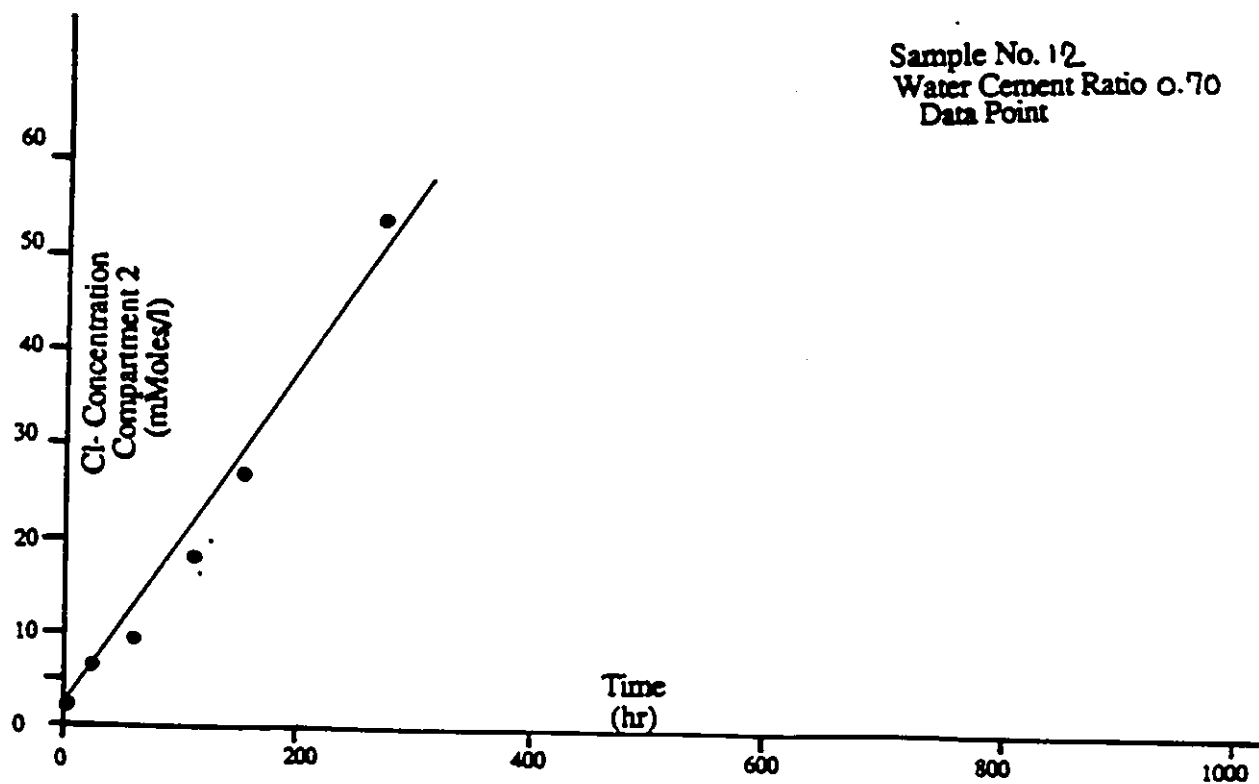


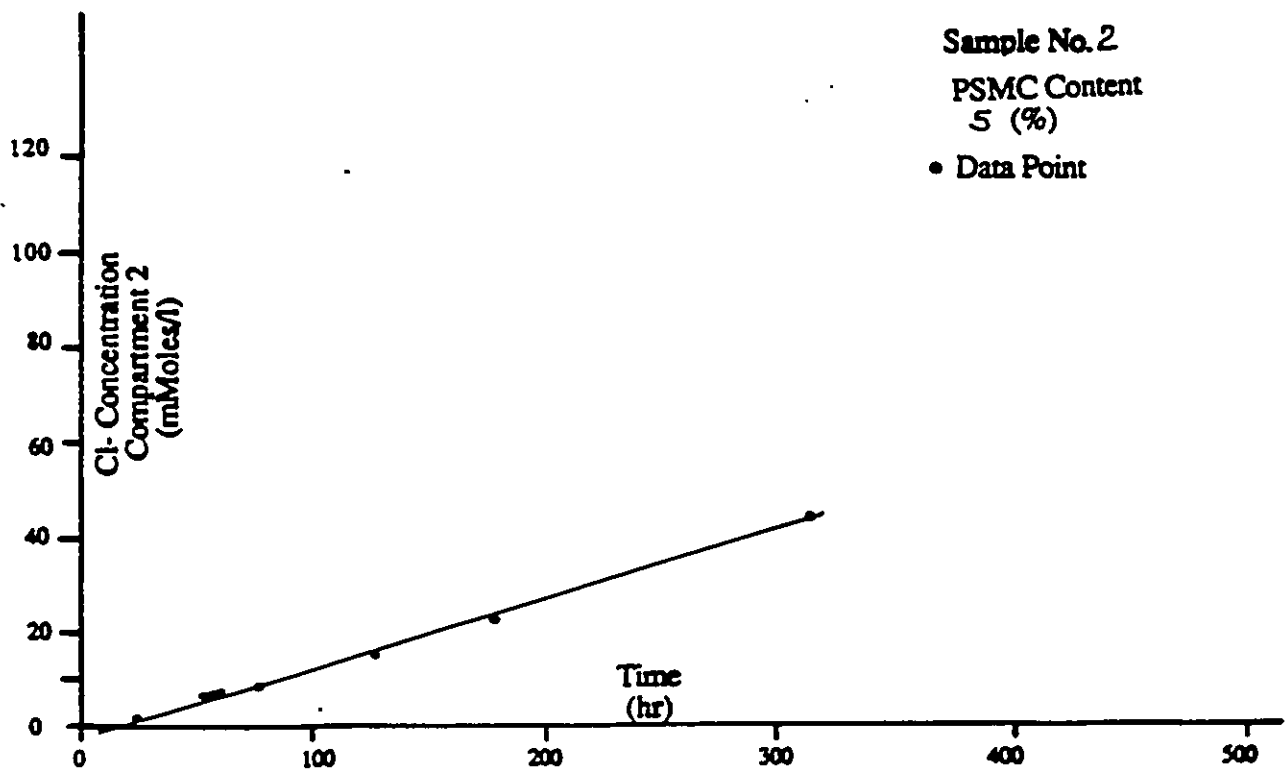
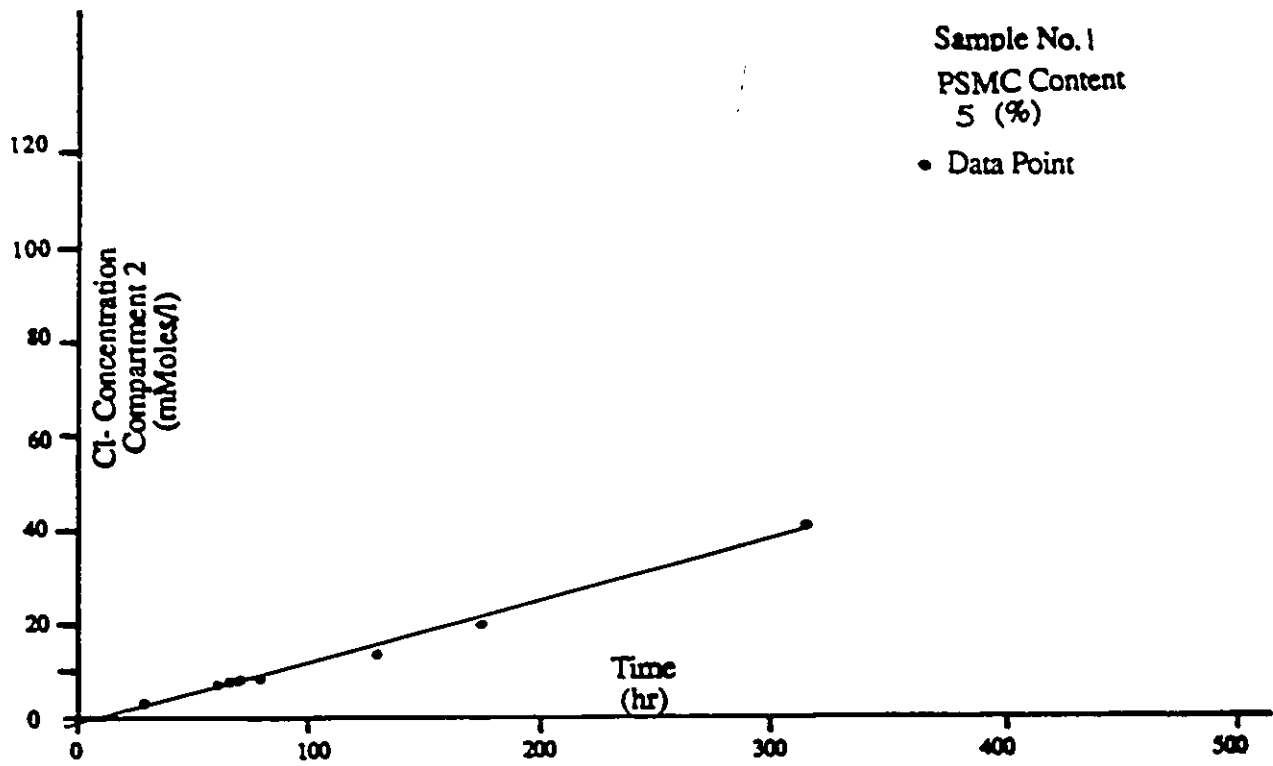


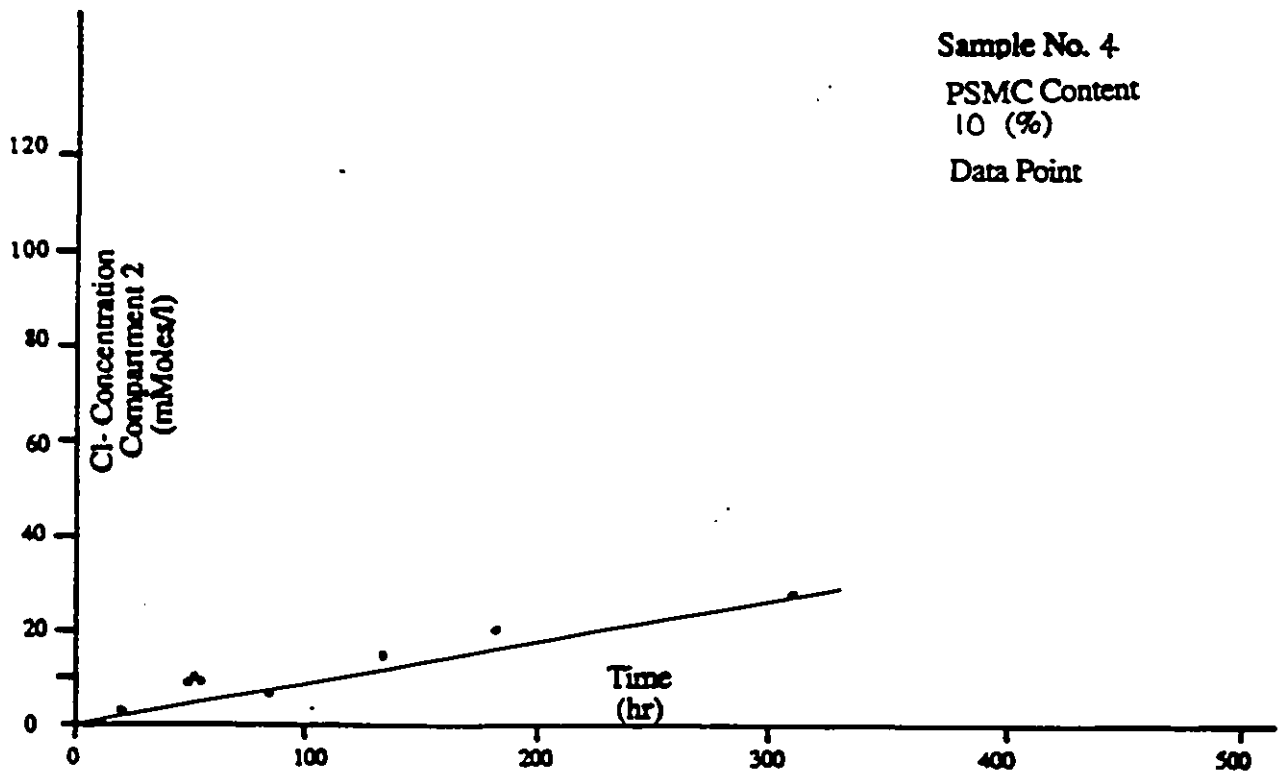
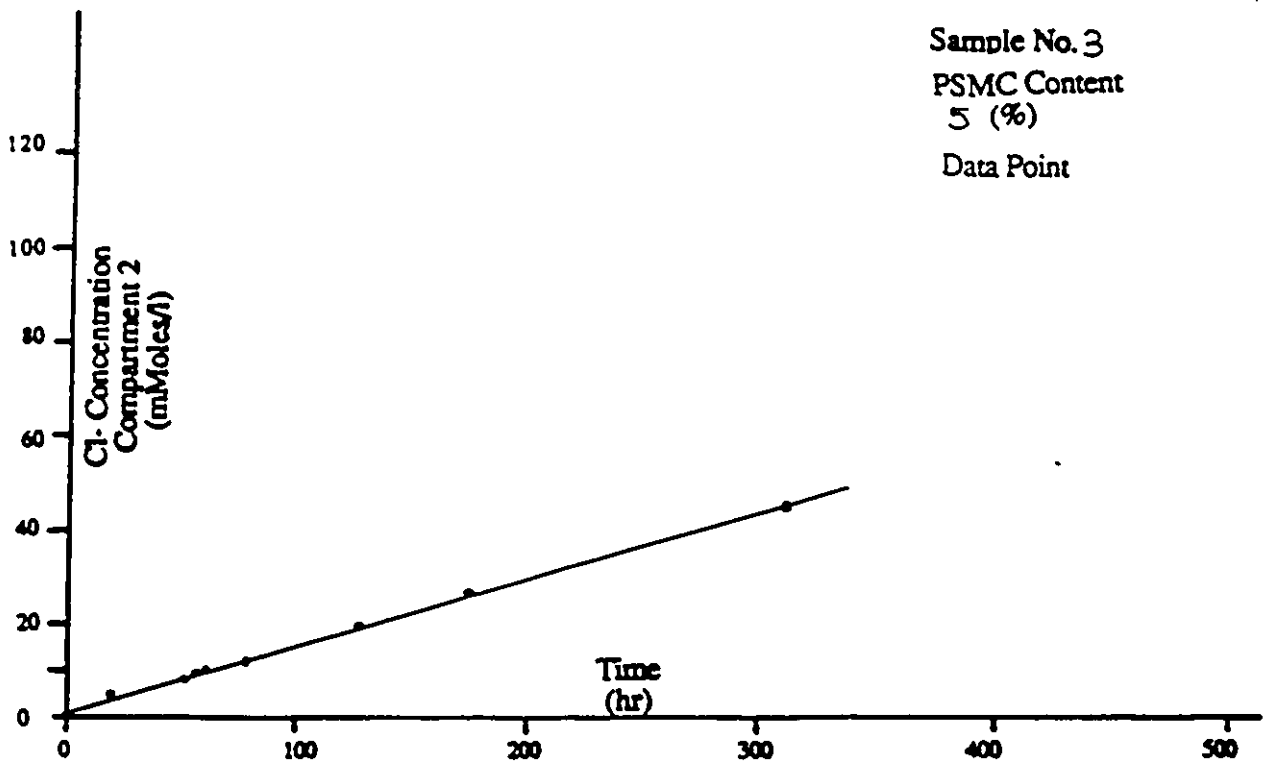
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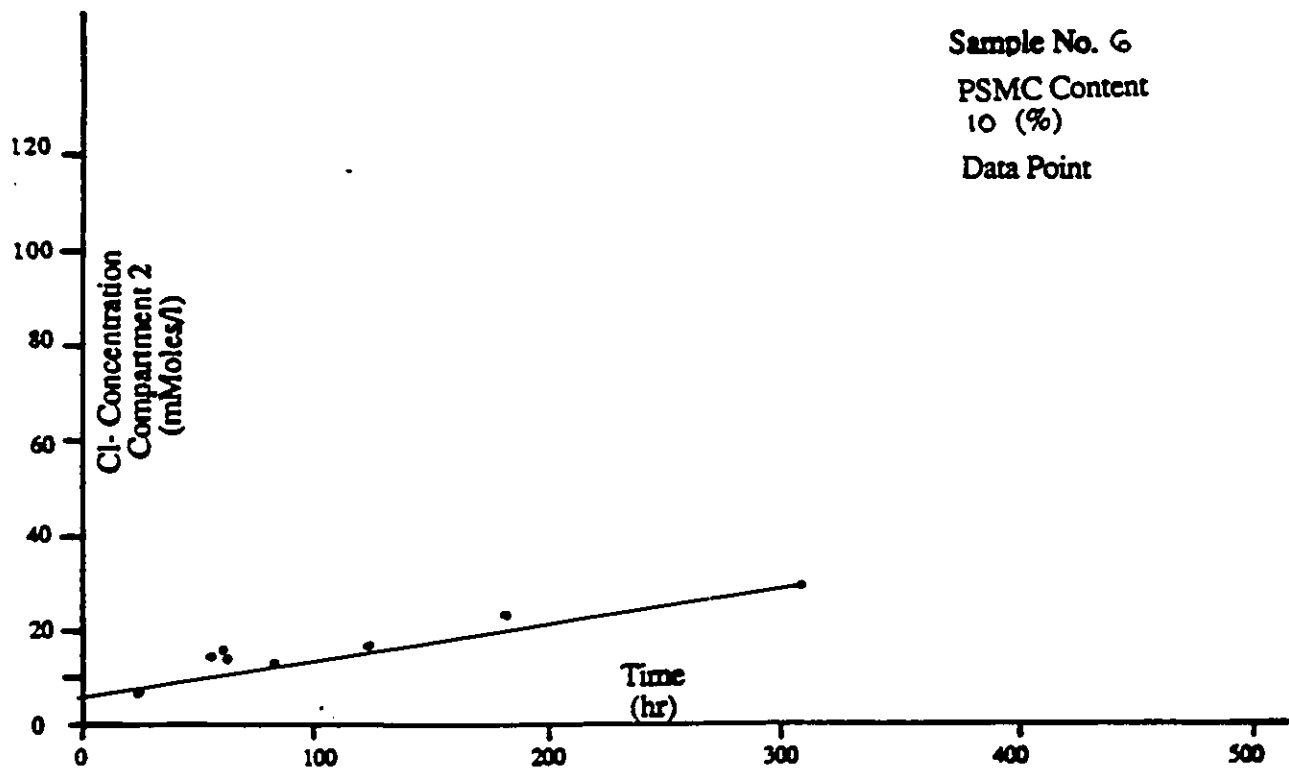
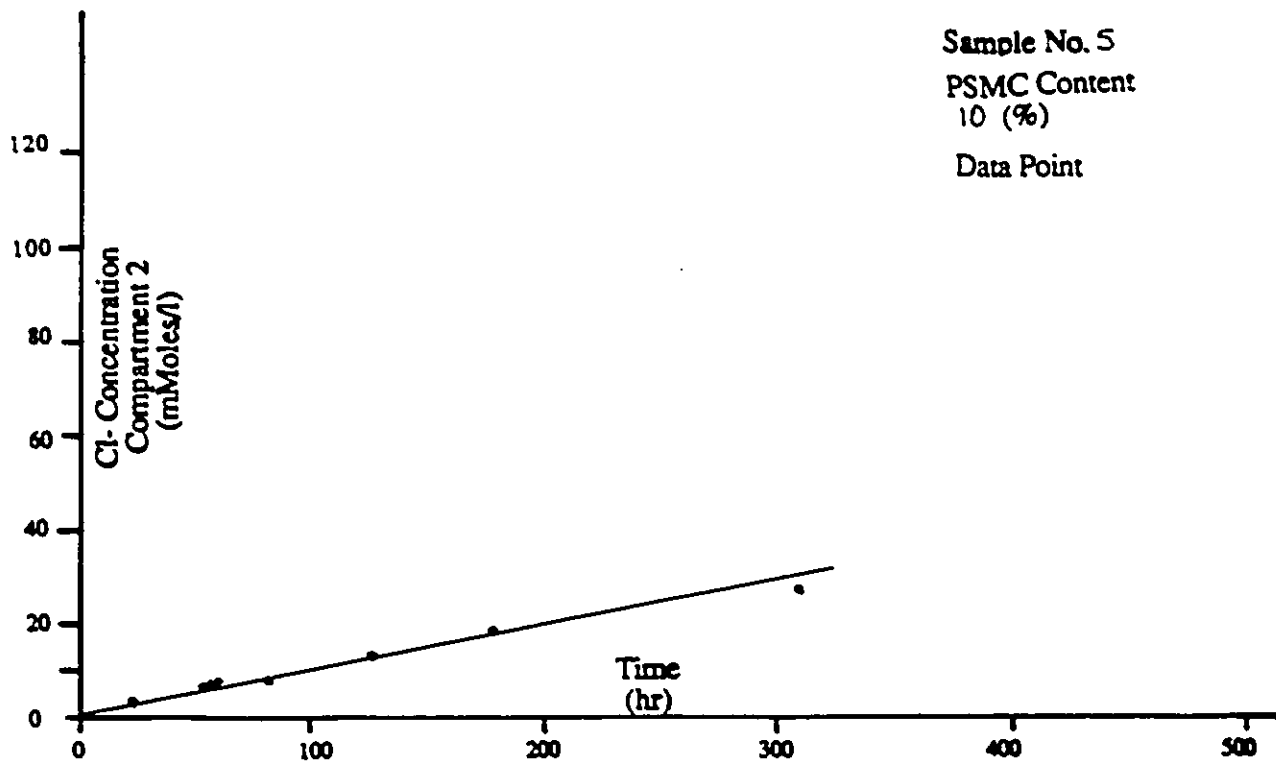


