Chloride Resistance of High Volume Fly Ash Concretes

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Abstract

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Allen Michael Idle

Costly reinforced concrete structures serve as foundations for the economic prosperity of a nation. The continued deterioration of concrete structures, due to corrosion of steel reinforcing rebar, requires the implementation of vast multi-million dollar rehabilitation projects to maintain an adequate level of service in these systems. The process of corrosion in reinforced concrete is largely due to the ingress and build-up of chloride ions in the capillary pores of concrete caused by the use of road salts and from contact/spray from seawater. Lowering the water to cement ratio and incorporating Supplementary Cementing Material's (SCM's) are effective methods of lowering the permeability of concrete to harmful chloride ions. Fly ash is used commonly because it is environmental and economical. However, the amount of fly ash which can be used in concrete is limited, because there are concerns (controversy) over the long-term durability of such structures when fly ash is used in high volumes. This thesis will investigate the chloride resistance of two types of Portland cements and two silica fume blended Portland cement concretes. Each of the four cement types was replaced with two Type CI fly ashes, with coal sources from Sundance, Alberta and from Rockport, Indiana, at 0, 20, 40, 60, and 80 replacement percentages. The chloride resistance was determined by the Rapid Chloride Permeability Test (ASTM C 1202-08) for each combination made. The Sundance fly ash showed greater resistance to chloride permeability than the Rockport fly ash, assumingly because of its lower carbon content, higher fineness, and increased pozzolanic activity.

Acknowledgements

I would like to thank Dr. M. R. Nokken for her guidance and expertise throughout this process. My appreciation also goes out to all the staff in the structure's laboratory and all the others who helped make this project possible.

Dedication

Dedicated to the patient and loving women in my life. They are my dearest Grandmother, my supportive Mother, and my kindest partner Melanie. Without them this would have not been possible.

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1.0 Introduction:

Throughout history, limited concern has been placed upon the harmful effects that many of the technological and industrial advancements made by civilization may have on the Earth. With recent attention and relative acceptance by humans that rising CO_2 emissions contribute largely to global warming (and other environmental issues) a turn towards more responsible and sustainable development has arisen in the 21st century. The current annual release of CO_2 gas in the atmosphere from all sources is estimated at over 23 billion metric tonnes per year (2005), and currently growing exponentially over time [1]. The cement industry is accountable for about 7 percent of this release (just under 2 billion tones per year) [1]. Each tonne of Portland cement produced requires the use of 4GJ of energy, and is responsible for the release of one tonne of CO_2 into the atmosphere [1, 2]. The expected annual production of cement is estimated to be well over 2 billion tonnes by the year 2010 [1].

It is vital that each sector of industry make continued efforts to reduce CO2 emissions [2]. The cement industry can help to reduce its emission contributions by increasing and encouraging the use of Supplementary Cementing Material's (SCM's) in its products. The three main types of SCM's used are: fly ash, ground granulated blast furnace slag, and silica fume. They are all by-products of various industrial processes [3, 4]. SCM's contribute to the hardening of concrete by pozzolanic or sometimes by a combination of hydraulic and pozzolanic activity [4, 5]. Pozzolans are defined as: "a siliceous or aluminosiliceous material that, in finely divided form and in the presence of moisture, chemically reacts with the calcium hydroxide released by the hydration of Portland cement to form calcium silicate hydrate and other cementing compounds" [5]. They are normally used in partial replacement of the Portland cement by mass in the concrete mixture. There are also other natural sources of pozzolans such as clays and some types of shales. Figure 1 displays some of the common types of SCM's used in concrete. From left to right they are Type C fly ash, metakaolin (calcined clay), silica fume, Type F fly ash, ground granulated blast furnace slag, and calcined shale.

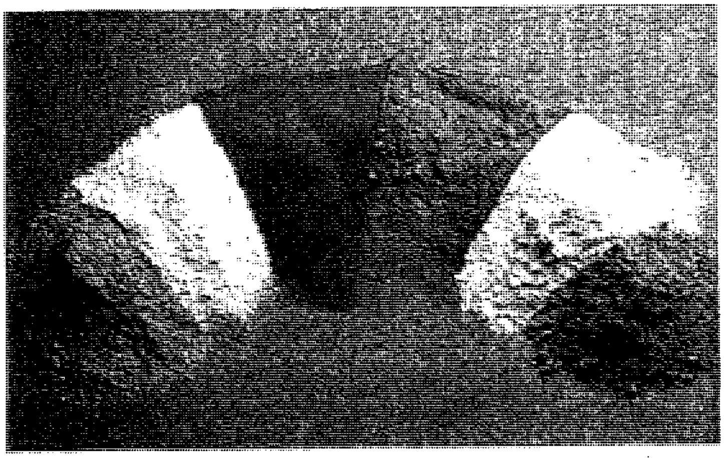


Fig 1.1 - Photograph of some common types of SCM's used in concrete [5].

Fly ash is the most widely used SCM [3]. It is relatively inexpensive and readily available. The worldwide production of fly ash is estimated at over 500 million tonnes [1]. However, less then 20 percent is used in the production of cement concrete [1]. The remainder is disposed by ponding or stockpiling; it may also be placed in landfills or used as road base material [1]. Disposal in this manner can be harmful, because fly ash contains various toxic metals (As, Cr, Se, Ti, Va) which can leach into surrounding ground-water (increasing cations) [1]. Concrete provides a safe place for potentially toxic fly ash [1, 6]. The hydration products of the Portland cement concrete (and the pozzolanic reaction of the fly ash) forms various chemical complexes which immobilize and trap many of the toxins found in fly ash inside the concrete [1, 7]. Using fly ash reduces the amount of energy used, CO_2 produced, and land use area required (to store fly ash) [8]. Using fly ash in concrete structures under the right conditions can also lead to other benefits such as improved economy, improved durability, improved workability, reduced heat of hydration, reduced bleeding and segregation [1, 9 - 11].

Nearly 25 percent of the world's CO_2 emissions come from the burning of coal products for thermal power generation. Considering this large contribution in CO_2 emissions, power generating utilities should also continue to encourage the use of their fly ash in the concrete industry, offsetting some of their own emissions. The concrete industry provides a logical and ideal place for the disposal of large quantities of fly ash, in both an economic and environmentally responsible manner [1]. It was said "When there is a sufficient economic incentive, producers of fly ash will overcome the problems that are hindering the high-value uses of the material" [1]. Promoting certain partnership programs between corporations and government such as the: Leadership in Energy and Environmental Design (LEED®) provides corporations with incentives (tax cuts) which encourage sustainable development.

Growing populations (9 billion by 2025) throughout the developed and developing worlds place ever-increasing supply demands on cement and concrete, for use in new and rehabilitated infrastructure [1]. This demand can not be met solely by the production of Portland cement. It will require increasing the use of SCM's (fly ash largely) in the construction industry [1, 2]. However, there are various hindrances and misconceptions limiting the use of fly ash. One of these issues pertains to concern over the long term durability of concrete, containing large volumes of fly ash. One of the major contributors, which reduces the durability of reinforced concrete structures, is due to corrosion of the steel reinforcement [9, 12, 13]. This is largely due to the ingress and build-up of chloride ion concentrations within the capillary pore structure of the concrete matrix. This thesis will investigate the chloride resistance of Portland cement concrete containing different proportions of fly ash and silica fume using the Rapid Chloride Permeability Test (ASTM C 1202-08) Concrete producers generally limit the maximum amount of fly ash used in concrete to around 25-35 percent replacement levels, depending on exposure conditions and governing regulations [1, 14]. This thesis will investigate fly ash replacement levels of 20, 40, 60, 80 percent of the Portland cement. Limited research has been done concerning the permeability (chloride resistance) up to such high fly ash replacement levels.

2. Literature review:

2.1 Fly Ash:

2.1.1 Description of Fly Ash:

Fly ash is collected from the combustion gases released during the burning process of ground or powdered coal for the production of power in thermal power generating plants [1, 3, 5]. The coal is burned at temperatures of 1500°C, which burns most of the carbon found in it [1]. Some non-combustible mineral impurities found in the coal (clay, shale, quartz, feldspar, dolomite and limestone) will however remain [1]. The molten mineral impurities rapidly cool down to temperatures of 200°C when they are released in the combustion gases after burning [1]. Because of this rapid cooling, the molten impurities form into particles which are spherically shaped and glassy in texture [1, 3, 15]. The fly ash particles can then be removed from combustion gases by way of bag filters and/or electrostatic precipitators [1, 5, 15]. The fly ash particles are described as tan to grayish in color [3]. The size of fly ash particles generally range from about 1μm to 100μm in diameter, with the usual size being about 20 μm [1, 3, 5]. The specific gravity of fly ash particles is usually in the range of 1.9 to 2.8 with surface areas in the range of 300m²/kg to 500m²/kg [3, 5]. It is also important to have fly ash which is consistent. The exact composition and effect of the fly ash on the concrete depends on the source of the coal and the combustion methods used [1, 3, 15,]. Power plants which maintain a more constant power production output, produce much more uniform fly ash compared to plants which have variable power production output (differences in burning temperatures) [1]. The degree of pozzolanic reaction of fly ash is mainly controlled by its fineness, calcium content and mineralogy [1].

2.1.2 Chemical Composition of Fly Ash:

The main chemical constituents of fly ash are silica, alumina, ferric, calcium, magnesium, alkali, and sulfur oxides as well as carbon (LOI – loss on ignition). Table 2.1 shows the chemical compositions of common types of fly ash used in Canada and the U.S by coal type.

Table 2.1 - Chemical Composition of Fly Ash by Coal Type [1]

Source	Percent by mass							
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Alkalies	SO_3	Ignition Loss
Bituminous, U.S.	55.1	21.1	5.2	6.7	1.6	3.0	0.5	0.6
Bituminous, U.S.	50.9	25.3	8.4	2.4	1.0	3.1	0.3	2.1
Bituminous, U.S.	52.2	27.40	9.2	4.4	1.0	0.8	0.5	3.5
Bituminous, Canada	48.0	21.5	10.6	6.7	1.0	1.4	0.5	6.9
Bituminous, Canada	47.1	23.0	20.4	1.2	1.2	3.7	0.7	2.9
Subbituminous, U.S.	38.4	13.0	20.6	14.6	1.4	2.4	3.3	1.6
Subbituminous, U.S.	36.0	19.8	5.0	27.2	4.9	2.1	3.2	0.4
Subbituminous, Canada	55.7	20.4	4.6	10.7	1.5	5.7	0.4	0.4
Lignite, U.S.	26.9	9.1	3.6	19.2	5.8	8.6	16.6	-
Lignite, Canada	44.5	21.1	3.4	12.9	3.1	7.1	7.8	0.8

2.1.3 Effect on Fly Ash Quality due to Higher Emissions Standards:

Increased emission standards which have been placed on power plant utilities are causing concerns over the quality of fly ash produced. To reduce NO_x (smog) emissions, power plant utilities, seek to modify the combustion products by lowering peak burning temperatures of the coal (1300°C) [16]. This temperature decrease causes increased levels of unburnt carbon, decreases the fineness, decreases the amount of spherically shaped particles, and decreases the amount of glassy texture of the fly ash [3, 16, 17]. Generally, unburnt carbon particles are coarser and can be separated through certain beneficiation and particle separation techniques. Screening, grinding, and air classification are some common methods to achieve this. Such methods also have the advantage of increasing the overall fineness. However, grinding can further decrease the amount of spherically shaped particles. To overcome the problem of decreased fly ash quality in Japan, fly ash classification has been revised, which now classifies fly ash into four different classes, largely based on carbon content and fineness [16]. Coal power plants also use what are referred to as "ammonia-based environmental control technologies" [17]. Ammonia is injected into the flue gas which converts the NO_x to N_2 [17]. This causes the fly ash to have high levels of ammonia. Ammonia removal is fairly costly and can destroy the pozzolanic activity of fly ash [17]. Problems of fly ash deterioration due to environmental regulations is of less concern in developing countries, where generally environmental standards are lower.

2.1.4 Fly Ash Classification:

In Canada, fly ash is divided into two main categories by CSA A23.5 as Type F and Type C. Type F fly ash is usually formed from the combustion of anthracite or bituminous coal and contains a low calcium content of less then 8 percent (the first five fly ashes in Table 2.1 are Type F) [5]. Type C which is derived mainly from lignite or sub-bituminous coals and has higher calcium contents (the last five fly ashes in Table 2.1 are Type C) [5]. In Canada, Type C has two sub-classes, Type CI and Type CH. Type CI fly ash has intermediate calcium levels of 8-20 percent and Type CH has higher calcium levels of more then 20 percent and less then 30 percent [5]. In the USA, fly ash is similarly classified as Type F and Type C according to ASTM C618.

2.1.4.1 Classification Based on Chemical Requirements:

The chemical requirements are summarized in Table 2.2. The moisture content is important because the fly ash will be hard to handle and sticky if it is too wet [4]. The loss on ignition is an indication of the carbon content found in the fly ash. High carbon levels have been shown to cause difficulty in ensuring proper levels in air entrainment in the concrete, because of the sensitivity of air entraining agents to high carbon levels [4, 17]. The main difference between the Canadian and U.S. standard on the classification of fly ash, are the limits placed on the combined sum of SiO_2, $Al2O_3$ and Fe_2O_3 for Type F and Type C fly ash. At one time, it was thought that this was a main indication of the pozzolanic contribution of the fly ash [4]. Various studies have shown that these limits have little correlation with the performance of fly ash [1, 4]. SO_3 limits were placed over the possible concerns in the setting and volume changes of the concrete, however this was shown not to occur [4]. The main problem with high sulfur levels is in the efflorescence and discoloration that can occur on the outer surface of the concrete [4]. The chemical composition is extremely variable in fly ash. However, pozzolanic properties are not highly governed by the chemistry [1]. Chemical requirements on fly ash can be misleading and hinder the increased use of fly ash [1].

Table 2.2 - Chemical Requirements for Fly Ash Use in Portland Cement Concrete [1]

	Canada CSA-A23.5		U.S. ASTM C 618	
	Type F	Type C	Class F	Class C
Free moisture, max. %	*	*	3.0	3.0
Loss on ignition, max. %	12.0	6.0	6.0**	6.0
(SiO_2+Al_2O_3+Fe_2O_3), min. %	-	-	70	50
CaO, max. %	-	-	-	-
SO_3, max. %	5.0	5.0	5.0	5.0

* The Canadian Standard does not contain any mandatory requirement for the free moisture content of fly ash. However, the user may exercise the option to require a maximum of 3.0% free moisture.

** The use of Class F fly ash containing up to 12% loss on ignition may be approved by the user if either acceptable performance records or laboratory test results are made available.

2.1.4.2 Classification Based on Physical Requirements:

The physical requirements placed on Types C and F fly ashes for the Canada and the U.S. standards, are shown in Table 2.3. A governing factor affecting the reactivity of the fly ash is its fineness [1, 18]. Fineness is determined by obtaining the proportion of the washed fly ash which is retained on sieve number 325 (45μm). Most modern coal fired power plants produce fly ash which easily meets the maximum requirements of the 34 percent retainment [1, 4]. Another important measure of fineness that was at one point used to determine the fineness in the U.S. standard is the specific surface area of the fly ash. This is commonly known as the Blaine fineness. However, because it is fairly fast and easy, the sieve method became the common test procedure for determining fineness. The strength activity index is a measure of pozzolanic reactivity. Fly ash is combined with lime, which cause the activation of the fly ash to occur. The amount of fly ash which has reacted is then measured as a percentage. It is also important that the physical properties are uniform, to ensure consistency of the concrete.

Table 2.3 - Physical Requirements for Fly Ash Use in Portland Cement Concrete [1]

	Canada CSA-A 23.5	U.S. ASTM C 618
Fineness 45 μm (No. 325) sieve residue, max. %	34	34
Water requirement Max. of control:	-	105
Soundness Autoclave expansion, max. %	-	0.8
Uniformity requirements: Specific gravity, max. % variation:	5	5
Fineness, 45 μm residue, Max. % variation:	5	5
Strength activity index With portland cement, 7 days or 28 days min. % of control:	68*	75*
With lime, 7 days at 55°C min. psi (MPa)	-	800 (5.5)

* The strength test values between different standards are not comparable because they are based on different mixture proportions and curing conditions.

2.1.5 Mineralogical Composition of Fly Ash:

The amount and type of glassy phase present in fly ash is also a governing factor which contributes to the degree of pozzolanic reactivity [1]. Fly ash is composed of material which is between 60-90 percent glassy in texture; the remainder is crystalline [1]. Type C (high calcium content) has a calcium aluminosilicate glass phase which is much more reactive than the Type F fly ash (low calcium content) aluminosilicate glass phase[1]. The crystalline phase of the Type C fly ash contains minerals such as: quartz, periclase, tricalcium aluminate, calcium aluminosulphare, anhydrite, calcium oxide, and alkali sulphates [1]. The crystalline phase of the Type F fly ash contains minerals such as: quartz, mullite, sillimanite, hematite, and magnetite [1]. None of the Type F crystalline phase minerals are reactive [1]. Where as, all but the last two minerals of the Type C fly ash are reactive [1]. Type C fly ashes are much more reactive and can have both hydraulic and pozzolanic reactions [1, 3, 4]. Whereas, Type F usually has only pozzolanic reactions [1, 3, 4].

2.1.6 Effect of Fly Ash on Water Requirements:

Fly ash addition will generally reduce water requirements in concrete mixtures [1, 19, 20]. There are three main reasons why the addition of fly ash will reduce water requirements. Firstly, the addition of fly ash will increase the packing density of the concrete [1, 21, 22]. The fine particles of fly ash pack into the spaces which would otherwise be filled with water, making it more compact (displaces the water from the spaces). The excess water increases the slump or workability of the concrete (for the same water to cement ratio), when compared to a normal Portland cement concrete without fly ash. Another way to look at this is that, the addition of fly ash will generally reduce the amount of water required to obtain a desired concrete slump consistency [10, 23]. It has been shown that the addition of fly ash can reduce the water requirements by 5-20 percent [1, 3]. This effect is increased as the degree of fly ash fineness increases [1]. Figure 2.1 shows the typical change in excess or free pore water as fly ash replacement levels and fineness increase, for a concrete with the same slump consistency.

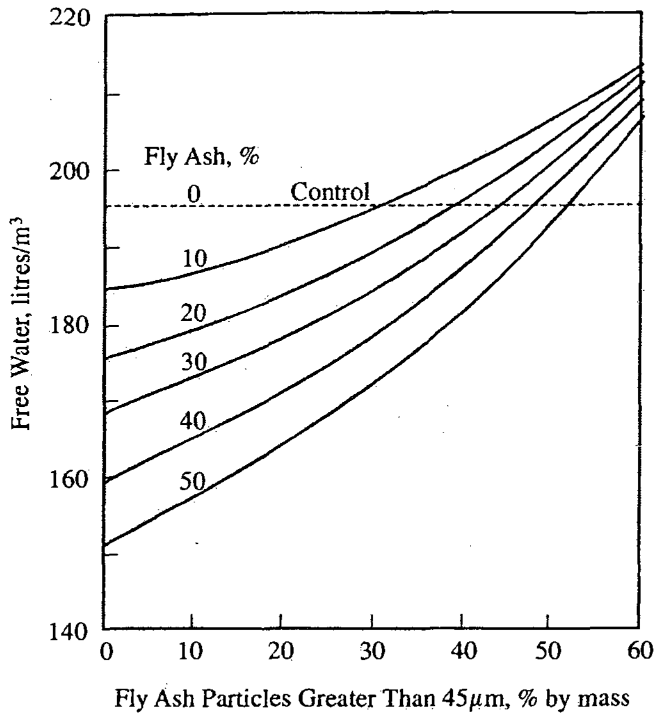


Fig 2.1 - Free water verses particle fineness for different fly ash replacement percentages [1].

Secondly, the smooth and spherical morphology of the fly ash particles cause what is termed a "ball bearing" effect, which makes the concrete more fluid (reduced friction) [1, 3]. Thirdly, electrical charges in cement particles cause them to flocculate to each other, causing water to be trapped inside the flocs [1]. The finely divided fly ash particles tend to gather (are adsorbed) over the surface of the larger cement particles, reducing attraction of the cement particles to each other [1, 3]. Reduced bleeding is also found in the concrete, because less water is required [5, 24]. Fly ash will also increase the cohesiveness of the concrete leading to reduced segregation [4].

