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THE EFFECT OF DE-ICING AGENTS ON WATER ADSORPTION PHENOMENA IN ROCK AGGREGATES

A Thesis

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of Windsor.

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CONTENTS

CHAPTER 1

CHAPTER 2

CHAPTER 5

APPENDIX A

APPENDIX B

TABLES

TABLES CONTINUED

FIGURES

FIGURES CONTINUED

ABSTRACT

Reviews of the mechanism of frost action in cement paste, concrete and aggregate are presented, with reference to the possible action of deicing agents. A Theoretical treatment of the influences of adsorbed cations on clay mineral surfaces on water adsorption is also presented.

Carbonate rocks of middle Ordovician to middle Devonian age were taken from aggregate producing quarries in Southern Ontario. The following were determined: water adsorption at 45 % and 95% humidity and approximately 20 C, alumina, silica and calcite/dolomite ratio, 24 hour and vacuum saturation adsorption and loss in the magnesium sulphate soundness test. A simple rapid method for the determination of the quantity of adsorbed water to a precision of 0.002% by weight was perfected.

Statistical analysis of the results indicated the following:

The adsorption of water by carbonate rocks is largely controlled by the amount of alumina (clay) in the rock. For equal amounts of clay at 45% humidity, limestones adsorb about 65% more water than dolomites. Treatment of rocks with 0.5 molar solutions of chlorides of the following cations increased adsorption at high humidities in the order: $K^+ < Li^+ < Na^+ < Mg^{++} < Ca^{++}$. Water adsorption was found to be one of the main factors influencing performance in the magnesium sulphate soundness test. The greater the adsorption the greater the loss in the sulphate test. Thus the action of deicing agents increases adsorption which results in a decrease in durability.

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INTRODUCTION

The 'Bare Pavement' policy adopted by Departments of Highways has led to the use of deicing agents in ever increasing amounts on North American roads. While their use enables more rapid transportation under winter conditions, this may not necessarily lead to an increased degree of safety (Adams 1973). The strain that these large amounts of salt place on the biosphere has been well documented by Keyser (1973). In addition to the deleterious effect on the environment, deicing agents cause decreased durability of concrete roads and structures. Research into how deicing salts cause this increased deterioration has been hampered until recently by lack of proper understanding of the mechanism of concrete deterioration under freezing conditions.

The deterioration of concrete cannot be properly understood unless observations of freezing of cement paste and aggregate are treated as separate yet related phenomena. The phenomena of freezing and the effect of deicing agents on cement paste is now moderately well understood. However the role that aggregate plays, in the disruption of concrete on freezing, is most important, yet is less well understood, this is due in part to extreme variability in the aggregates physical characteristics. This study was performed in an attempt to learn how deicing agents influence the performance of rock aggregates in concrete. A review of literature suggested that water adsorption by rock aggregates may influence the performance of aggregate in concrete. Literature reviewed in chapter 2 suggests that the application of a deicing salt may significantly alter the water adsorption properties of rock aggregates. This work was extended to investigate how the variation in mineralogy caused variation in the water adsorption characteristics of rock aggregates. The amount of water adsorbed by carbonate aggregates should be related to the internal surface area of the rock, which in turn should be significantly related to the clay content of the aggregate.

Deicing agents are chemicals which are used on road surfaces to prevent the formation of ice and to melt ice and snow. They work by forming a solution in water, changing the hydrogen bonded structure of the water, which lowers the freezing point. Any substance soluble in water depresses the freezing point; however, the common deicing agents are: sodium chloride, calcium chloride, ethyl alcohol and ammonium chloride. Usually sodium chloride is used because it is generally the cheapest. In very cold climates, calcium chloride or a 1:3 mixture of $CaCl_2$:NaCl may be used. Calcium chloride causes a greater reduction in freezing point (-50°C) than sodium chloride (-20°C). Also calcium chloride releases heat on going into solution, thus speeding the melting process. The many factors that influence the melting rate of snow and ice, were discussed by Keyser (1973) in a comprehensive review paper.

CHAPTER 1

THE MECHANISM OF FROST ACTION IN CEMENT AND CONCRETE AND THE EFFECT OF DEICING AGENTS

INTRODUCTION

Before a proper understanding of the disruption caused by deicing agents can be formed it is essential to understand the mechanism by which concrete deteriorates under freeze/ thaw conditions. Any study of the mechanisms of concrete deterioration under frost conditions should treat the cement paste and aggregate as two separate,yet related systems. This also applies to the effect of deicing agents upon cement paste and on the aggregate in concrete.

MECHANISM OF FROST ACTION IN CEMENT PASTE

Powers in 1945 proposed the hydraulic pressure mechanism to explain the force causing disruption of cement paste under freezing conditions. Ice forming in pores expands by about 9% by volume. According to Powers theory, in a saturated or nearly saturated porous material,this expansion will drive unfrozen water away from the site of ice formation. If the rate of freezing is rapid enough, pressure caused by the resistance to flow of water through the microporous paste may be sufficient to exceed the tensile strength of the paste and disruption and failure will occur.

Further experimental work caused Powers and Helmuth (1953) to propose another mechanism which seemed better able to explain experimental results observed. They observed an initial contraction on cooling below 0°C of about twice that predicted by the coefficient of thermal expansion. They attributed this to the progressive dessication of the cement paste. They also found that after freezing occurred, dilation continued while the temperature was held constant. They proposed that since ice growing in a cavity has a much lower vapour pressure than that of water, water will migrate toward the ice through the paste and be condensed in the form of ice in the cavity. If the water in the pores has dissolved solute (cement alkalies) this will be concentrated at the point of freezing as the weak solution migrates to the cavity. This concentrated solution may have a vapour pressure the same as that of the ice and thus will not freeze and the two phases will be at equilibrium. Water will still migrate toward the cavity which contains ice and concentrated solution since it has a vapour pressure greater than that of the two phase system. When the cavity is filled by ice and concentrated solution, expansion may take place caused by the osmotic pressure so generated. Expansion may also be caused by the force generated by growing ice crystals in the larger pores,in the same manner as growing salt crystals may exert destructive pressures. While certain pores may be expanding, the surrounding paste tends to shrink as a result of water being drawn from it toward the cavities containing ice. The volume change of the material as a whole is the resultant of the two processes operating. Continued dilation,,observed at constant temperature after a period of freezing,may be due to the fact that normal rates of cooling are too fast for equilibrium to be established rapidly and thus water is still migrating through the porous , though not very permeable paste,towards sites of freezing.

Recent work by Litvan (1972 ,1973a,1973b, 1975) on the phase transitions of adsorbates has led to another proposed mechanism of frost damage to cement paste. This, like Powers' and Helmuth's (1953) hypothesis, utilises the idea of moisture migration in cement paste due to disequilibrium caused by differing vapour pressures between ice and water. The actual mechanism, however, differs from that of Powers' and Helmuth. Litvan (1972) proposed that the mechanism causing disruption is ...'the desorption or expulsion of water resulting from reduction of the relative humidity'. Adsorbates that shrink on freezing, cause a similar dilation to that of water when cement paste is frozen (Litvan 1975). Litvan concluded that the observed dilation of cement paste on freezing is not caused by expansion of ice in the paste.

Water contained in the pores and capillaries of a porous body has a reduced vapour pressure as predicted by Lord Kelvin's equation (Adamson 1960,p.57). This water will not freeze until the vapour pressure of ice is equal to that of the water in the pores. The narrower the pore, the lower the vapour pressure above the mensicus and hence the temperature at which it will freeze. Water, whose vapour pressure is greater than that of ice at any prevailing temperature will be at disequilibrium and will either condense as ice or migrate toward the outside of the body and freeze there. Because cement paste has a wide range of pore sizes, lowering temperature and hence vapour pressure, results in continuous dessication as the pores empty (Litvan 1972) If the water is unable to escape from the porous body, dilation occcurs. The longer the migration path, the less water will escape at a given rate of temperature drop for a given degree of saturation. A body of small minimum dimension should dilate less than one of a larger minimum dimension due to a shorter migration path. Litvan (1972) observed that on freezing, the length of a cement paste specimen 0.05 in. thick did not increase as much as that of a specimen 0.125 in. thick under the same conditions.

Air-entrained pastes do not expand excessively on freezing since they are not saturated. The air voids are sufficiently large so that they will not fill with water by capillary action even at high humidities. These voids provide reservoirs into which water can flow from desiccating paste on the reduction of vapour pressure with cooling below 0° C. Normal cement paste, is not protected in this manner and if critically saturated will deteriorate when frozen (Litvan, 1972). The degree of saturation theoretically needed to produce dilation is 91.7 percent. However, due to the heterogenous nature of cement paste and other porous media a degree of saturation below this theoretical point may often produce dilation. MacInnis and Lau (1971) investigated the dilation of concrete at different degrees of saturation on cooling and noticed that complete saturation was not necessary to produce dilation. Dilation could be produced when the concrete was only 80 - 90% suturated.

Void space and pore size distribution (determined largely be water/cement ratio and air-entrainment), permeability, degree of saturation, specimen size and rate of cooling are all significant variables which determine the durability of cement paste. The ASTM test (C666) has poor reproducibility and relevance to field conditions because many of these variables are not sufficiently controlled by the procedures of the test (Litvan 1973b). Furthermore, it is highly likely that under field conditions the concrete will be subjected to periods of drying between periods of freezing. Powers (1955) and Litvan (1973b) critically reviewed ASTM soundness tests and suggested ways in which they might be improved, in operation and in quantitative measure of the damage incurred.