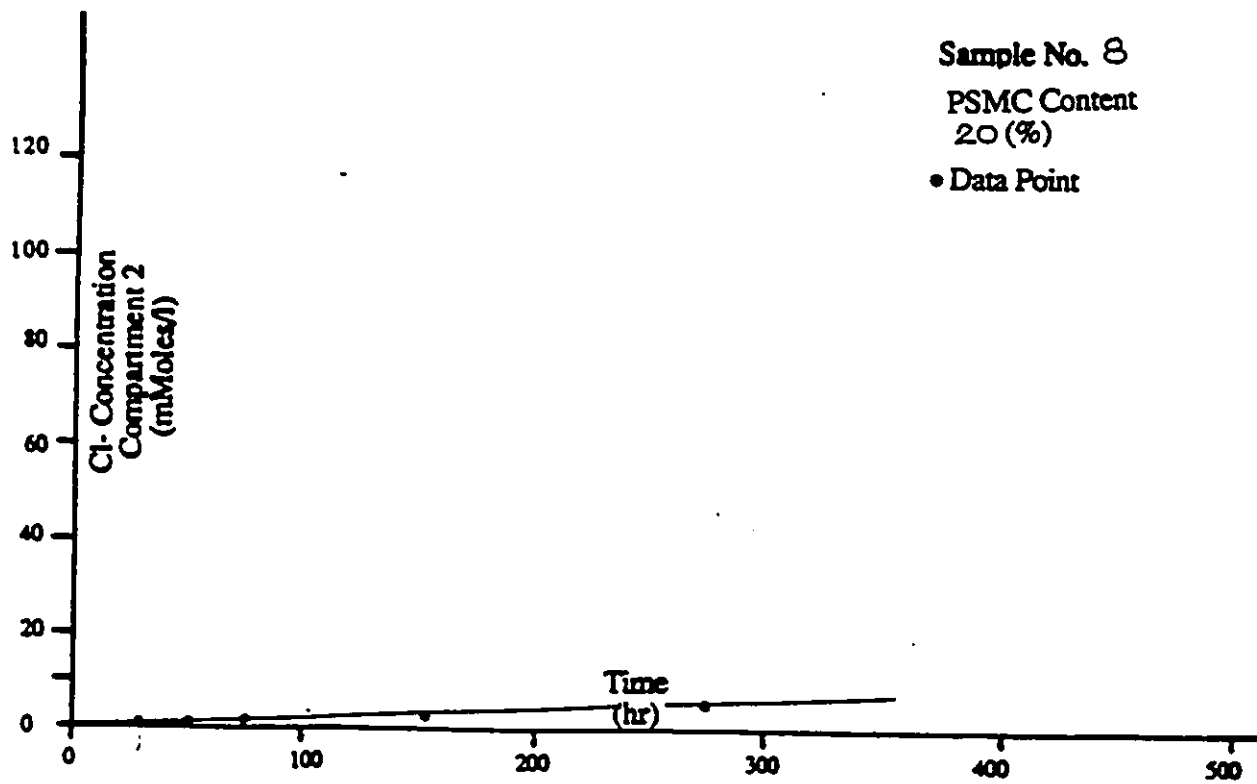
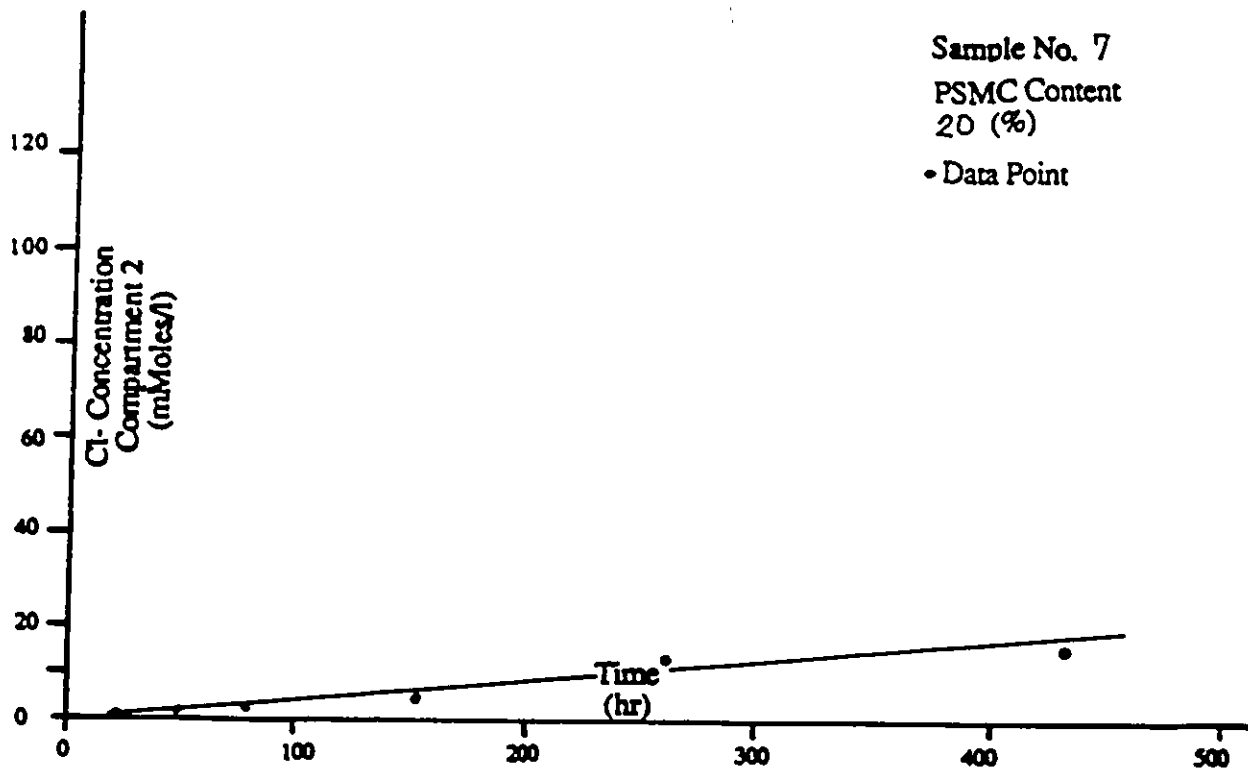
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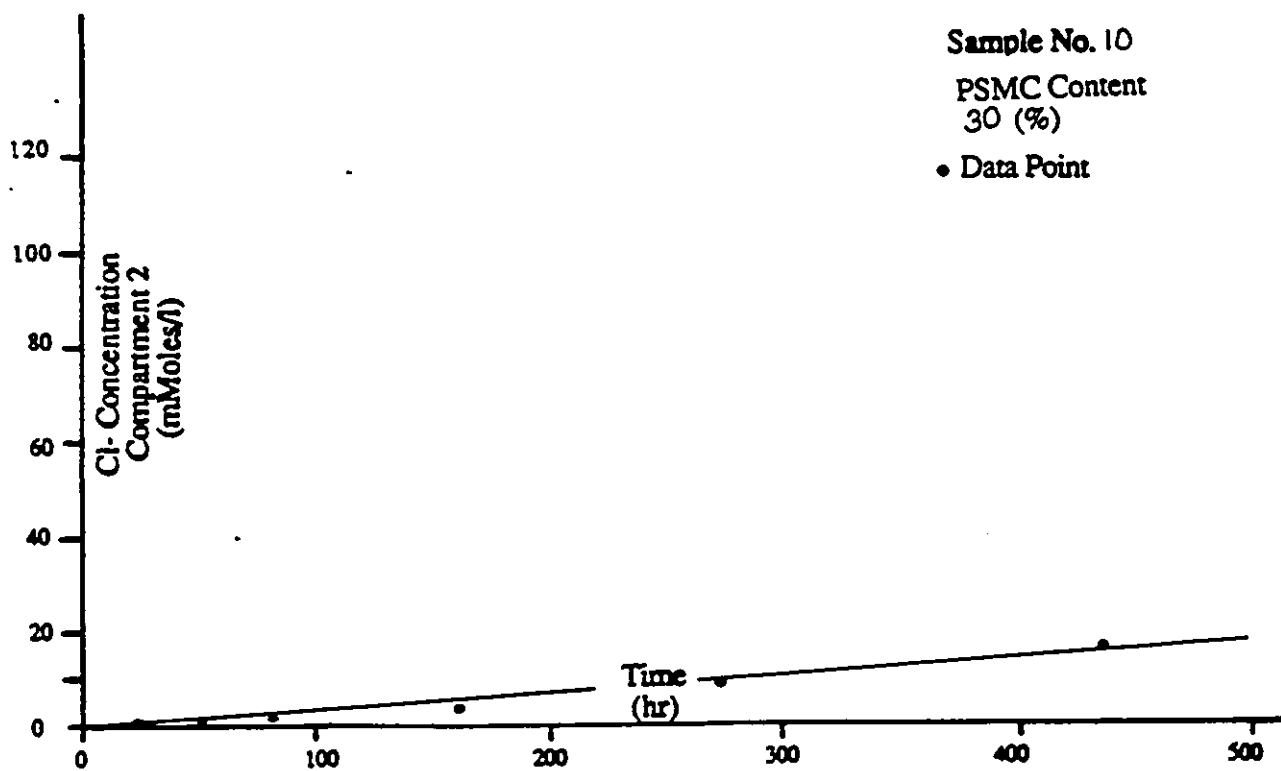
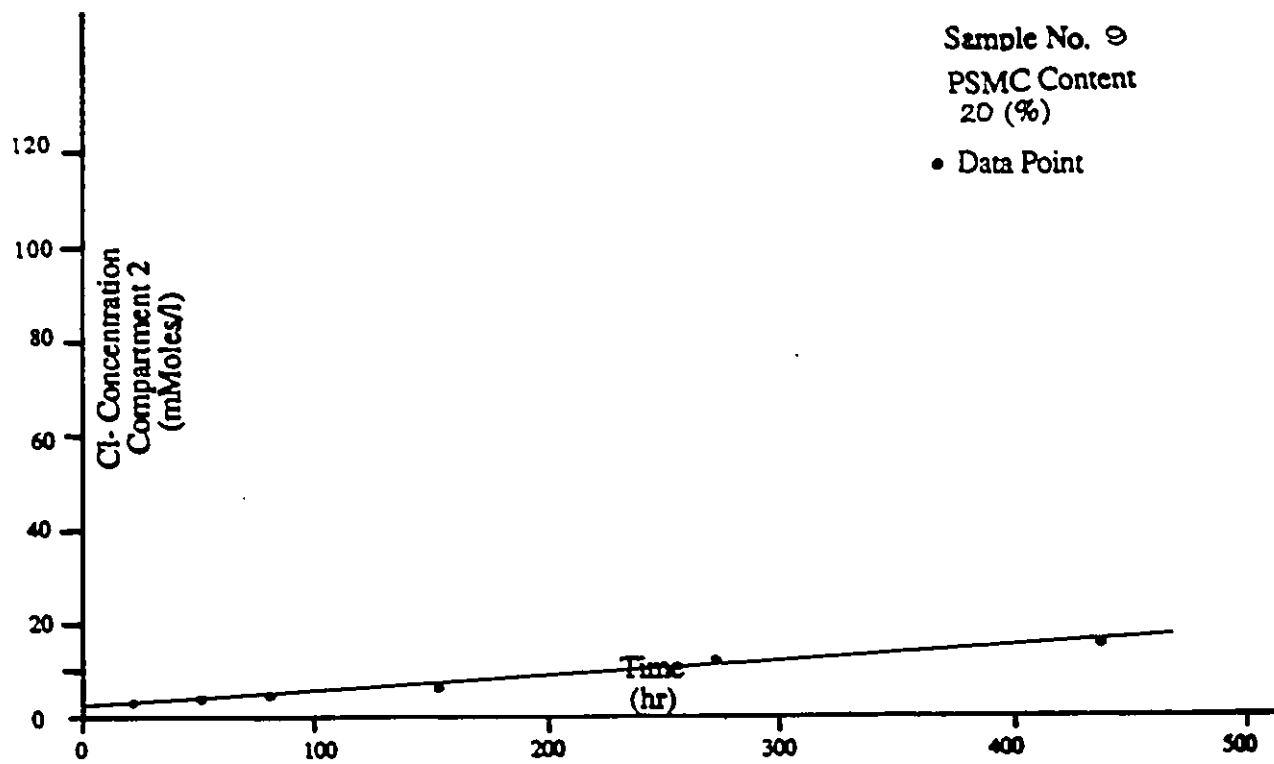