2.1.7 Effect of fly Ash on the Hydration Process:

The silica and aluminum oxides of the fly ash react with calcium hydroxides (formed during the hydration process) to form calcium silicate hydrate and calcium silicate aluminate hydrate gel [7, 25]. Therefore, there are much lower calcium hydroxide concentrations in the pore water and cement paste when fly ash is used [26]. The addition of fly ash into a concrete mixture generally retards the hydration process or time of setting. Sufficient generation (time) of the hydration products between the Portland cement and water is needed, before the pH of the concrete rises high enough, to then cause activation (reaction) of the fly ash. The glassy material of the fly ash will not break down (activate) until the pH of the moisture in the pore structure has increased to around 13.2 [3]. Once the glassy material is activated it will form into a well compacted cement or otherwise known as aluminosilicate gel [27]. This is known as (termed) the alkali activation of fly ash [27].

2.1.8 Effect of fly Ash on the Strength of Concrete:

The variability of fly ash makes it difficult to predict the exact outcome of strength development. Testing is required for each specific fly ash type and percent replacement for a given concrete. Some general remarks can be made. The replacement of fly ash in a Portland cement concrete generally lowers the compressive strength compared to that of a Portland cement only concrete with the same mix proportions (same water to cement ratio) [3, 28 - 31]. The rate of strength gain is also slower than that of normal Portland cement [32].

Table 2.4 shows the compressive strength values, over time, of the average of six Type F and four Type C fly ashes. They all have replacement levels of 25 percent fly ash (of the Portland cement). One control made of only of Portland cement is also shown. The pure Portland cement concrete has higher strengths then both fly ash types, for all ages. Type C has higher compressive strengths than Type F, for most ages. The reason that Type C fly ash usually gains strength sooner, is because it contains higher calcium levels [1, 3]. The calcium oxide reacts hydraulically to form cementing compounds sooner. The value in compressive strength of a fly ash and Portland cement concrete can reach that of pure Portland cement concrete, after longer periods of time (curing) [33]. Care should be taken when early formwork removal is needed for fly ash cement concretes (can have lower early strength).

Table 2.4 – Compressive Strengths for Concretes made with Portland Cements and Portland Cement Concretes Made with 25 Percent Class F and Class C Fly Ash Replacement [3]

Cementitious material	*Compressive strength, MPa (psi) at age (days):*						
	1	*3*	*7*	*14*	*28*	*91*	*365*
Portland cement	12.1 (1750)	21.2 (3070)	28.6 (4150)	33.9 (4910)	40.1 (5810)	46.0 (6670)	51.2 (7420)
Class F fly ash (25%)	7.1 (1030)	13.9 (2010)	19.4 (2820)	24.3 (3520)	30.3 (4400)	39.8 (5770)	47.3 (6860)
Class C fly ash (25%),	8.9 (1290)	19.0 (2760)	24.1 (3490)	28.5 (4140)	29.4 (4260)	40.5 (5880)	45.6 (6620)

Although, pure Portland concrete generally has higher strength values, relative to a similar one containing fly ash, the incorporation of fly ash can still provide a concrete with adequate strength [1, 31, 33]. Moreover, many concretes containing fly ash incorporate the use of a superplasticizing agent to further reduce the water to cement ratio. This serves to increase the compressive strength [35, 36]. Figure 2.2 shows the compressive strength results for an ordinary Portland cement concrete which has (OPC +S) and has not (OPC) been superplasticized and a Portland cement concrete with a 20 percent replace of Type F fly ash which has (OPC +PZ +S) and has not (OPC +PZ) been superplasticized. The pure Portland cement concrete still outperforms the fly ash mixtures with or without the use of a superplasticizing agent. However, the superplasticized concrete containing fly ash is still impressive with high early strength. The use of fly ash with the use of a superplasticzer to reduce the water to cement ratio can have a higher compressive strength than to that of a pure Portland cement concrete [28, 37]. A recent study into the mixture proportioning methodology of concretes containing fly ash has shown that 7 day and 91 day compressive strengths of over 50MPa and 90MPa respectively can be achieved for fly ash replacement levels of 60 percent [38]. Another study, with fly ash replacements of 30 percent, found compressive strengths of over 80MPa and 100MPa for 28 day and 90 day test dates respectively [14].

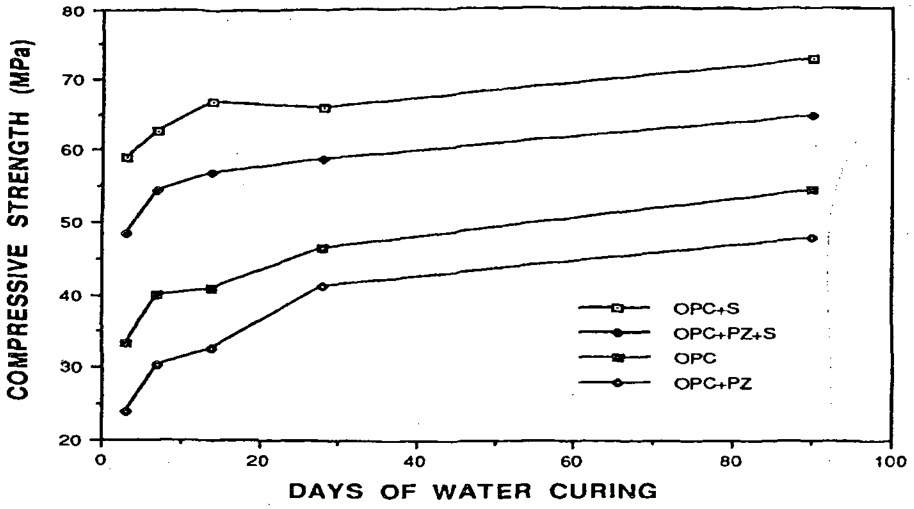


Fig 2.2 - Compressive strengths for concretes made with Portland cement and Portland cement with fly ash, both of which have and have not been superplasticized [35].

2.1.9 Effect of Fly Ash on Permeability:

The main ways in which fly ash reduces permeability are by particle packing effect, pozzlanic reactions, and reducing water requirements [1]. Generally speaking, fly ash Portland cement concretes are considered to be more and then less permeable relative to regular Portland cement concretes at early stages (~ 7 days) and later stages (~3 months) of concrete curing respectively [3, 39]. Permeability (chloride penetration) generally decreases with increasing fly ash replacements, given sufficient curing time [22, 29, 30, 33, 40, 41]. It has also been shown that permeability decreases with increasing fly ash particle fineness [32]. It has been shown that the use of both Type F and Type C fly ashes show good long term durability and resistance to chloride ion penetration [20, 42]. In one study of fly ash use in concrete, with replacements between 15 to 70% percent of

Portland cement, showed good resistance to chloride permeability after one year (low coulomb readings <1000 coulombs) [43]. However, the concrete made with 70 percent fly ash replacement had fairly high coulomb reading early on at 2 months [43]. This is shown in Figure 2.3.

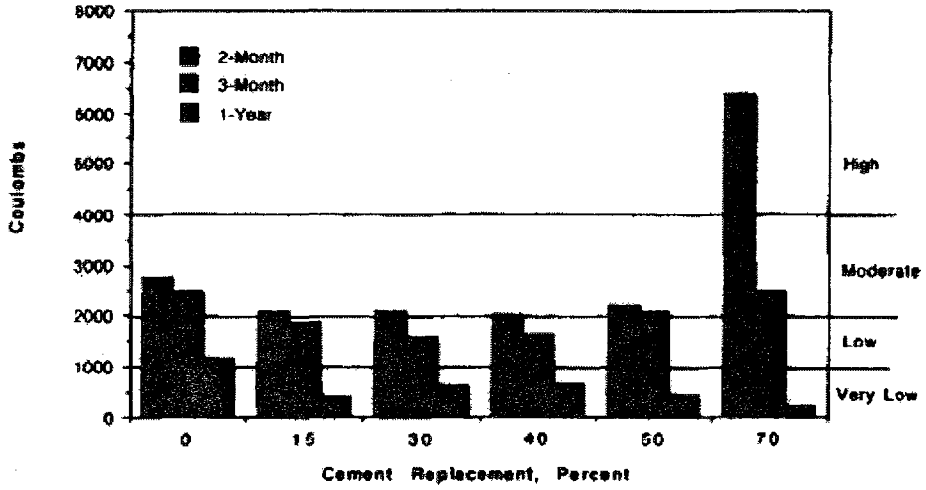
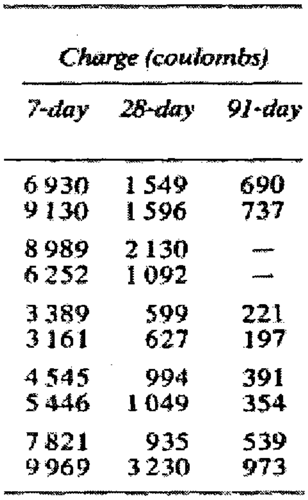


Fig 2.3 - Coulomb readings for different fly ash replacement percentages at 2, 3, and 12 months of curing [43].

In another study of fly ash use in concrete, with different types of fly ashes at replacements between 54 to 58 percent, all the mixtures showed good resistance to chloride ion penetration after 91 days (<1000 coulombs), shown in Table 2.5 [44].

Table 2.5 - Coulomb Readings for Different Fly Ash Types [44]



Charge (coulombs)		
7-day	*28-day*	*91-day*
6 930	1 549	690
9 130	1 596	737
8 989	2 130	—
6 252	1 092	—
3 389	599	221
3 161	627	197
4 545	994	391
5 446	1 049	354
7 821	935	539
9 969	3 230	973

2.2 Silica Fume:

2.2.1 Description of Silica Fume:

Silica fume is a by-product of the production of silicon and ferrosilicon alloys. High-purity quartz and coal are combined in an electric arc furnace and heated to temperatures of 2000°C to produce these alloys [3, 24, 45]. In the United States, nearly 20 thousand tonnes of silica fume is used in the construction industry per year [24]. The worldwide use is over 150 thousand tonnes [24]. Filters are used to collect the silica particles which condense in the cooling combustion gases. The silica fume particles are described as amorphous (glassy) and spherically shaped [3, 24]. The particles are about 0.1-0.12μm in diameter, almost 100 times smaller than a cement grain (15μm). The surface area of silica fume is in the range of 15,000-25,000m^2/kg and has a specific gravity of about 2.2 [3, 5, 24]. Silica fume is highly pozzolanic which is largely due to its extreme fineness [3]. Concretes containing silica fume have high strength and durability (high chloride penetration resistance) [34, 46]. The chemical composition of silica fume is over 90% SiO_2 for silicon alloys. Ferrosilicon alloys have somewhat lower SiO_2 levels and contain varying levels of Fe_2O_3 and are considered less pozzolanic [3, 45]. This use of silica fume is limited to special projects because it has low availability and therefore high costs [24].

2.2.2 Silica use in concrete:

Silica fume is used because it is known to decrease permeability and increase the strength of concrete [41, 47]. Silica fume fills void spaces between the larger cement particles which would otherwise be occupied by water [4, 5, 24, 45]. It is usually used at replacement levels of 5 – 10% of that of the mass of the cement binder [5]. It has been shown that replacement of 10% of the cement binder with silica fume can decrease the water permeability coefficient from 1.6×10^{-5} to 4×10^{-8} cm/s [24]. The large surface area of the silica fume causes it to adsorb more water, therefore, increasing the water requirements in the concrete mix [24]. Usually, the addition of water reducing admixtures is incorporated into the concrete mix design when silica fume is used. The fineness of the silica fume makes the concrete more cohesive which reduces bleeding and segregation of the fresh concrete.

2.3 Corrosion of Steel Reinforcement:

It has been said: “Paradoxically, modern concrete structures, with metallic reinforcements, are less durable than the ancient un-reinforced concrete structures” (Roman structures) [48]. Corrosion of metallic rebar is the most significant and widespread deteriorative process suffered by reinforced concrete structures [49]. Most of the reported failures of reinforced concrete structures are seldom attributed to mechanical failure, but large numbers are caused by the corrosion of reinforcing rebar [9]. The rehabilitation cost due to corrosion of rebar in reinforced concrete structures in the U.S.

alone, was estimated to cost between 350 billion to 1 trillion American dollars per year [6, 12].

The word corrosion is derived from the Latin word *corrodere* meaning: "to gnaw to pieces" [50]. Corrosion in metals is the process by which they return from a high energy state to a lower one [4]. There are few metals that are naturally found in their metallic state except for the noblest ones such as gold, silver and copper. Manufactured metallic metals (steel) require the input of large amounts of energy for their production. Therefore, they are less stable and will eventually corrode. Resistance of reinforcing rebar in concrete to corrosive elements is dependent on the type of reinforcing steel used, and the pH of the pore water found in the concrete (high pH protects steel) [51]. The availability of corrosive elements to the reinforcement is determined by the ability of the concrete cover layer, between the outside surface and the steel rebar, to resist the penetration of these elements (chlorides, water and oxygen) [51]. This is a function of the concretes cover's permeability and thickness [51, 52].

2.3.1 Steel Rebar:

Rebar is available in many different types of steel alloys. Plain carbon steel is composed mainly of iron and less than about 2 percent of carbon. The carbon serves to strengthen the steel, however, this also makes it less ductile. Other metals such as: chromium, manganese, tungsten, vanadium or molybdenum can also be used in varying proportions to produce a wide range of steel alloy grades with different properties (increased corrosion resistance, increased yielding and strength limits) [12]. One of the best types of steel alloys used to prevent corrosion is stainless steel; however it is very expensive [3, 6, 12]. Stainless steel can be used throughout a structure or can be used selectively in parts of a structure that are the most likely to suffer from corrosion [6]. Stainless steel is commonly used by the Ontario Ministry of Transportation in components of structures which are exposed to severe conditions such as expansion joints, dams, barrier walls, and sidewalks [53]. Stainless steel is extremely durable in corrosive environments, because they have what is commonly described as a protective passivity layer which is "self healing" (It will reform itself if scratched). Stainless steels generally reduce the long term rehabilitation costs and increase the initial capital costs [3]. Steel rebar may also undergo various surface treatments such as epoxy-coating and galvanization processes which can also help in the protection against corrosion. The use of various steel alloys and different surface treatments, have all been shown to be effective in adding to the resistance of corrosion under the right conditions [3]. However, in a recent study by the Ontario Ministry of Transportation, the use of epoxy-coated rebar has been shown to have poorer performance (shorter service life of only 20 years for some bridges) than was expected (75 years); its use has been discontinued in some jurisdictions [53]. For example, the Perley Bridge found in Hawkesbury, Ontario had an epoxy-coated rebar deck installed in the year 1979 which then had to undergo extensive rehabilitation in 1998, due to delamination of the road surface caused by corrosion of the epoxy-coated rebar [53]. Regular carbon steel is the most widely used type of steel currently placed in reinforced concrete structures, because of its availability and low initial cost [23]. However, carbon steel will easy corrode under aggressive exposure conditions.

2.3.2 Alkalinity Protection of Steel Rebar:

Embedded carbon steel rebar in concrete is normally protected from the process of corrosion by the high pH of the pore water of the concrete. The pH is normally above 12 for Portland cement concrete, commonly in the range of 12.6 to 13.5 [3, 12, 45]. This high pH causes the formation of a passive gamma iron oxide film layer (γ-Fe_2O_3) which surrounds and protects the steel inside this layer from reacting with outside elements [45, 54]. Corrosion of the steel rebar can occur when this film is removed or penetrated [3]. This primarily occurs from the processes of carbonation and chloride attack [1, 4, 6, 49].

2.3.3 Carbonation:

Carbonation is mainly caused by atmospheric carbon dioxide reacting with calcium hydroxides found in the cement to form calcium carbonates [5]. Sulfur oxide, nitrogen oxide and carbonic acid are also known to cause carbonation [55]. The carbonation process does not actually directly cause the steel rebar to corrode [3]. Carbonation lowers the pH of the concrete to around 6 to 9 [3, 5, 12]. This process commences from the outer surfaces of the concrete and progresses inwards over time, at a rate of about a few millimeters a year [54]. If the carbonated concrete reaches the steel rebar, the lowered pH levels cause the removal of the protective passive oxide layer around it. This process can cause chloride induced corrosion to initiate sooner (at lower concentrations) [3 - 5]. It has been shown that for concretes containing high volumes of fly ash which have low water to cement ratios (high strength) and have been well cured, carbonation is not an issue [56, 57, 58]. In one study, a concrete containing 50 percent fly ash replacement, with 45 MPa strength, had a predicted service life of 100 years based on carbonation [59]. In another Study, the depth of carbonation was only 4mm after three and a half years for a concrete containing fly ash [58]. This is due to the dense structure and low permeability of this type of concrete [56].

2.3.4 Chloride Attack:

Chloride induced corrosion of steel rebar is caused by ingress and gradual build up of free chloride ions inside the capillary pore structure of the concrete [8]. Generally speaking, the intensity of steel corrosion increases with an increase in chloride concentrations [60]. These chlorides are soluble and travel throughout the moisture found in the capillary pore structure of the concrete. Chloride ions will attack and penetrate the protective oxide film surrounding the rebar. Over time, once chloride concentration levels have reached certain threshold values, deterioration of the passive layer will commence. This process can cause localized pitting to occur as shown in Figure 2.4. The reactions are as follows [3]:

$$Fe^{++} + 2Cl^{-} \rightarrow FeCl_2$$

$$FeCl_2 + 2H_2O \rightarrow Fe(OH)_2 + 2HCl$$

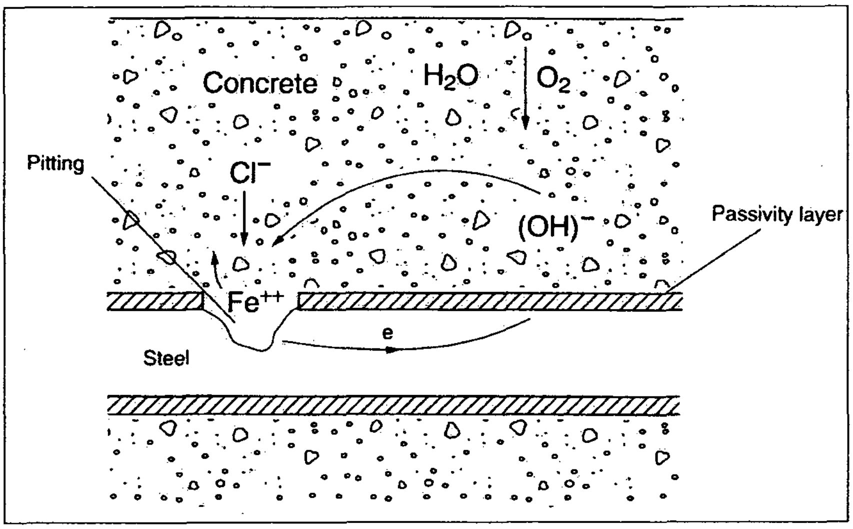


Fig 2.4 - Process of pitting [3].

2.3.5 Chlorides in concrete:

Chlorides can be found in concrete in two ways, namely bound or free. Bound chlorides are trapped and cannot move inside the concrete. They can be chemically or physically bound. Bound chlorides are not available for the corrosive reaction with steel. It is only the free chlorides which may contribute to the corrosion of steel rebar, at a given time. Bound chlorides can become unbound by processes which lower the pH (carbonation) [12].

2.3.5.1 Bound Chlorides:

Chlorides become chemically bound by reacting with the hydration products of the cement. There are two main hydration products that the chlorides will react with to become bound. The first, is a reaction with the products C_3A to form calcium chloroaluminare ($3CaO.Al_2O_3.CaCl_2.10H_2$) also known as "Friedel's salt" [3]. The second is a reaction with the products C_4AF to form calcium chloroferrite ($3CaO.Fe_2O_3.CaCl_2.10H_2O$) [3].

Physically bound chlorides are the ones which collect and are trapped (adsorbed) on the surfaces of the gel pores of the cement matrix [3]. In Figure 2.5 a model of the cement paste is shown. The black dots represent the gel particles (crystallized hydrates) and white areas represent voids. The gel pores are the small white spaces (voids) between the gel particles in the Figure [3].