Cement paste of high water/cement (W/C) ratio (which increases its porosity), suffers more from the effect of freezing and thawing than does cement paste of low W/C ratio. Litvan (1973b) found that a 0.4 W.C ratio paste dried at about the same rate as a paste with a W/C ratio of 0.8, yet there was a large increase in porosity and amount of adsorbed and absorbed water in the latter. Litvan attributed the greater frost susceptibility of pastes of high W/C ratio to an increase in the amount of water to be expelled on freezing. This water increases with an increase in W/C ratio ..."without the benefit of increased permeability". Since the mechanism proposed by Litvan is essentially rate controlled, the increased susceptibility to frost action of saturated cement paste with a high rather than low W/C ratio, is not surprising, as much more water will have to be moved in a given time to prevent failure. Verbeck and Landgren (1960) considered, however, that the permeability of paste depends upon the W/C ratio. "For well hydrated pastes the permeability may be increased by as much as 100 fold as the water/cement ratio is increased from 0.40 to 0.70 by weight". Neville (1972) found that the permeability of cement paste was controlled both by the degree of hydration and the W/C ratio of the cement paste. He considered that a reduction in the W/C ratio from 0.7 to 0.3 lowered the co-efficient of permeability a thousandfold. Thus Litvan's (1973b) hypothesis appears to be invalid if, in fact, increased W/C ratio does increase permeability as well as 'freezable' water.

Dunn and Hudec (1965) formulated the hypothesis that the principle cause of disintegration of some rocks was the expansion of adsorbed water on cooling. They proposed that adsorbed water was relatively rigid and not very mobile. However, work on the nature of adsorbed water in clays suggests that at least above -30 C this is not the case, because adsorbed water has the properties of a two dimensional fluid (Anderson 1972). Since cement paste has a relatively large specific surface area, it will also have significant quantities of adsorbed water: thus Dunn and Hudec's principle would also be applicable to cement. Powers (1972) considered that the force causing the disruption observed by Dunn and Hudec was either that of osmotic pressure, or swelling of the rock due to the action of adsorbed water on the clay within the rock.

MECHANISM OF FROST ACTION IN AGGREGATES

Rock aggregates are less uniform in pore size and pore size distribution than cement pastes. Some aggregates have large pores and, as a result, a small specific surface area while others have extremely small pores and hence a large specific surface area, not unlike cement pastes. Thus hypotheses formulated to explain freezing phenomena in cement paste may be applied with certain modifications to rock aggregates (Powers 1975).

Verbeck and Landgren (1960) subscribed to Powers' (1945) theory to explain the failure of aggregates due to freezing. Powers attibuted the failure of cement paste and concrete to hydraulic pressures set up as a result of flow of water away from regions of freezing to accommodate expansion due to ice formation. Litvan's (1972) hypothesis attributing water movement to reduction in relative humidity may also operate. In either case, moving water appears to be the destructive agent. Therefore, many factors recognized as important by Verbeck and Landgren (1960) in determining aggregate performance are still relevant.

Verbeck and Landgren (1960), like others before and since, (Powers 1955, Litvan 1972), recognized the importance of the degree of saturation, porosity and permeability of aggregate and cement paste in determining the resistance of concrete to freezing. They introduced the concept of critical aggregate size, that is: "that size above which a particle of aggregate in not able to accommodate hydraulic pressures as a result of freezing." Aggregates of low permeability (fine pores) have a small critical size. Aggregates of high permeability can have a large critical size. They found that rocks of very low absorption (less that 0.1% by weight) can probably accommodate tensile stresses due to freezing even when completely saturated. Concrete made from these aggregates may withstand hundreds of freeze-thaw cycles with only minor damage (Powers 1975).

The degree of saturation at any particular humidity depends largely on the pore volume and pore size distribution of the aggregate. An aggregate with fine pores such as a trap rock or argillaceous dolomite will attain a much higher degree of saturation at any particular relative humidity than a rock with large pores such as a biohermal dolomite. Figure 1 shows that even at 100% relative humidity (R.H.) the dolomite will not be completely saturated; yet the microporous trap rock will be almost completely saturated. Verbeck and Landgren also considered that a rock of fine pore size would reach a high degree of saturation much more rapidly than one of large pore size even if the rocks had the same porosity.

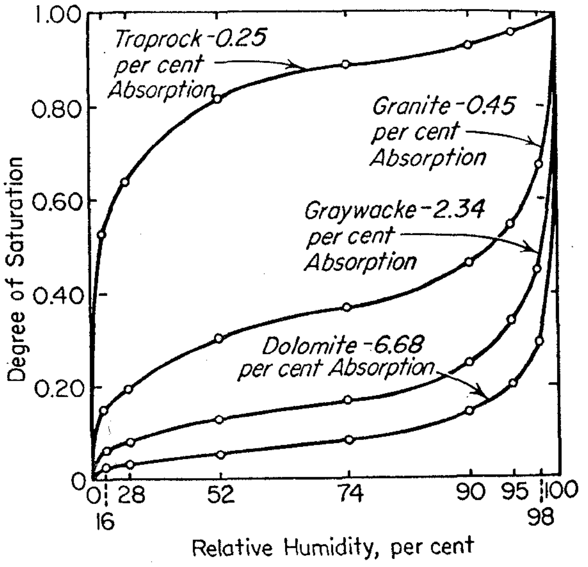


FIG. 1. Degree of saturation against relative humidity for rocks of different pore size distributions, from Verbeck and Landgren (1960), p. 1066.

The greater the degree of saturation, the greater the percentage of the absorbed water that will have to be expelled on freezing to allow for the expansion accompanying ice formation. Thus, the degree of saturation of an aggregate is of extreme importance because: "the hydraulic pressure created during freezing is a direct function of the amount of water that must be expelled from the freezing zone" (Verbeck and Landgren 1960 p. 1075). While the driving mechanism as visualized by these authors may not be the correct one, their conclusions are still valid since, as implied by Litvan's hypothesis, the greater the amount of water at disequilibrium, the greater the damage on freezing. Large voids in a rock not filled at the prevailing humidity will act as relief reservoirs for the water expelled on freezing in the same manner as air-entrained bubbles. Thus the dolomite in Fig. 1 will have ample pore space on freezing at 98% R.H. to accommodate water, yet the microporous trap rock will have very little space for accommodation since it is almost completely saturated.

Both Powers' (1945, 1955) and Litvan's (1972) hypotheses regard water as the destructive agent. On freezing aggregate, water may be prevented from moving by low permeability or the blocking of pores by ice. The hydraulic pressures produced may be destructive if there are not unfilled void spaces to relieve this pressure.

From brief consideration of the factors outlined above, it may be readily understood that any factor that increases the degree of saturation of the aggregate particle, at any relative humidity, will tend to decrease its durability on freezing.

MECHANISM OF FROST ACTION IN CONCRETE

On cooling concrete, water from a saturated aggregate particle will be expelled and will migrate into the cement paste. Naturally the larger the aggregate particle, the smaller the unit external surface area. Thus for a given porosity, degree of saturation and rate of freezing, more water has to be expelled per unit surface area for a larger aggregate particle than a smaller particle. The greater the amount of water flowing through a given unit area of interface, the greater will be the pressure induced by the flow of water. Thus it is possible that sufficient tensile stress may be developed to cause disruption and failure near a paste-aggregate boundary. This is more likely to occur for a large aggregate particle than a small particle of the same porosity and degree of saturation. If this hypothesis is correct, concrete made by using a reduced maximum aggregate size should be more durable than concrete made using a larger size. This has in fact been observed by many workers (Verbeck and Landgren 1960, MacInnis and Lau 1971, Powers 1975).

The important role played by aggregates in concrete durability has been demonstrated. Air-entrainment does not fully protect concrete unter the conditions of the accelerated freeze-thaw test ASTM C666 (Powers 1975). The time taken to fail will be a function of the rate of saturation of the particles of aggregate, other factors being constant. Remembering Verbeck and Landgren's (1960) conclusion that microporous rocks will reach a high degree of saturation more rapidly than a macroporous rock under the same conditions, it should be possible to predict the durability of concrete, given a knowledge of the pore size distribution of the aggregate and the properties of the cement paste.

EFFECT OF DEICING AGENTS ON CONCRETE AND CEMENT PASTE

The poor performance of concrete in the presence of deicing agents has been recognized for some time (Amfelt 1943). There are two main effects of deicing agents on concrete durability:

1. Concrete specimens saturated in solutions of deicing agents show an increased dilation on freezing compared to specimens saturated in water (Whiting 1974). Whiting also

found the greatest dilation occurred following freezing in 3% solutions of sodium chloride.

2. Surface scaling: This phenomenon is the separation of thin layers of cement paste from the surface of concrete. Brown and Cady (1975) attributed failure of this nature to the hydraulic pressure mechanism which they related to the degree of saturation and the deicer concentration gradient in the paste. They considered that it was a paste phenomenon and not directly related to the performance of the aggregate. Litvan (1975) considered that the best prevention against this problem was a reduction in porosity. This phenomenon shall not be considered further in this thesis.

Verbeck and Klieger (1957) found that solutions made of 3% by weight deicing agent produced a greater deterioration of concrete than with either lower or higher concentrations, regardless of the type of deicer used (NaCl, $CaCl_2$, Urea and ethyl alcohol). This has been confirmed by later studies (Whiting 1974, Browne and Cady 1975, Litvan 1975). Whiting (1974) found that concrete specimens, previously saturated in different concentrations of sodium chloride solution, increased the amount of adsorbed water at constant relative humidities in proportion to the concentration of the sodium chloride. Thus a specimen previously saturated in 10% NaCl adsorbed more water than a specimen previously saturated in 3% NaCl. Experiments conducted by Vos and Tammes (1969) showed relationship of adsorbed water to the content of NaCl in porous materials (Fig 2). Whiting (1974) and Litvan (1975) both noticed that the maximum dilation was obtained at low (3 - 5%) concentrations of deicer. Litvan found that this relationship held, with varying W/C ratios both for normal

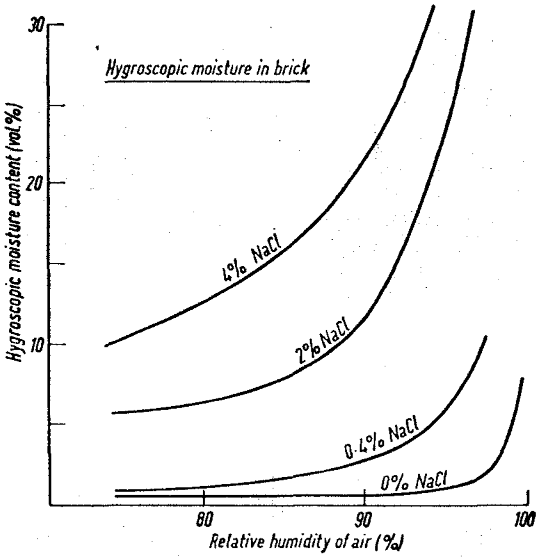


FIG 2. Hygroscopic moisture in brick depending on the relative humdity of the air and the content of NaCl. From Vos and Tammes (1969).

and air-entrained cement pastes (Fig 3).

