2.1. Introduction

Supplementary materials such as fly ash, slag and silica fume when used in concrete production have been found to be beneficial in improving several properties including strength (as a result of pozzolanic reaction) and permeability (as a result of reduction in porosity and refinement of the microstructure) thereby reducing ingress of water and other harmful salt solutions and in many cases reducing the overall production cost. Strength improvements due to the addition of mineral admixtures is due to the pozzolanic reaction taking place, which typically starts after seven days and causes in increase in the amounts of C-S-H gel which is known to be the strength imparting component in concrete. Studies have also shown that a combination of fly ash and slag improves the strength of concrete at all ages similar to the addition of silica fume (Tan and Pu, 1998). The use of supplementary materials has found widespread applications in the construction industry also because of its tendency to act as a panacea for durability related problems. Plain concrete mixes if used in mass concrete construction like dams would result in very high heat of hydration thereby leading to problems like thermal cracking. The use of materials like fly ash or slag offers the possibility of reducing the temperature rise almost in direct proportion to amount of Portland cement replaced (Mehta and Monteiro, 1997). Durability to chemical attacks is improved with the use of
most fly ashes and slag’s mainly due to the pore refinement of concrete made with such materials. Experiments have shown that cement pastes containing 10-30% low calcium fly ash causes significant pore refinement in the 28 to 90 day curing period (Manmohan and Mehta, 1981).

Since this research pertains to the performance of concrete containing supplementary materials under cold weather conditions, further discussion would be restricted to this topic. Some of the major concerns regarding the inclusion of fly ash or slag in concrete are slow strength gain at early ages and effectiveness of air-entraining agent due to presence of carbon in fly ash, which can pose problems in providing a stable air-void system. Both of the above concerns can affect the freeze thaw and salt scaling resistance of concrete. ACI Committee 201 on durability of concrete has set forth specific guidelines for production of durable concrete under freezing conditions. These include adequate air entrainment, adequate compressive strength (4000 psi prior to freezing) and a period of air-drying prior to being subjected to freezing conditions. Naik and Singh (1991) investigated the use of high volume fly ash for use in structural concrete. Inclusion of Class C fly ash in concrete at replacement ratio of 1:1.25, resulted in lower values of compressive strength and splitting tensile strength at early ages up to 7 days. Beyond 7 days, concrete incorporating class C fly ash exhibited consistently higher compressive strength compared to the reference concrete at all the tested levels of fly ash up to 70% of cement replacement.

Earlier studies have shown that lower replacement levels of cement with fly ash or slag in the range of 20-35% is optimum in order to have satisfactory durability to frost conditions (Nasser and Lai, 1993). Concrete with higher water to binder (w/b) ratio is
more susceptible to problems related to deicer salt scaling and internal micro cracking due to freeze and thaw cycles (Bilodeau et al. 1991). Also, problems of dispersion of the air-entraining agents due to high carbon contents in the fly ash have been reported. Researchers have argued that as long as sufficient air content and spacing factor is provided, high carbon contents in fly ash do not pose a problem (Sturrup et al. 1983). There have been reports in the literature that the pressure method for determination of air content indicated a significantly lower air volume than did the microscopical analysis (Hover, 1988). This is believed to be due to the increase in internal bubble pressure, which accompanies a reduction in bubble diameter. The calculated error between the actual air content and the meter reading was found to be significant only in air bubbles smaller than 10 µm whereas for bubbles greater than 50 µm, the error was insignificant. However, for practical purposes, it is believed that bubbles less than 10 µm in diameter cannot exist in concrete because high internal pressures associated with such small diameters would force the air into solution. It is believed that finer cements can improve concrete durability due to the reduction in average size of the capillary pore. There have also been reports of the detrimental influence of high alkali/high C\textsubscript{3}A cements on the scaling resistance of concrete (Marchand et al. 2000). Rodway (1998) tested five different fly ashes covering a wide range of lime contents, which were used as 25 % replacement in concrete mixtures. It was found that regardless of the lime content of the fly ash, satisfactory air void size and spacing values could be obtained to produce durable fly ash concrete.