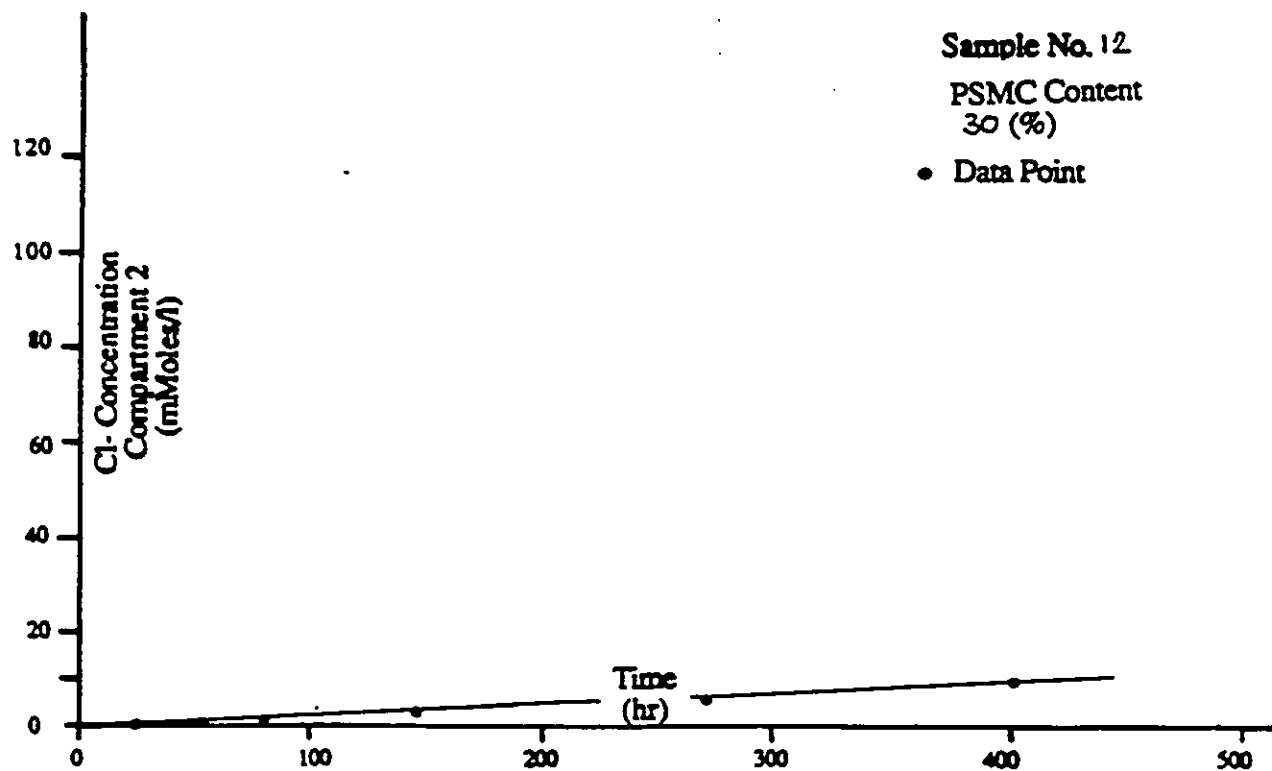
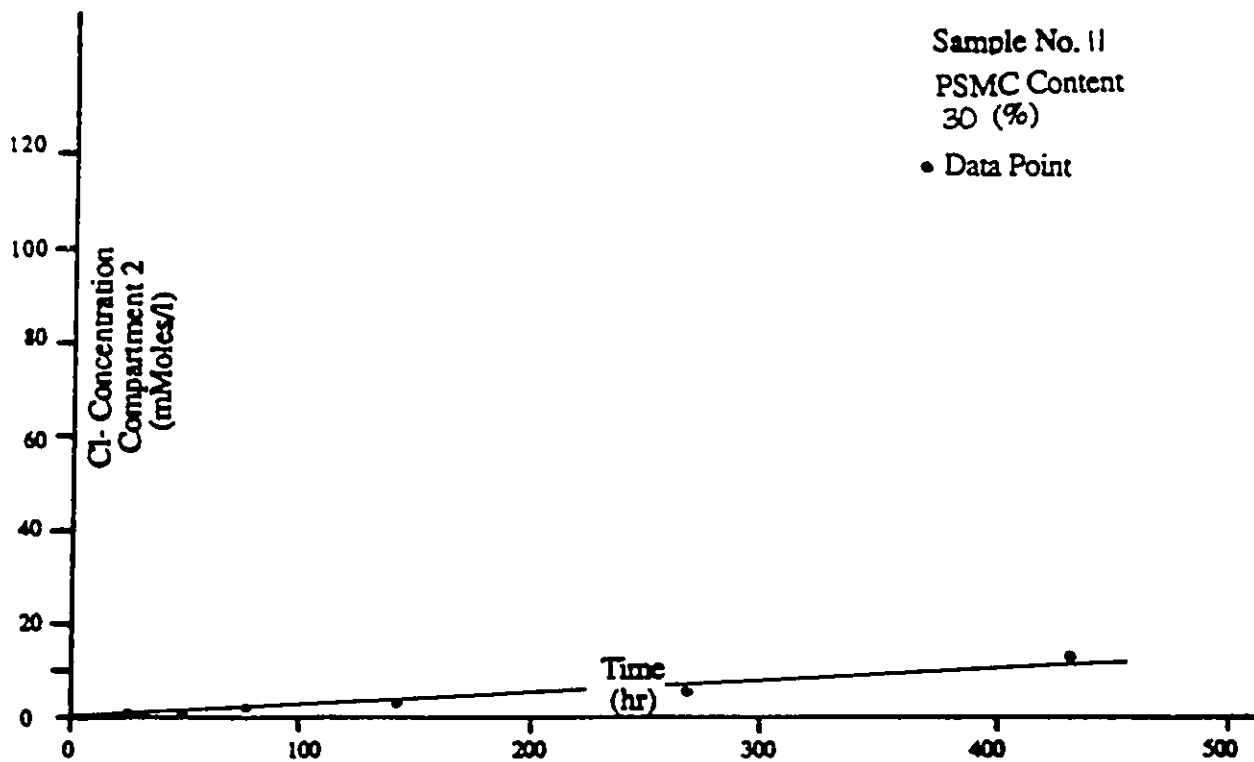


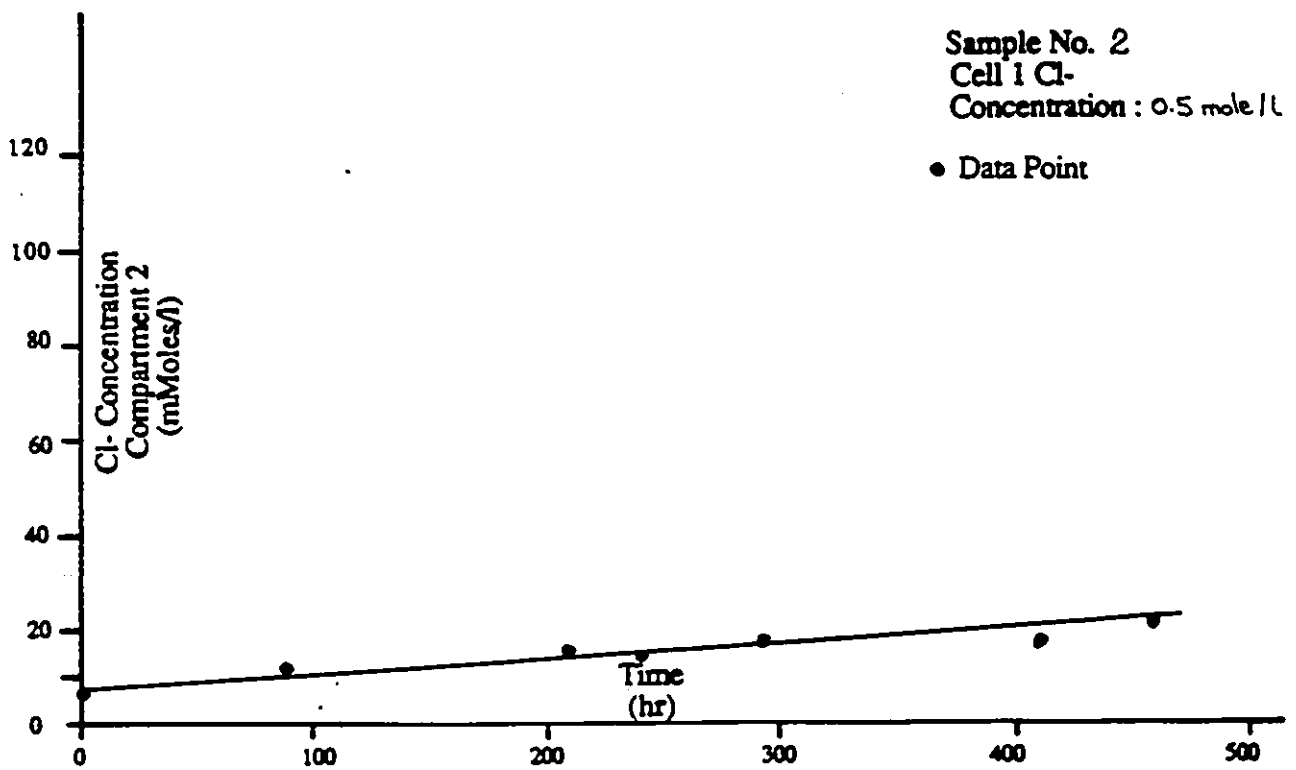
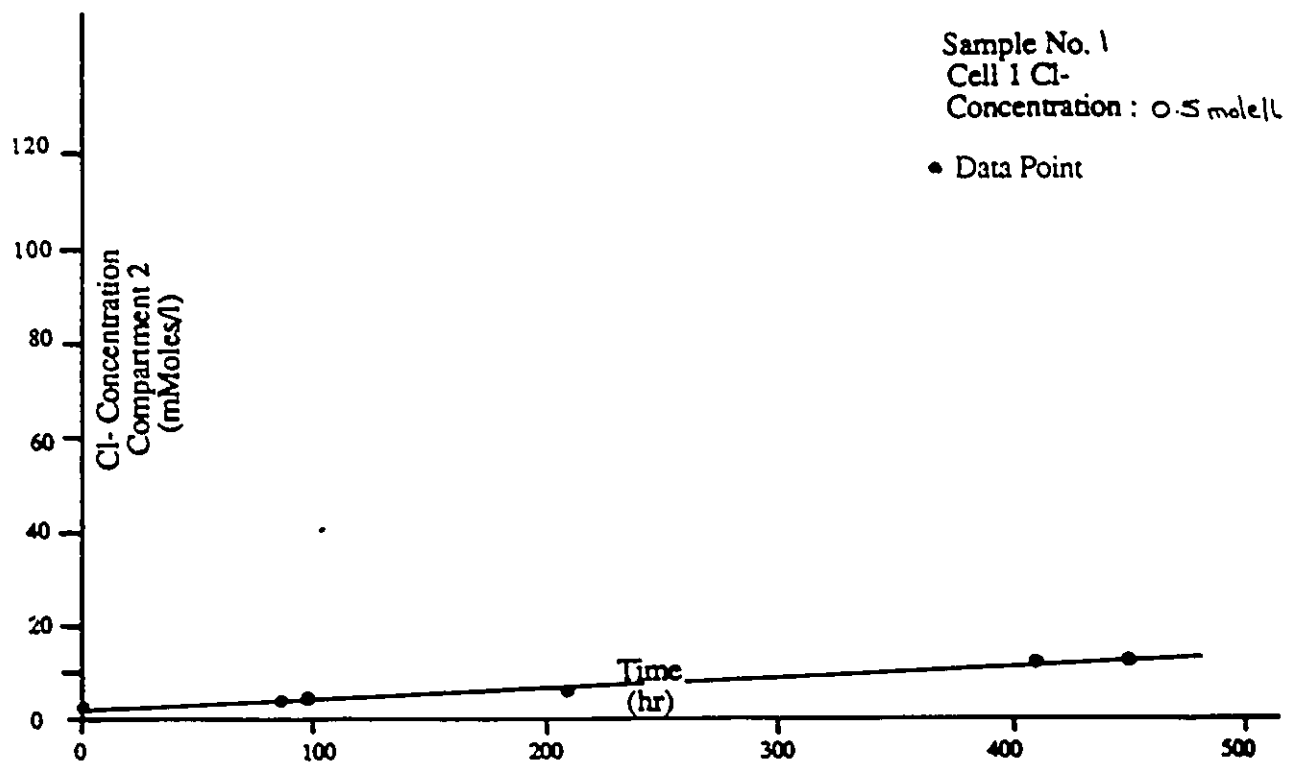