Litvan (1975) attributed the action of deicers to the high degree of saturation they cause when cement pastes are immersed in them. This he considered was a consequence of the reduced vapour pressure of the solutions. Thus specimens soaked in more concentrated solutions should have been more nearly saturation and so might have been expected to show greater dilations. From consideration of Fig 3.,it will be seen that this was not in fact the case. There must be some factor controlling dilation,other than the degree of saturation.

Litvan (1975) froze cement pastes and conducted differential thermal analysis (D.T.A.) and length change measurements. He found that pastes saturated in water showed a narrow range of freezing temperatures with a single exothermic peak at about -9° C. On freezing pastes saturated in different concentrations of sodium chloride solution,he found a much wider range of freezing temperatures with two exothermic peaks. The low temperature peak always occurred at about -25° C, and its size was

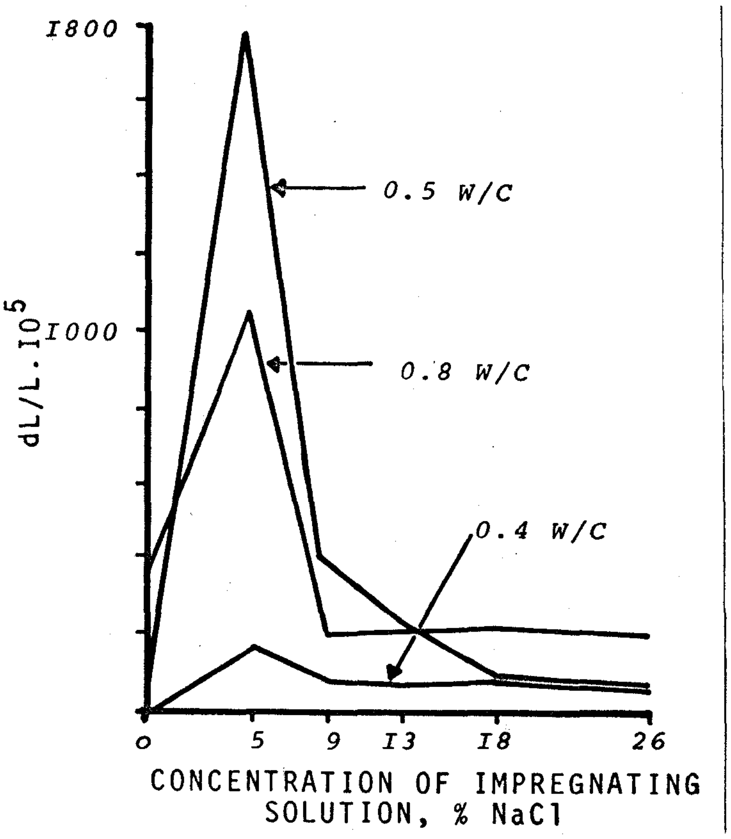


FIG 3. Overall expansion (difference between minimum on cooling and maximum on warming) as a function of deicer concentration. From Litvan (1975).

increased with increased salt concentration. The -9°C peak showed a size inversely proportional to the salt concentration. Litvan proposed that the increased dilation and destruction of paste frozen in low concentrations of deicers was due to two opposing effects. These were: an increased degree of saturation and a broadening of the freezing temperature with increased concentration of deicer. He postulated that:"these effects oppose each other and result in most severe conditions at low (5%) concentrations...". He implied that at about -9°C,more water was flowing in the system (in a response to relative humdity changes) than at any other temperature of deicer concentration. He observed that a 0.5 W/C air-entrained paste in 5% NaCl showed a far greater expansion on cooling from -10°C to -20°C than that observed for the paste saturated at other concentrations.

Litvans's work implies that more water is frozen in a given time at moderate deicer concentrations. There is, however, a major difficulty in this. Dunn and Hudec (1972) investigated the freezing of aggregates, some of which may have had a pore size distribution not unlike the cement pastes investigated by Litvan (1975). When comparing samples cooled to -20°C and saturated in pure water, with those saturated in a 10% sodium chloride solution, they found that 8 of 11 samples showed, on the average, a decrease of about 50% in the amount of water frozen. They ran most of their experiments to -20°C and only rarely went as low as -20°C and did not observe any freezing of water below -12°C. These results were based on data obtained by D.T.A where the amount of water frozen was proportional to the area under the recorder trace. It seems probable that Dunn and Hudec (1972) never observed the low temperature exothermic peak found by Litvan (1975); thus there may not be a reduction in total water frozen following saturation in solutions of deicers.

Litvan (1975) attributed the increased saturation observed, due to deicing agents, to the reduced vapour pressure of the deicer solution. This increases the saturation of the paste by hygroscopic action. Since this is a physical, rather than a chemical process, Litvan postulated that all deicers will show an increased saturation and a broadening of freezing temperature ranges with increased concentration, resulting in maximum dilation of specimen saturated in 5% solution. Litvan found that specimens saturated in urea and in sodium chloride solutions showed similar relationships in terms of the heat change and dilation on freezing. Verbeck and Kleiger (1957) found that moderate concentrations (3%) of NaCl, $CaCl_2$, urea and ethyl alcohol solutions, produced the greatest deterioration on freezing. Therefore, the action of deicers is primarily a physical phenomenon.

CHAPTER 2

THE EFFECT OF DEICING AGENTS ON ROCK AGGREGATES

INTRODUCTION

The freezing of aggregate, in a weak solution of a deicing agent, increases the deterioration of the aggregate. The New York freeze-thaw test (N.Y. Test method 208-62) for coarse aggregate, calls for the saturation of the aggregate in a 10% sodium chloride solution. This decreases the number of cycles needed before measureable deterioration takes place.

Dunn and Hudec (1972) found that 8 of the 11 rocks studied showed increased absorption following saturation in a 10% sodium chloride solution, when compared to absorption in pure water. They reported a reduction in the total amount of water freezing on cooling to -20°C following saturation in sodium chloride solution. However, as discussed in the previous chapter, they failed to observe freezing below -12°C and a possible low temperature exothermic peak. This may have resulted in the observed reduction in the amount of water frozen. Dunn and Hudec attributed the reduction in the total water frozen to the sodium chloride increasing the amount of adsorbed (unfreezable) water, in relation to the total water content. More recent work by Rigbey (1975) confirmed in part the findings of Dunn and Hudec. He found that rocks previously treated in a 5% sodium chloride solution showed an increase in adsorbed water at 45% and 98% relative humidity. He also found that the amount of absorbed water was increased on average by 11%.

It appears that there are two processes by which it might be possible for rock to increase its adsorbed and absorbed water.

1. An enhancement of the surface sorptive properties of alumino-silicate minerals within the rock as suggested by Fisher (1972).
2. An increase in the amount of water held in capillaries due to the hygroscopic nature of solutions of deicers. Water vapour is attracted towards partly filled capillaries due to the lower vapour pressure of the solution (Litvan 1975).

How does an increase in adsorbed and absorbed water result in decreased durability of aggregate? Or is there some other associated factor which causes an increase in deterioration? In view of work by Litvan (1975) and others (Verbeck and Kleiger 1957, Whiting 1974) it is probable that maximum deterioration is obtained using a 3-5% sodium chloride solution. Hudec (personal communication) reports that the destructiveness of deicing solutions on aggregate does in fact peak at intermediate concentrations (3-5%).

HYDRATION

The hydration of sodium chloride, when added to water, is a process of interaction between ions of sodium and chlorine and the molecules of water. This interaction not only affects bonds between ions and the molecules of water but also the structure of the water in the solution. Horne (1970 & 1972) presented diagrammatic models of the structure of pure water and the water structure near a sodium ion. Sodium enhances the hydrogen bonding of the water. Immediately adjacent to an ion is a 'primary hydration' sheath of four strongly bound, tightly electrostricted water molecules. At increasing distances from the ion, the water is less influenced by the ions' coulombic field. Horne (1972) suggested that clusters of 'structured' water molecules are larger and more molecules are affected due to the presence of a sodium ion than are found in pure water. He considered that at 20°C there were 40 water molecules in the total hydration atmosphere of a sodium ion. At present, the nature of the hydration of anions is not properly understood.

The close hydration of ions in aqueous solutions is frequently represented as the strong binding of nearby molecules. This is characterised by the number of water molecules bound or the so called hydration number of the ion. This concept is only justified in the case of strongly hydrated ions (Sanioilov 1972). The hydration number of an ion depends on its radius and charge. For instance, lithium and sodium can, theoretically, closely bind four molecules.

IONIC SPECIES	ΔE (K cal per mole)
Li	.73
Na	.25
K	-.25
Mg	2.61
Ca	.45

TABLE 1. Values of ΔE of hydration. From Fisher (1972)

The above table shows the energy of hydration of various ions in an infinitely dilute aqueous solution. A large positive ΔE corresponds to strong hydration. While these values are somewhat idealised, they do show the relative hydration of the respective ions. Note that potassium shows a negative energy of hydration which results in a net destruction of the hydrogen bonded water structure. Sodium and lithium form a bond between their ions and the nearest molecules of water and also enhance bonds between adjacent water molecules, resulting in an increase in clustering of water molecules.