High volume fly ash (HVFA) concrete that contain fly ash in excess of 50 % replacement levels have been produced with the fly ash inter ground with cement or
added to the mixer as separate batch materials. The former also known as blended HVFA cements exhibit improvements in all properties (like mechanical strength, durability to freeze thaw resistance) except resistance to deicing salts when compared to the concrete in which the fly ash and cement were added separately at the mixer (Bouzoubaâ et al. 2001). HVFA is also known to improve the later age performance to strength and chloride ion penetration (Ramezanianpour and Malhotra, 1995).

2.2. Case studies of the durability of concrete containing supplementary materials to freeze thaw and scaling resistance

The two forms of damage in concrete due to exposure under cold weather conditions commonly reported are: internal cracking due to the freeze thaw action and surface scaling in the presence of deicer salts. This section discusses results from selected case studies.

Various binary and ternary blends were tested in a study at Virginia Department of Transportation (VDOT) and all combinations showed satisfactory durability factors after 300 cycles of freezing and thawing and only one binary blend (having 60 % slag) showed mass loss in excess of 7 % (Lane and Ozyildirim, 1999).

Naik et al. 1995 found that properly cured air-entrained concrete mixtures, one containing 40% Class F fly ash and another containing 50 % Class C fly ash had excellent resistance to freezing and thawing. The 40 % Class F fly ash concrete showed moderate scaling but the 50 % class C fly ash concrete showed severe scaling after 50 cycles of freezing and thawing. The same authors also pointed out the effectiveness of
the Class F fly ash in improving the resistance to chloride ion penetration compared to the Class C ash. In yet another study, Barrow et al. (1989) found that neither the strength nor the water to binder ratio is a governing factor in determining the scaling resistance of concrete containing fly ash. They observed that for a given curing temperature, the best scaling resistance was exhibited by concrete that did not contain any fly ash. Langan et al. (1990) observed poor scaling resistance in concrete with 50% fly ash. All four fly ash paving mixtures tested in this study showed visual ratings of 5 (worst rating) for scaling resistance after 5 or 10 cycles of freeze-thaw. It was observed that addition of superplasticizer resulted in an increase in spacing factor, which corresponds to reduced durability factors.

Nasser and Lai (1993) found that increasing the curing period did not increase the frost resistance. Incorporating 35 to 50% fly ash in concrete was detrimental to frost resistance even though the specimens were cured for 80 days. However, these authors found that 20% fly ash in concrete resulted in satisfactory performance (durability factor greater than 60%) and 35% fly ash resulted in doubtful to satisfactory performance (durability factor between 40 and 60%). These authors also found from SEM micrographs that decrease in the freezing and thawing resistance may be due to slow displacement of microcrystalline Ca (OH)₂ and fibrous ettringite hydrates from the dense C-S-H zones to the air voids during freeze-thaw cycling.

Marchand et al. (1992) found that only blended silica fume cement concrete cured with membrane forming curing compound displayed mass of scaled off particles below 1.5 kg/ m². Addition of fly ash or slag resulted in poorer resistance to scaling compared to the blended silica fume cement. Test results by Pigeon et al. (1996) indicate that the
higher porosity of the surface layer tends to reduce the deicer salt scaling resistance of wood troweled laboratory samples during the first cycles of freeze-thaw. Microstructural investigations have shown a higher porosity level at the top level as opposed to the bulk of the concrete. The 40% fly ash mixtures tested by the above researchers showed good scaling resistance despite having slow rate of reaction. The mass of scaled particles for this particular mix was 0.02 kg/m² after 10 cycles of freezing and thawing. The above research was based on the maximum scaling limit of 1 kg/m² adopted from the Swedish standard. It is believed that the mass of scaled particles increase with the amount of fly ash during the first 10 cycles as the amount of bleed water and the duration of bleeding at the surface increases; resulting in an increased porosity of the surface layer (Marchand et al. 2000).

Bilodeau et al. (1991) found that increasing the water to binder (w/b) ratio resulted in increased amount of scaling. They observed a lot of variability in the results from scaling tests on fly ash concretes. Also, increased replacement levels of cement with fly ash resulted in increase in the amount of scaling (Naik et al. 1995). For most mixtures tested, good scaling resistance (less than 0.8 kg/m² recommended by the Ministry of Transportation of Ontario, Toronto) was observed only after 3 days moist curing.