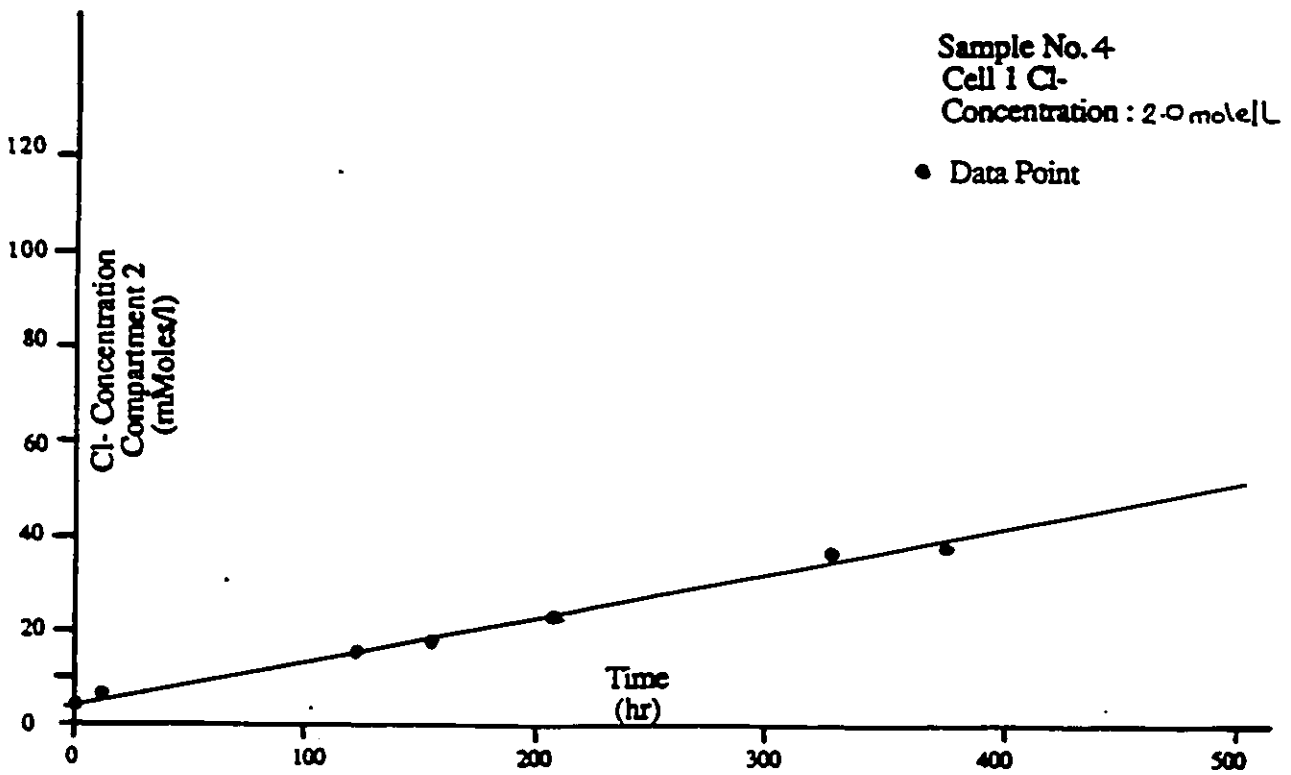
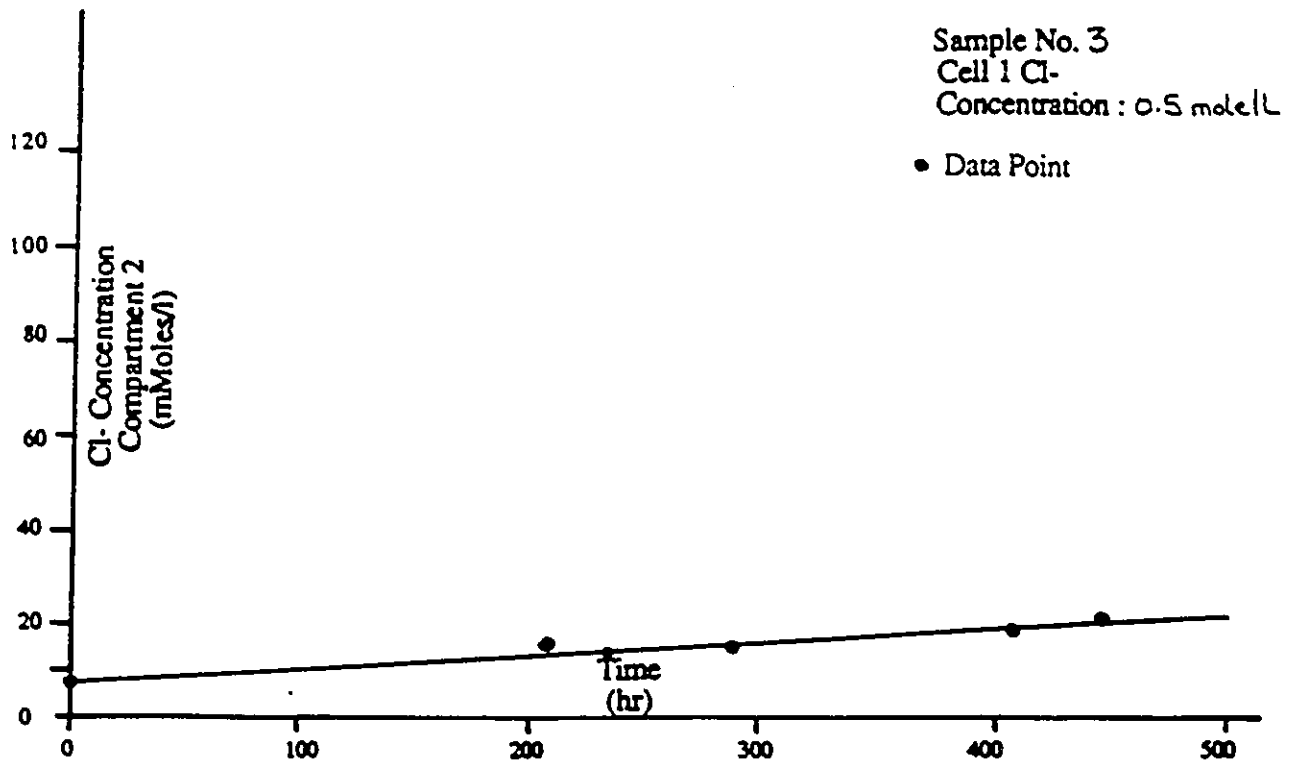


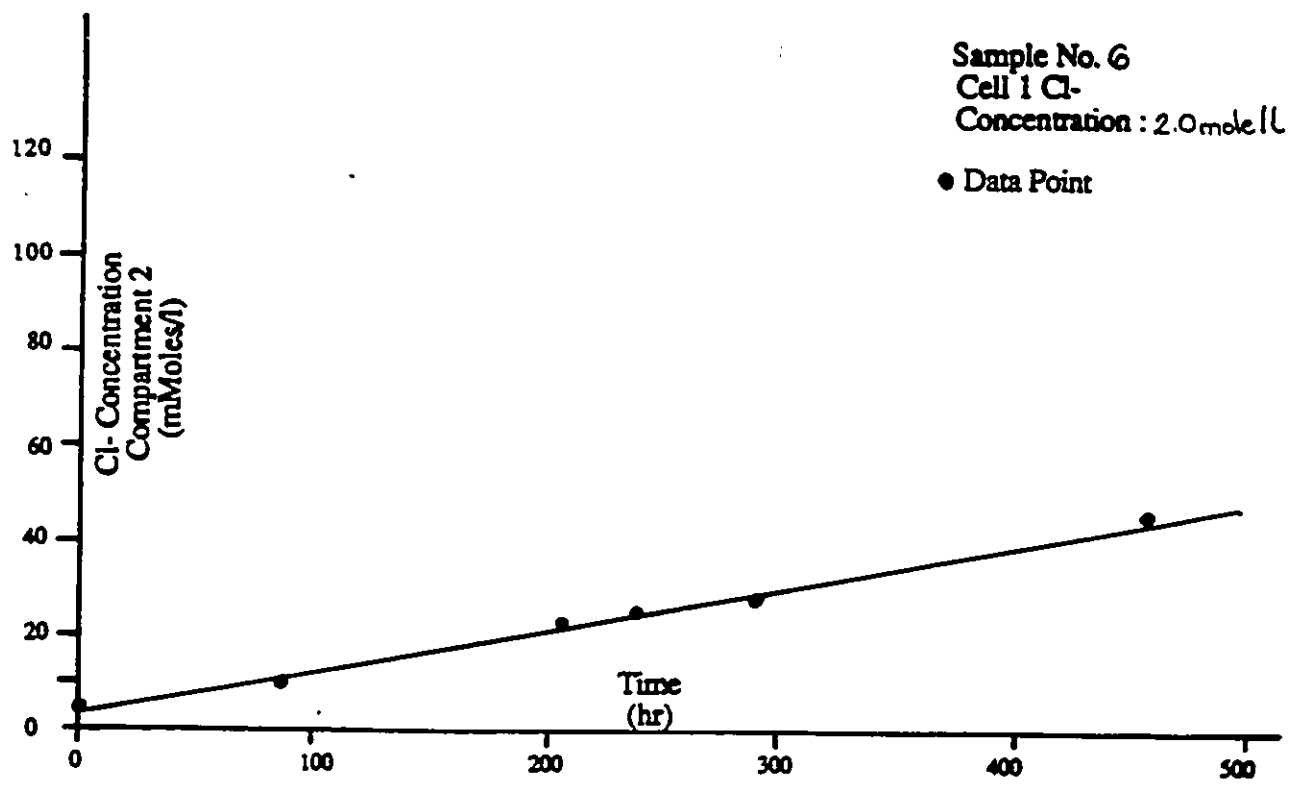
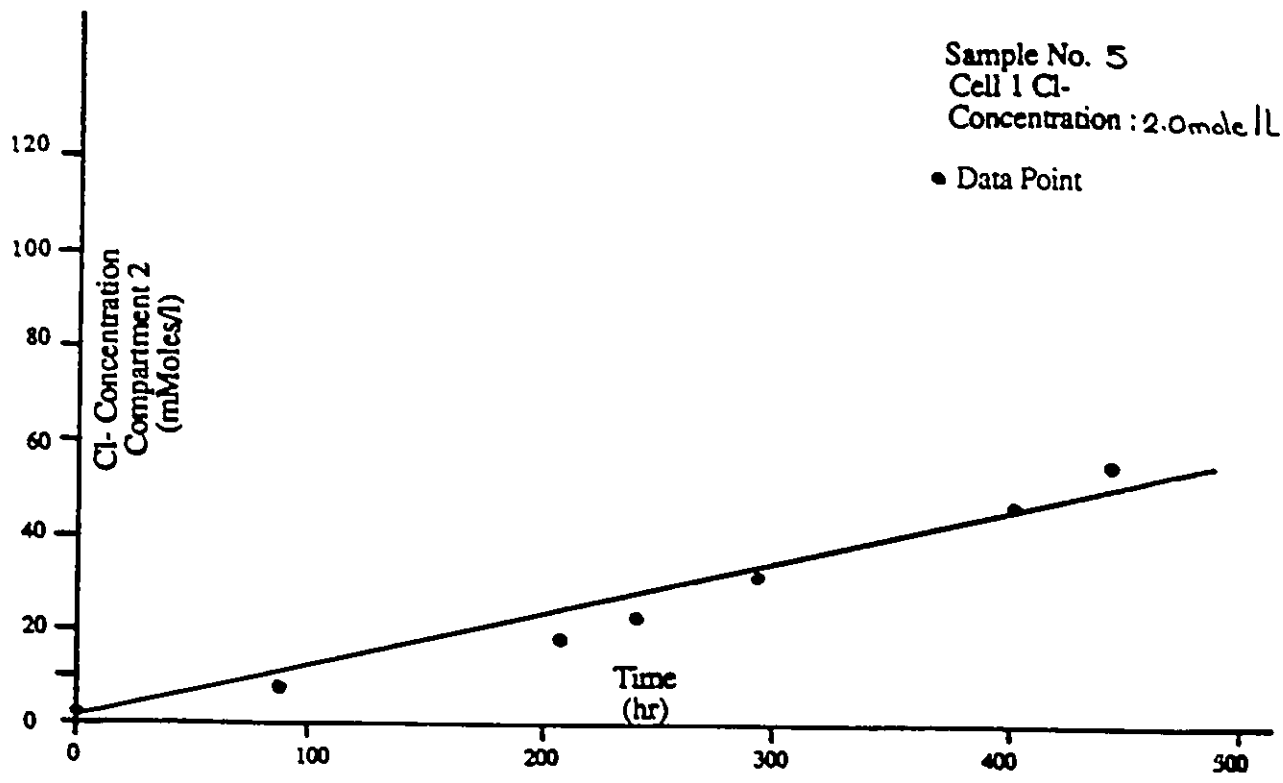


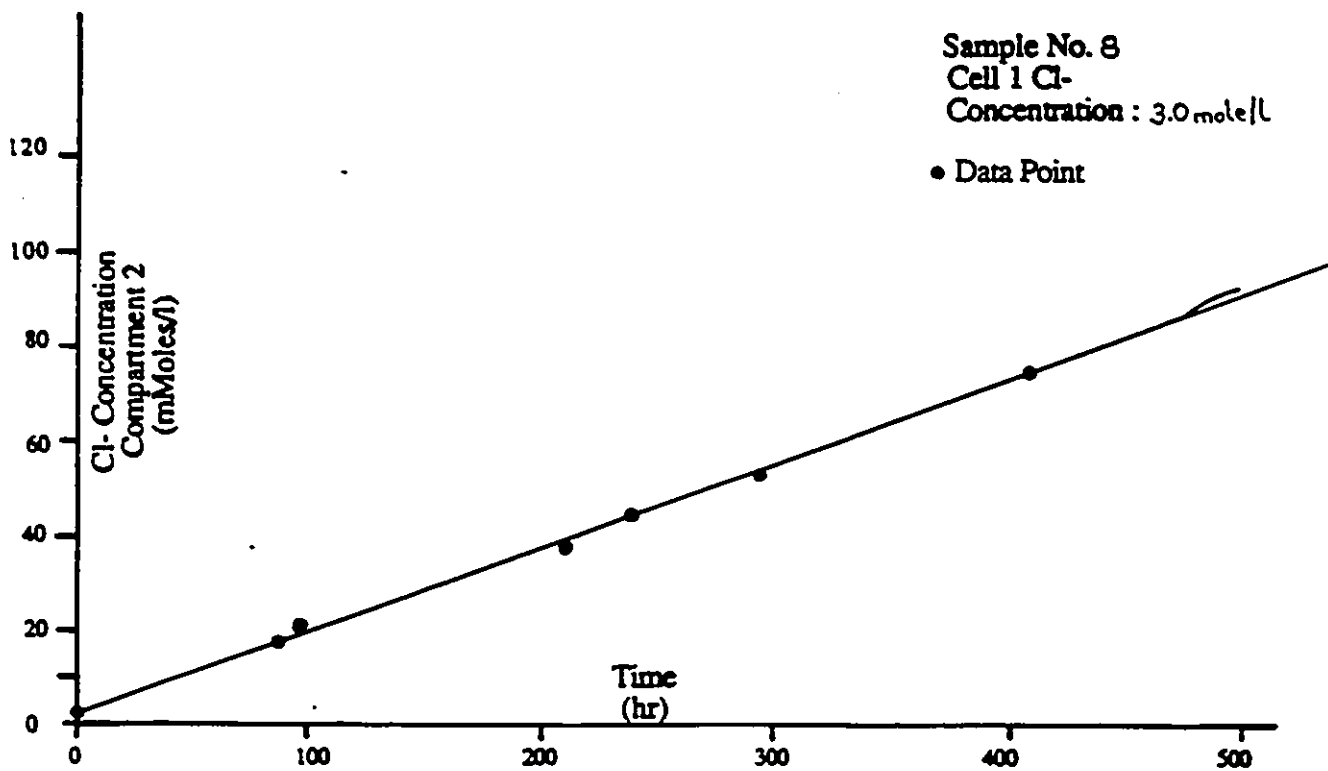
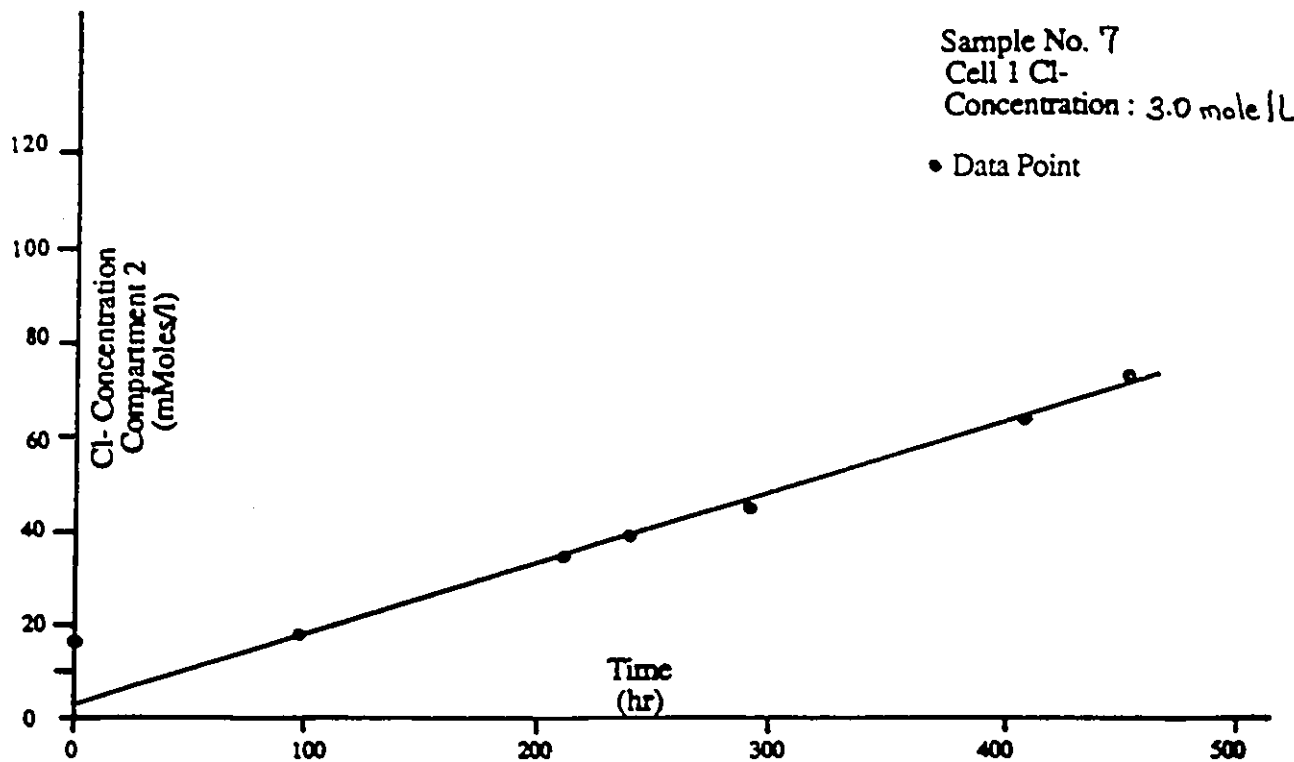