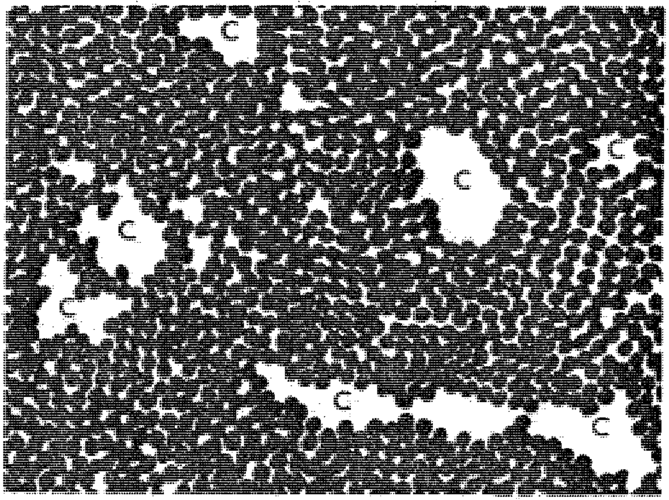


Fig 2.5 - Representation of cement paste matrix [3].

2.3.5.2 Free Chlorides:

Free chlorides ions are found in the larger capillary pore structure of the cement matrix (shown by the larger white spaces labeled “C” in Figure 2.5). They are free in the sense that the soluble chloride ions can travel throughout the network of interlinked capillary pores of the concrete, provided there is sufficient moisture levels [3].

2.3.6 Sources of chlorides:

Bound chlorides usually result from the incorporation of chlorides into the mixture of the fresh concrete. They may come from chemical admixtures (calcium chloride), contaminated water, or aggregates [3].

The main source of free chlorides is from externally soluble chlorides which penetrate through the surface and to a lesser extent from chlorides which may have been incorporated into the mix, which have not become bound by the hydration process [3]. External chlorides mainly come from the use of de-icing salts ($NaCl$ or $CaCl_2$) placed on roadways and from contact with seawater or seawater spray [3]. It has been shown that the incorporation of fly ash into the concrete mix increases the percentage of bound chlorides and reduces the amount of free chlorides (the fly ash activation products trap the chloride ions), provided it has been well cured [61].

2.3.7 Mechanisms of Corrosion:

To understand the process of corrosion it is useful to use a simplified and theoretical model as the one shown in Figure 2.6. The Figure depicts an electrochemical cell, similar to process found in reinforced concrete which suffers from corrosion. For the process of corrosion to progress, the presence of anodic and cathodic sites must exist. The anode site involves the oxidation of the iron in the rebar which causes releases of electrons [3, 5, 45]. The reaction is:

$$Fe \rightarrow Fe^{++} + 2e^-$$

The anode and cathode must be joined together to complete the cell. The electrons which have been released at the anode travel easily through a metallic (electronic conductor) connection and are consumed at cathode sites. Hydroxide ions are then formed at the anodic site when the electrons fuse with the oxygen and hydrogen found in the solution [45]. The hydroxyl ions then flow through an electrolyte (ionic conductor) from the anode to the cathode, completing the cycle.

The reaction is:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

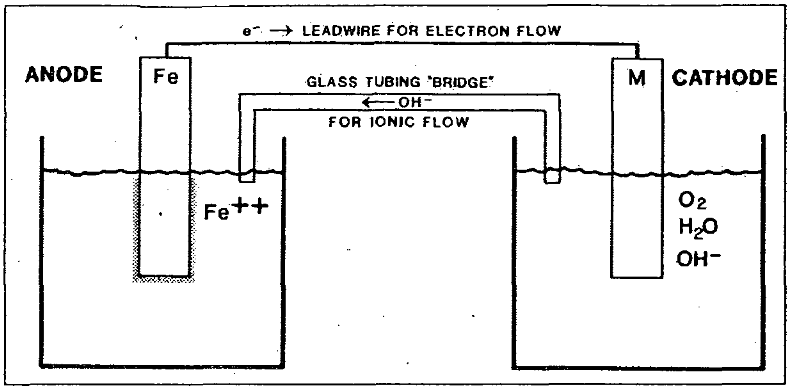


Fig 2.6 - Theoretical model of the corrosion process [54].

The actual process is more complex in real life, however the principles are similar. The reactions are shown in Figure 2.7.

anodic reactions:

$$\begin{aligned} \mathrm{Fe} &\rightarrow \mathrm{Fe}^{++} + 2e^{-} \\ \mathrm{Fe}^{++} + 2(\mathrm{OH})^{-} &\rightarrow \mathrm{Fe(OH)}_2 \quad \text{(ferrous hydroxide)} \\ 4\mathrm{Fe(OH)}_2 + 2\mathrm{H}_2\mathrm{O} + \mathrm{O}_2 &\rightarrow 4\mathrm{Fe(OH)}_3 \quad \text{(ferric hydroxide)} \end{aligned}$$

cathodic reaction:

$$4e^{-} + \mathrm{O}_2 + 2\mathrm{H}_2\mathrm{O} \rightarrow 4(\mathrm{OH})^{-}.$$

Fig 2.7 - Anodic and cathodic reactions [3].

Anode sites are located where the passivity layer has been removed, commonly where pitting of the rebar has occurred, as discussed previously (i.e. Figure 2.4) [9]. Once the passive layer has become penetrated, the iron inside the steel is exposed to elements, in the pore solution, to form the corrosion products which we commonly refer to as "rust". The "rust" products formed at the anode are more specifically described as "the collective sum of the complexes of ferrous (Fe++) and ferric (Fe+++) oxides, hydroxides, chlorides and hydrates" [4]. Anodic regions become increasingly acidic and cause chloride concentrations to increase as the corrosion process proceeds. Anodic areas become more acidic because of the hydrolysis of the corrosion products [9]. The negatively charged chloride ions are attracted to positive anodic areas, which contributes to further depassivation [9]. This reaction releases electrons which travel easily through the rebar itself, or other steel wires which hold the rebar in place (bolsters and bar chairs), to the cathode sites.

The process of corrosion in reinforced concrete is dependent on the presence of moisture and oxygen. The concrete serves as an electrolyte for the movement of hydroxide ions. The hydroxyl ions formed at the cathode sites must travel through the moisture found in the capillary pore structure of the concrete (shown in Figure 2.8).

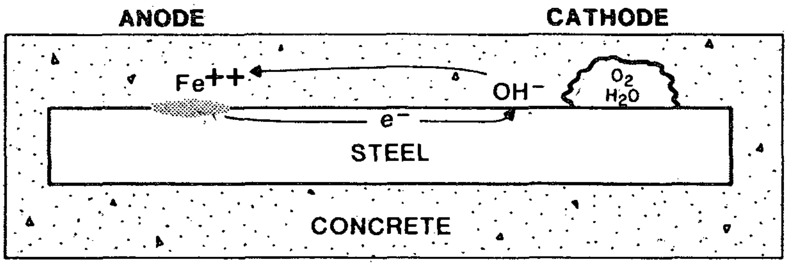


Fig 2.8 - Electrochemical cell formed in reinforced concrete [54].

There will be little corrosion if the concrete is fairly dry with moisture levels below 60 percent relative humidity even at high chloride concentration of up to 5kg/m^3 [3, 62].

The optimum moisture level for the formation of corrosion in reinforced concrete is between 70 to 80 percent relative humidity [3]. Because oxygen is consumed in the reaction at the cathode, the cathode regions are usually located in dryer areas of the concrete element(s). Air permeability is known to decrease as the moisture content increases (this is because the capillary pores are filled with water) [63]. As illustrated below in Figure 2.9, if the entire reinforced concrete element is submerged there is much less oxygen. Therefore, the corrosion potential is decreased. When the structure is partially submerged, the cathode area will generally form above the water surface [12]. In Figure 2.10, cathodes are usually formed in dryer areas, potentially where rebar is exposed from cracking.

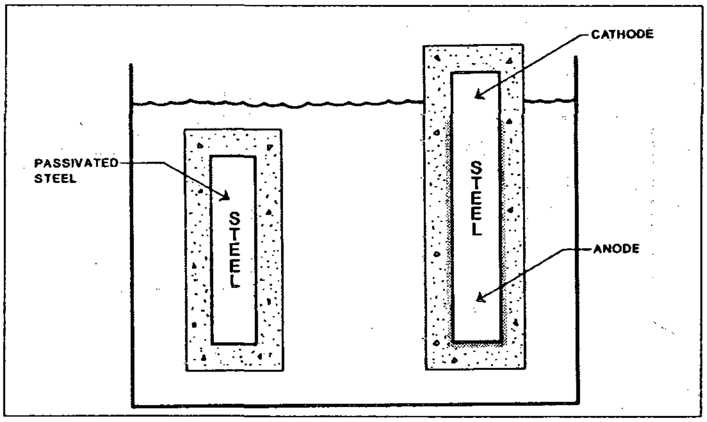


Fig 2.9 - Representation of a reinforced concrete structure which is submerged or partially submerged [54].

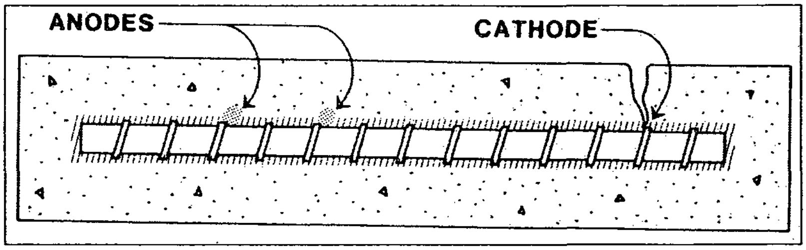


Fig 2.10 - Representation of potential anodic and cathodic areas along a rebar [54].

What normally "drives" the cell is the potential differences caused by differing concentrations of chloride ions, hydroxide ions, and oxygen [4, 45]. As stated, electrons can flow easily through the metal of the rebar. What determines largely the rate or speed of corrosion, is the ease at which ions can flow through the capillary pores of the concrete [45]. This is commonly referred to as the "resistance of the cell" [45]. The governing factor determining resistance or corrosion rates is permeability (moisture content, pore structure and pore water composition) [3, 15, 12, 24, 45]. A low resistance concrete would have higher permeability and a higher rate of corrosion.

2.3.8 Example of Chloride Induced Corrosion:

Figure 2.11 depicts one of the common case situations where corrosion of embedded steel rebar frequently occurs. It is typical of a bridge deck, ramp or floor of a parking garage, where roads salts are used. Water and chloride ions enter into the concrete from the wet surface (puddles) on top of the concrete slab. The steel rebar mat, located in the top part of the slab forms into the anodic region. High levels of moisture and chloride ions cause the removal of the passive layer and expose the iron in the steel rebar to the surrounding hydroxide ions. The electrons flow easily from the anodic site down through the connected rebar (or holding wires and other bent bars) down to the lower mat. The lower mat is where the cathodic region is located. The bottom surface of the slab is drier which allows oxygen to enter through it easier. It has been shown that the use of cement containing fly ash and silica fume can increase the durability and strength of concretes used in bridge decks [64, 65].

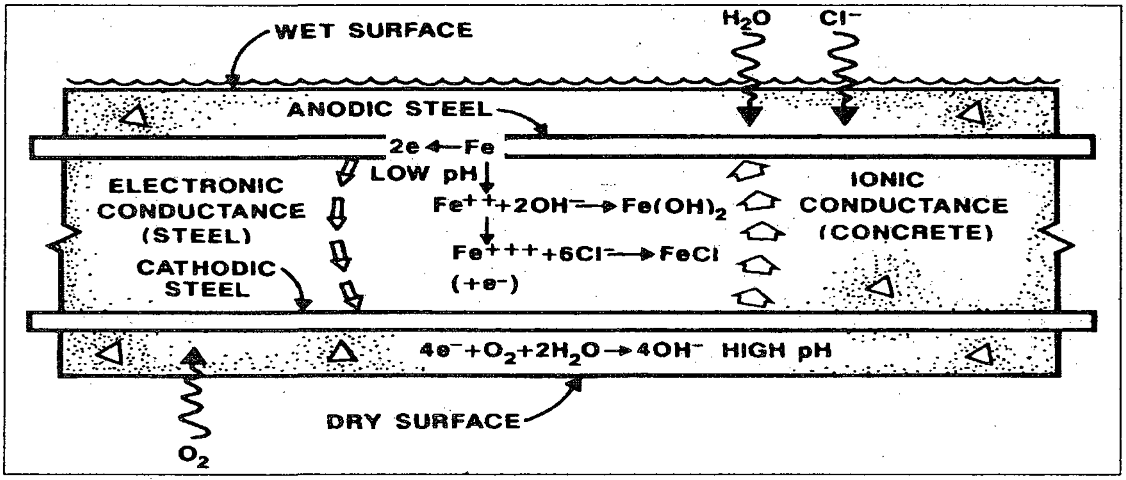


Fig 2.11 - Depiction of the corrosion process in the deck of a bridge [4].

2.3.9 Structural Damage of Reinforced Concrete due to Steel Corrosion:

Two predominant reasons, in which corrosion of the steel reinforcement is harmful to reinforced concrete structures is caused by the reduction in the cross sectional area of rebar and from the associated volume increases associated with the process of corrosion [9]. Pitting and corrosion reduce the cross sectional area of the reinforcing steel rebar, which thus reduces the strength and ductility of the structure [49, 66, 67]. The products of steel corrosion can occupy a volume of over 600 percent or more than the original steel rebar [3]. Such volume increases are restricted by the surrounding hardened concrete. Stresses build up in the concrete until they can no longer be held. This results in the cracking, spalling and delamination of the outer cover of concrete (As shown in Figure 2.12). Removal or cracking of the concrete cover will allow for increased access by corrosive elements into the concrete, potentially causing a further increase in the rate of corrosion.

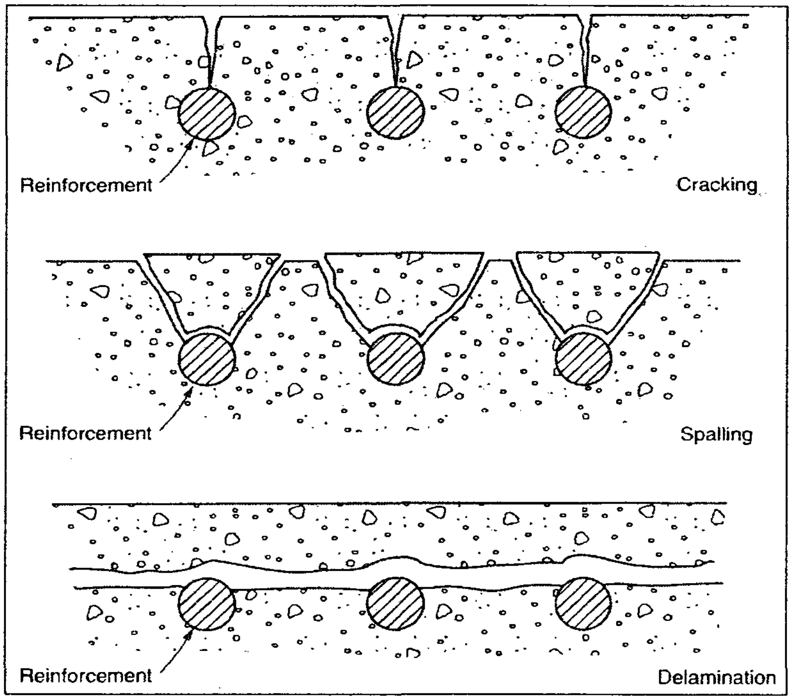


Fig 2.12 - Reinforced concrete suffering from cracking, spalling, and delamination [3].

Another important reason why corrosion of steel is harmful to structures is due to bond deterioration and loss of anchorage between the rebar and the concrete, and the associated decrease in the maximum load which can be sustained [49, 68, 69]. As the rebar becomes "rusted" the bond between the concrete and rebar is diminished. The bond between the rebar and concrete is important because tensional stresses in the concrete elements are transferred to (held by) the reinforcement through the shear force generated between the ribs of the rebar and the concrete [69, 70]. The rebar could potentially loose anchorage with the concrete surface (slip), with potentially disastrous effects.

2.3.10 Chloride Concentration Threshold Levels:

For the removal of the protective oxide layer, chloride concentration levels must reach certain threshold values at the surface of reinforcement [9]. An exact value is difficult to determine, because it is dependent on the exposure conditions and the type of cement used. The chloride concentration itself is dependent on the depth from the surface of the concrete. Some of the chloride threshold values, found by various researchers, for the inducement of corrosion are listed in Table 2.6.

Table 2.6 - Chloride Concentration Thresholds [71]

Researcher(s)	**Year**	**kg/m^3 of concrete**
Lewis	1962	0.7
Hausmann	1967	0.2 - 2.8
Berman	1972	0.77
Clear and Hay	1973	0.6 - 0.9
Clear	1974	0.66
Stratfull, Jaukovich, and Spellman	1975	0.66
Cady	1978	0.6 - 1.3
Browne	1982	1.33
Pfeifer, Landgren, and Zoob	1986	0.5 - 0.9

The chloride threshold is largely dependant on the pH of the pore water in the concrete. At lower pH values (potentially caused by carbonation) the chloride ions can penetrate the passivity layer of the rebar at lower concentrations levels, as shown in Figure 2.13 [3, 15].

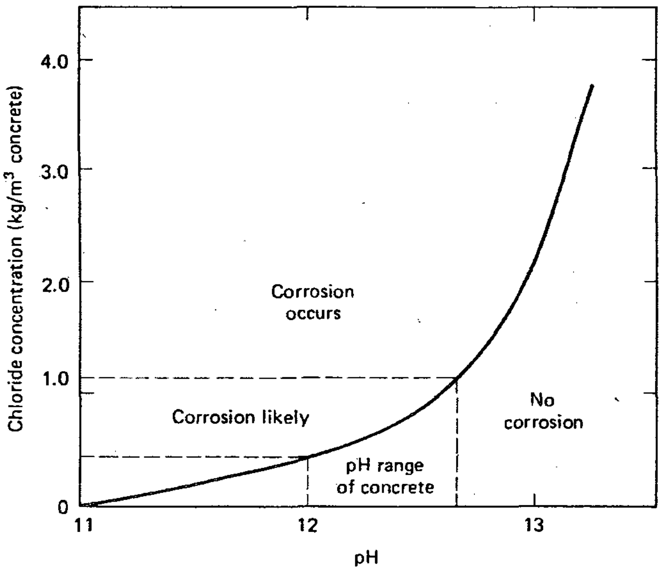


Fig 2.13 - Effect of Chloride Concentration versus pH Levels on Corrosion likelihood [15].

It is generally believed that depassivation will commence once the ratio of chloride ions to hydroxide ions has surpassed 0.6 [45, 72]. It has also been shown that fly ash may reduce the pH of the capillary pore water. Hydroxide ions are consumed during pozzolanic reaction of the fly ash [26, 73, 74]. Because the hydroxide ion concentration is lowered, the corrosion threshold ratio of chloride ions to hydroxide ions would increase

[74]. However it has also been shown that the benefits in reduced permeability, due to fly ash addition, outweighs this negative effect [73].

The chloride concentration levels are highest on surfaces which have been exposed the most to chlorides, and decrease inwards (depth from surface) [9]. One way for determining the potential (theoretical) chloride concentration for a given exposure duration and depth, is by using Fick's second law of diffusion [9]. It is given as:

$$\frac{\partial C_{x,t}}{\partial t} = D_c \frac{\partial^2 C_{x,t}}{\partial x^2}$$

where $C_{x,t}$ is the chloride concentration at depth, x, at time, t,
D_c is the chloride diffusion coefficient of the concrete,
x is the depth from the exposed surface of the piles,
and t is the exposure duration.

Fig 2.14 - Fick's second law of diffusion [75].

From the solution of Fick's law, theoretical curves for the chloride concentration versus depth, for different exposure times can be created for a variety of conditions (seawater salt concentration and cement type). A good example where this has been used, is a case involving concrete piles which were extracted from a Singapore harbor. Figures 2.15 through 2.17, show the chloride concentration profiles for the atmospheric, tidal, and submerged zones of the concrete piles respectively. These graphs were verified by taking chloride readings at different depths and locations along the length of the actual piles removed from the harbor, and were shown to have good correlation. The upper part (atmospheric zone) of the pile is subjected only to sea spray/splashing and remains much drier than the other two zones. This zone was described by the researchers as having the least amount of corrosion [75]. The tidal zone would be between the high and low level marks of the sea tide and was shown to have the highest chloride concentrations and structural damage. The main reason that the chloride concentration is high in the tidal zone is due to the alternating drying and wetting conditions which causes capillary absorption (suction) of chlorides (chlorides are "drawn" into the concrete as it dries) [3, 12, 49, 75]. This zone is similar to the example depicted in Figure 2.11, about the bridge deck being cyclically exposed to road salts under alternating wetting and drying conditions. The researchers describe some of the piles in the tidal zone as spalled with visibly corroded rebar, missing links, cracks and rust stains running the length of the rebar [75]. It has been shown that the chloride concentration of the capillary pore water can actually be higher than that of the seawater [3]. The submerged zone would always be underwater, therefore constantly saturated. One would think that this area would have the highest concentrations, however it does not suffer from this absorption effect. The researchers of the project described the submerged section as being in good condition with no cracks with lower amounts of rust stains [75]. It has been shown that a concrete exposed to constant moisture conditions will have less chloride ingress than that exposed to cyclic wetting and drying condition [76]. The Singapore study also found chloride threshold values for the initiation of corrosion at 0.025 and 0.05 percent of the mass of concrete (0.575kg/m^2 and1.15kg/m^2) for the atmospheric and tidal/submerged zones respectively. The chloride corrosion inducement thresholds can vary, even within the same structure.