2.3. Factors influencing durability of concrete under cold weather conditions
There are several critical factors influencing the durability of concrete under cold weather conditions. These are discussed in the following sub-sections.
2.3.1. Stable air-void system

Research has shown that proper air void spacing is the most critical factor determining the resistance of concrete to freezing and thawing (Marchand et al. 1996, Pigeon et al. 1987, Pigeon et al. 1996). When the air voids are close together, the surrounding cement paste does not expand when it is frozen, thereby preventing crack formation. ASTM C 457 (1998) specifies a maximum air-void spacing of 0.008 inch (200 µm) for concrete exposed to freezing and thawing cycles. For a given concrete, the critical spacing factor can be defined as the value below which concrete will not be damaged by internal cracking when submitted to a given freeze-thaw cycle test. For concrete with water – cement ratio of 0.3, exposed to cycles of freeze thaw, it was observed that the critical spacing factor was 300 µm for condensed silica fume concrete and 400 µm for plain cement concrete (Pigeon et al. 1987). Klieger and Gebler (1987) observed that organic matter content in fly ash was the most significant factor affecting retention of air voids in fresh concrete. Total carbon content and loss on ignition of the fly ash showed less correlation with retention of air content in fresh concrete than did organic matter content. Class C ash was found to retain a greater amount of entrained air than the Class F fly ash. In general, air – entrained concretes with or without fly ash showed good resistance to freezing and thawing when moist cured at 23 °C, but the Class F ash showed lower resistance when compared to concrete made with Class C ash when cured at low temperatures.

Apart from the spacing factor of 200 µm which is most commonly used for specifying durability, field concrete having air content values in the range of 5-8% are also thought of as being durable. Though this is generally true, it may not always be the
case. It is normally assumed that concrete containing air content of about 6% has a spacing factor of about 200 µm. Figure 2.1 shows that concrete containing air content of 6% can have spacing factors ranging from 100 µm to 400 µm (Saucier et al. 1991). Conversely, a spacing factor of 200µm can be obtained with concrete with air content as low as 4% and as high as 9%. Hence, when producing concretes that will be exposed to cold weather conditions, it is always safer to specify the critical spacing factor value instead of completely relying on the air content values as is done in field construction.

Figure 2.1: Relation between air content and spacing factor (Saucier et al. 1991)

2.3.2. Strength, slump and cementitious material content

Swenson (1969) suggested some requirements for concrete to be durable to the effects of freezing and thawing and salt scaling. For severe exposures, it was recommended that air-entrained concrete should have strengths in the range of 3500-4500 psi. Also, the water to cement ratio should not exceed 0.45 and slump should not exceed 3 ½ in. He also recommended that finishing is critical as excessive laitance is vulnerable to frost action, especially in the presence of de-icing salts. Micro structural investigations of concrete
subjected to salt scaling indicate a higher porosity close to the surface compared to the bulk of concrete (Pigeon et al. 1996). Higher slump of concrete may result in higher bleed water at the top surface, rendering the surface susceptible to damage due to deicer salts.

Studies by Gebler and Klieger (1986) indicated that higher compressive strength of concrete is essential in improving the scaling resistance of concrete. Average compressive strengths of 3500 psi, 4460 psi and 4910 psi was reported for three concrete mixtures (cured at 4.4 °C) containing Class F fly ash, Class C fly ash and plain cement respectively. They reported that as the compressive strength increases, deicer scaling resistance generally improves. The cementitious material in the Class C and Class F mixture was 517 lb/yd³ and for the plain cement mixture was 474 lb/yd³. There are also recommendations that minimum cementitious material of 564 lb/yd³ and maximum water to cementitious material ratio of 0.45 should be adopted for satisfactory performance of concrete subjected to deicer salts (Kosmatka et al. 2002).