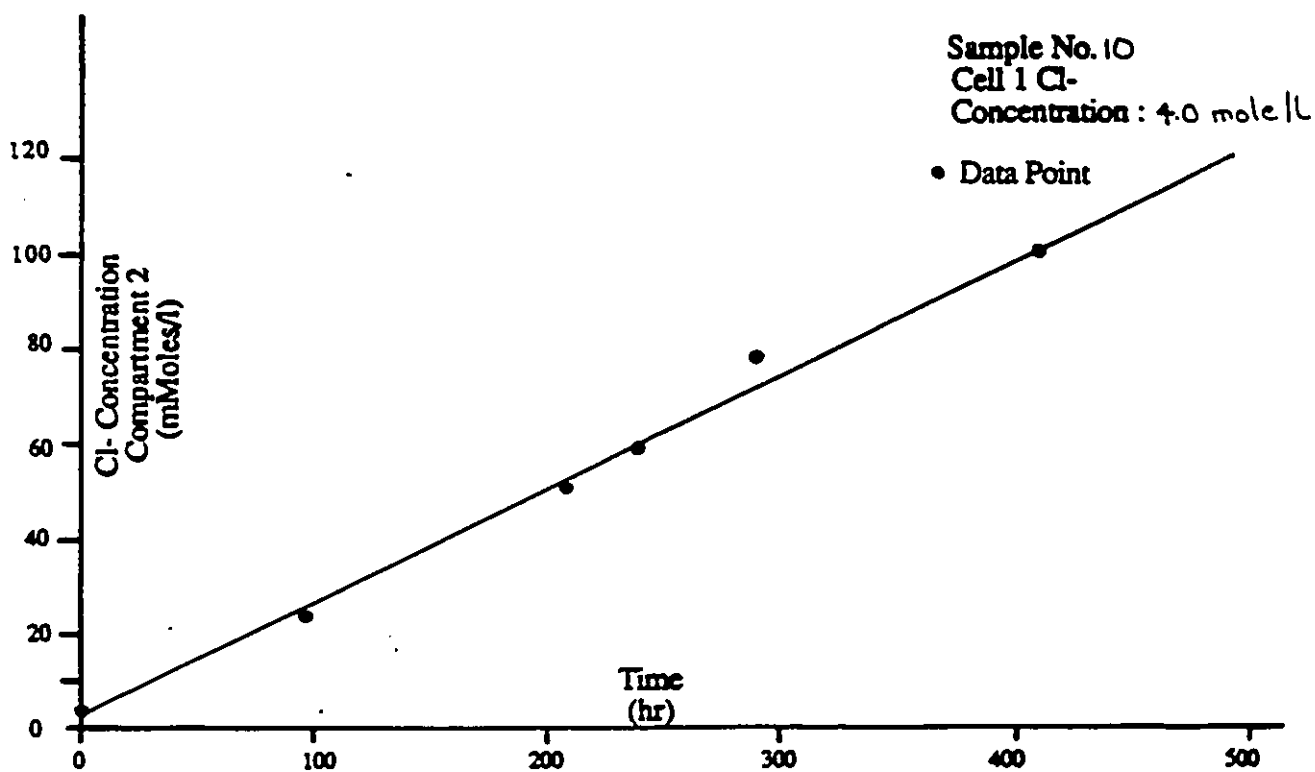
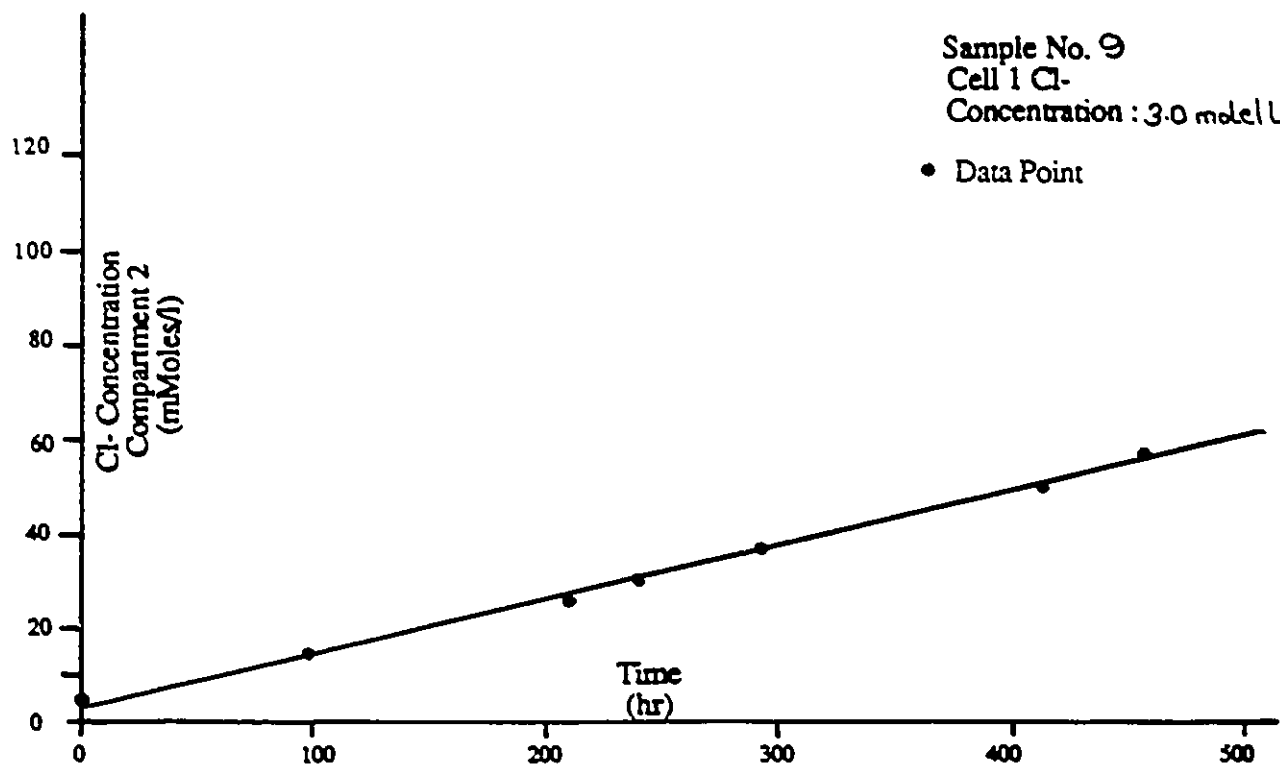


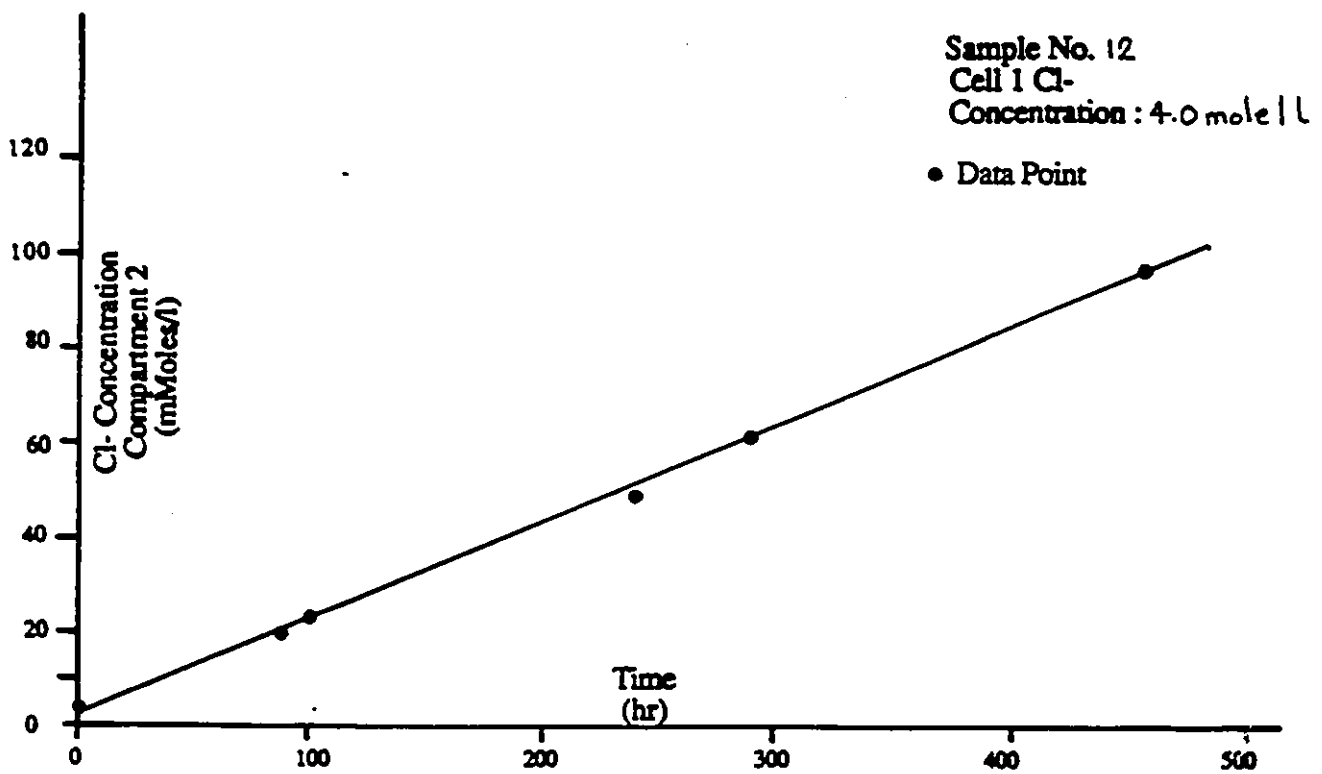
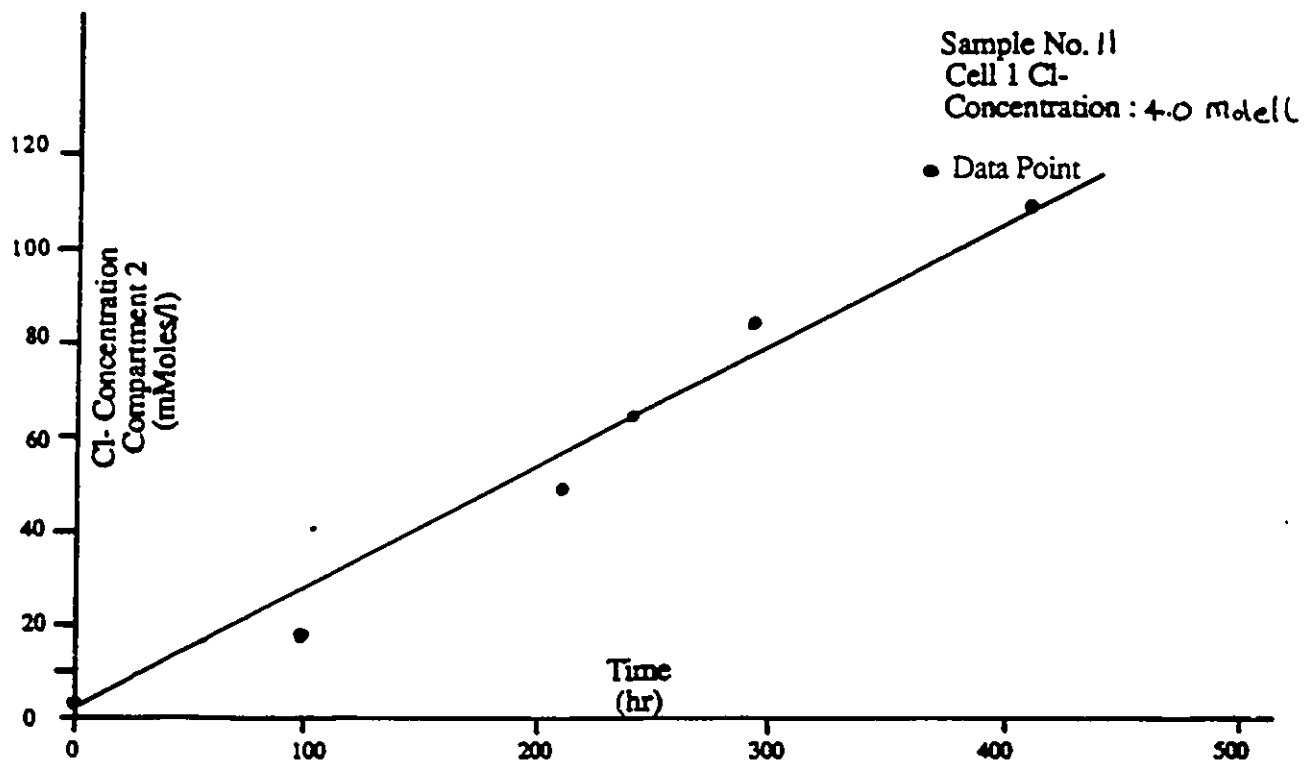