Robinson and Stoakes (1959) found that the energy of hydration of group 1A cations increased with a decrease in ionic radius, i.e., Li< Na< K< Cs . Thus lithium hydrated more strongly than sodium. There appears to be some disagreement over the actual values of energy of hydration, due in part, to different assumptions about the nature of the chlorine ion. However, the relative relationship of the order of hydration of monovalent cations is clear.

ADSORPTION IN ROCKS

The phenomenon of adsorption of very thin layers (one or two molecules thick) of gas or liquid on surfaces is well documented by Adamson (1960). Boyd (1971) investigated the theoretical and thermodynamic considerations of the adsorption of water on clay surfaces.

The greater the surface area, the more adsorbate will be held by the adsorbent. Table 2 gives some figures for the surface area of various minerals, determined by nitrogen adsorption techniques. Note, however, that the values obtained can vary according to the technique employed. It will be seen from the table, that in carbonate rocks, the minerals calcite, dolomite and quartz play a subordinate role in adsorbtion to clay minerals even though the layer may constitute only one or two percent of the rock.

MINERAL	SURFACE AREA
Kaolinite	13.2 m^2/g
Montmorillonite	85-800 m^2/g
Fullers Earth	310 m^2/g
Halloysite	14.2 m^2/g
Silica gel	520 m^2/g
Illite	120-350 m^2/g
Dolomite	.743 m^2/g
Calcite	.714 m^2/g
Quartz	very low

TABLE 2. Surface area of some minerals. From Boyd (1971).

THE EFFECT OF CATIONS ON ADSORPTION

A geologist of necessity works on a complex material with many variable parameters. In order to understand the effect of cations on water adsorption,it is necessary to look to other, yet related fields.

Considerable work has been done by agronomists and others on the adsorption of water in clay systems. Clays may be obtained in a relatively pure and homogenous form which may be investigated by the use of X-ray techniques and calorimetry. Their structure, physical and chemical properties are known and have been extensively studied. They are particularly well suited for the study of adsorption phenomena since they have very large specific surface areas.

How relevant will be an investigation of the properties and variables affecting adsorbed water on clays to actual rock systems? Illites are the dominant clay minerals in shales and mudstones and occur in other sediments such as limestones (Deer, Howie and Zussman 1966). Robbins and Keller (1952) reported that illite was the most common clay mineral present in limestones of Palaeozoic age. They also reported restricted occurrences of kaolinite and montmorillonite. Roy et al (1955) found that illite and varying amounts of mixed-layer clays were the dominant clay minerals in the carbonate rocks from Iowa. Dunn and Hudec (1972) found that the dominant clay mineral in the argillaceous dolomites that they studied was illite with minor kaolinite and chlorite. Unlike the montmorillonites these clays do not take up interlaminar water; only their external faces are available for adsorption of water. Dolar-Mantuani and Laakso (1973) in an investigation of an argillaceous limestone from the Trenton formation found that the illite present was mixed with 15% of a swelling mineral, probably montmorillonite. Whether a rock contains swelling or non-swelling minerals is probably not important in terms of the amount of water adsorbed because particle size is probably more important. Anderson et al (1973) found, in an investigation of the phase composition of clay-water systems, that for a unit surface area, kaolinite had considerably more unfrozen (adsorbed) water than montmorillonite. On the other hand, Deer et al (1966) stated that kaolinite had little or no surface adsorbed water. The surface of kaolinite available for adsorption is all external while the external surface of montmorillonite only constitutes 10-20% of the total surface available for adsorption. Since every surface must take up adsorbed fluids which depend on the partial pressure of the fluid phase, kaolinite must adsorb fluids in the same manner as any other adsorbant. The quantity taken up will depend largely on the surface area available. Deer et al were perhaps expressing the belief that kaolinite has a small specific surface area. Anderson et al (1973) concluded that as a first approximation that the interaction between clay and water decreases with distance and applies in the same manner and degree to all alumino-silicate surfaces. Thus, neglecting cation exchange phenomena, it seems that investigations on one group of clay minerals may, at least, be applied qualitatively to other clay minerals.

The phenomenon of cation exchange shown by most clay minerals is well known. Utilizing this, it is possible to manufacture montmorillonite clays with predominantly one species of cation filling the available exchange sites. This allows the influence of different species of cations on adsorbed water to be investigated. The variations in the thickness of the interlamellar water may be studied by observing the variations in the interlaminar spacing by X-ray diffractometry. Montmorillonite has an extremely large specific surface area compared to other clay minerals; thus surface effects will be dominant.

Some of the earliest work concerning the effect of different cations on the properties of adsorbed water was published by Anderson and Low (1958). They examined the density of adsorbed water on lithium, sodium and potassium montmorillonites and found that at a distance of 10A from the clay surface the density of the water was: Li 0.975, Na 0.972, K 0.981. This they attributed to the disrupting effect of the cations on the hydrogen bonds of the water in the order $K < Li < Na$. This work has been confirmed by Sposito (1973). Robinson and Stoakes (1959) favoured a degree of hydration in the sequence: $Li < Na < K < Cs$. Since hydration results in the interaction between cation and water molecules being increased through an increase in the strength of hydrogen bonding, it might be expected that lithium would have the strongest bonding and hence form the most dense phase on hydration of lithium montmorillonite.

In an investigation on the variation in b spacing of montmorillonite with various cations, Ravina and Low (1972) found that the cations enhance the b dimension in the order K< Li< Na. These authors concluded that the exchangeable cations affect the configuration of the clay lattice and that this in turn affects the structure of the expitaxial water. This may, to some extent, explain the results obtained by Anderson and Low (1958). The minimum density found with sodium, as the adsorbed cation, is perhaps not directly due to hydration but rather to the sodium affecting the crystallographic dimensionsof the montmorillonite lattice and hence the 'crystalline like' water. Since most of the adsorbed water on montmorillonite is interlayer, it does not follow that the same relationship need be found for illite and kaolinite.

CATION AND ANION ADSORPTION ON CLAY MINERAL SURFACES

Clay mineral surfaces have positive edges and negative face charges. This may be due to isomorphous replacement of Al^{3+} for Si^{4+} in the tetrahedral layer or of Mg^{2+} for Al^{3+} in the octahedral layer, broken bonds, or lattice defects (Wayman 1967). Since the ratio of edges to plane surfaces of clay minerals is small, clays possess a net negative charge. The charge is, however, dependent on pH. Under acid conditions , hydrogen may be adsorbed on clays creating a positive surface. Under most conditions the greater cation exchange capacity compared with anion exchange capacity supports a net negative charge on the clay mineral surfaces.

Water and other polar liquids are readily adsorbed to clay surfaces by hydrogen bonding. In a similar manner ions of salts in electrolytic solutions are also attracted and adsorbed to clay surfaces. Cations surrounded by their hydration shells will be adsorbed on the negatively charged surfaces, which results in a double layer effect as predicted by the Guoy-Chapman theory. This phenomenon should apply equally to water and to solutions of electrolyte (Wayman 1967).

Cations and anions may also be chemisorbed rather than adsorbed on clay surfaces. Chemisorption is characterised by high heats of adsorption, considerably in excess of 10 Kcal/mole (Wayman 1967). This type of adsorption is probably irreversible. However, Van Olphen (1961) and Norrish et al (1961) considered that cations were unlikely to be held by other than electrostatic forces, so that chemisorption of cations was unlikely.

Fisher (1972), in a review of adsorption phenomena on clay surfaces, found that the Gouy-Chapman double layer thickness depends on the concentration and valency of the charged ions. An increase in concentration or valency will reduce the thickness of the double layer (Bear 1964). Anions will be negatively adsorbed (repulsed) away from a negative clay surface. Wayman (1967) considered that a double layer would occur at positive clay surfaces. Since the Gouy-Chapman model considers charges as points and fails to account for ionic radius, it has certain limitations (Bear 1964). Both Fisher (1972) and Wayman (1967) considered it an effective tool in accounting for clay surface phenomena. The more recent treatments of this subject are similar in many important points. Neilsen (1972) predicted that the thickness of the double layer of adsorbed ions should be of the order of 20-300A.

The properties of the double layer influence various phenomena such as reverse osmosis and also the amount of water adsorbed on clay surfaces attracting different cations.

HYDRATION OF CATIONS ON CLAY SURFACES

Wayman (1967), in a discussion of the adsorption of water on clay surfaces, noted that hysteresis occurred between the desorption and adsorption isotherms of montmorillonite and illite. Kaolinite did not show any hysteresis. Furthermore desorption although almost complete for kaolinite is less complete for illite and montmorillonite at zero partial pressure of water. Wayman attributed this to the character of the bond between adsorbate and adsorbent. This hysteresis is most likely to occur with clays which have adsorbed ions that hydrate strongly.