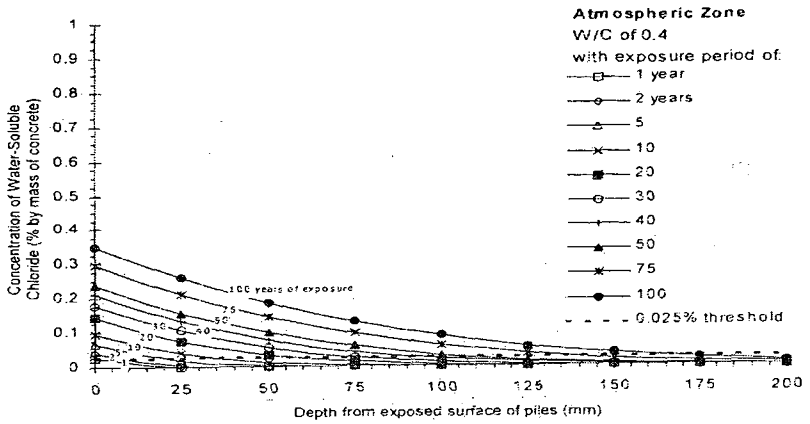


Fig 2.15 - Chloride concentration profiles for the atmospheric zone of the piles [75].

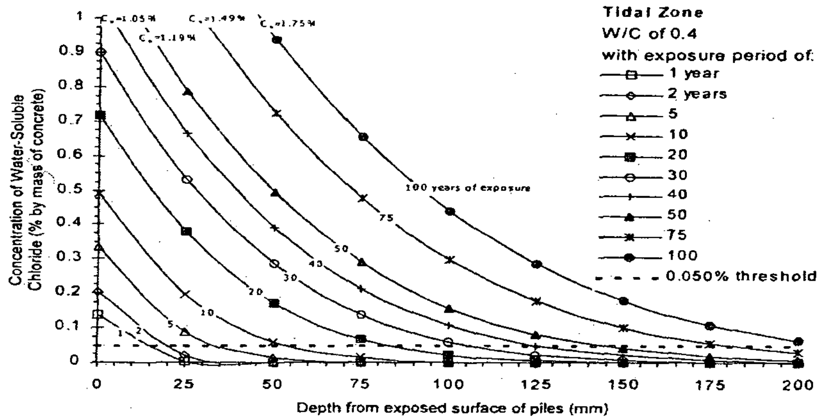


Fig 2.16 - Chloride concentration profiles for the tidal zone of the piles [75].

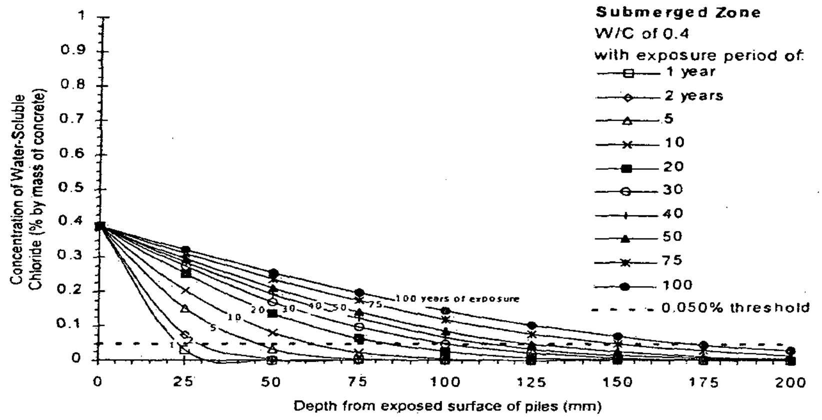


Fig 2.17 - Chloride concentration profiles in the submerged zone of the piles [75].

A study by the Norwegian Public Roads Administration of the Gimøystraumen Bridge found that the chloride concentrations varied considerably at different locations tested throughout the structure. The bridge is located along the harsh Norwegian coastline and is subjected to continued weathering from the sea. The study's goal was to produce a detailed "map" of the chloride concentrations in the concrete bridge [77]. To do this, 900 chloride-ion profiles were taken from the bridge [77]. The study concluded the chloride ion concentration levels were controlled by four factors. The first is the height above sea level, high chloride concentrations of over 1.0 ($3kg/m^2$) percent of the cement weight were found at heights up to 15m above sea level [77]. The second is windward/leeward effect, the leeward sides were defined as being sheltered from wind and precipitation [77]. It was found that leeward sides had chloride concentration about twice as high as the windward sides [77]. The third is the size and shape of exposed surfaces, it was found that the chloride ingress was about three and a half times higher closer to the columns than to that of the mid-span of the bridge [77]. This could be related to drainage f water from the road surface. The fourth is the micro climate (temperature, humidity) at the bottom of the columns; the chloride levels were high in this area [77]. The study also carried out extensive studies of over 300 bridges exposed to marine conditions, and concluded that chloride concentrations were much lower and took longer to reach the rebar in concretes which have lower water to cement ratios, with additions of fly ash and silica fume (<25 percent replacement) [77]. It was also concluded in a recent CANMET study, of concrete panels which were exposed to 10 years of arctic marine environmental exposure, that the use of fly ash (20-25 percent replacement) and silica fume (up to 10 percent replacement) or a combination of the two had a better resistance to chloride ion penetration than to that of purely Portland cement concrete [78].

2.3.11 Chloride Limitations:

There are maximum limitations placed on the amount of chlorides which can be present in the concrete. There are two approaches which can be taken in determining limitation values. The first, limits the total chloride content or the sum of the bound and free chloride in the concrete. The European Standard limits the maximum of the total chloride content to under 0.4 percent of the mass of concrete [3]. The second, places limits on only the free chlorides found in the concrete. In Canada and the US, the maximum allowable concentration of the water soluble (free) chloride ions in concrete is 0.15 percent of the mass of concrete (summarized in Table 2.7). The requirements placed on prestressed concrete elements are even more limiting. Because the wire cables are so highly stressed, a problem known as "stress corrosion cracking" can occur [4]. An equivalent loss in the cross-sectional area in prestressed cable can be more catastrophic, compared to regular rebar [4].

Table 2.7 - Maximum Chloride Levels in Concrete [5]

Type of member	**Maximum water soluble chloride ion (Cl^-) in concrete, percent by mass of cement**
Prestressed concrete	0.06
Reinforced concrete exposed to a moist environment or chlorides or both	0.15
Reinforced concrete exposed to neither a moist environment nor chlorides	1.00

* Requirements from CSA A23.1-Section 15.1.6.

2.3.12 Classification of Exposure Conditions and Requirements:

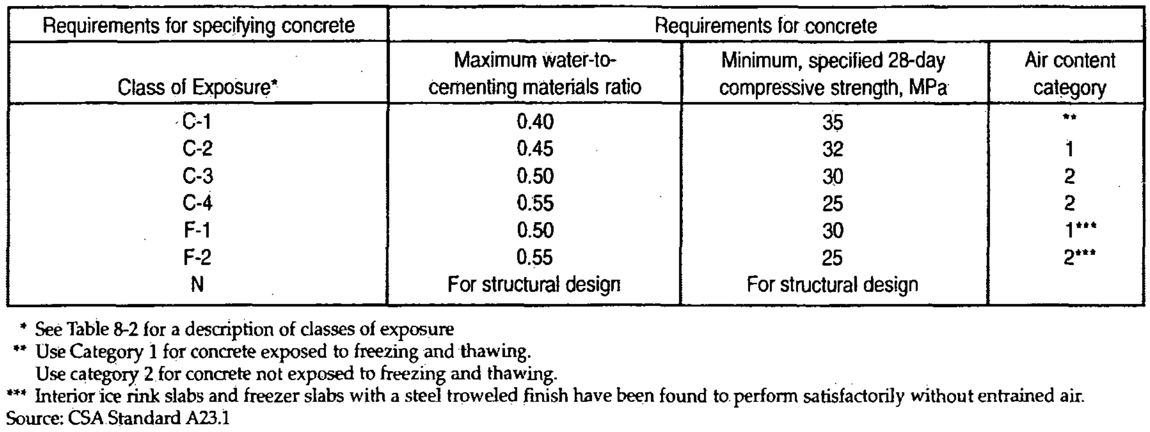
The CSA Standard A23.1, lists certain exposure conditions which may be suffered by concrete structures (summarized in Table 2.8). Depending on these conditions, they are classified into the different categories (C-1, C-2, C-3, C-4, F-1, F-2, N). Depending upon the classification, certain requirements must be satisfied to ensure and maintain the durability of the structure (summarized in Table 2.9 and Figure 2.21).

Table 2.8 - Concrete Exposure Condition Classification [5]

C-1	Structurally reinforced concrete exposed to chlorides with or without freezing and thawing conditions. *Examples:* bridge decks, parking decks and ramps, portions of marine structures located in tidal and splash zone
C-2	Non-structurally reinforced (plain) concrete exposed to chlorides and freezing and thawing. *Examples:* garage floors, porches, steps, pavements, sidewalks, curbs and gutters
C-3	Continuously submerged concrete exposed to chlorides but not to freezing and thawing. *Examples:* underwater portions of marine structures
C-4	Non-structurally reinforced concrete exposed to chlorides but not to freezing and thawing. *Examples:* underground parking slabs on grade
F-1	Concrete exposed to freezing and thawing in a saturated condition but not to chlorides. *Examples:* pool decks, patios, tennis courts, freshwater pools, and fresh water control structures
F-2	Concrete in an unsaturated condition exposed to freezing and thawing but not to chlorides. *Examples:* exterior walls and columns
N	Concrete not exposed to chlorides nor to freezing and thawing. *Examples:* footings and interior slabs, walls and columns

Notes:
(1) "C" classes pertain to chloride exposure.
(2) "F" classes pertain to freezing and thawing exposure only.
(3) "N" class pertains to nonexposure to either chlorides or freezing and thawing.
Source: CSA Standard A23.1

Table 2.9 - Requirements for the Class of Exposure [5]



Requirements for specifying concrete	Requirements for concrete		
Class of Exposure*	Maximum water-to-cementing materials ratio	Minimum, specified 28-day compressive strength, MPa	Air content category
C-1	0.40	35	**
C-2	0.45	32	1
C-3	0.50	30	2
C-4	0.55	25	2
F-1	0.50	30	1***
F-2	0.55	25	2***
N	For structural design	For structural design	

* See Table 8-2 for a description of classes of exposure

** Use Category 1 for concrete exposed to freezing and thawing.
Use category 2 for concrete not exposed to freezing and thawing.

*** Interior ice rink slabs and freezer slabs with a steel troweled finish have been found to perform satisfactorily without entrained air.

Source: CSA Standard A23.1

2.3.12.1 Requirements on Water to cement Ratio:

For the case of reinforced concrete exposed to chlorides C-1, a maximum water cement ratio of 0.4 is required. The effect of lowering the water to cement ratio, is to lower the permeability of the concrete and increase strength. With a lower amount of water in the mix, the concrete will be denser with fewer voids and less permeable. Figures 2.18 and 2.19 show the effect of varying water to cement ratio on strength and permeability respectively. The strength decreases and permeability increases as the water to cement ratio increases.

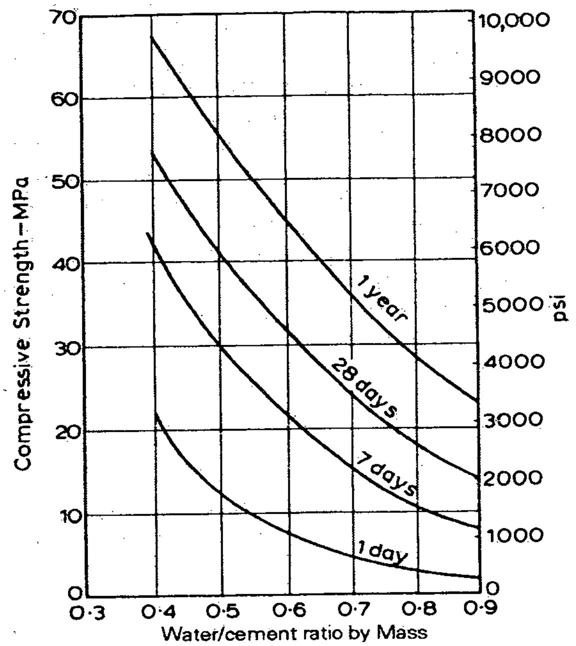


Fig 2.18 - Compressive strengths for concretes made with varying water to cement ratios [3].

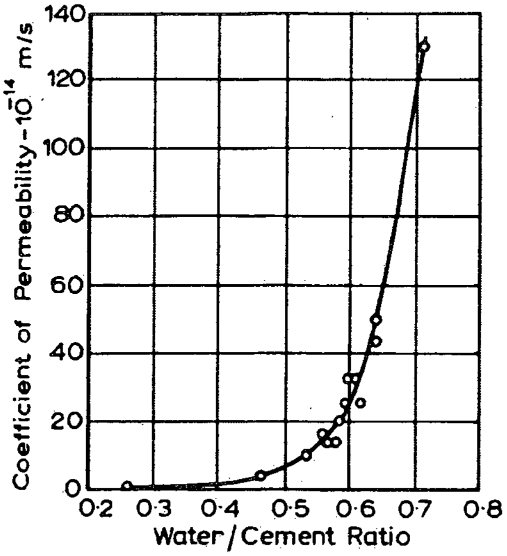


Fig 2.19 - Permeability coefficient for concretes made with varying water to cement ratios [3].

It has also been shown that to improve long-term durability, the rebar and concrete interface should be free from voids [79]. At high water to cement ratios, water can gather on the underside of rebar (wall-effect) where corrosion is more likely to occur [1]. Figure 2.20 shows the results obtained from the Rapid Chloride Permeability Test for a concrete of varying water to cement ratio. The test (RCPT) assumes a correlation between increasing cumulative charge and increase permeability.

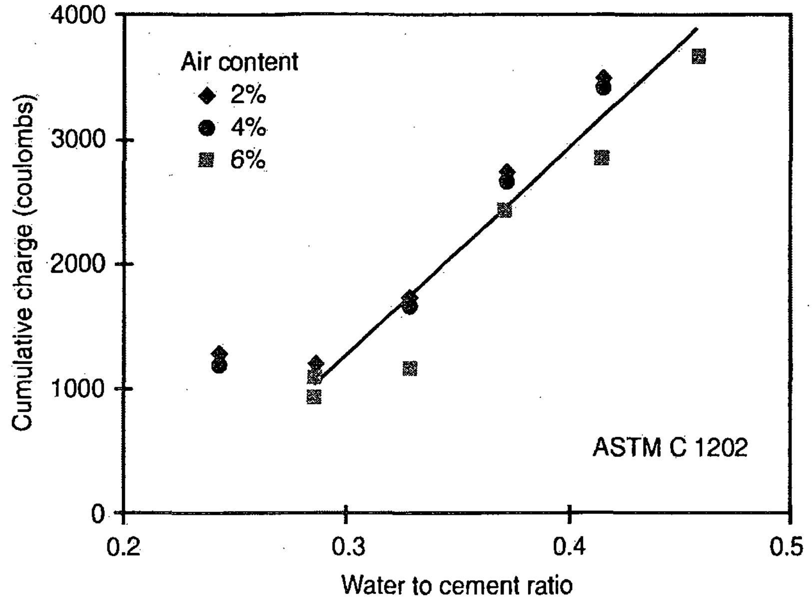


Fig 2.20 - Cumulative charge readings for a Portland cement concrete made with varying water to cement ratios [5].

For reinforced concrete, which may be prone to potential durability problems and therefore weakening, increasing the strength requirement is logical. This also has the effect of ensuring that the products of hydration have been well formed. It has been shown that there is a strong correlation between the amount of capillary pores found in concrete containing fly ash (porosity) and its strength [80].

2.3.12.2 Requirements on Air Entrainment:

There are also requirements on the minimum levels of percent of air-entrainment found in the concrete which will be exposed to chlorides. At the bottom of Table 2.10 the two categories of air-entrainment are listed. The percent of air-entrainment is dependent on the maximum size of the course aggregates. This is because as the maximum sized aggregate decreases, the proportion of fines and cement (mortar) increases, requiring an increase in the overall percent of air-entrainment in the concrete (the requirement is for the percent of air entrainment for concrete not cement).

Table 2.10 - Recommended Water and Air Content Proportions by Canadian Standards [5]

	Water, kilograms per cubic metre of concrete, for indicated sizes of aggregate*							
Slump, mm	10 mm	14 mm	20 mm	28 mm	40 mm	56 mm**	80 mm**	150 mm**
	Non-air-entrained concrete							
25 to 50	207	199	190	179	166	154	130	113
75 to 100	228	216	205	193	181	169	145	124
150 to 175	243	228	216	202	190	178	160	—
Approximate amount of entrapped air in non-air-entrained concrete, percent	3	2.5	2	1.5	1	0.5	0.3	0.2
	Air-entrained concrete							
25 to 50	181	175	168	160	150	142	122	107
75 to 100	202	193	184	175	165	157	133	119
150 to 175	216	205	197	184	174	166	154	—
CSA A23.1 Recommended total air content percent†								
Category 1	6 to 9	5 to 8		4 to 7		—	—	—
Category 2	5 to 8	4 to 7		3 to 6		—	—	—

* These quantities of mixing water are for use in computing cementing material contents for trial batches. They are maximums for reasonably well-shaped angular coarse aggregates graded within limits of accepted specifications.

** The slump values for concrete containing aggregates larger than 40 mm are based on slump tests made after removal of particles larger than 40 mm by wet screening.

† See Tables 9-1 and 9-2 for class of exposure and corresponding air content category.

Adapted from CSA Standard A23.1, ACI 211.1, and ACI 318. Hover (1995) presents this information in graphical form.

Table 2.11 presents the recommended percent of air-entrainment for the American and British Standards. The values are allowed a tolerance of ±1.5 percent of that listed. The three standards are all fairly similar.

Table 2.11 - Recommended Water and Air Content Proportions by American and British Standards [3]

Maximum size of aggregate		*Recommended total air content of concrete (per cent) for level of exposure:*		
		ACI 201.2R-92$^{11.92}$		*British BS 8110:Part 1:1985*
mm	*in.*	*Moderate*	*Severe*	*Subject to de-icing salts*
9.5	⅜	6	7½	7
12.5	½	5½	7	—
14	—	—	—	6
19	¾	5	6	5
25	1	5	6	—
37.5	1½	4½	5½	4
75	3	3½	4½	—
150	6	3	4	—

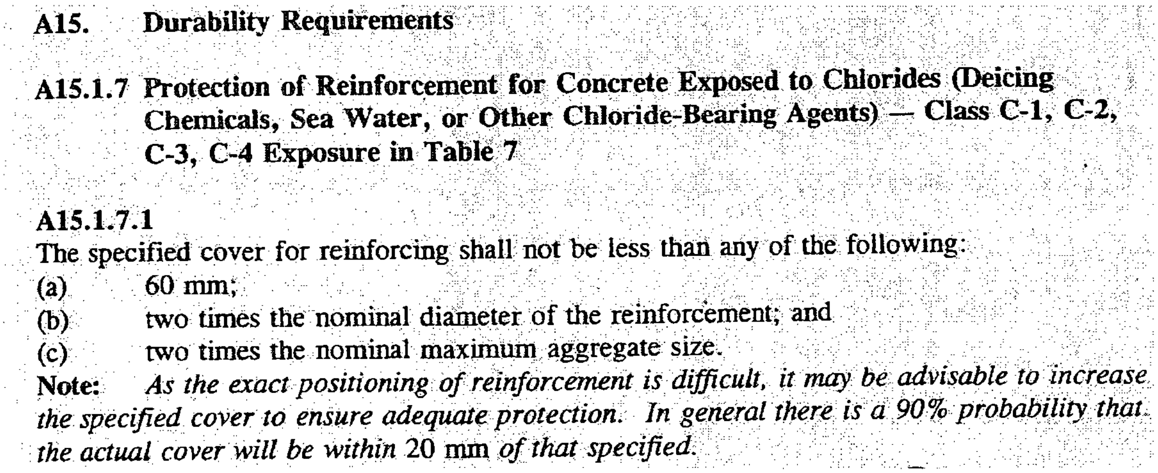
Air-entrainment is achieved by the addition of certain chemical admixtures, some commons ones are listed in Table 2.12. These admixtures cause microscopic air bubbles to form in the hardening concrete. The entrained air bubbles are not interconnected and do not contribute to permeability. The benefit of having more of these air bubbles is to provide space for the expansion of water as it freezes inside the concrete. The increased percent of air-entrainment in the concrete can also have other benefits. The increase in air content makes the concrete more workable [81]. It also can slightly reduce the permeability of the concrete as shown by Figure 2.20. The addition of SCM's can increase the amount of air-entrainment admixture, necessary to achieve a desired percent of air-entrainment in the concrete [4].