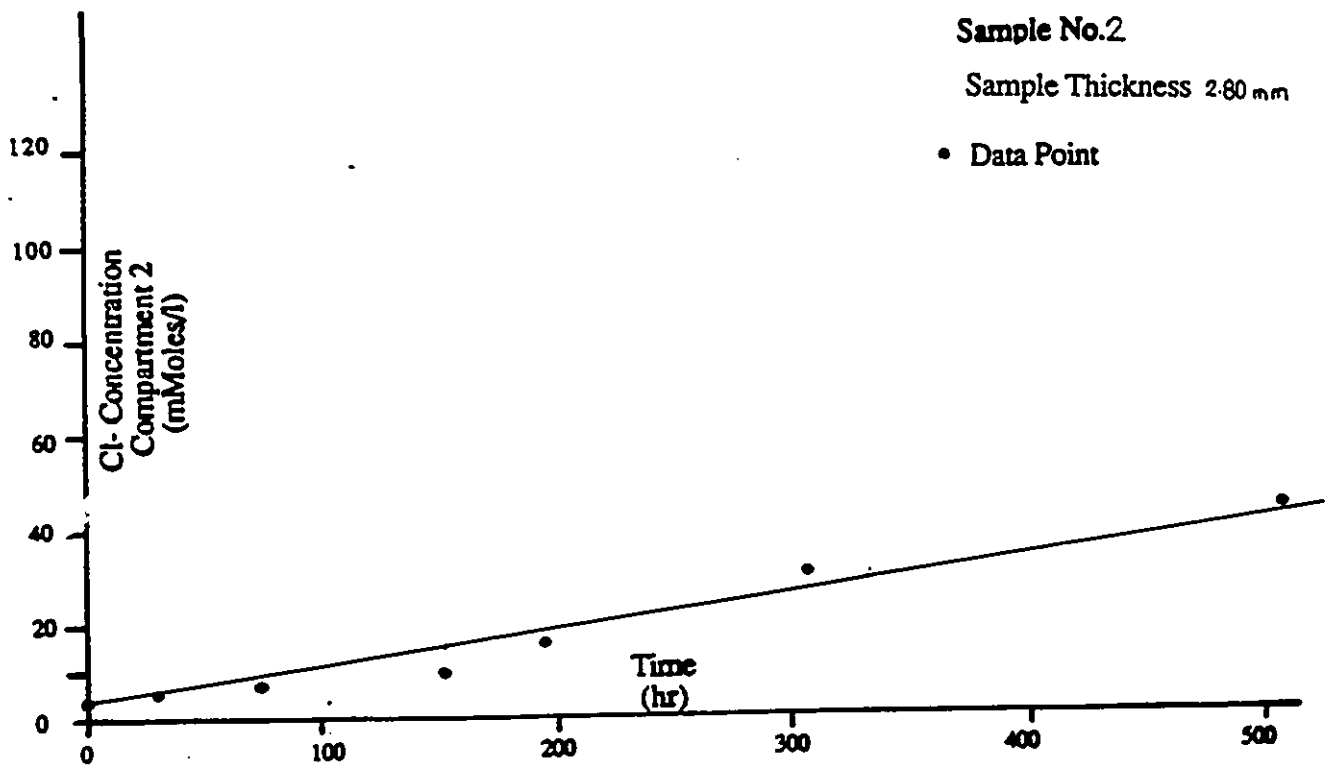
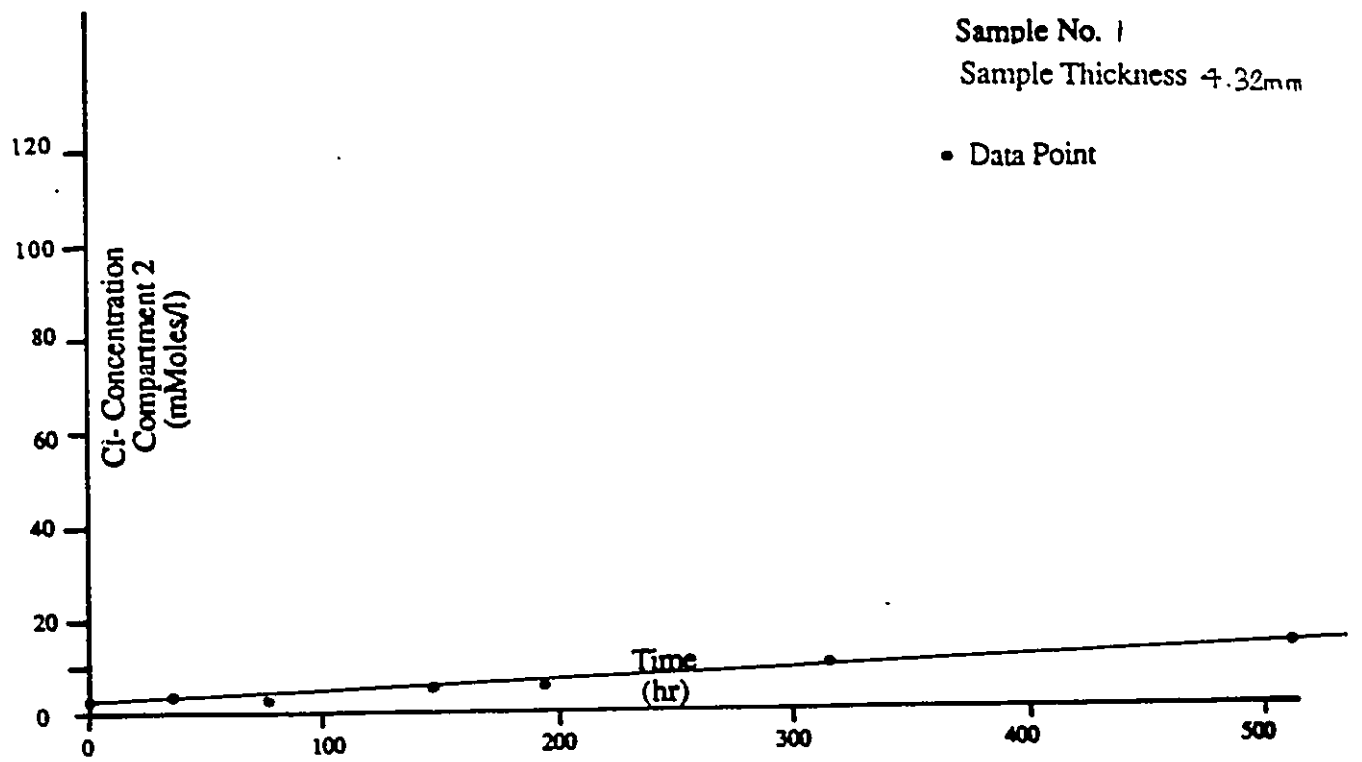


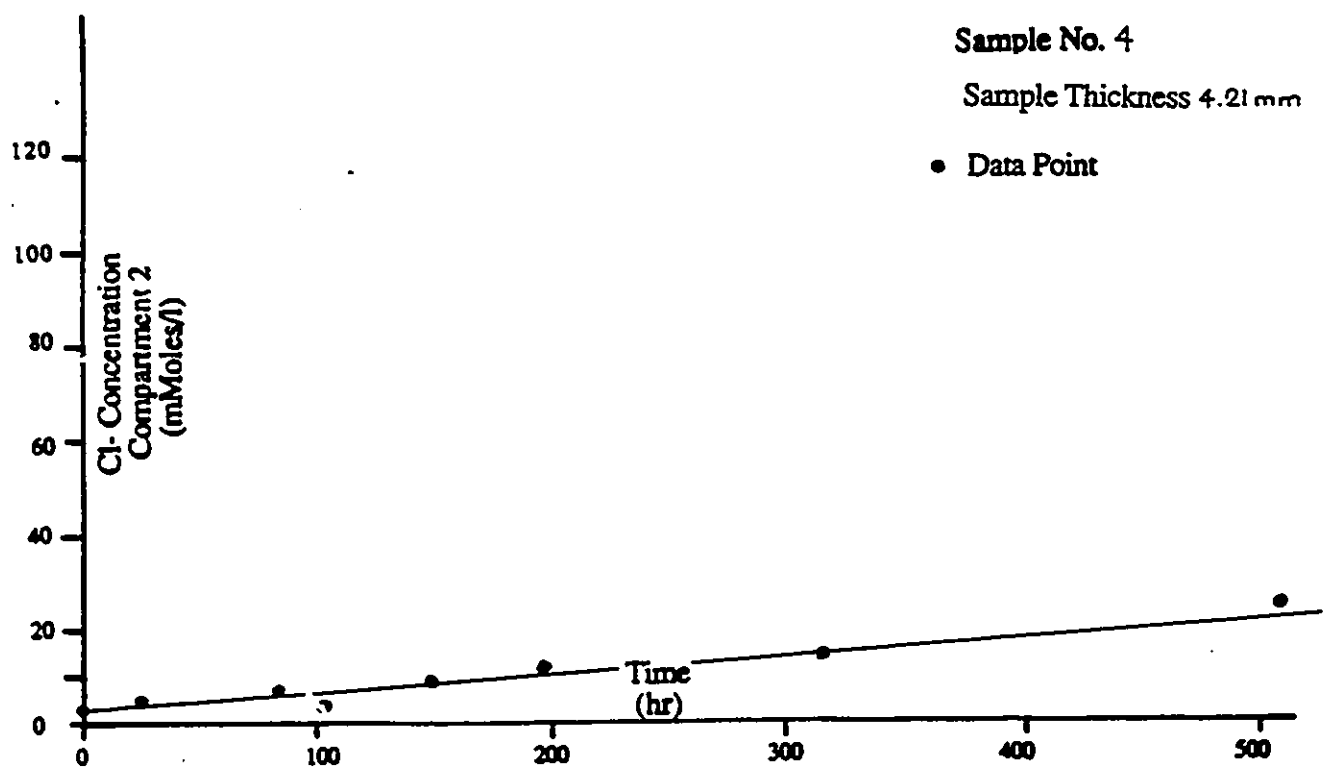
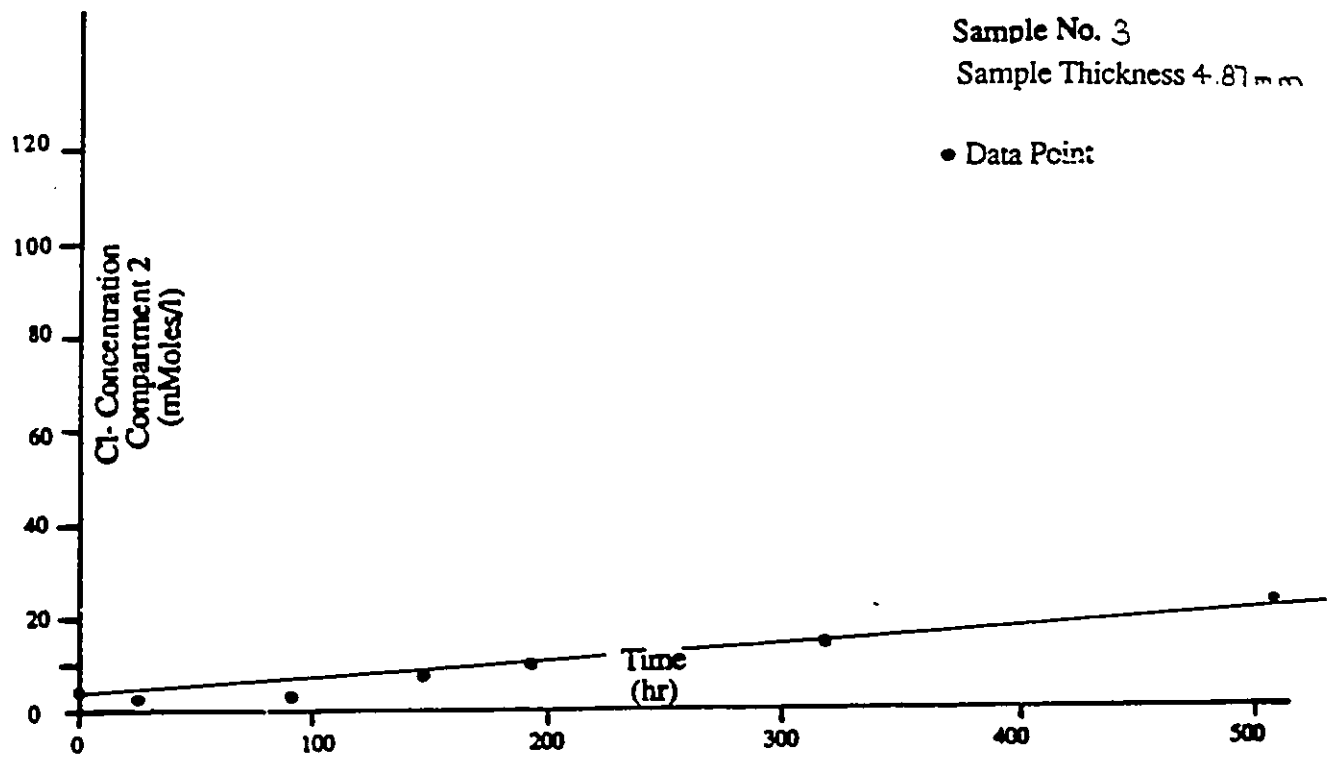