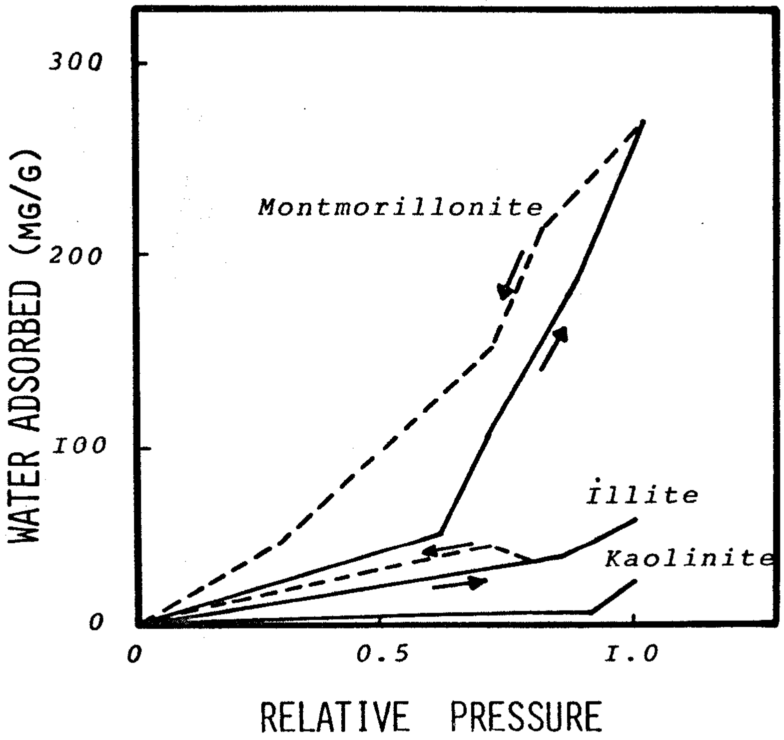


FIG 4. Water vapour adsorption and desorption on various clays. From Wayman (1967, p.149).

Hendricks (1940) stated that Na^+, H^+, K^+ and trivalent ions were not hydrated in clay water systems. Grim (1962) found that there was a considerable difference of opinion as to whether adsorbed cations were hydrated, i.e. surrounded by a definite envelope of water molecules. He considered that the degree of hydration depended on the nature of the cation, the clay mineral and the amount of water. More recent work suggests that adsorbed cations on clays are hydrated (Oster and Low 1963, Shainberg and Kemper 1966).

Oster and Low (1963) found lower activation energies for ion movement at high water contents as compared to those at medium and low water contents. This they attributed to a less coherent structure of water and the absence of appreciable ion-surface interaction at high water contents. Their study was on the interlamellar water in montmorillonite,but they considered that the same factors should influence the conductance of water layers on external surfaces of all clays. Therefore, as water content increases, the ions should have a greater opportunity to dissociate from the surface.

Shainberg and Kemper (1966) considered the hydration status of various cations on montmorillonite. They found that potassium lost its water of hydration between a relative humidity of 40% and 25%, sodium between 25% and 10% and lithium had not lost its water at 5% R.H. These conclusions were confirmed in part by Lahav _et al_ (1973) who found that in a completely dry montmorillonite all the exchangeable cations were close to the surface. In air dried clay, the cations became hydrated as a fuction of the relative humidity.

Water vapour adsorption isotherms on montmorillonite with different species of cations show that the quantity of water

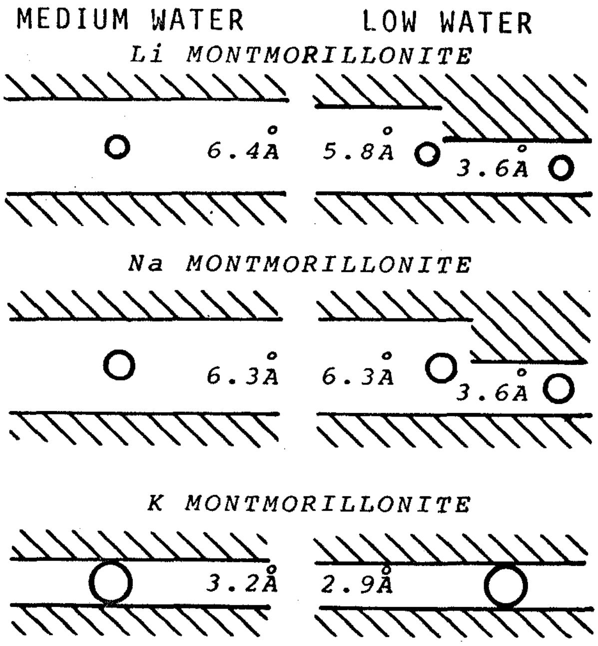


FIG 5. The interlamellar spacings of Li, Na and K montmorillonites at the water contents used by Oster and Low. The spacings shown for Li and Na at low water contents represent the maxima and minima found. Oster and Low (1963).

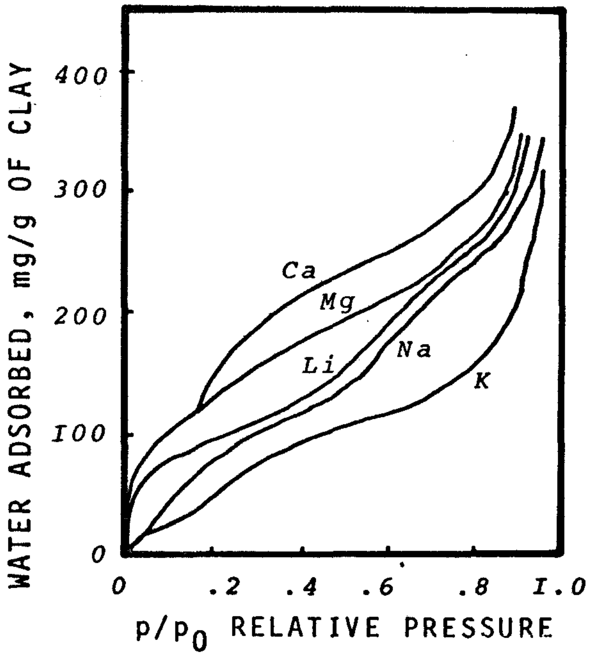


FIG 6. Water vapour isotherms of homoionic montmorillonite saturated with different monovalent and divalent cations. From Anderson (1967, Figs 1 & 2).

adsorbed is dependent on the nature of the adsorbed cation (Anderson 1967).

THE MOBILITY OF ADSORBED WATER

Ling (1972) presented evidence,based on the measurement of the dielectric constant which indicated that the rotational freedom of water molecules was restricted in the adsorbed layer. Anderson (1967) considered that nuclear magnetic resonance data showed a substantial reduction in the mobility of the first layer. Thermal agitation,however, was sufficent to permit the complete exchange with D_2O, thus indicating that the water retains the mobility of a two dimensional fluid. Anderson _et al_ (1973), in a later paper,considered that below -30°C the adsorbed layer was considerably less mobile.

In an investigation of the diffusion of sodium ions in montmorillonite, Murrman _et al_ (1968) found that the diffusion coefficient depended primarily on the unfreezable water content, i.e.the film thickness of adsorbed water. Since the film thickness decreased with decreasing temperature, the ions were confined more closely to the clay surface, where mobility was restricted. Anderson (1972),in an investigation of the ionic migration in frozen Antarctic soil found that the movement of the sodium ions was many times slower than that of chlorine ions. This may be explained by the fact that the positively charged sodium ions will be attracted and impeded by the negative surface of the alumino-silicate particles, unlike the negatively charged chlorine ions which will be repelled or negatively adsorbed. He calcuated that the thickness of the adsorbed water in which the ions were moving was of the order of 6 Å. While the mobility of adsorbed water is restricted when compared to bulk water, it is still relatively mobile at least above -30°C (Anderson 1972). This is in contrast to Dunn and Hudec (1972) who concluded that adsorbed water ..."is all tightly held, not particularly mobile".

VARIATION IN THICKNESS OF THE ADSORBED WATER LAYER

In an investigation of the migration of interlamellar water during freezing and thawing of Wyoming bentonite, Anderson and Hoekstra (1965) noticed that the amount of unfrozen water was governed principally by the temperature and to a lesser extent by the exchangeable cation. Their results are shown graphically in Figure 7. The thickness of this unfrozen interfacial water at 0°C to -5°C ranged from 50Å to about 9Å; below -5°C and down to liquid nitrogen temperatures,

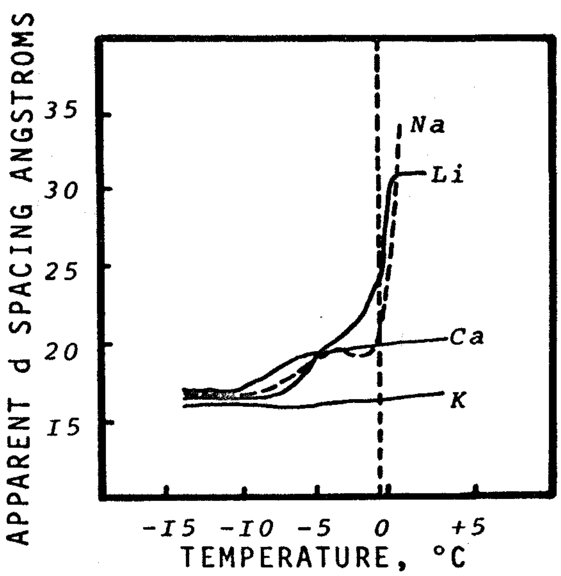


FIG 7. The change in d spacing for several bentonites, during the warming portion of a freeze/thaw cycle. The dotted line represents the temperature at which the diffraction pattern of ice was last seen. (Anderson and Hoekstra, 1965).

the thickness diminished from about 9Å to 1Å. At about -15°C the thickness of the interfacial water zone was about 6-7Å, the effect of the interchangeable cation was small. This corresponds to a thickness of water on each alumino-silicate surface of just over one layer (Anderson 1967). Anderson and Hoekstra (1965) observed that on melting,the inter-lamellar spacings increased rapidly, thereby demonstrating the temperature dependence and the relative mobility of the inter-lamellar water. Notice the relationship of sodium, lithium,and potassium on the d spacing and hence on the amount of adsorbed water. Note also the apparent anomalous behaviour of the sodium which may be due to its control of the b spacing of the montmorillonite lattice as suggested by Ravina and Low (1972). This work agrees well with conclusions reached by Deer et al (1966) and Gillott(1968,p.110) who considered that the amount of water taken up by sodium montmorillonite was continually variable and that this clay had the greatest potential for expansion. Anderson (1967) reported that at -5°C, 0.83, 0.99, 0.75 gms of unfrozen water were found per gm of clay in Li, Na and K montmorillonites respectively. At -15°C a similar relationship was found between the ionic species, i.e. Li 0.81, Na 0.86 and K 0.72 gms of water per gm of clay. This would appear to confirm the findings of Anderson and Hoekstra (1965). Anderson (1967) considered because of conflicting data that it was uncertain what portion of the unfrozen water was extralamellar. However Anderson and Tice (1971) suggested that the adsorbed water layer may be thicker on an external surface (kaolinite) than on an interlamellar surface (montmorillonite).