2.3.3 Curing

Curing plays an important role in reducing the permeability of concrete. This is particularly true for concrete containing supplementary materials as the dependence on curing increases with an increased replacement level of cement. Experiments done to determine the frost resistance of non air-entrained high strength concrete containing silica fume reveal some shortcomings of ASTM C666, which recommends only 14 days of curing prior to first exposure to freezing and thawing cycles (Cohen et al. 1992). Silica fume and other pozzolanic materials may require much higher time for hydration and self
desiccation in order to cause a reduction in the amount of freezable water. It was found that the compressive strength of concrete with 50% fly ash was more adversely affected by inadequate curing (Thomas, and Mathews, 1994). The fly ash concretes showed less oxygen permeability compared to OPC concretes at the same strength levels irrespective of the curing applied. Ballim (1993) suggested that increasing the duration of moist curing is a more effective way of extending the durability of concrete than increasing the cement content.

Bilodeau et al. (1991) found the mass of scaling residue to reduce significantly when membrane curing was used instead of moist curing. Langlois et al. (1989) found that the use of curing compound can result in scaling resistance as good as that of concrete moist cured for 14 days, but the results seemed to vary with the type of curing compound used. They also found accelerated heat curing of specimens to have a very detrimental influence on the scaling resistance.

2.3.4. Rate of freezing

Freezing rate is considered to be an important parameter specifying the freeze-thaw durability of concrete. It is believed that higher the rate of freezing, lower should be the spacing factor. For concrete prepared with w/c ratio between 0.5 and 0.6, Powers (1949) proposed a critical spacing factor value of 250 µm for a freezing rate of 11 °C/h. Different concrete mixtures having a constant w/c ratio of 0.5 but having variable spacing factors were subjected to F/T cycles (Pigeon et al. 1985). The critical spacing factors for various freezing rates were evaluated from length change measurements done at the completion of 300 cycles. It was found that the critical spacing factor reduces
significantly when the freezing rate is increased from 2 to 6 °C/h. Malhotra (1982) reported that concretes with spacing factor values in the range of 250 to 300 µm can resist 300 cycles of freezing and thawing in water when the freezing rate is 8 °C/h. His test results indicated that though the test results obtained from ASTM C666 procedure B (freezing in air, thawing in water) were identical to test results from procedure A (freezing and thawing in water), concretes frozen in water exhibited surface scaling after 300 cycles whereas those frozen in air did not.

2.3.5. Carbon content of fly ash

It has been reported that concrete containing fly ash can be durable to the effects of freezing and thawing provided it has a stable air-void system. There have been reports of carbon content in the fly ash reducing the effectiveness of air-entraining agent. Sturrup, Hooton and Clendenning (1983) found that doubling the carbon content required a double dosage of air-entraining admixture for entraining about 6.5 ± 1 % air. They mentioned in their findings that as long as the required air contents are obtained, carbon content in the fly ash does not adversely affect the performance of fly ash concrete to the effects of freezing and thawing.

2.3.6. Degree of hydration

Degree of hydration is an important tool in determining the amount of internal water present in a paste mixture, which can be useful in predicting the performance in similar concrete mixtures under freezing conditions. In a binary system containing cement and fly ash, determining the fly ash reaction products besides the cement hydration products
becomes essential. Selective dissolution procedures have been adopted to determine the degree of fly ash reaction. Lam et al. (2000) found that in HVFA pastes containing 45% and 55% fly ash, more than 80% of the fly ash remains unreacted even at the age of 90 days. They also found the non-evaporable water contents ($W_n$ %) of fly ash pastes to be lower than the plain cement pastes at a given water to binder ratio. Roy (1989) found that the hydration rates are greatest in silica fume pastes, followed by OPC pastes and fly ash pastes. It was found that the degree of reaction of silica fume is much greater than fly ash pastes even at 90 days primarily due to silica fume’s high specific area and that the overall reaction with Class C ash is greater than the Class F ash after a few days. XRD patterns have shown that the hydration products of OPC with fly ash and slag are very similar and that at the age of 90 days, slags showed better pozzolanic activity than fly ash (Sharma and Pandey, 1999). It has also been verified that hydration of the fly ash causes a densification of the microstructure, as the SEM studies show etching of glassy materials around the ash and at ages beyond 28 days, the fractured surface deposits comprise of round, toroidal plates with compositions similar to C-S-H (Berry et al. 1994).