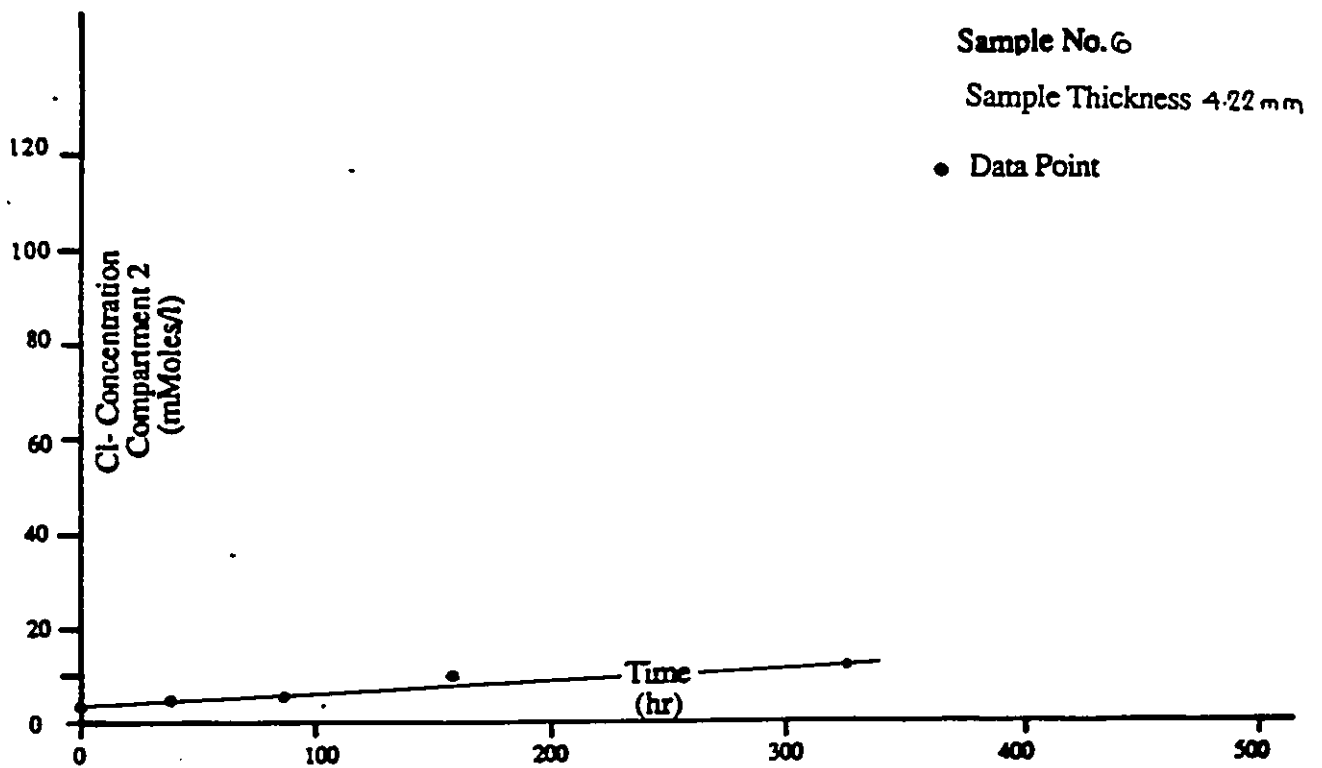
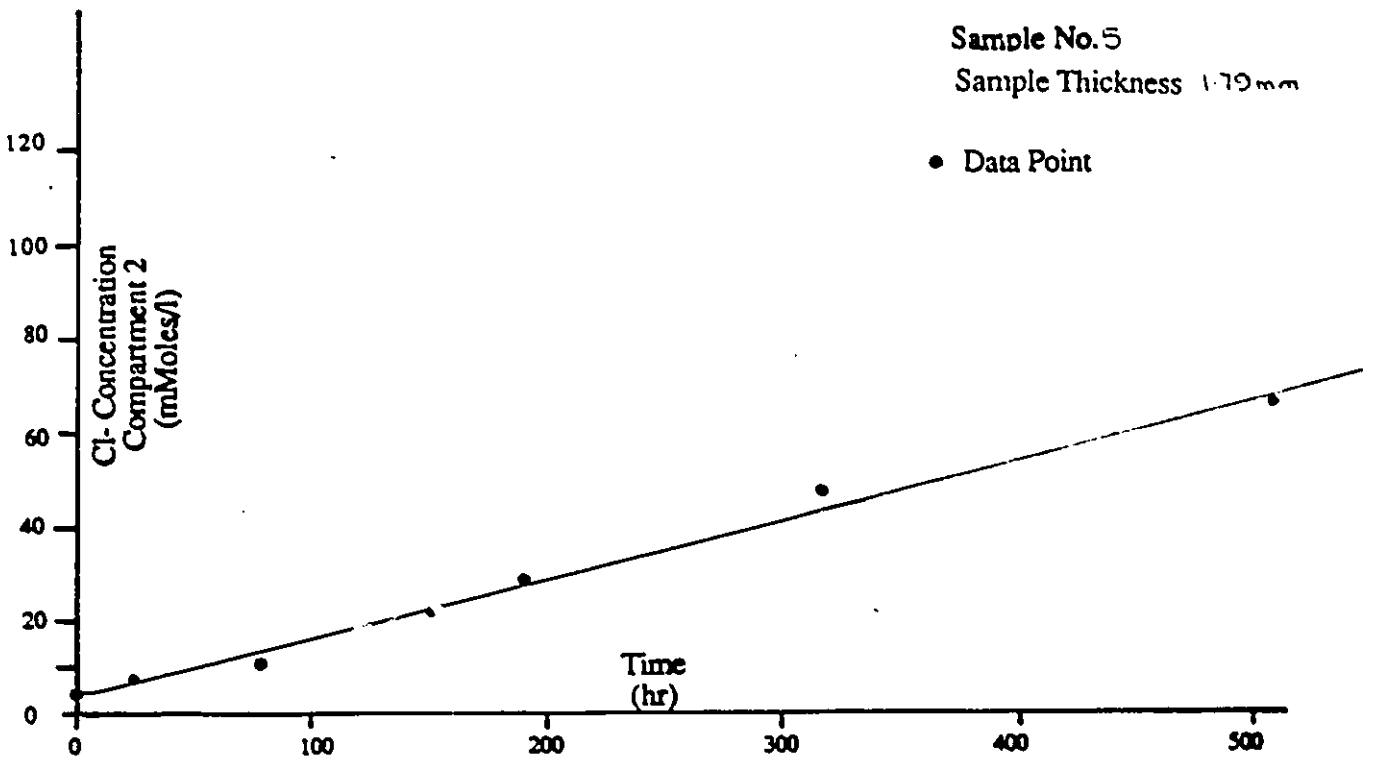


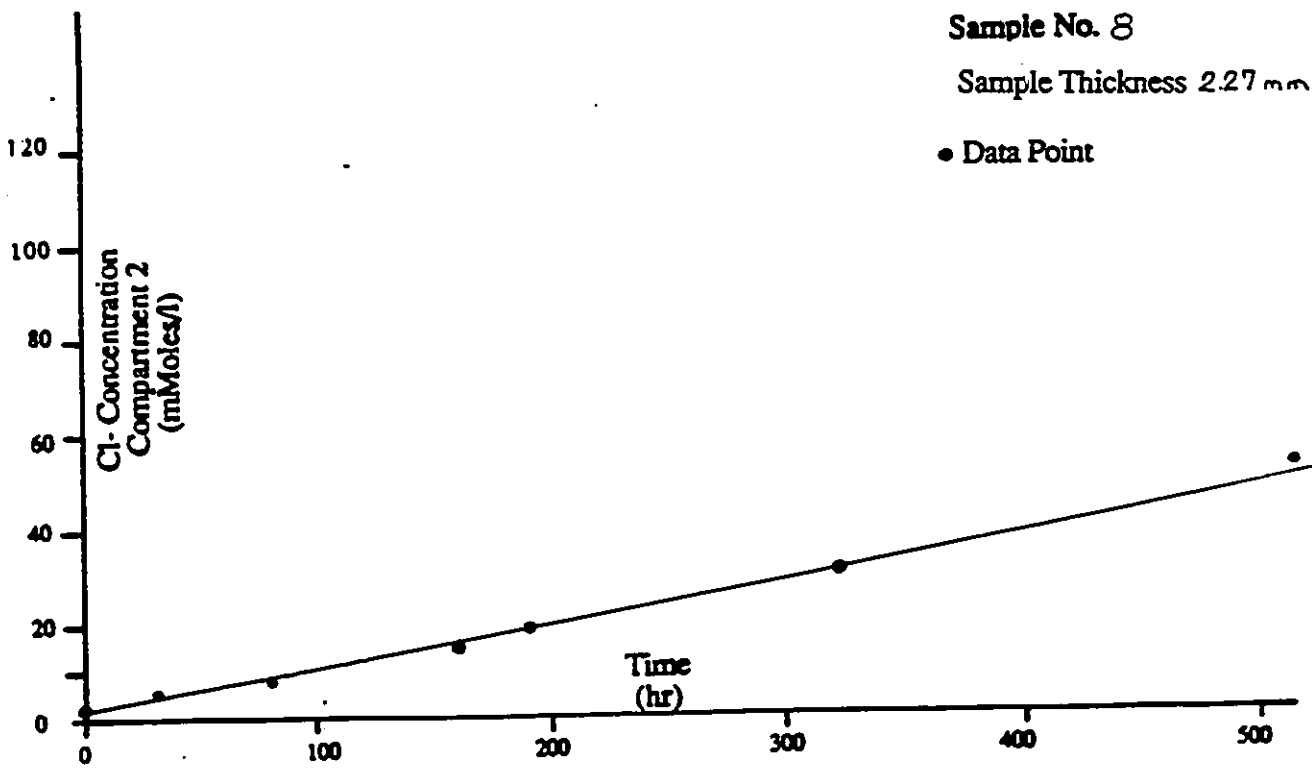
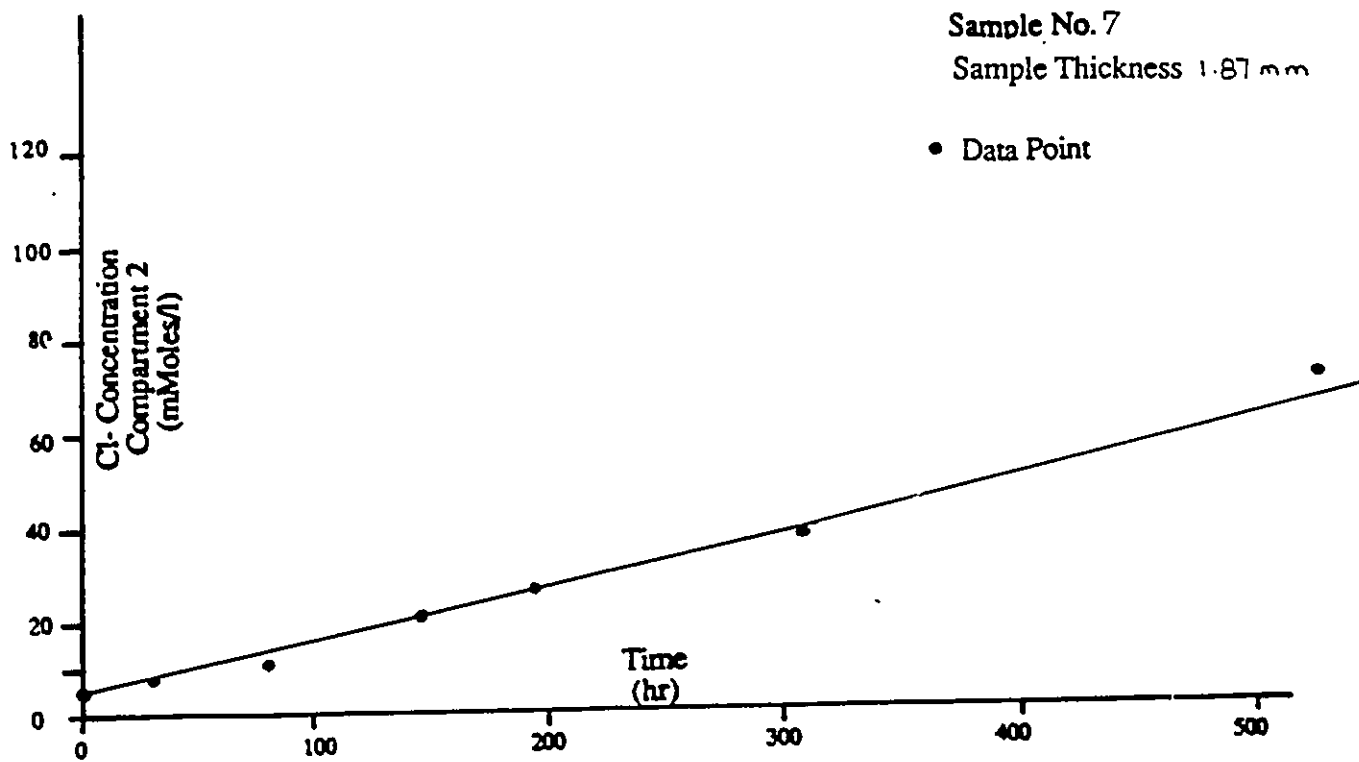


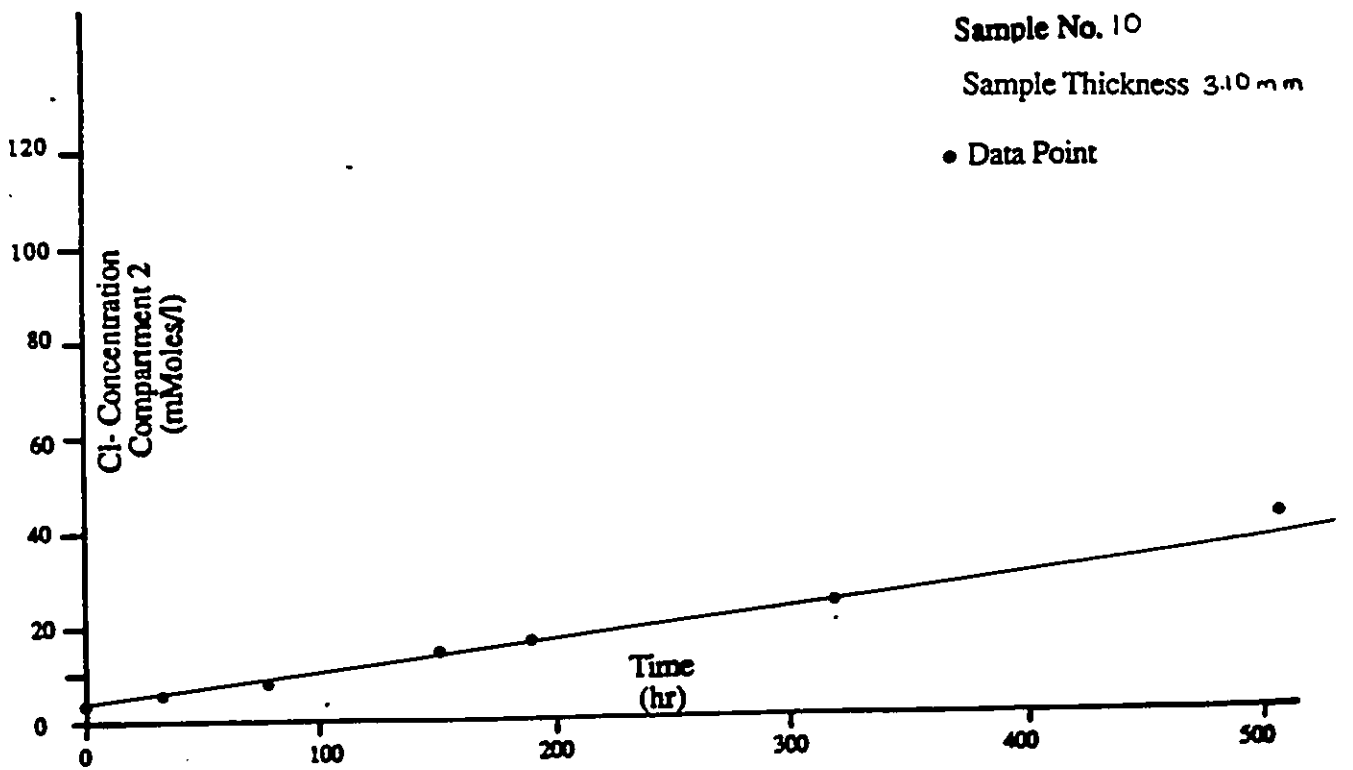
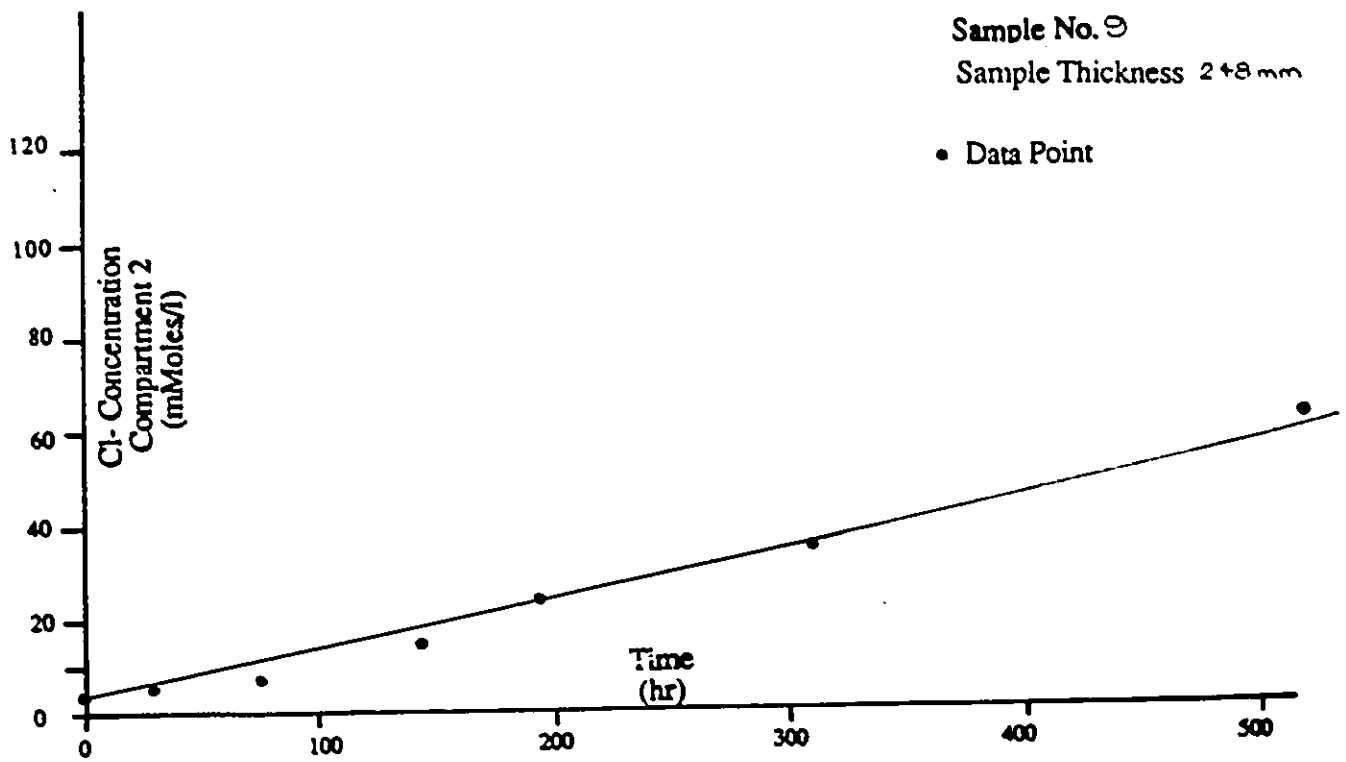