Table 2.12 - Common types of Chemical Admixtures [4]

Classification	Chemical Description	Notes and Performance Characteristics
Wood derived acid salts Vinsol Resin®	Alkali or alkanolamine salt of a mixture of tricyclic acids, phenolic, and terpenes	Rapid air generation, especially in low slump mixes. Minor air gain some air loss possible with continuous mixing. Mid-sized air bubbles. Compatible with all admixtures. Some air loss possible.
Tall Oil	Fatty acid—major component; tricyclic acids—minor	Slower air generation. Air may increase with prolonged mixing. Smallest air-voids among common agents. Compatible with all admixtures.
Vegetable oil acids	Alkali and alkanolamine salts of coconut fatty acids	Relative to wood rosins, slower air generation, both air gain and air loss possible with continuous mixing. Small to mid-sized air-voids, and compatible with all admixtures.
Synthetic detergents	Alkyl-aryl sulfonates and sulfates (e.g., sodium dodecylbenzenesulfonate)	Rapid air generation. Minor air loss with mixing. Coarser bubbles. Not compatible with naphthalene sulfonate-based HRWR. Applicable for cellular concretes.
Synthetic workability aids	Alkyl-aryl ethoxylates	Primarily used in masonry mortars.
Miscellaneous	Alkali/alkanoloamine acid salts of lignosulfonate Oxygenated petroleum residues Proteinaceous materials Animal tallow Saponin	Older technologies not currently used as concrete air-entraining agents.

2.3.12.3 Requirements on the Depth of Concrete Cover:

The Canadian standard places the same requirements on the concrete cover depth for all classes of exposure to chlorides. It is shown in Figure 2.21 the 3 minimum conditions that must be met for Canadian standards. For rebar less than 30mm in diameter, the cover would be a minimum of 60mm. For rebar diameters larger then 30mm, the cover must be two times its diameter. As the diameter of the rebar increases, so does the potential for increased expansive forces due to corrosion. Therefore, more cover is needed to resist these forces. The limitation placed on the cover depth due to the size of the maximum aggregate size, is because the aggregates can be up to 1000 times more porous than Portland cement mortar [4]. Large aggregates can effectively reduce the concrete cover depth.



A15. Durability Requirements

A15.1.7 Protection of Reinforcement for Concrete Exposed to Chlorides (Deicing Chemicals, Sea Water, or Other Chloride-Bearing Agents) — Class C-1, C-2, C-3, C-4 Exposure in Table 7

A15.1.7.1

The specified cover for reinforcing shall not be less than any of the following:

(a) 60 mm;

(b) two times the nominal diameter of the reinforcement; and

(c) two times the nominal maximum aggregate size.

Note: *As the exact positioning of reinforcement is difficult, it may be advisable to increase the specified cover to ensure adequate protection. In general there is a 90% probability that the actual cover will be within* 20 mm *of that specified.*

Fig 2.21 - Minimum cover requirements for reinforced concrete structures under Canadian standards [82].

The minimum depth of cover recommended by The American Concrete Institute is 2 inches (~50mm) for concrete place in forms and exposed to weather or ground conditions and three inches (~75mm) for concrete place without formwork (on ground) [83]. Concretes exposed to heavy road salting and harsh marine exposure conditions should be taken equal to ground conditions (3"). A recent study conducted on reinforced concrete structures in marine environments in China suggested values of between 50-70mm of concrete cover [84]. The Architectural Institute of Japan recommends that for exterior concrete structures exposed to heavily chloride-rich environments, that the concrete cover be a minimum of 90mm [55]. A recent study, on durability based design procedures for the mitigating of corrosion in reinforced concrete, has recommended that the ratio of the concrete cover to bar diameter should be selected at 3 to 4 [73]. However, if the concrete cover becomes too thick, wire mesh should place within the cover [73]. The depth of cover (when there is no wire mesh used) should not exceed more then about 80-100mm [3].

2.3.13 Curing:

The importance of proper curing practices can not be overlooked. The products of hydration are about two times greater in volume than that of the original cement [9]. These products will partially fill in the spaces (voids) occupied by water reducing permeability [9, 85]. Proper curing ensures sufficient time for the hydration process to proceed. Figure 2.22 shows the effect of 1 day of moist curing versus 7 days of moist curing. It was shown that concretes made with higher water to cement ratios are more affected (lower compressive strength and high permeability) by the type of curing conditions, than those made with lower water to cement ratios [87, 88].

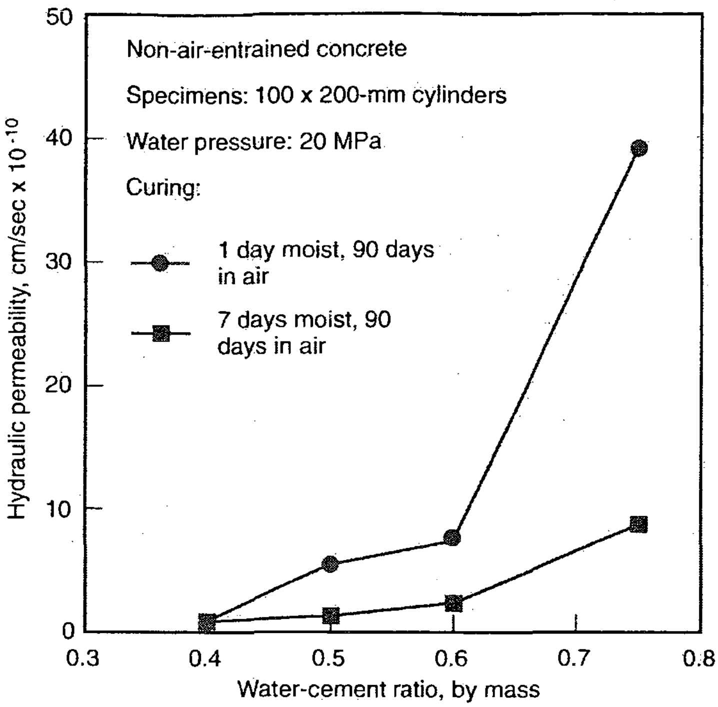


Fig 2.22 - Hydraulic permeability for concretes made with varying water to cement ratios under different curing conditions [5].

Figure 2.23 shows the differential pore size distribution versus pore size for different water to cement ratios and curing practices, in a normal Portland cement mortar mix. Gel pores are not considered. Line number 5 has a water to cement ratio of 0.6 and was left in the mold for 1 day then spent 6 days in water and 105 days at 20°C and 60% relative humidity. Line number 6 is the same except it was kept at 68 percent relative humidity. Line number 7 is the same as 5 except the water to cement ratio is 0.75. Line number 11 is the same as 5 except there was not 6 days of initial moist curing in water but just 111 days. As lines 5 and 6 have lower pore sizes, it is evident that curing is an important factor leading to lower permeability. However, the most important factor which reduces permeability is the water to cement ratio as shown. High water to cement ratios lead to larger capillary pore size distributions and diameters, which facilitate the ease of movement of moisture and other ions throughout the cement concrete.

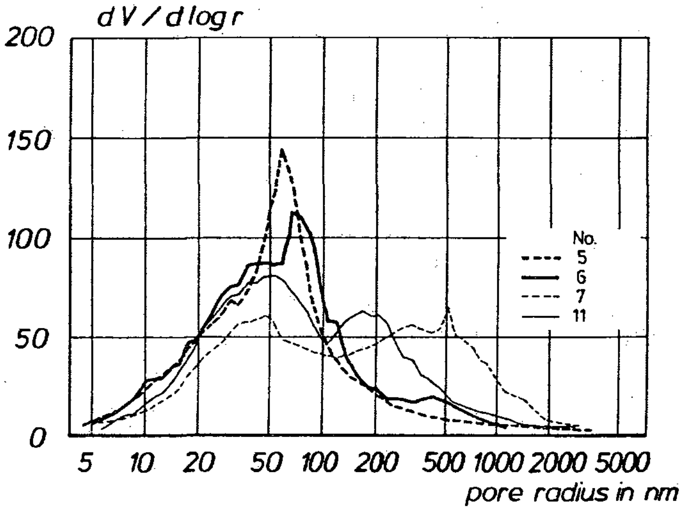


Fig 2.23 - Differential pore size distribution versus pore radius for different water to cement ratios and curing practices [89].

The effect of curing is especially important in cement concrete which contains fly ash [85, 86, 89]. Well cured concrete containing increasing amounts of fly ash will show a corresponding increase to the resistance of chloride ion penetration (permeability) [86]. However, in the same study under uncontrolled curing conditions, increasing amounts of fly ash can show a corresponding decrease in the resistance to chloride ion penetration (permeability) [86]. Figure 2.24, shows the effect of three different curing conditions (CC1: uncontrolled curing, left out in the lab until date of testing, CC2: 7 days initial moist curing in 20°C water bath then placed in a curing room at 20°C and 60% r.h., CC3:

7 days initial moist curing in 30°C water bath than placed in a curing room at 20°C and 60% r.h.). All the mixtures showed lower coulomb ratings with improvements in the curing conditions. For the two moist curing conditions, the coulomb rating decreases with the increasing addition of fly ash. The coulomb rating however increases under the uncontrolled curing conditions for increasing fly ash amounts. The graph is also useful for displaying the effects of age and curing temperature on fly ash reaction. Over time, fly ash will continue to become less permeable as the pozzolanic reaction continues. Fly ash has increased pozzolanic reactivity at higher initial internal temperatures [90]. At lower temperatures, fly ash can significantly retard the curing process [5]. Under winter conditions heating up mixing water or using accelerating admixtures can help to increase the rate of curing [3].

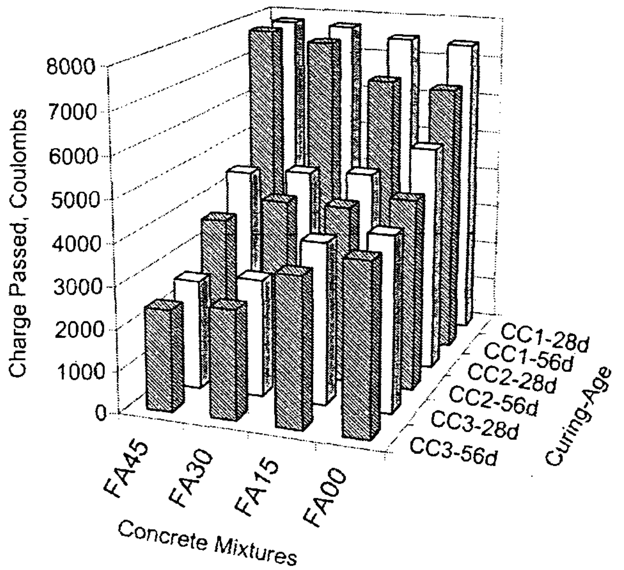


Fig 2.24 - Cumulative charge for concrete made with different percentages of fly ash and under different curing conditions [86]

2.4 The Rapid Chloride Permeability Test:

The Rapid Chloride Permeability Test (RCPT) is useful for an indication of a concrete's ability to resist internal chloride ion penetration through its capillary pores when saturated. The test is a method of indirectly measuring concrete's permeability. To measure permeability, the method assumes a relationship between permeability and the amount of current which can pass through the water inside a concrete sample's capillary pore structure. Standardized sample disks of 100 mm (4 inch) diameter and 50mm (2 inch) height are prepared from the concrete which is potentially going to be used for the construction of a structure. During testing, the disk samples have a solution of 3 percent NaCl forming a chloride source cell on one side and on the other side there is a chloride collecting cell filled with a solution of 0.3 N NaOH (see Figure 3.1). To test a sample, a potential difference of 60 V is applied through it for six hours; the cumulative charge is then calculated. The principle of this test is the accelerated movement of chloride ions by an external power source [91]. This test method can also be used to test the concrete in existing structures. A coring rig can be used to drill into a structure producing a 4" diameter core sample. The sample is then cut to the standard length of 2" with a diamond saw. The samples are then placed into a vacuum desiccator. The samples are submerged in water inside a vacuum chamber. The vacuum chamber is then pressurized using a pump. Additional air is forced into the top of the vacuum chamber pushing downward on the water surface, causing the pores of the concrete to fill with water. The samples are then tested for the 6 hours as mentioned previously. This testing method has been shown to be a good indication of a concrete ability to resist chloride ion penetration in a relative short duration of time [91]. However, there are three main shortcomings to this method.

The first is that SCM's can alter the chemistry of the pore water, and this test method can be sensitive to this change [91]. The second is that there is no direct correlation between the charge passed and the behavior of chloride movement [91]. The third is that the current passed through the sample, can heat it and the pore water up, affecting results [91].

3. Materials and Procedures

To test the effect of fly ash replacement on chloride resistance, the testing consisted of making various combinations of concrete using 4 different types of Portland cement and two types of fly ash at various replacement levels. The materials used and the testing procedure are described in this section.

3.1 Cementing Materials:

The four types of Portland cement and the two fly ashes used are listed below:

3.1.1 Portland Cement:

1. St. Constant, CSA Type GU cement, St. Constant, Quebec
2. St. Constant, CSA Type GUb-7SF cement, St. Constant, Quebec
3. Herndon, ASTM Type I cement, Herndon, Virginia, and
4. Brookfield, CSA Type GUb-7SF cement, Brookfield, Nova Scotia

The two St. Constant cements were selected because of their high alkali content in order to determine the effect of cement alkalinity on chloride resistance (Cements are categorized as high alkali with $Na_2O_e > 0.6$). Herndon and Brookfield have low alkali contents. Two of the cements used, indicated as GUb-7SF, were silica fume blends in order to investigate the effect of silica fume on the chloride resistance of concrete containing fly ash. The chemical composition of the Portland cements are in Table 3.1.

Table 3.1 - The Chemical Composition of the Cements used (wt %)

	ST CONSTANT GU	ST CONSTANT SF	HERNDON	BROOKFIELD SF
SiO_2	19.22	24.38	19.71	26.57
Al_2O_3	4.75	4.82	4.35	4.33
TiO_2	0.21	0.22	0.20	0.34
P_2O_5	0.29	0.24	0.08	0.04
Fe_2O_3	2.24	2.24	2.64	2.62
CaO	62.2	59.15	62.76	59.1
MgO	2.61	2.33	3.74	1.19
Na_2O	0.24	0.26	0.17	0.1
K_2O	0.95	0.91	0.60	0.59
Mn_2O_3	0.06	0.06	0.06	0.09
SrO	0.26	0.23	0.05	0.07
LSO_3	4.11	3.46	2.39	2.9
LOI @ 1000°C	2.22	1.20	2.80	1.59
Na_2Oe	0.86	0.85	0.56	0.48

3.1.2 Fly Ash:

Two Type CI fly ashes were used in this study. Although both fly ashes are categorized as Type CI (8%<CaO<20%), they represent either end of the category at 10.94 and 16.35% CaO.

1. Sundance Fly Ash. Type CI, Sundance, Alberta, and
2. Rockport Fly Ash Type CI, Rockport, Indiana

The chemical compositions of the fly ashes are in Table 3.2.

Table 3.2 - The Chemical Composition of the Fly Ashes used (wt %)

	Sundance	Rockport
SiO_2	54.67	44.28
Al_2O_3	22.93	20.96
TiO_2	0.65	1.43
P_2O_5	0.09	0.83
Fe_2O_3	3.82	6.93
CaO	10.94	16.35
MgO	1.16	3.69
Na_2O	2.97	1.21
K_2O	0.71	1.29
Mn_2O_3	0.06	0.03
SrO	0.11	0.26
LSO_3	0.17	0.8

Table 3.2 Continued - The Chemical Composition of the Fly Ashes used

BaO	0.5	0.58
ZnO	0.01	0.02
Cr2O3	0.00	0.02
LOI @ 750°C	0.40	1.13
Na2Oe	3.43	2.04

3.2 Coarse and Fine Aggregates:

The coarse aggregate consisted of crushed limestone with a maximum particle size of 10mm. The fine aggregate is a natural aggregate. Both the coarse and fine aggregates met ASTM C 33 and are from the Greater Montreal area.

3.3 Water:

City of Montreal tap water was used in the mixing of the concrete. Distilled water was used to make sodium chloride and sodium hydroxide solutions.

3.4 Mixing and Preparation of Samples:

There were 36 different concrete mixture combinations made and tested. Four of the combinations were of pure Portland cement as the binder. The other 32 combinations were each of the Portland cement combined with one of the 2 fly ash types. For the 32 different combinations, the fly ash replaced 20%, 40%, 60%, and 80% of the Portland cement binder (i.e. 8 sets of 4). The combinations were tested at 7, 28 and 56 days after mixing. For each of the 3 test dates, 3 samples were needed for each of the given concrete mixture combinations to ensure repeatability. Therefore, 9 samples were made for each of the 36 combinations totaling 324 samples.

3.5 Sample Specification and Casting:

The sample shape and size were cylinders which are 100mm (~4") in diameter by 50mm (~2") in height in accordance with ASTM C 1202-08 (Rapid Chloride Permeability Test). For all samples, a water to cement ratio (w/c) of 0.44 was used. Originally a water to cement ratio of 0.4 was choose. However mixtures made with only Portland cement were not sufficiently workable. To make 9 samples of each of the 36 combinations a volume equal to 10 of the cylinders was mixed, so there would be excess material available. For mixing, 4.56 kg of coarse aggregates, 3.51 kg sand, 1.67kg binder and 730ml of water was blended in a concrete mixer for about 3-4 minutes. Table 3.3 summarizes the mixture proportions for the different fly ash replacements. The concrete was then poured into PVC plastic cylindrical molds. The molds were first lubricated (WD40) for easy of extraction. The samples were capped for the first 24 hours then placed in a saturated lime-water solution for curing until testing. All mixing, storage and testing of the samples was done at room temperature of approximately 24° C.

Table 3.3 - Mixture Proportions (in grams)

Fly Ash Replacement%	0%	20%	40%	60%	80%
water	730	730	730	730	730
cement	1667	1333	1000	667	333
fly ash	0	333	667	1000	1333
coarse	4562	4562	4562	4562	4562
fine	3513	3513	3513	3513	3513

3.6 The Rapid Chloride Permeability Test:

The RCPT system is manufactured by GERMANN INSTRUMENTS, Inc. which consists of software, Microprocessor Power Supply Unit (MPSU), and cells. The cells house the concrete samples for testing. When a cell is attached to a sample, reservoirs are formed between the faces of the sample and the cell walls (see Figure 3.1). One reservoir is filled with sodium chloride (3% NaCl) solution and connected to the negative terminal of the MPSU. The reservoir on the other side of the sample is filled with a sodium hydroxide (0.3 N NaOH) solution and connected to the positive terminal of the MPSU. When the test commences, the current in milliamps is recorded every five minutes while the voltage is maintained at 60 Volts for 6 hours of testing. The cumulative charge in Coulombs is then calculated by the software for the 6 hours of testing time.