APPLICATION OF MONTMORILLONITE ADSORPTION PHENOMENA TO OTHER CLAY MINERALS

To what extent can the findings of investigations on montmorillonites be applied to other clay minerals such as illites and kaolinites? Lahav and Anderson (1973) considered that, as a rough generalisation, the thickness of the adsorbed water layer and its variation with temperature applied to all silicate minerals. There are however important qualifications such as the complications caused by the expanding lattice clays which appear to have two distinctly different interfacial zones (Anderson and Tice, 1971).

The nature of the exchange properties of the different clay minerals should have a considerable effect on the quantity of adsorbed water. It might be expected that a mineral of low exchange capacity such as kaolinite would have less adsorbed water than a mineral of high exchange capacity such as montmorillonite.

CLAY TYPE	CATION EXCHANGE
Kaolinite	3-5
Montmorillonite	80-150
Illite	10-40
Vermiculite	100-150
Chlorite	10-40

TABLE 3. Cation exchange capacity of clay minerals in milli-equivalents per 100 g. From Grim (1962).

In montmorillonite and vermiculite, the net negative charge resulting from substitutions within the lattice cause about 80% of the total cation exchange capacity. Since surface area will increase with a decrease in particle size, it follows that the smaller the mineral size, the greater the cation exchange capacity. Wayman (1967) reported that the unit surface charge densities of kaolinite and montmorillonite are similar but that the much larger surface area of montmorillonite will result in a larger total surface charge and hence greater exchange capacity expressed per unit weight. It seems that the particle size rather than the nature of the alumino-silicate surface will be the most important factor in determining cation exchange capacity and water adsorption.

The rate of cation exchange varies with the mineral species, concentration, and nature of the cations and the anions. In general the reaction for kaolinite is almost instantaneous, slower for montmorillonite, and requiring more time, perhaps hours, for illites and chlorites (Grim 1962).

As further evidence of the ability and the effect of the adsorption of an exchangeable cation on a clay surface, a paper by Sherard et al (n.d.) is instructive. In an investigation of piping in earth dams caused by dispersive clay, they found that the ability of a clay to disperse was related to the sodium ion concentration. Thus only clays that adsorb sodium will influence this dispersion. They found montmorillonite was important, kaolinite relatively unimportant but that some illites also showed dispersive properties. It follows that some illites are capable of adsorbing sufficient sodium ions to radically alter their properties in water. This is especially important since most of the clay minerals in carbonate rocks are illites (Robbins and Keller 1952). It also shows that illites may well show a similar response to adsorbed water influenced be exchangeable cations, as montmorillonite. Thus work cited in the earlier part of this chapter may well be applicable to clay minerals other than montmorill-

CHAPTER 3

SAMPLE COLLECTION AND EXPERIMENTAL PROCEDURE

SAMPLE COLLECTION

Bulk samples of carbonates were collected in the spring of 1975 from aggregate quarries throughout Southern Ontario. Where possible,they were taken from freshly worked quarry walls. Each sample consisted of a single bed of a distinctive lithology. See Figure 8 for the location of the samples.

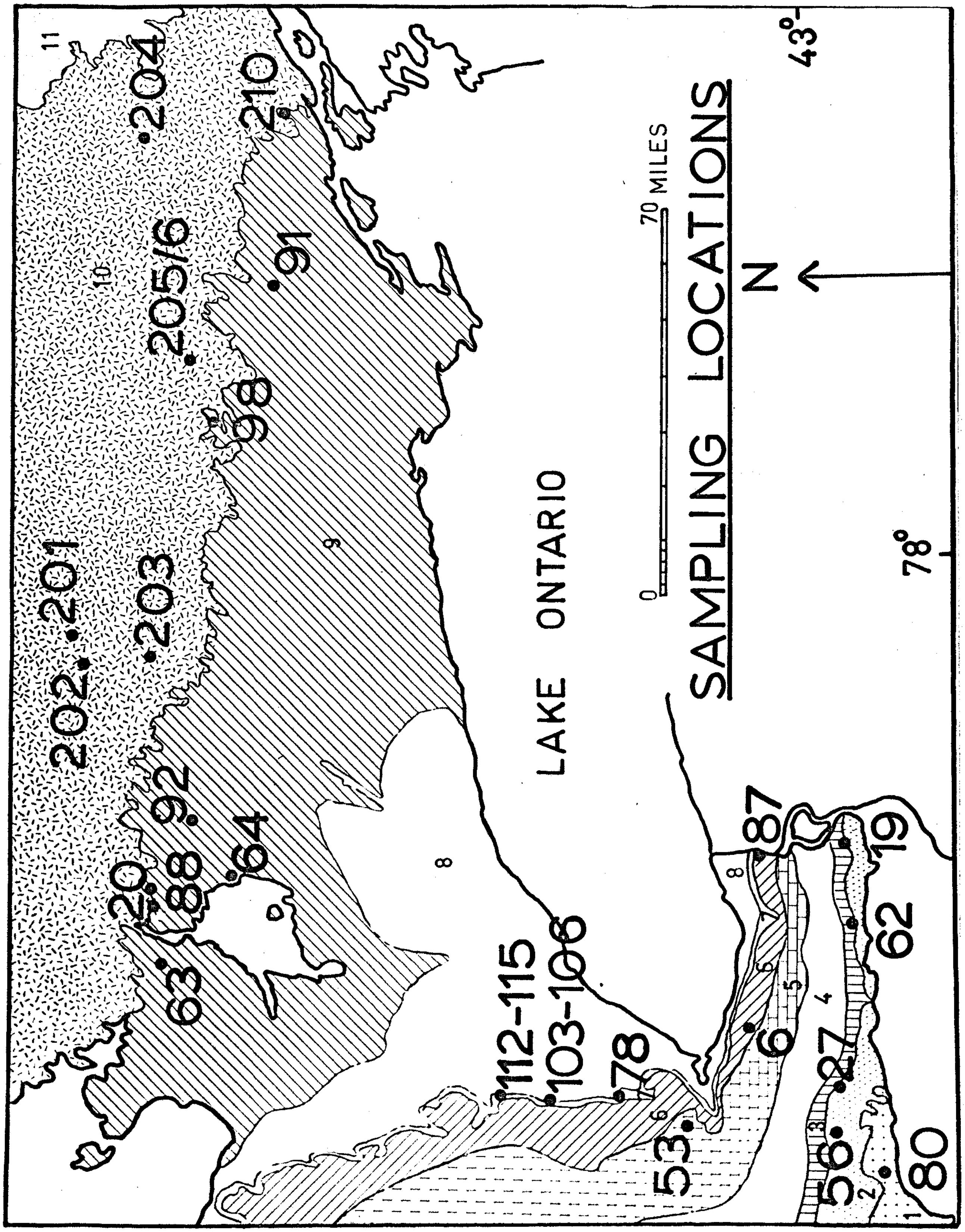
The location of most quarries was designated by the number taken from the Ontario Division of Mines map of Limestone quarries (1971 Map # 2264) and described by Hewitt and Vos (1972).

Each sample from a particular quarry was numbered and when added to the quarry location number, identified the sample. Thus sample # 12 from quarry # 56 had the # 56.12.

It should be noted that the samples collected did not necessarily represent typical aggregates used for concrete.

At location #98 there was a company producing chips from various quarries in the Madoc area for use in terrazzo floors. Samples 98.03 to .07 are probably true marbles from the Grenville province, and 98.01 and .02 are limestones from the Simcoe group (Trenton-Black River). These samples were taken from stock.

FIG 8. Map of sample collection locations, Legend P.T.O.



LEGEND

MIDDLE DEVONIAN

1 DUNDEE FORMATION, Limestone.

2 BOIS BLANC FORMATION, Cherty limestone.

UPPER SILURIAN

3 BASS ISLANDS (BERTIE) FORMATION, Dolomite.

4 SALINA FORMATION, Dolomite, shale, gypsum and salt.

MIDDLE & LOWER SILURIAN

5 GUELPH FORMATION, Dolomite.

6 LOCKPORT-AMABEL FORMATIONS, Dolomite.

7 CLINTON AND CATARACT GROUPS, Sandstone and shale.

UPPER ORDOVICIAN

8 QUEENSTON FORMATION, Red shale. WHITBY FORMATION, grey and black shale.

MIDDLE ORDOVICIAN

9 SIMCOE GROUP (TRENTON-BLACK RIVER), Limestone. Includes LINDSAY, VERULAM, BOBCAYGEON and GULL RIVER FORMATIONS.

LOWER ORDOVICIAN

11 BEEKMANTOWN GROUP, Dolomite and sandstone.

PRECAMBRIAN

10 Rocks reworked by GRENVILLE orogeny.

Samples of the Medina sandstone were taken from quarries in the Georgetown area. These locations were designated by adding 100 to the quarry number given in Hewitt (1968). Thus sandstone quarry #3 became sample location #103.

Samples of igneous and metamorphic rocks taken from various locations in the Grenville province were designated by a location number of greater than 199.

Location 210 was a road cut in the limestone of the Simcoe group (Trenton-Black River).

EXPERIMENTAL PROCEDURE

Outline

The samples were crushed, sieved, washed and split into six subsamples each weighing approximately 175g. A seventh subsample of 300g was submitted to the Ministry of Transportation and Communications for magnesium sulphate testing.