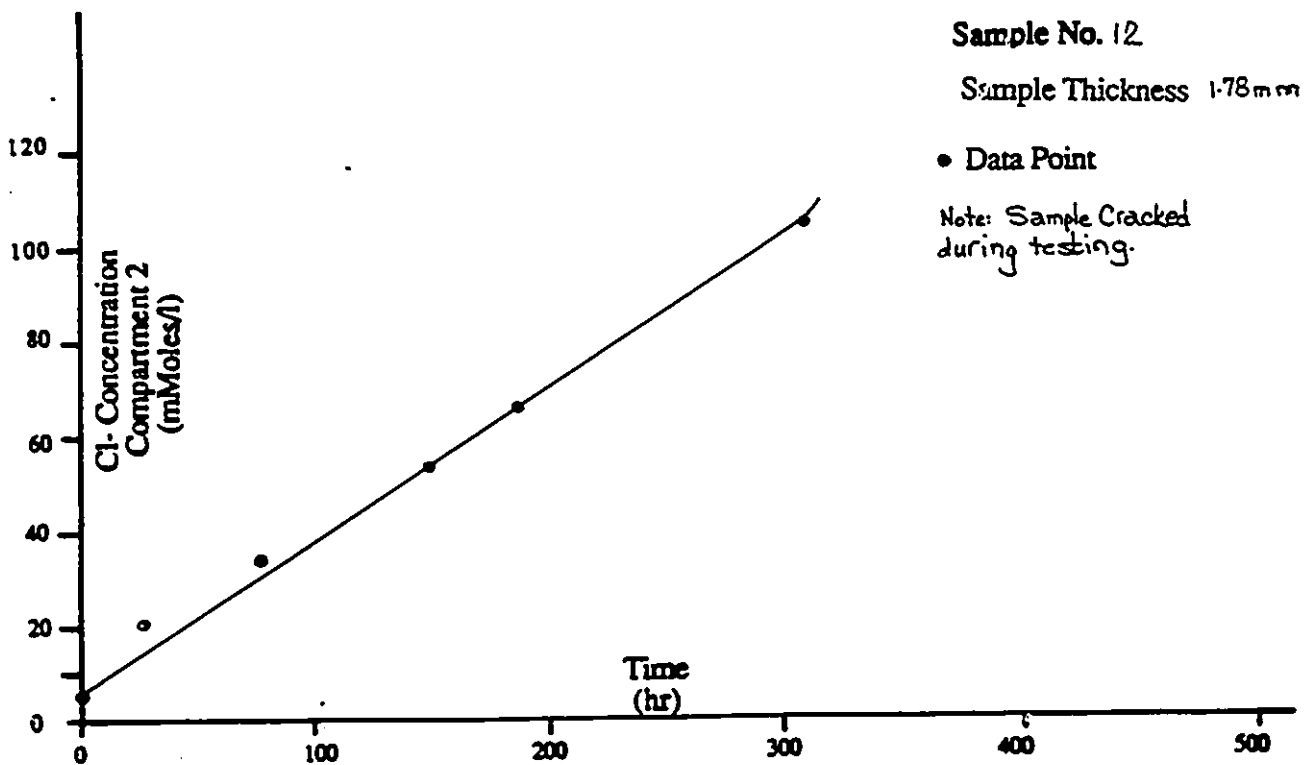
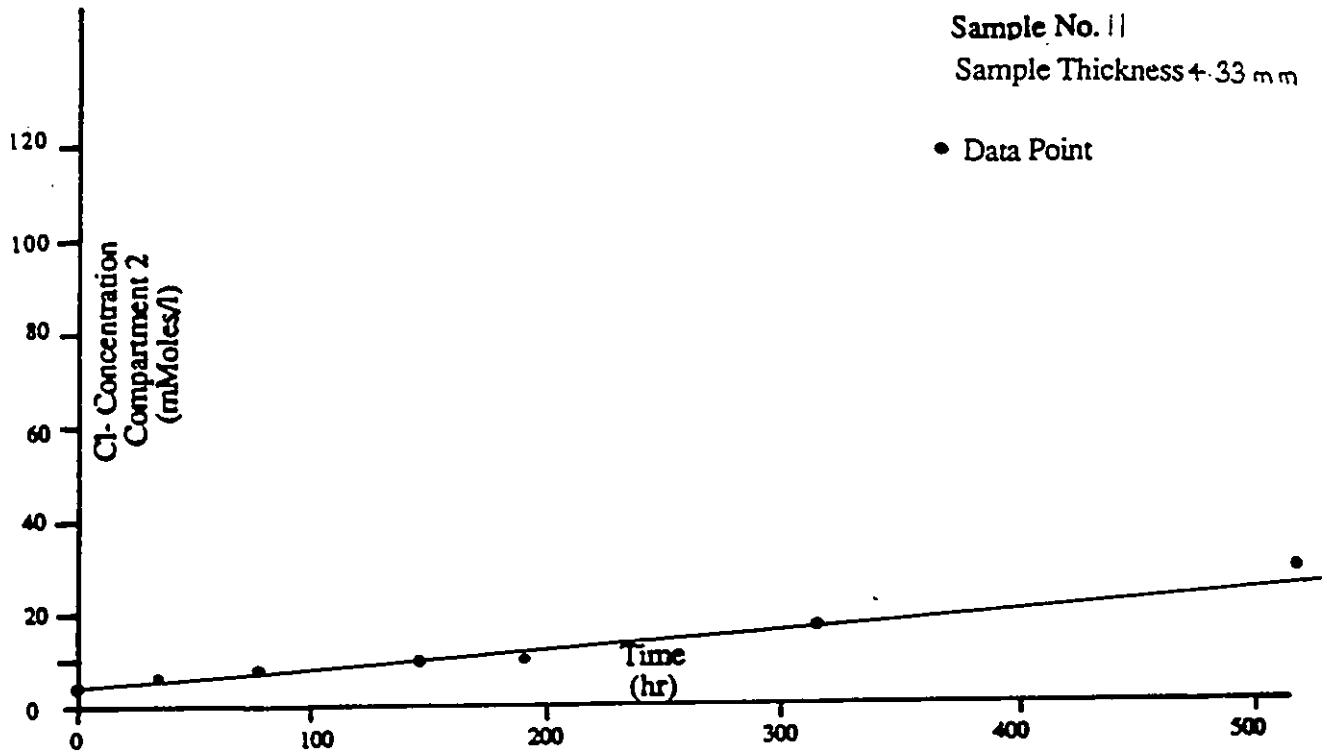












Appendix D

Sample Calculation of D_{Cleff} from Chloride Ion
Concentration/Time Data

Below is presented a sample calculation of $D_{Cl_{eff}}$, specifically for Cell 12 during the experiment wherein the water:cement ratio was varied. The water cement ratio of the disk installed into this cell was 0.7.

From Chapter 3, Equation (10) reads:

$$C_2 = D_{Cl_{eff}} \frac{AC_1}{Vl} t \quad (D1)$$

Where C_2 is the chloride ion concentration in cell 2 of the diffusion cell, A is the cross sectional area of the cement paste disk under study, l is the disk thickness, V is volume of cell 2 and t is time.

Table D1 : Experimental Data for Cell 12 Water:Cement Ratio 0.7

Time (hrs)	Electrode Potential (mV)	Chloride Ion Concentration C_2 (Moles/Litre)
0	75.4	0.0026
24	53.2	.0061
48	40.4	.0099
96	25.1	.0179
144	15.0	.0263
264	-3.5	.0535

Cell 1 Chloride Ion Concentration = 1.0 Moles/Litre.
Sample Thickness = 4.11 mm.

By linear regression the slope of the c_2 versus time plot is 19.2×10^{-5} moles/litre hr.

The ratio of explained to total variance (r) is 1.0.

From equation (D1) the slope of the C_2 versus time plot is related to D_{cleff} by the equation (D2).

$$m = D_{cleff} \frac{Ac_1}{Vl} \quad (D2)$$

rearranging equation (D2) yeilds

$$D_{cleff} = \frac{mlT}{c_1} \quad \text{where } T = \frac{V}{A} \quad (D3)$$

T in all cases was 9.9 cm. For m in moles/l hr, l in mm, C_1 in moles/l hr, and desiring D_{cleff} in cm^2/sec , the final formula for computing D_{cleff} becomes:

$$D_{cleff} = \frac{m(\text{moles/lhr}) l(\text{mm}) T(\text{cm})}{c_1(\text{moles/litrehr})} \times \frac{1 \text{ hr}}{3600 \text{ sec}} \frac{1 \text{ cm}}{10 \text{ mm}} \text{ cm}^2/\text{sec} \quad (D4)$$

$$D_{cleff} = \frac{ml}{c_1} \times 0.000275 \quad (D5)$$

In this case, where $m = 19.2 \times 10^{-5}$ moles/lhr, $l = 4.11$ mm and $c_1 = 1.0$ moles/l, D_{cleff} is as calculated below:

$$D_{cleff} = 19.2 \times 10^{-5} \times \frac{4.11}{1.0} \times 0.000275 \quad \text{cm}^2/\text{sec} \quad (D6)$$

$$D_{cleff} = 217 \times 10^{-9} \text{cm}^2/\text{sec} \quad (D7)$$

Appendix E

Boundary Layer Solution for Diffusion 'Lag Time' using
an Unagitated Diffusion Cell

Presented below is a boundary layer penetration solution to determine the time required for the chloride ion to diffuse 40 mm, which approximates the distance between the face of the disk and the port for fluid removal in diffusion cell type apparatus as used in this study and in others.

Consider a diffusion cell as illustrated in Figure E.1.

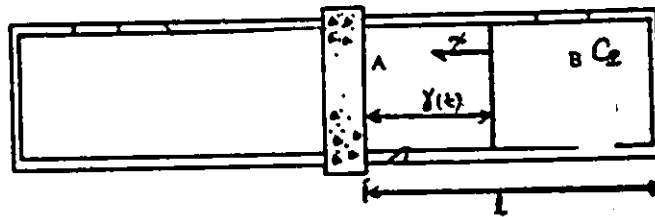


Figure E.1 : Cross Section of Typical Diffusion Cell
Defining x and γ .

This problem can be treated as a penetration type problem, and in terms of this type of solution two distinct time domains can be defined. The first time domain extends from time = 0 to time t_p and is the time from the initiation of diffusion until the time when γ is equal to l . This is defined as the penetration time. The second time domain extends from t_p to infinite and is the time required for the concentration profile to become uniform. In this analysis we are only interested in the first domain. γ is a

function of time and diffusivity, and behaves as a scale factor. The first step in this process is to define γ on the interval between $x = 0$ and $x = 1$.

In Domain I

$$\text{at } t = 0, \quad \frac{\partial C_2}{\partial x} = 0 \quad (E1)$$

$$t > 0 > t_p \quad C_2 = f(x, t) \quad (E2)$$

$$\text{at } t = t_p, \quad \gamma(t) = 1 \quad (E3)$$

Assuming a parabolic behaviour for the concentration profile, and that the concentration of chloride ion at the face of the disk is equal to C_1 , then a good approximation of the profile is

$$C_2 = C_1 \left(\frac{x^2}{\gamma^2} \right) \quad (E4)$$

Ficks second law states the following :

$$\frac{\partial C_2}{\partial t} = D \frac{\partial^2 C_2}{\partial x^2} \quad (E5)$$

Integrating both sides of equation (E5) with respect to x on the

bounds from 0 to γ , and changing the order of differentiation yields

$$\frac{d}{dt} \int_0^\gamma C_2 dx = D \frac{\partial C_2}{\partial x} \Big|_0^\gamma \quad (E6)$$

$$\frac{1}{D} \frac{d}{dt} \int_0^\gamma C_2 dx = \frac{\partial C_2}{\partial x} \Big|_\gamma - \frac{\partial C_2}{\partial x} \Big|_0 \quad (E7)$$

Recalling that

$$\frac{\partial C_2}{\partial x} \Big|_0 = 0 \quad (E8)$$

and

$$C_2 = c_1 \frac{x^2}{\gamma^2} \quad (E9) \quad \frac{\partial C_2}{\partial x} = \frac{2C_1 x}{\gamma^2} \quad (E10)$$

Equation (E7) becomes

$$\frac{1}{D} \frac{d}{dt} \frac{1}{3} C_1 \gamma = \frac{2C_1}{\gamma} \quad (E11)$$

Rearrangement yeilds

$$d\gamma^2 = 6Ddt \quad \text{Initial condition } \gamma(0) = 0 \quad (E12)$$

Which yields the following solution

$$\gamma = \sqrt{6Dt} \quad (E13)$$

So the approximate concentration profile in the penetration domain ($t < t_p$) is given by

$$C_2 = C_1 \frac{x^2}{6Dt} \quad (E14)$$

The time required for the chloride ion to diffuse 40 mm is equal to the time at which γ is equal to 40 mm. Assuming that D is equal to $1.2 \text{ E-}5 \text{ cm}^2/\text{sec}$, for γ equal to 40 mm is $2.22 \text{ E}5$ seconds, or approximately 2.6 days.

Publications

1. Kevin A. MacDonald and D.O. Northwood, *The Corrosion of Steel Reinforced Concrete Structures in Chloride Containing Environments*, Presented at the 6th Asian-Pacific Corrosion Control Conference, Singapore, September 1989. Published in Proceedings, Asian-Pacific Materials and Corrosion Association, Sydney, Australia, 1989, pp. D14-D18.
2. D.F. Watt, Xu Jian Zhou, K. MacDonald, D.O. Northwood, and P.P. Hudec, *Using Pyrolyzed SMC Ash as an Additive to Concrete*, Presented at Recycling Plastics in New England..Now and in Future, Society of Plastics Engineers Regional Technical Conference, Waterbury, Connecticut, June 3,4 1991. Published by the SPE, 1991, pp. 65-72.
3. D.F. Watt, J. Xu, K.A. MacDonald and D.O. Northwood, *The Recycling of Scrap Automotive Polymer Composite by Pyrolysis and Incorporation into Concrete*, Presented at Materials Processing and Performance, Melbourne, Australia, September 2-5, 1991. Published in Proceedings, Institute of Metals and Materials, Australasia, 1991, pp. 19-22.

Vita Auctoris

Kevin MacDonald was born in 1966 in Toronto, Ontario. After Graduating from De La Salle "Oaklands" College School in 1985, he obtained a Bachelors Degree in Chemical Engineering from the University of Windsor in 1989. He is currently a candidate for the degree of Master of Applied Science in Engineering Materials at the University of Windsor. He hopes to graduate in the spring of 1992.