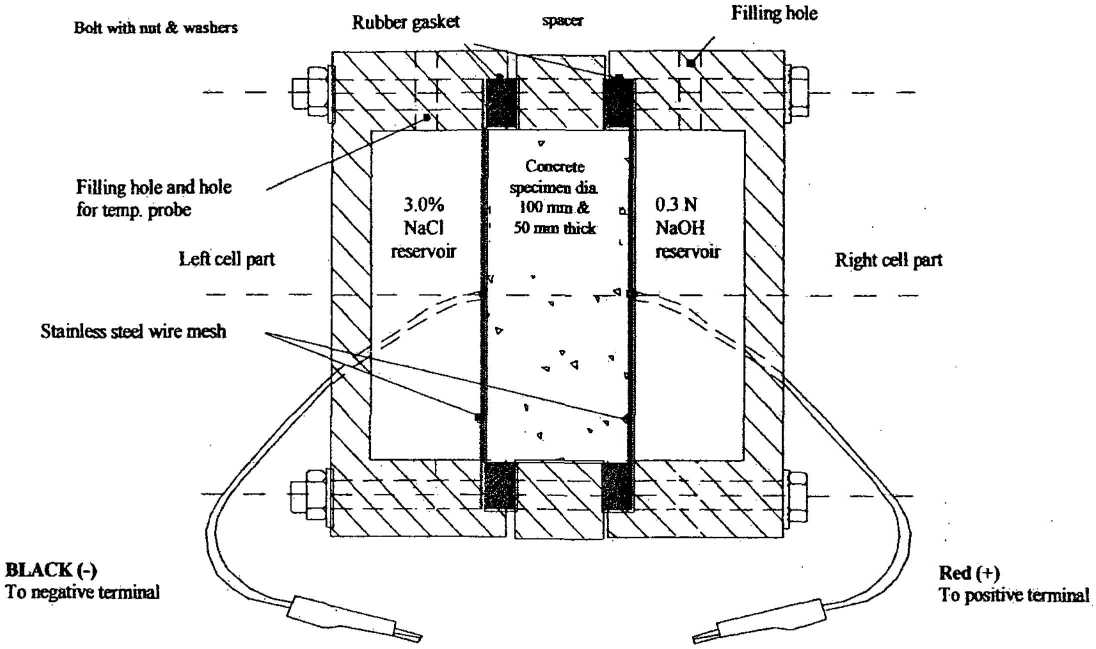


Fig 3.1 - Depiction of the concrete sample within a testing cell [92].

The MPSU passes a current flowing through the solution in the reservoirs and the pores of the saturated concrete sample. The MPSU is connected to a PC with the installed software, which records the data collected. The current in Coulombs is a measure of chloride permeability according to this method (Table 3.4).

Table 3.4 - Chloride Ion Permeability Classification Based on Coulomb Readings [92]

Coulombs	Chloride Ion Permeability
>4000	High
4000-2000	Moderate
2000-1000	Low
1000-100	Very low
<100	Negligible

4. Results and Discussion:

4.1 Rapid Chloride Permeability Test Results:

Figures 4.1 through 4.8 display the average Coulomb (cumulative charge) values, determined by the RCPT, for the concrete samples in this study (the average values are in the appendix). In each of the Figures, one of the four types of cement with one of the two types of fly ashes, for 0, 20, 40, 60, and 80 percent fly ash replacement is displayed. For each specific combination of cement and fly ash, the 3 test dates of 7, 28, and 56 days are all shown within the same graph. At 7 days of curing, concretes containing increasing amounts of fly ash generally displayed a corresponding increase in the coulomb values relative to the amount of fly ash replacement. The increase generally resembles a linear relationship. At 7 days of curing, the fly ash in the concrete has only just begun to activate. The majority of the pozzolanic reaction of the fly ash occurs after this date. The increases in the coulomb readings with increasing amounts of fly ash are largely due to the removal of Portland cement. As curing progresses to 28 and 56 days, the coulomb values decrease relative to 7 days depending on the cement type, and whether or not the cement has been blended with silica fume, prior to fly ash replacement. The coulomb readings are also dependent on the type of fly ash used. The evaluation of the effects of varying ingredients are examined separately in each of the following sections.

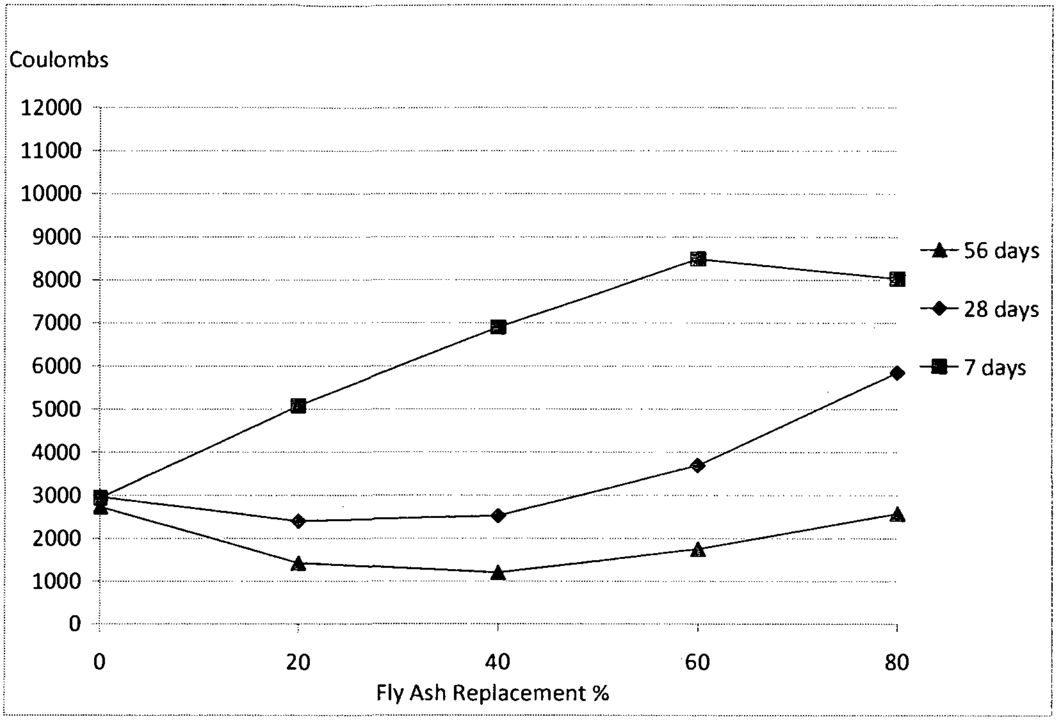


Fig 4.1 - St. Constant Portland cement with increasing Sundance fly ash replacement.

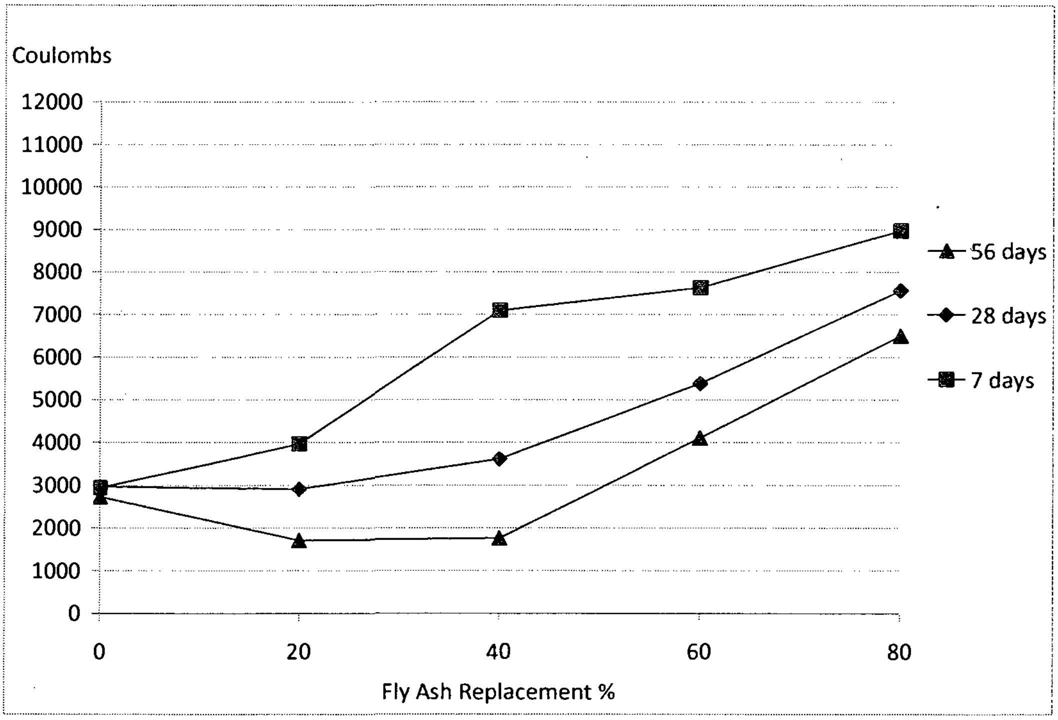


Fig 4.2 - St. Constant Portland cement with increasing Rockport fly ash replacement.

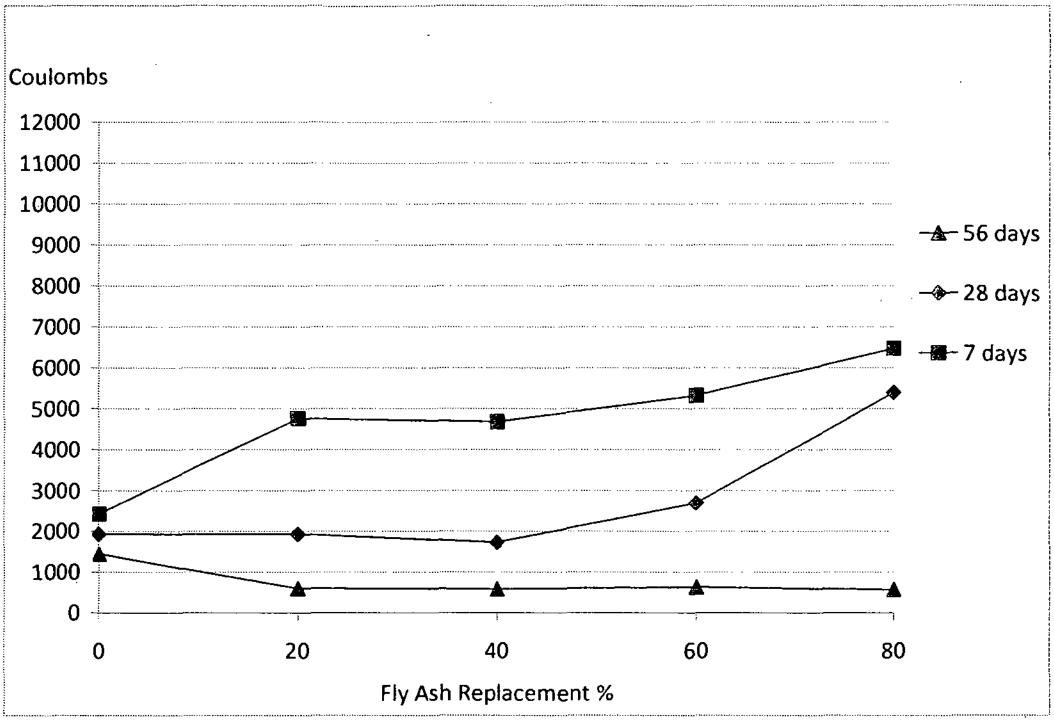


Fig 4.3 - Herndon Portland cement with increasing Sundance fly ash replacement.

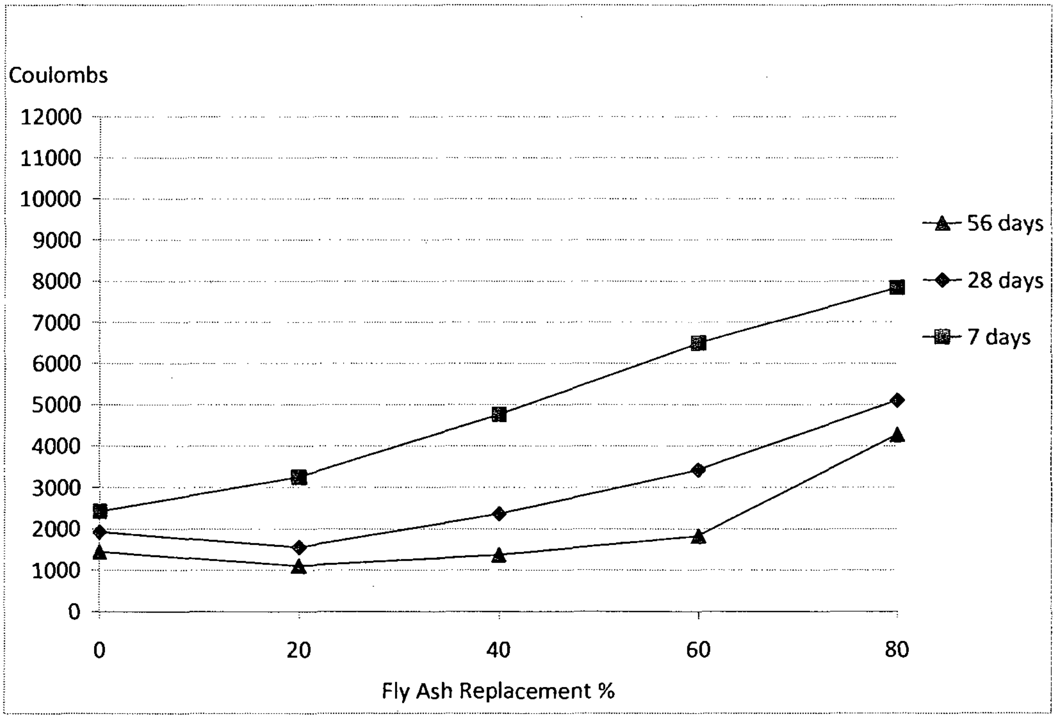


Fig 4.4 - Herndon Portland cement with increasing Rockport fly ash replacement.

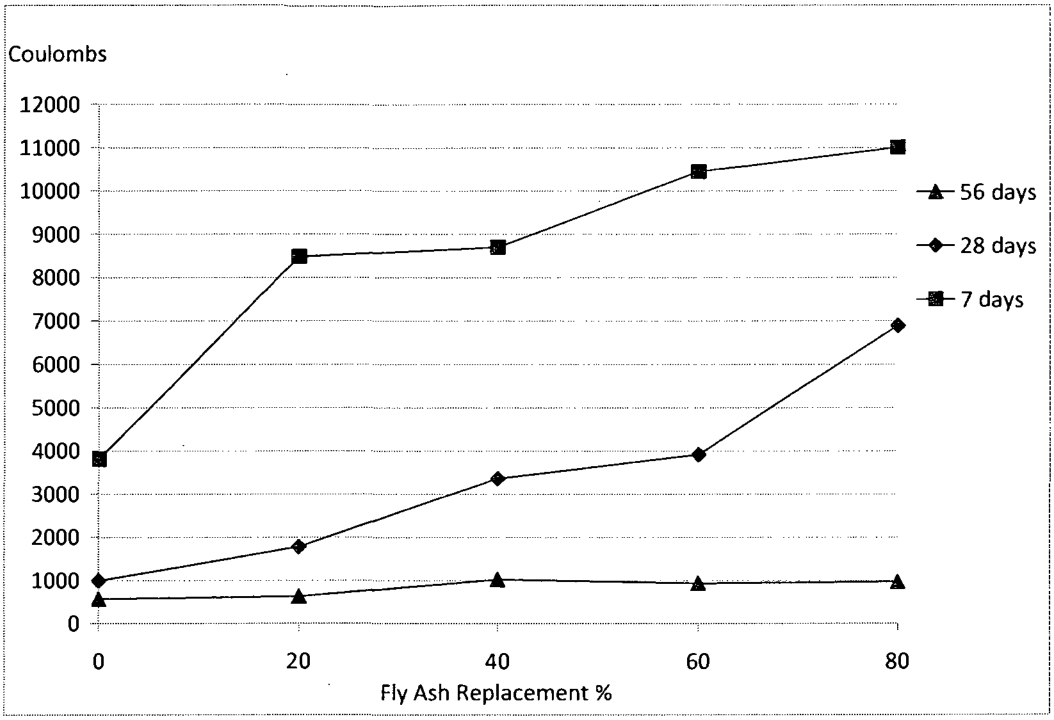


Fig 4.5 - St. Constant SF Portland cement with increasing Sundance fly ash replacement.

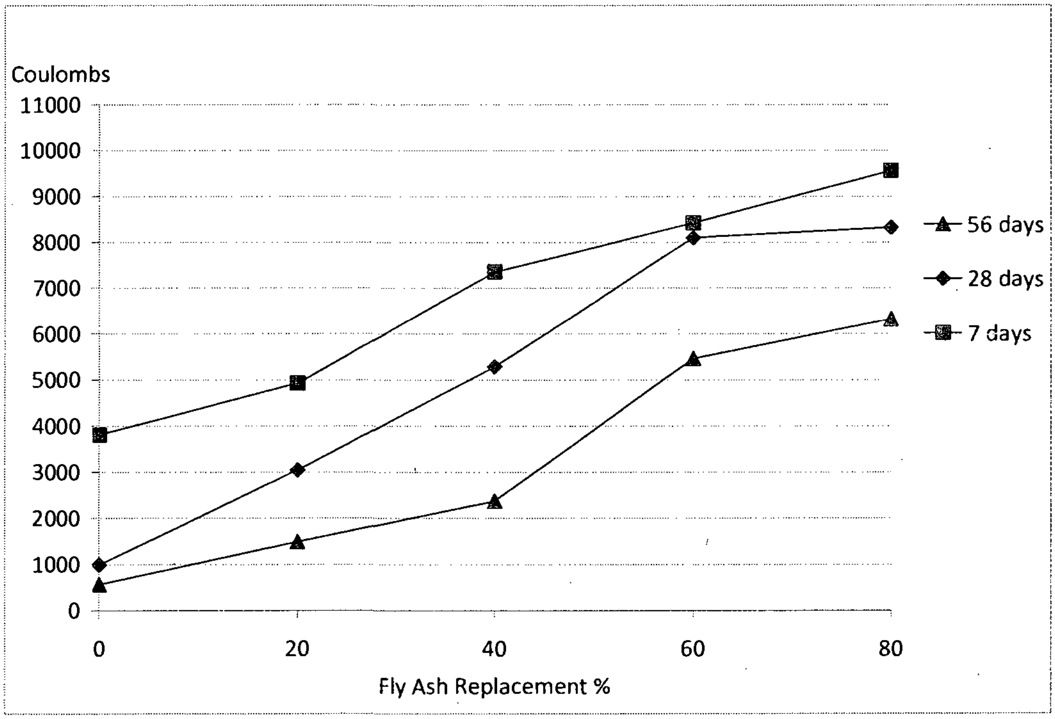


Fig 4.6 - St. Constant SF Portland cement with increasing Rockport fly ash replacement.

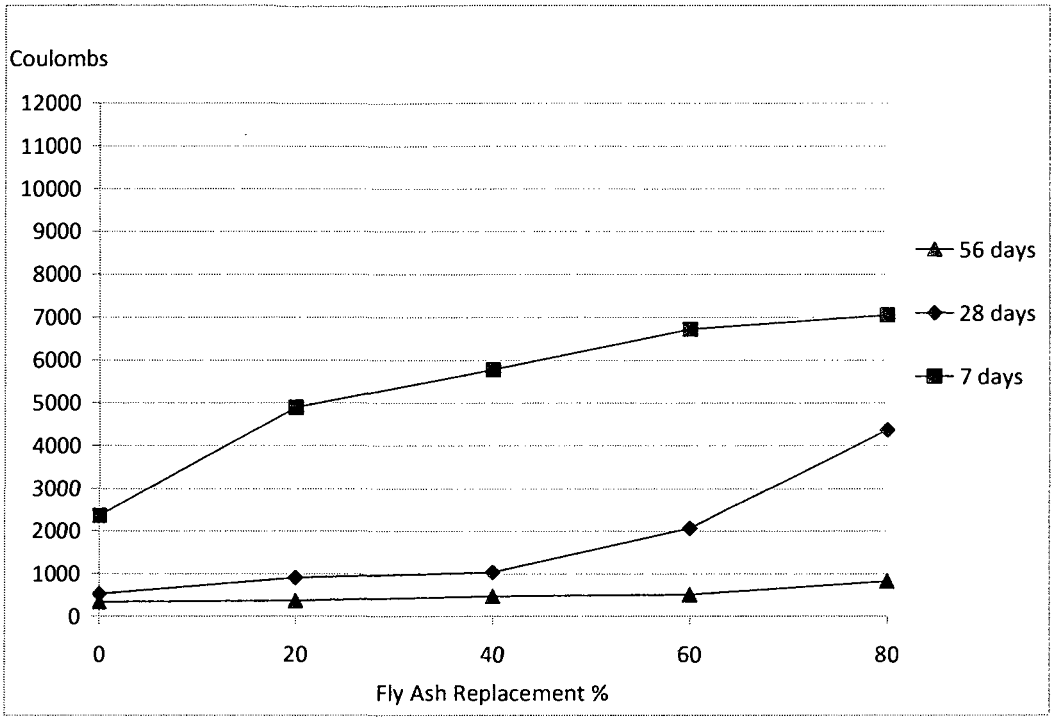


Fig 4.7 - Brookfield SF Portland cement with increasing Sundance fly ash replacement.