The amount of water adsorbed by the samples at 45% and 95% relative humidity (R.H.) was measured. These measurements were made on the samples in their 'as received' state and also after immersion in 0.5M solutions of univalent and divalent chlorides. A sixth sample was treated with an antiflocculating agent and the amount of adsorbed water also determined.

In the unsalted sample the amount of absorbed water was determined after 24 hours saturation and under vacuum saturation conditions. Finally the volume of the dry samples was obtained by using a mercury displacement technique.

A representative subsample was taken from each sample of carbonate rock and major element chemical analysis performed by using X-ray florescence techniques.

Sample Preparation

The samples collected were crushed using a Chipmunk jaw crusher, sieved and separated into the following sizes, 1/2" - 3/8", 3/8" - #4. The 3/8"- #4 (ASTM E-11) sieve size material was washed and dried. It was then split into six 175g subsamples,using a gill or riffle splitter, and stored.

In the case of the sandstones and igneous and metamorphic rocks, only two subsamples were taken, because it was considered unnecessary to submit them to the full range of salts. Only a few of these samples were submitted for magnesium sulphate testing.

Adsorption Experiments

Drying Cycle

The samples were placed in paper bags in a forced air circulating oven at a temperature of 105 - 110°C for a period of 24 hours. They were then transferred into a weighing cup and weighed hot on a Satorius single pan balance to a precision of 0.001g. When weighed, the samples had a temperature of greater than 100°C, thus it was physically impossible for them to adsorb water.

The temperature change of the balance, above the pan was monitored and a temperature increase of the order of 7-8° C was noted under constant use. Because this temperature increase was fairly constant after the first few weighings, all the oven dry weights of the samples were thought to be comparable, if not absolute weights. The sample and weighing cup being hotter than the surrounding air might be expected to cause convection currents so making the reading of the extremely sensitive balance somewhat variable. This was observed and it was only possible to weigh to 0.001g although the balance will read to 0.0001g. The 175g sample size made further precision unnecessary.

The reason for weighing the samples hot was based on observations of a control experiment. A sample when allowed to cool before weighing, adsorbed considerable amounts of water even though it was stored over phosphorous pentoxide which is an extremely efficient dessicant.

After weighing, the sample was transferred to a clean 40 dram plastic container with a 'snap on' lid.

Adsorption Cycle

The oven dry samples in plastic containers, were placed in a humidity chamber and left without lids to equilibriate for a period of 72 hours. The humidity chambers consisted of wooden and plexiglass boxes 28" x 12" x 18" in size. There was a shelf at half height for storing samples, below which were trays with solutions of appropriate salts for maintaining the desired humidity. The air within the boxes was circulated by means of a small electric fan. The boxes were provided with 'gloves' enabling work to be performed inside them without affecting the atmosphere within. These boxes were originally designed and built by Whiting (1974) for studies on the adsorption of water by concrete.

To attain a relative humidity of 43-45%, a supersaturated solution of potassium carbonate $K_2CO_3.2H_2O$ was used. This humidity would be maintained by keeping the temperature between 18.5 C and 24.5 C. This was approximately the temperature range in the laboratory. To maintain a relative humidity of 95%, a supersaturated solution of sodium sulphite $Na_2SO_3.7H_2O$ was used. This humidity would be maintained at 20 C which was the approximate mean temperature found in the laboratory.

After a period of 72 hours the samples were assumed to have reached equilibrium with the surrounding atmosphere. Without opening the box, the plastic containers were resealed with the plastic lids. Although these containers were not absolutely airtight, they sufficed for this purpose. As a further precaution the containers were kept in the chambers until needed.

The samples were removed one at a time, emptied into the weighing cup and weighed as before to determine the amount of water adsorbed. The samples were then replaced in the plastic containers and allowed to reach equilibrium at 95% R.H. for a further 72 hours, before the adsorbed water was again determined by weighing.

Salt Solution Saturation

Five subsamples were placed in containers and vacuum saturated in 0.5M solutions of NaCl, LiCl, $CaCl_2$, $MgCl_2$ and 5g/l sodium hexametaphosphate (Calgon) respectively. The containers were covered to minimize evaporation losses and allowed to stand for a period of 72 hours. The samples were then drained and were dried for a period of 24 hours.

The same procedure as described above was used to determine the water adsorbed by the salted samples at 45% and 95% relative humidity.

Due to shortage of material the sample group used for adsorption experiments with sodium hexametaphosphate was saturated in a 0.5M solution of KCl and the water adsorption determined as described above.

Sources of Error in Adsorption Experiments

To determine whether the 72 hours allowed to establish equilibrium between the samples and the atmosphere in the humidity chambers was sufficient, the following experiment was performed. A 250g sample of oven dry shale was suspended from a balance pan and placed in a 95% humidity atmosphere. Readings of the balance were taken for a period of three days. The results are presented graphically in Fig 9.

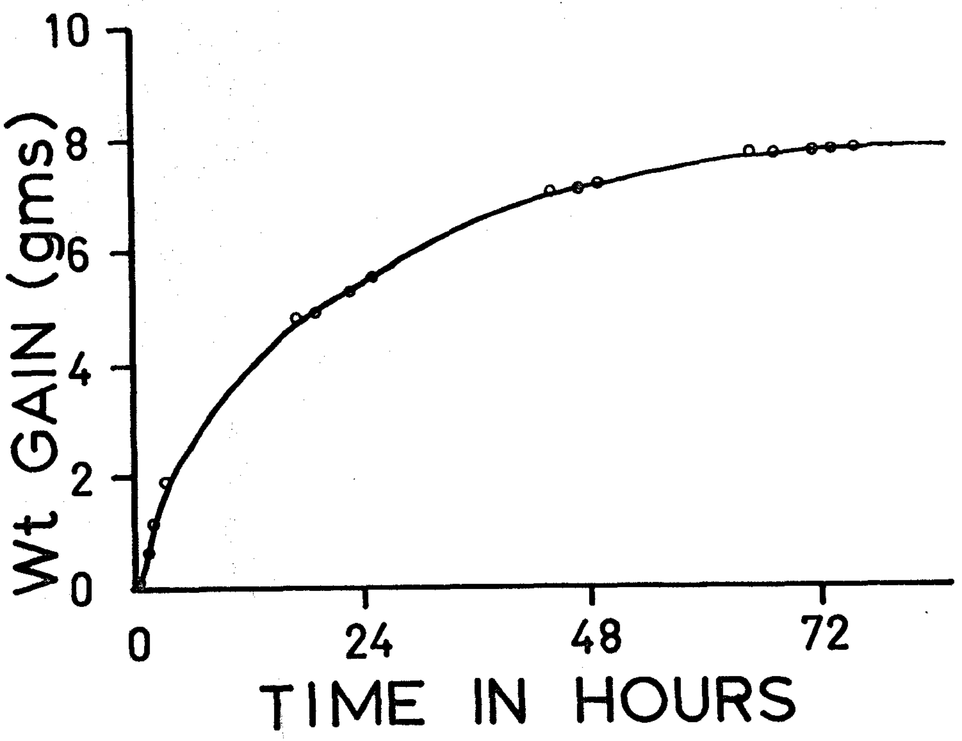


FIG 9. Weight increase of 250 g of oven dry shale in a 95% relative humidity atmsophere.

The conditions differed from those under which the adsorption experiments on samples were run, in that the humidity chamber was not filled with other samples. Thus the full applicability of the results obtained on the shale may be questioned. The results do show, however, that after a period of about three days the rate of adsorption of water is approaching zero. Thus it appears that a period of 72 hours is sufficient to approach equilibrium between a sample and the prevailing atmosphere. This confirms the work of Dunn and Hudec (1965) who found a period of 72 hours was sufficient to establish almost complete equilibrium between a sample and the atmospheric moisture.

Rigbey (1975) reported significant weight changes of his samples during the weighing procedure of the order of 0.005. - 0.01g in thirty seconds. During the present series of experiments a similar precedure to determine weight changes during the weighing was followed, namely, weighing a sample thirty seconds after removal from the humidity chamber both at 45% and 95% relative humidity and thereafter every thirty seconds for three minutes. The data was then extrapolated back to determine the weight the sample should have had at time 0, i.e. in the humidity chamber. The weight changes were found to be negligible when weighing to 0.001 g.

This contrast in results may be attributed to the fact that Rigbey's samples were contained in paper envelopes which adsorb appreciable quantities of water and have a large external surface area. The samples in this study were contained in plastic weighing cups. No correction was thought to be necessary for weight change during the weighing procedure. An effort was made, however, to weigh the samples 15 seconds after removal from the humidity chambers.

As described previously, oven dry weights were taken at a temperature of about 100°C. As a result no inaccuracies caused by uptake of adsorbed water could have occurred. Uplift forces due to temperature contrasts between the sample and surrounding air were considered small and constant and thus no correction was thought necessary.

Because the samples were sealed in the atmosphere in which they equilibrated, they had no opportunity for gain or loss of adsorbed water before the weighing procedure. The only instance in which it was possible for a significant loss to occur was in the transferral of material from the weighing cup to the plastic container and back again. Great care was taken during these procedures.

There are three weighings necessary to determine the amount of adsorbed water at 45% and 95% relative humidity:

1. oven dry weight, 2 45% R.H. weight, 3. 95% R.H. weight. Before each series of weight determinations, the balance was calibrated with a set of standard weights. Assuming that no loss of material occurred in transferral and that the weights are accurate to 0,001g, the total error in determining the percent of adsorbed water due to weighing twice is 0.002g Because the samples have an average oven dry weight of 175g, the total error will be 0.0011%. If a further error of 0.001g occurred by loss of sample, the total error will be 0.003g, which is an error of 0.0017%. This would appear to be excellent, as the range of adsorbed water values is of the order of 1.0 - 0.02 %. Thus recorded values would appear to be accurate to a good degree of certainty.