2.4. Maturity method

In concrete construction, it is essential to know the in-place strength of concrete so that construction schedules could be planned in advance and executed so as to have maximum economic benefits. The maturity technique uses temperature history collected during the curing period to find an equivalent age needed to achieve desired level of strength under different temperatures. Maturity techniques are being used extensively in current
pavement construction practices as a tool to predict the strength of concrete, which in turn can be useful in deciding the period of curing required before the pavement can be opened to traffic. The devices commonly used to measure temperature in concrete are thermocouples or other sensors like thermistors, which are inserted into the concrete at required depths. The temperature is collected by a data logger (which stores the temperature data), to which instructions like the time interval for temperature collection are transferred by means of a software code.

Under isothermal curing conditions, the strength gain of concrete can be described by a hyperbolic curve having three parameters: (1) the limiting long-term strength, $S_u$, (2) the rate constant, $k_t$ and (3) the age $t_o$ when rapid strength development is assumed to begin (Tank and Carino, 1991). Another important parameter called the activation energy, $E_a$. Activation energy is defined as the energy required to initiate a reaction or the minimum energy needed to form an activated complex during a collision between reactants. $E_a$ is related to the rate constant through the Arrhenius function, which was found to accurately account for the influence of temperature differences on strength gain (Carino, 1991, Carino et al. 1983). The maturity method has been used to accurately monitor and predict the strength gain of rapid concrete pavement repairs during the curing period (Okamoto and Whiting, 1994). The prediction using the maturity method however seemed to underestimate strengths at early ages. Pinto and Hover (1990) found that the initial and final set times could be predicted for any mixture provided the activation energy is obtained. Early age curing temperatures have been found to influence the ultimate strength of concrete. McIntosh (1956) reported that for equal maturities, specimens exposed to low early age temperatures were weaker at early maturities but
stronger at later maturities. Many other researchers also reported this “cross-over” effect where lower early age curing temperatures resulted in higher ultimate strengths.

2.5. Water ingress in concrete

The resistance of concrete to ingress of harmful salts or to that of water depends upon the permeability of the system. In other words, a denser microstructure of concrete not only ensures less ingress of harmful salts, which can cause problems related to corrosion of the reinforcing steel, but also reduces water absorption, which is important with respect to improving the durability of concrete to freezing and thawing cycles. Millions of dollars are spent every year towards rehabilitation of bridge decks, which deteriorate over time mainly due to the corrosion of reinforcing steel. Also, water filling of air voids has been experimentally proven to be the most probable cause of high scaling in virgin concretes (Jacobsen et al. 1997). In an unsaturated system, water flows within a porous media under the action of a capillary force, which in turn depends on the pore structure of the material. Thus the capillary force is the strongest when the material under consideration is completely dry and becomes small in saturated conditions. In concrete, the water absorption could be influence by the porosity of the aggregate, porosity of the cement gel matrix, the packing geometry of the constituent particles like sand, coarse aggregate and in some cases due to the inclusion of air - entraining admixtures (Hall and Yau, 1987). High permeabilities in concrete are often related to poor compaction practices or to the use of higher water - cement ratio or to the non-inclusion of supplementary materials, which are known to refine and reduce porosity.
Sorptivity test that involves the theory of capillary suction can be used to determine the cumulative absorption as well as the rate of ingress of water in the concrete. The above method in which the depth of water penetration is proportional to the square root of time may thus be useful in studying the quality of concrete surfaces subjected to wet and dry cycling (Gopalan, 1996, Hall, 1989, Hall and Yau, 1987, Martys and Ferraris, 1997). Gopalan (1996) found that when adequate curing was provided, 37% reduction in sorptivity was observed in a mix containing 40% fly ash. He also reported that under fog cured conditions, the sorptivity of fly ash concrete was lower than OPC concrete, but under dry curing, the sorptivity of the fly ash concrete was higher than the OPC concrete. Studies have also been done to study the effect of surface finish on the sorptivity of concrete. It is believed that cut sections are not the most appropriate samples to be used as cutting might introduce microcracks in the concrete. McCarter (1993) tested the top, bottom and cut surfaces for their sorptivity and found the top surface to have the highest sorptivity values followed by the bottom and cut surfaces.