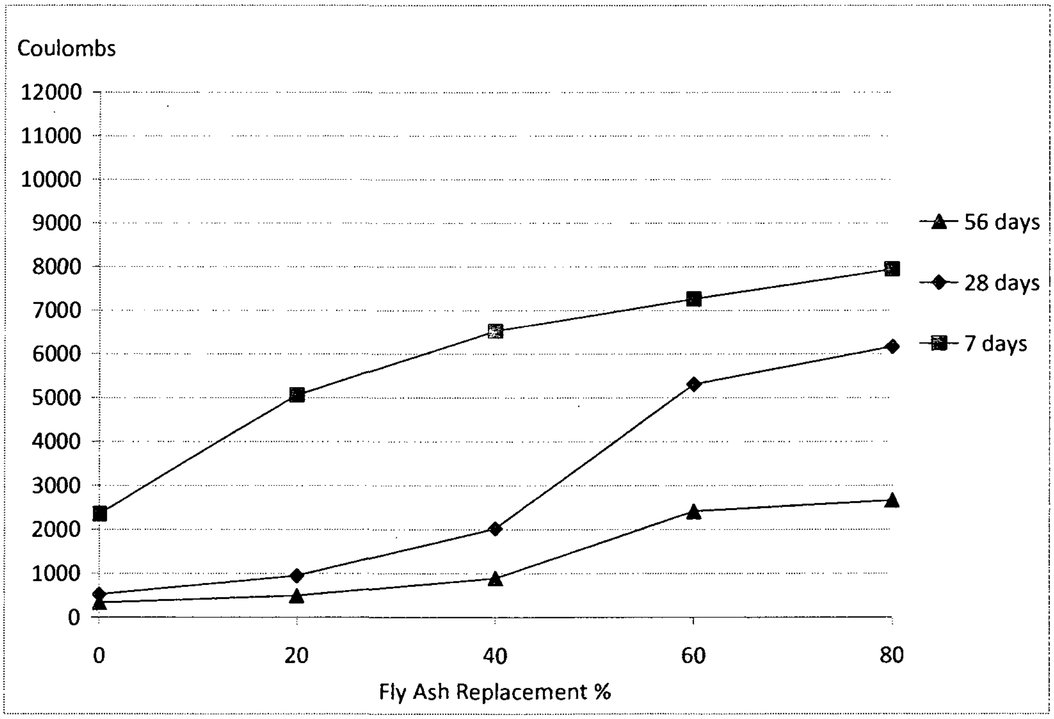


Fig 4.8 - Brookfield SF Portland cement with increasing Rockport fly ash replacement.

4.2 Effect of Silica Fume on Permeability:

The beneficial effects of incorporating silica fume into concrete, to lower permeability, can clearly be seen in Figure 4.9. The Figure shows the result for all four types of cement concretes made without any fly ash replacements. The incorporation of 7 percent blended silica fume into the St. Constant cement concrete reduced the cumulative charge readings from 2729 coulombs to 565 coulombs, at 56 days. The pure Herndon cement concrete had values of 1442 coulombs, at 56 days. The silica fume blended Brookfield cement concrete had the lowest reading of all at 333 coulombs, at 56 days.

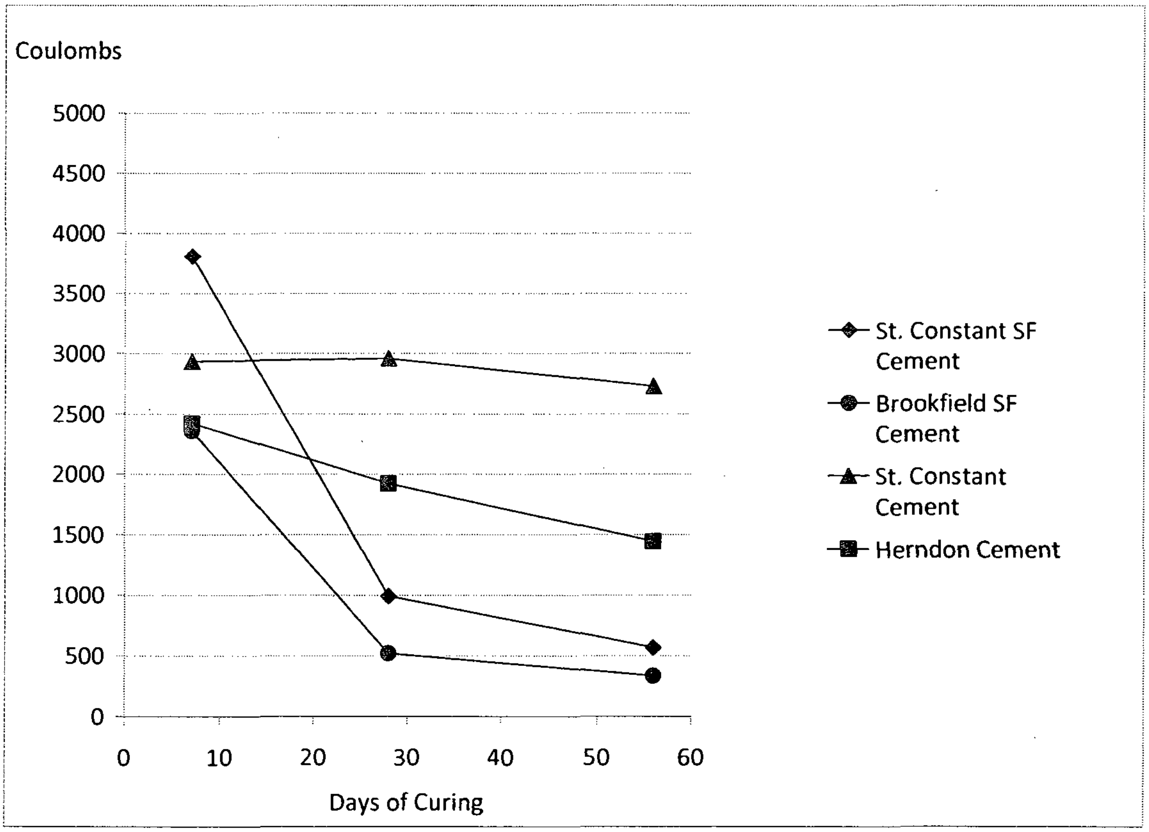


Fig 4.9 - Portland cement concretes with (7%) and without (0%) silica fume blending (SF).

4.3 Effect of Fly Ash Addition in Concretes Containing Cements with and without Silica Fume Blending:

The Canadian standards commonly uses 56-day values of the RCPT to asses the long-term resistance of concretes to chloride ion penetration. Figures 4.10 and 4.11, shows the results from RCPT at 56 days for cement concretes with and without silica fume blending respectively, containing various fly ash replacement percentages.

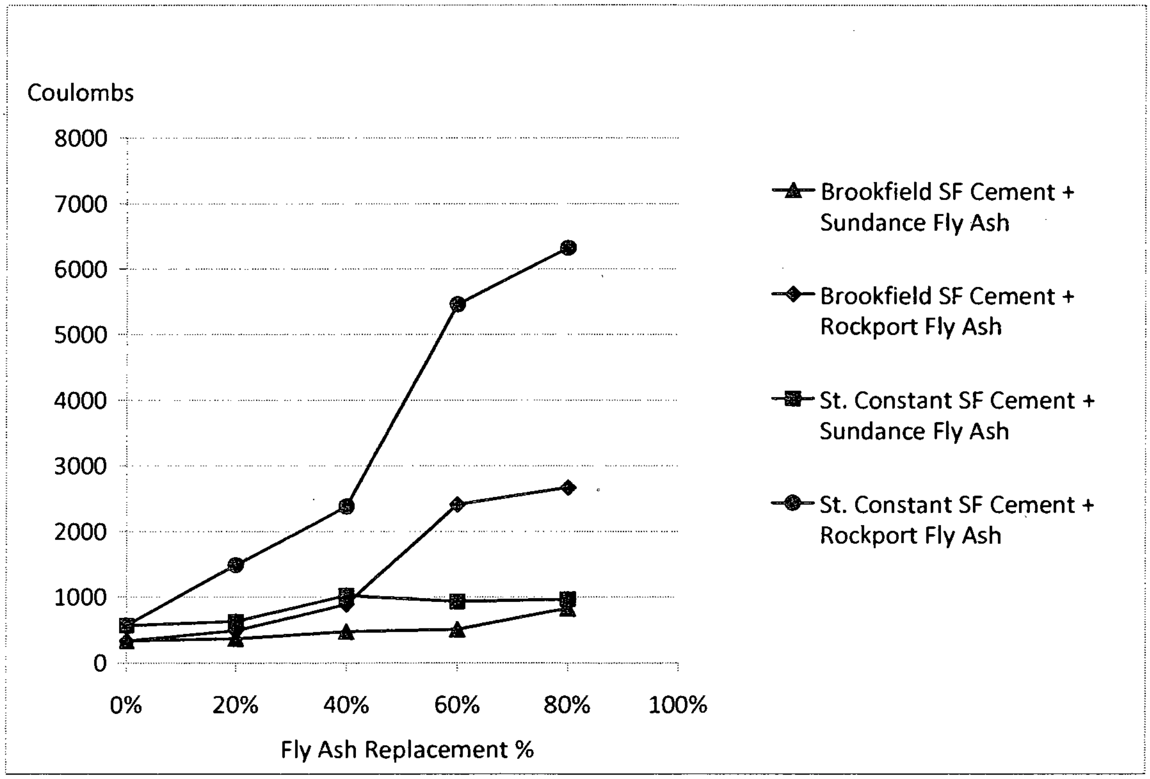


Fig 4.10 - Fly ash addition in silica fume (SF) blended Portland cement concretes at 56 days.

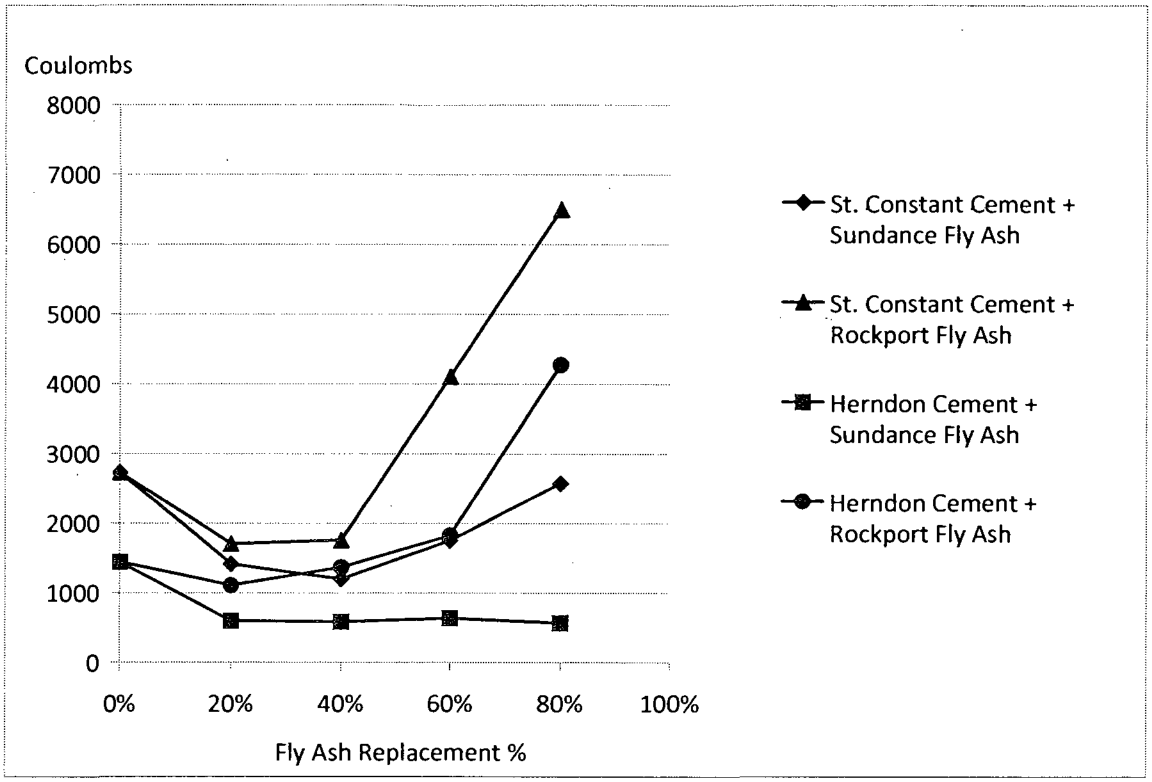


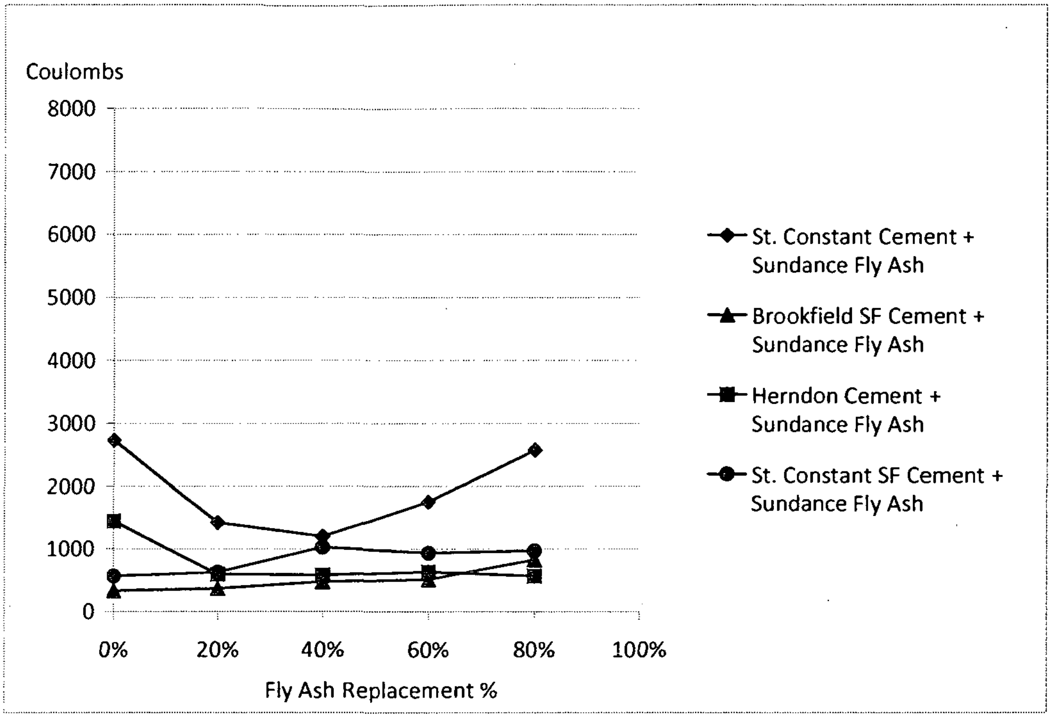
Fig 4.11 - Fly ash addition in regular Portland cement concretes at 56 days.

The effect of silica fume blending is noticeable at lower levels of fly ash replacement. The benefits of fly ash addition, in silica fume blended cements, become less so as fly ash replacement percentages increase. The reason for this is that the silica fume has been blended with the cement prior to fly ash replacement. The amount of silica fume when there is no fly ash replacement is 7 percent of the cement binder. However, at 20, 40, 60, and 80 percentages of fly ash replacement, the total amount of silica fume found in the cement binder (Portland cement and fly ash) decreases to 5.6, 4.2, 2.8, and 1.4 percent of the cement binder respectively. In other words, we are seeing two different effects occurring simultaneously, the positive effects of fly ash addition and the negative effects of silica fume reduction. The negative effect of silica fume reduction, outweighs the benefit of fly ash replacement, for the silica fume blended cements. This can make fly ash replacement appear to be "negative" in cements blended with silica fume prior to fly ash replacement. For instance, when the two silica fume blended cements are partially replaced with 20 and 40 percentages of fly ash, the coulomb readings increase, relative to the silica fume blended Portland cement values with no fly ash replacement, at 56 days (particularly in the case of the Rockport fly ash). However, for the Portland cement concretes made without silica fume blending (Figure 4.11), replacements of 20 and 40 percentages of fly ash, lowers the coulomb readings relative to the pure Portland cement (0%) values, at 56 days. The values obtained for concretes with only fly ash replacement (no silica fume) are fairly consistent to that of other studies without silica fume blending (as in Figures 2.3 and 2.24, and Table 2.5). Although the increased replacement of fly ash in silica fume blended cements increase the coulombs values relative to those with lower fly ash replacement, they were still generally lower then the concretes made without silica fume blending with only fly ash. In other words, inclusion of silica fume in Portland cement concretes containing fly ash replacements results in concretes which are more resistant to chloride ion penetration than to that of Portland cement concretes with only fly ash replacement (no silica fume), for similar replacement levels.

4.4 Effect of Fly Ash Type:

4.4.1 Replacement with Sundance Fly Ash:

The Sundance fly ash generally outperformed the Rockport in the resistance to chloride ion penetration. The Brookfield and St. Constant silica fume blended cement concretes performed the best with Sundance fly ash, with coulomb values corresponding to very low (<1000) chloride ion permeability, at 56 days. The Herndon cement combined with Sundance fly ash also performed well, with coulomb values correspond to very low and low (1000-2000) chloride ion permeability, at 56 days. The St. Constant cement made with Sundance fly ash had coulomb values correspond to low to moderate (2000-4000) chloride ion permeability, at 56 days. This is shown below in Figure 4.12.

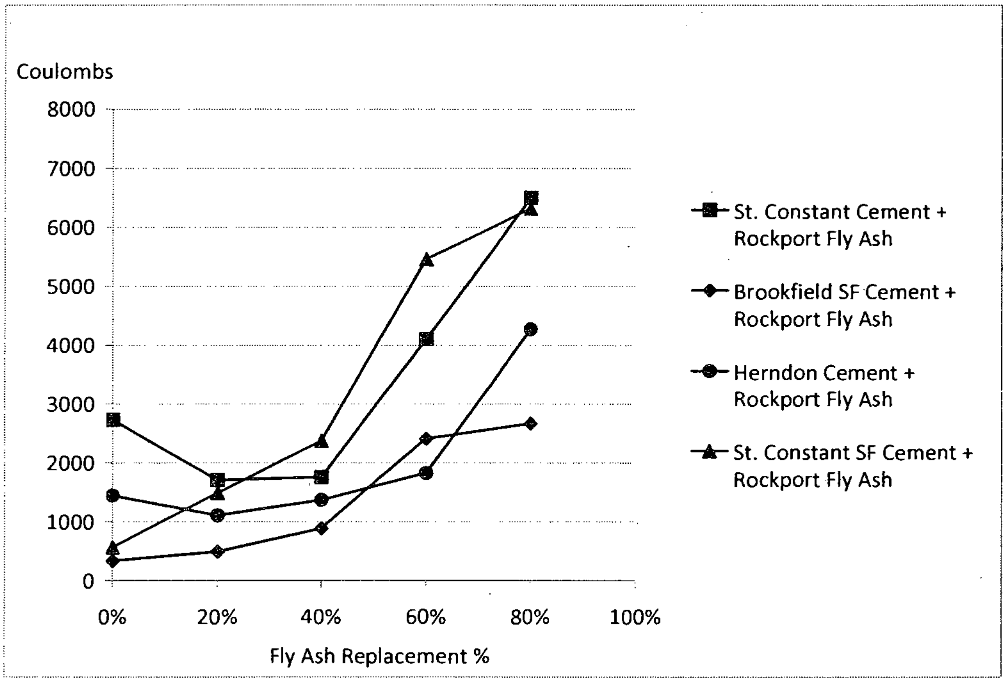


4.12 – Coulomb values for the Portland cement concretes made with Sundance fly ash replacement.

4.4.2 Replacement with Rockport Fly Ash:

The Brookfield silica fume blended cement combined with Rockport fly ash at 20 and 40 percent replacements showed very low chloride ion permeability, at 56 days. The Brookfield silica fume blended cement combined with 60 and 80 percent Rockport fly ash replacements showed moderate chloride ion permeability, at 56 days. The St. Constant silica fume blended cement combined with Rockport fly ash at 20 and 40 percent replacement showed very low to low chloride ion permeability respectively, at 56 days. The St. Constant silica fume blended cement combined with Rockport fly ash at

60, and 80 percent replacement showed high (>4000) chloride ion permeability respectively, at 56 days. The Herndon cement combined with Rockport fly ash at 20 to 60 and 80 percent replacement had moderate to high chloride ion permeability respectively, at 56 days. The St. Constant cement combined with Rockport fly ash at 20 to 40, and 60 to 80 percent replacement showed moderate and high chloride ion permeability respectively, at 56 days. This is shown in Figure 4.13.



4.13 – Coulomb values for the Portland cement concretes made with Rockport fly ash replacement.

4.4.3 Reasons for Superior Performance of Sundance over Rockport Fly Ash:

At 56 days of curing, concretes containing Sundance fly ash showed much lower coulomb values than the Rockport fly ash, especially at 60 and 80 percent replacement levels. Although the Rockport had higher calcium content, it did not out perform the Sundance fly ash in this study. The possible reason for this is that the Sundance fly ash has lower carbon levels (LOI) relative to the Rockport fly ash. Low carbon levels are indicative of finer fly ash [3]. From one source, the percent retained on the 45μm sieve, for similar Sundance fly ash, was 16 percent [93]. From another source, the percent passing the 45 μm sieve, for similar Rockport fly ash, was 22 percent [11]. Also from these two sources the pozzolanic reactivity index determined at 7 days, was 94.5 percent and 85.5 percent for the Sundance and Rockport fly ashes respectively [11, 93]. From the data, we can determine that for the Portland cements used in this study to make concrete, Sundance fly ash replacements of up to 80 percent generally will have low chloride ion permeability. For the Portland cement concretes made with the Rockport fly ash, replacements of up to 40 percent will have low chloride ion permeability. This is not to say that the Rockport fly ash will not have low chloride ion permeability at 60 and 80 percent replacements at later dates. The pozzolanic reactions of the fly ash will continue for some time at 56 days, and could very well reach that of the Sundance provide sufficient curing time. For example, in Figure 2.3 the concrete made with 70 percent fly ash replacement had drastically reduced coulomb values from those recorded at two months to that after three months of curing.

4.5 Relationship between Compressive Strength and Cumulative Charge:

Figure 4.14, shows the relationship between the coulomb values obtained from the RCPT and compressive strength for certain mixtures of concrete studied, determined at 28 days. A linear trendline of all data points is also shown. It is apparent that there is a relationship between strength and coulomb values (cumulative charge). Generally as concrete strength increases the resistance of concrete to chloride ion permeability increases. The compressive strength of concrete is known to be related to the degree of porosity in a given concrete mixture [3]. Although porosity is different from permeability there is a strong correlation between the two. Therefore it is generally expected that at higher coulomb values (high permeability/porosity), the strength should likewise decrease. The results obtained from the compressive strength tests support the findings obtained from the RCPT.

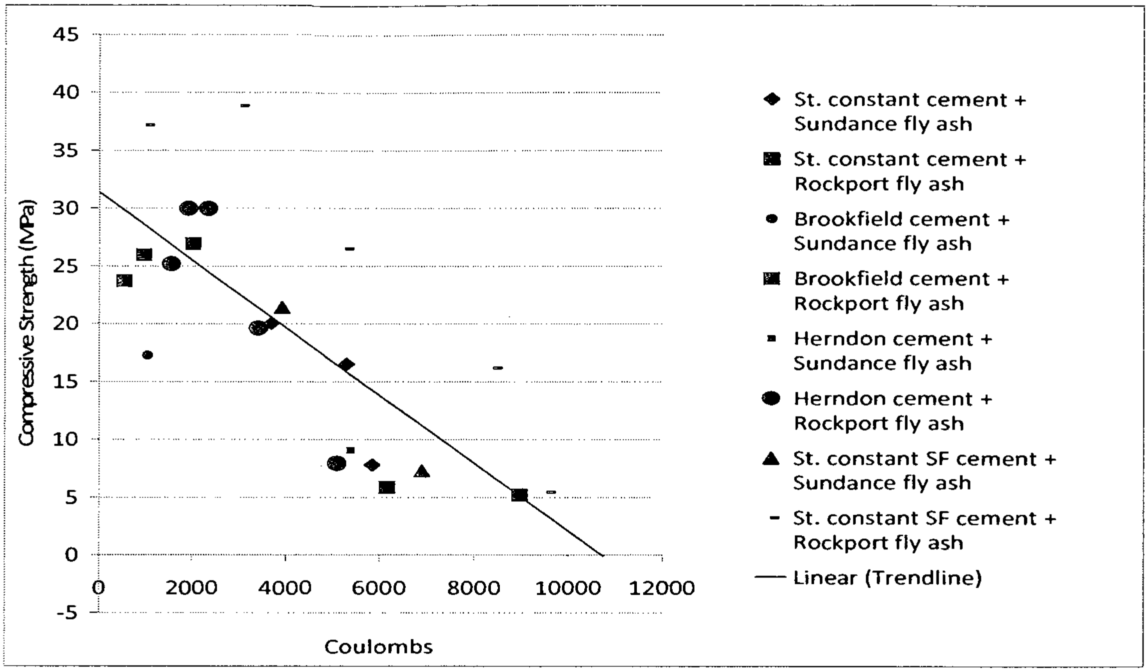


Fig 4.14 - Relationship between compressive strength and cumulative charge readings [94].

4.6 Effect of Portland Cement Alkali Content on Permeability:

Higher alkali contents (2 % NaOH addition by mass of fly ash) are known to increase activation of pure fly ash concretes [95]. The effect with which the cements' alkali content has on the permeability of concrete was considered by comparing the high alkali cements with the low alkali cements. Only concretes without silica fume blending, have been considered. The samples made with St. Constant cement with an Na_2O equivalent of 0.86 have higher coulomb readings than the samples made with Herndon cement with an Na_2O equivalent of 0.56. This is true for all cements made with either Sundance or

Rockport fly ashes, at all percentages of replacements, at all dates tested (7 day, 28 day, and 56 day). Figure 4.15 and 4.16, show the St. Constant cement and Herndon cement coulomb values at 56 days of curing for the Sundance and Rockport fly ashes respectively.

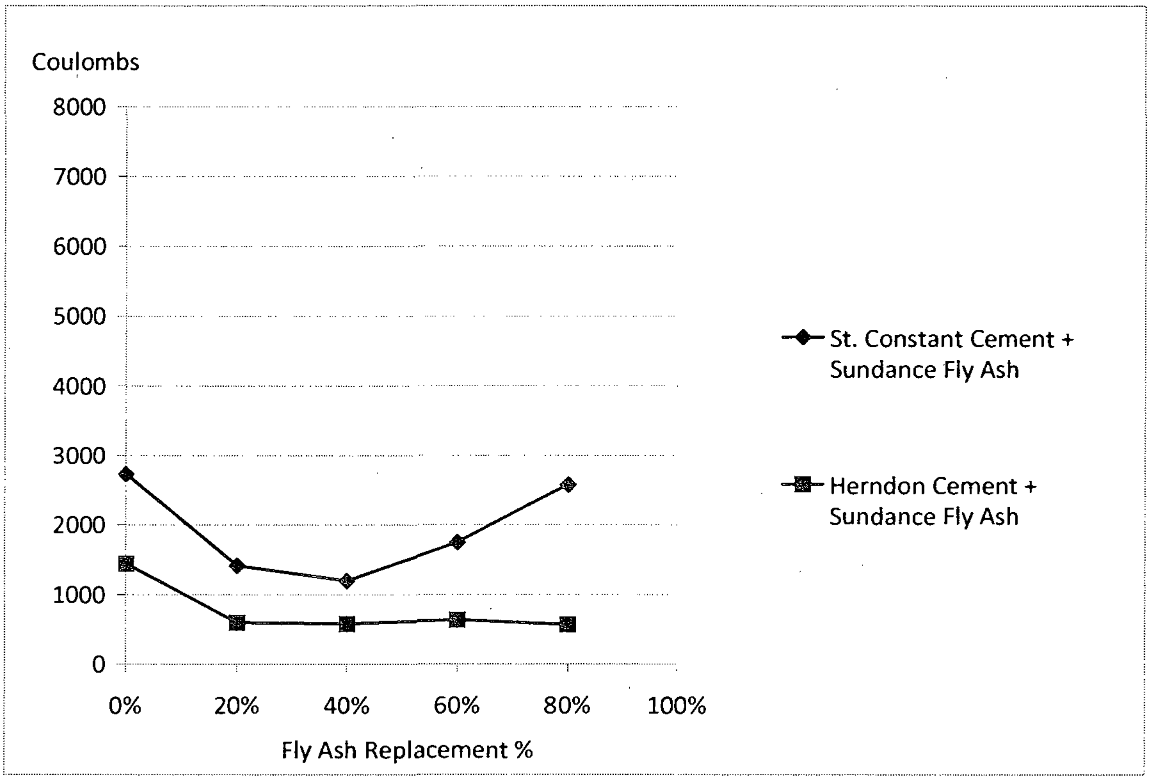


Fig 4.15 - St. Constant and Herndon cement concretes made with Sundance fly ash

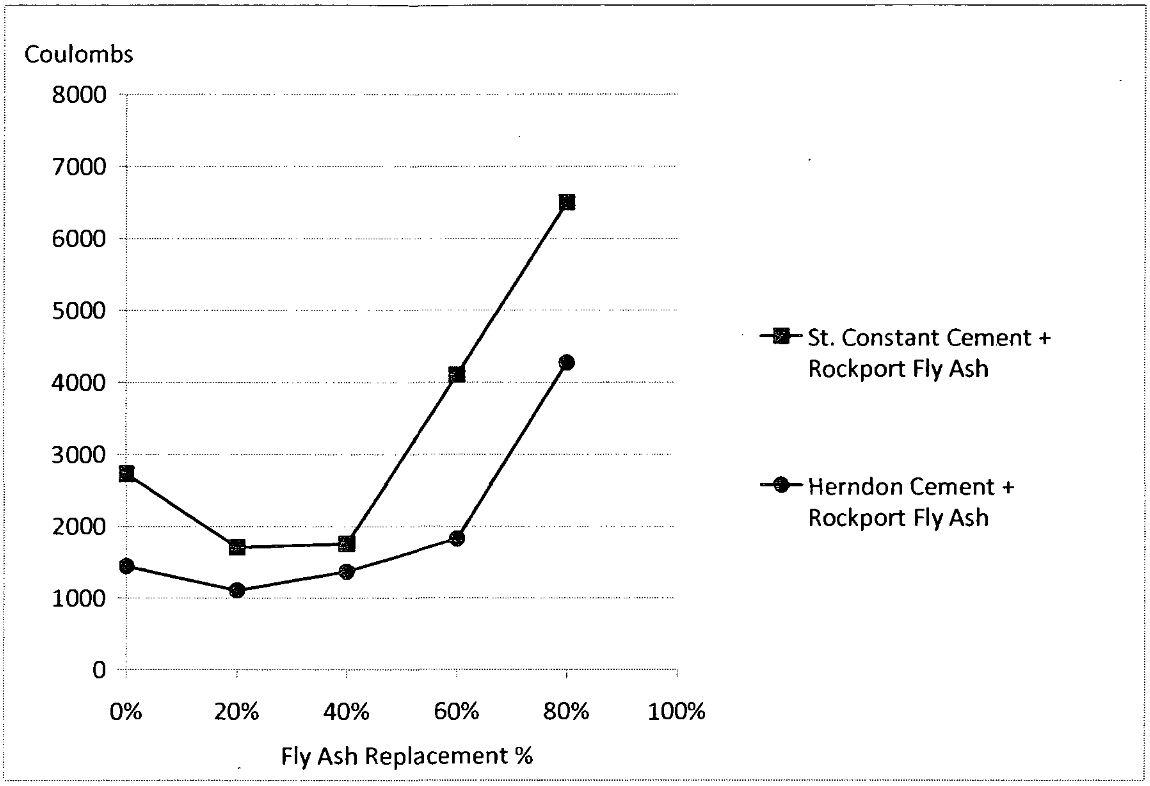


Fig 4.16 - St. Constant and Herndon cement concretes made with Rockport fly ash.

Concretes made with only Portland cement (without fly ash), which have higher alkali contents (0.6 – 1.25 Na_2O equivalent) have been shown to have hydration products which have a microtexture/microstructure which is more porous and reticular (increased network/interlinking of pores) [96]. This negative effect is believed to outweigh the potential benefits, which are characteristic of higher alkalinity in the aid to fly ash activation, for this study.

The influence of the Portland cements' alkali content on the activation of fly ash depends on the proportions of Portland cement to fly ash. In the above graphs, the higher alkali content of the St. Constant potentially causes the convergence and then divergence of the two lines in each graph shown. For concretes with no fly ash replacement, the high alkali content has a negative effect on the Portland cement (more permeable). This is why it is believed to have higher coulomb readings at zero percent fly ash replacement in the Figures 4.15 and 4.16. At 20 and 40 percent fly ash replacements, this effect continues. However, the higher alkali content of the St. Constant cement potentially causes greater activation of the fly ash relative to the cements with lower alkali content (Herndon) , which acts to offset/counter the negative effects which the higher alkalinity possibly have on the hydration products. It is believed this is likely why the higher line (higher alkali content) converges downward on the lower one. However, at higher levels of fly ash replacements (60 and 80 percent) there is much less Portland cement (alkali content) relative to fly ash, to cause such benefits in the activation of the fly ash. This could explain the divergence of the lines.

4.7 Possible Sources of Errors:

As mentioned in section 2.4, a shortcoming of the RCPT is that as the 6 hours of testing progresses the temperature rises as well. This also causes the current to gradually rise. The cumulative charge (in coulombs) is defined as equal to the area under the coulomb versus time graph (recorded by the RCPT machine). The RCPT machine is also designed so that if the current should exceed 500mA, it will shut off automatically. Some of the mixtures with high coulomb values did not run the full 6 hours. This occurred mainly for mixtures tested on day 7, and for mixtures with high replacement percentages of fly ash. For these cases, the cumulative charge was determined by averaging it out to 6 hours and by the predicted results obtained from the RCPT software. This would result in some degree of error. However, because the rise in current over the six hours is quite slow is can be assumed accurately as constant value. The largest source of error (is believed) in this study arises from the variable nature of concrete mixtures (for example, differences in the properties and proportions of fine and course aggregates in the concrete mixtures).

5. Conclusions:

1. Partial fly ash replacement of Portland cement in concrete was shown to have adequate resistance to chloride ion penetration for certain cases. This is true for replacements of Sundance fly ash up to 80 percent, and for certain Rockport fly ash up to 40 percent replacement.

2. The replacement of fly ash with silica fume blended Portland cement did not lower the coulomb values relative to the silica fume blended concrete without fly ash replacement, at 56 days. This was due to the reduction of silica fume as fly ash percent replacements increases.

3. Silica fume blended Portland cement concretes with replacements of fly ash, had higher resistance to chloride penetration than concretes made with ordinary Portland cements without silica fume blending containing replacements of fly ash.

4. The Sundance fly ash was generally found to have lower coulomb values than the Rockport Fly ash, due to increased pozzolanic reactions.

5. The higher alkali content of the St. Constant cements likely caused more activation of the fly ash, relative to the cements with lower alkali contents.

6. Recommendations:

1. Fly ashes with lower carbon contents, which are therefore finer, should be selected over ones which are less so whenever possible, when concretes with higher resistance to chloride ion penetration is needed.

2. The inclusion of 5-10 percent silica fume in high volume fly ash concretes can be beneficial, and lead to further increases in the resistance to chloride ions.

3. The long-term resistance to chloride ion penetration, in high volume fly ash concretes, can not always be determined after just 56 days of curing. For concretes made with only pure Portland cement, it is recommended performing the RCPT after 28 days of curing. However, for concretes containing large volumes of SCM's such as fly ash, where pozzolanic reactions can take much longer it is recommended to perform such tests later on, perhaps after 90 days of curing.

4. The use of cements with higher alkali content or additions of NaOH could be used to increase activation of fly ash, provided that the negative effects of higher alkali content do not overly effect the morphology of the hydration products.

5. When the results obtained from this study are compared to that of others, results have fairly good correlations. Increasing fly ash replacement will generally

reduce chloride ion permeability provide ample curing times. However, in studies where the water to cement ratios are lower than the ones used in this study (0.44), the concretes generally have lower coulombs values, over lesser durations of curing (the opposite is true for higher ones). Therefore, concretes mixtures containing fly ash should have the lowest possible water to cement ratios possible (~0.35).

7. Future Work:

1. Additional data is needed to fully characterize the compressive strength development over time, for comparison with the results obtained from the RCPT, of the fly ash and Portland cement concrete mixtures in this study.

2. The effect of cement alkalinity needs further research for concrete mixtures containing fly ash. It was not proven that the high alkalinity of the St. Constant cement necessarily caused the increase in coulombs values, because of harmful effects of higher alkalinity to the products of hydration. Addition of NaOH to increase overall alkalinity in a fly ash and Portland cement concrete mixture should also be investigated further. It could be possible that additions of NaOH could lead to further "harmful" increase in the coulomb values in pure Portland cement concrete mixtures, while also causing larger "beneficial" (increased fly ash activation) reductions in the coulomb readings, for Portland cement concretes with fly ash replacements.

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9. Appendix:

ASTM C 1202 Coulombs at 7 days

mixture	Fly Ash Content				
Fly Ash %	0%	20%	40%	60%	80%
St. Constant Cement + Sundance Fly Ash	2934	5074	6898	8484	8025
St. Constant Cement + Rockport Fly Ash	2934	3964	7088	7628	8967
Brookfield SF Cement + Sundance Fly Ash	2355	4891	5770	6718	7046
Brookfield SF Cement + Rockport Fly Ash	2355	5057	6526	7258	7941
Herndon Cement + Sundance Fly Ash	2419	4758	4678	5319	6471
Herndon Cement + Rockport Fly Ash	2419	3243	4758	6482	7836
St. Constant SF Cement + Sundance Fly Ash	3808	8476	8700	10440	*11000
St. Constant SF Cement + Rockport Fly Ash	3808	4924	7352	8420	9554

*test went over 500mA

ASTM C 1202 Coulombs at 28 days

mixture	Fly Ash Content				
Fly Ash %	0%	20%	40%	60%	80%
St. Constant Cement + Sundance Fly Ash	2960	2396	2517	3689	5850
St. Constant Cement + Rockport Fly Ash	2960	2904	3606	5375	7559
Brookfield SF Cement + Sundance Fly Ash	520	907	1032	2060	4372
Brookfield SF Cement + Rockport Fly Ash	520	943	2021	5307	6159
Herndon Cement + Sundance Fly Ash	1922	1926	1718	2691	5393
Herndon Cement + Rockport Fly Ash	1922	1549	2354	3414	5104
St. Constant SF Cement + Sundance Fly Ash	992	1775	3361	3916	6887
St. Constant SF Cement + Rockport Fly Ash	992	3040	5283	8095	8319

ASTM C 1202 Coulombs at 56 days

mixture	Fly Ash Content				
Fly Ash %	0%	20%	40%	60%	80%
St. Constant Cement + Sundance Fly Ash	2729	1414	1196	1747	2574
St. Constant Cement + Rockport Fly Ash	2729	1703	1755	4102	6499
Brookfield SF Cement + Sundance Fly Ash	333	366	475	508	826
Brookfield SF Cement + Rockport Fly Ash	333	490	887	2410	2665
Herndon Cement + Sundance Fly Ash	1442	595	580	632	567
Herndon Cement + Rockport Fly Ash	1442	1105	1366	1823	4271
St. Constant SF Cement + Sundance Fly Ash	565	628	1020	930	964
St. Constant SF Cement + Rockport Fly Ash	565	1486	2374	5458	6318