There are, however, possible inaccuracies introduced by variation in the relative humidity, especially at 95%, due to variation in the temperature (18-24°C) at which the samples were equilibrated. Small variations in temperature may cause quite large variations in humidity. These variations may not be important at relatively low humidities where capillary filling does not take place (45% R.H.). However, at high humidities (95% R.H.) where capilliary filling occurs, quite small temperature variations may cause large variations in the water adsorbed. During experimentation the chambers were kept in the same positions in the same laboratory which was maintained at as constant a temperature as possible.

Leaching Experiments

An experiment was devised to study the effect of leaching by distilled water of the previously salt saturated rocks on their adsorption properties. Samples of rock specimens saturated in

0.5M solutions of NaCl, LiCl and $CaCl_2$ were chosen. Upon completeion of the normal adsorption experiments each sample was placed in a filter funnel and covered with distilled water. Distilled water was dripped on to the immersed sample at a rate of 120-240 ml hr^{-1}. The leaching process was continued for a period of 24 hours. The sample was removed, air dried, and then placed in a paper bag and oven dried. Adsorption determinations were then performed on the leached samples according to the procedure previously described.

Absorption Experiments

Introduction

Traditional methods of determining the water absorption (percent by weight) of coarse aggregate (ASTM C127) are inaccurate when performed on samples of small particle size and less than about 3000g. This is because of the method of determination of the saturated samples' 'surface dry' weight. When samples of small diameter are used, inaccuracies are introduced due to the large external surface area and the subjective assessment of what constitutes 'surface dryness'. However, the Ministry of Transportation and Communications reports good repeatability when ASTM procedures are followed.

All the samples were crushed to less than 1/2 an inch in diameter and there was insufficient material to determine adsorption following standard methods. The method adopted by Rigbey (1975) was followed to determine the water absorption of the samples. Absorption was calculated by determining the specific gravities of particles, retained on the #4 sieve, under three conditions: 1. Specific gravity after 24 hours' saturation, 2. specific gravity after vacuum saturation and 3. specific gravity of the oven dry sample.

$$\% \text{ Absorption} = \frac{\text{saturated S.G.} - \text{dry S.G.}}{\text{Dry S.G.}} \cdot 100 \quad \ldots \text{ Eqn } 1$$

Both 24 hour and vacuum saturated absorption may be calculated by substituting the appropriate specific gravities in the above equation. The 24 hour and vacuum saturated absorption was determined using glass weighing bottles with ground glass stoppers.

Specific Gravities of Saturated Samples

A weighing bottle of known weight was filled with 175g of oven dry sample. The weight of the bottle and the sample was determined on a top loading Mettler balance to 0.01 g. The bottle was then filled with degassed water and allowed to stand for 24 hours. The bottle was then fitted with its ground glass stopper, being careful to exclude all air bubbles, dried externally and then reweighed. The bottle was placed without its stopper in a vacuum dessicator which was next evacuated to approximately 10 mm of mercury and allowed to stand for a period of 72 hours. After this, the bottle was removed from the dessicator and fitted with its ground glass stopper, dried externally and reweighed. The saturated sample was then removed from the bottle and air dried. The bottle was refilled with degassed water, fitted with its stopper as before, dried externally and reweighed.

The 24 hour saturation specific gravity may be found by substitution of the appropriate weights in the following equation:

taken from Rigbey (1975).

$$\text{24 hour saturation S.G.} = \frac{L(W_2 - W_1)}{(W_4 - W_1) - (W_3 - W_2)} \quad \text{...Eqn 2}$$

Where: W_1 = Wt of weighing bottle

W_2 = Wt of weighing bottle and dry solid

W_3 = Wt of weighing bottle, solid and water

W_4 = Wt of weighing bottle and water alone

L = Specific Gravity of water

Vacuum saturated specific gravity may be calculated by substituting the weight of the bottle, solid and water after 72 hour vacuum saturation for W_3 in the above equation.

Dry Specific Gravity

As discussed previously, the saturated surface dry weight is subject to inaccuracies when used on small particle sizes. Rigbey (1975) eliminated this problem by using a mercury displacement volumeter, originally designed by P.P.Hudec, to measure the volume of the sample.

Certain modifications were made to the mercury displacement volumeter enabling easier and more accurate measurement. The position of the calibrated piston was noted when the mercury reached a marked level in a capillary tube. A calibration curve was constructed by determining micrometer readings for piston positions when various standard volumes were placed in the sample chamber. Very good correlation was obtained between piston position and volume.

As a result of the samples having been through many wetting and drying cycles, some samples had deteriorated and fractured. The samples were resieved on an #4 sieve, oven dried and then weighed to an accuracy of 0.01g. They were allowed to cool to room temperature, placed in the chamber of the mercury volumeter and their volumes determined from the calibration curve.

A malfunction of the micrometer screw prevented the accurate determination of dry volume. The method, however, is sufficiently accurate if the equipment is working correctly. It is imperative when using this technique that a mercury vacuum cleaner be used to clean up the small, but unavoidable spills, that occur from time to time. In view of the dangers and difficulties associated with working with mercury, it is felt that the ASTM method for large sample sizes should be used if it is at all possible. Thus in future it is recommended that the ASTM absorption test be performed before size reduction is effected.

The dry S.G. was calculated by substitution of the appropriate determinations in the following equation:

$$\text{Dry S.G.} = \frac{\text{oven dry weight}}{\text{volume}} \quad \text{.... Eqn 3}$$

Calculation

The saturation specific gravities (24 hour and vacuum saturated) and the dry specific gravity were used in equation #1 to determine the percent by weight absorption for both 24 hour and vacuum saturation immersion.

The percent unfilled voids after 24 hour saturation was calculated for each sample using the following equation:

$$\begin{array}{c}\text{Percent}\\ \text{unfilled voids}\end{array} = \frac{\text{Vac.sat.absorp.} - \text{24 hour absorp. } 100}{\text{Vac.sat. absorption}} \quad \text{... Eqn 4}$$

The dry specific gravity was not used in this calculation, therefore errors due to the malfunctioning volumeter were not introduced. The results of these absorption experiments are presented in Table 24.

Chemical Analysis

A representitive 20-25g portion of each sample of carbonate was taken from the 3/8"-#4 sieve size. This fraction was reduced in a shatterbox to a size of 200 mesh (75 microns) or finer. Four grams of this sample were then taken and used to make a borax pellet. The pellets were then dried for about 2 days. They were then analysed by X-ray fluorescence using a Phillips 1410 X-ray machine. The oxide percentages of the elements magnesium, calcium, aluminium and silica were determined using the standards 1b and 88a. The results are presented in Table 25.

Magnesium Sulphate Test

The magnesium sulphate test (ASTM C88) is designed to estimate the resistance of rocks to deterioration under freeze-thaw conditions. The test consists of soaking,a clean, graded sample of rock aggregate in a saturated magnesium sulphate solution. After 16 hours of soaking the sample is removed, drained and then dried in an oven at 105°C to constant weight. After a number of cycles (5 in Ontario) the sample is washed, dried, sieved and weighed. The soundness loss is the proportion passing a certain sieve size expressed as a percentage of the original weight. ASTM specifications call for final sieving on a sieve a size smaller than the sieve on which the sample was retained. On a 3/8" - #4 sample the ASTM loss is expressed as that % passing the #5 sieve. For reasons of consistency, the Ontario Ministry of Transportaion and Communications reports the loss passing both the retaining and the smaller sieve.

It is worth noting that the specifications in the ASTM test description should be rigidly adhered to, to obtain reliable results. When slightly different procedures are followed by different laboratories, totally inconsistent results are obtained.

Hygroscopic Nature of Salts

A simple experiment was devised in an effort to determine if increases observed in adsorbed water held by salt soaked rocks were due in part to the hygoroscopic action of entrapped salts.

Salts were placed in aluminium trays containing glass beads of known weight. The salts were dried in an oven at 105 - 110°C until they attained a constant weight. They were then removed from the oven and weighed to 0.001g. They were placed in a 45% humidity chamber for a period of 72 hours and reweighed. Any increase in weight was assumed to be due to water taken up by hydration or hygroscopic action. A similar experiment was performed at 95% relative humidity. The results are presented as the amount of water taken up by 1 mole g weight of salt (Table 21 in Appendix A).

CHAPTER 4

RESULTS AND DISCUSSION

INTRODUCTION

The results of experiments described in chapter 3 are presented in Appendix A. Due to the volume of data accumulated, some form of statistical analysis was necessary. The main techniques used were: 1. mean and standard deviation, 2. linear regression of two variables and, 3. correlation coefficient or measure of the correspondance between the two variables. The statistical work was performed using programs on a Wang computer, the capability of which was more than sufficient for the treatments desired. Results of statistical computations are presented in this chapter. In the following discussion the results obtained by statistical analysis are interpreted in the light of adsorption phenomena in rocks.

SELECTION OF SAMPLE GROUPS

To enable greater differentiation between the effects of deicer solutions on rocks, it was found useful to divide the carbonates into limestones and dolomites. Those rocks with a Cao:Mgo ratio between 4:1 and 1.4:1 were classified as dolomites. Most carbonates were either predominantly dolomite or limestone with very few of the intermediate composition. There were a small number of samples (56.11-56.13) which proved to have more than 60% clay and free silica; these were excuded from the analysis.

A histogram of the quantity of alumina in 0.2% increments in the carbonates was made to see whether the distribution was unimodal or polymodal. The result is hown in Figure 10. There appears to ba a natural division at about 1% alumina. The carbonates were thus divided into two groups depending on their alumina or clay content, i.e. those with less than 1% alumina were classed in the low alumina group and those with alumina greater than 1% in the high alumina group. Harvery _et al_ (1974) found a similar yet less well defined distribution. They divided their carbonates into high and low alumina groups at 0.9% alumina.

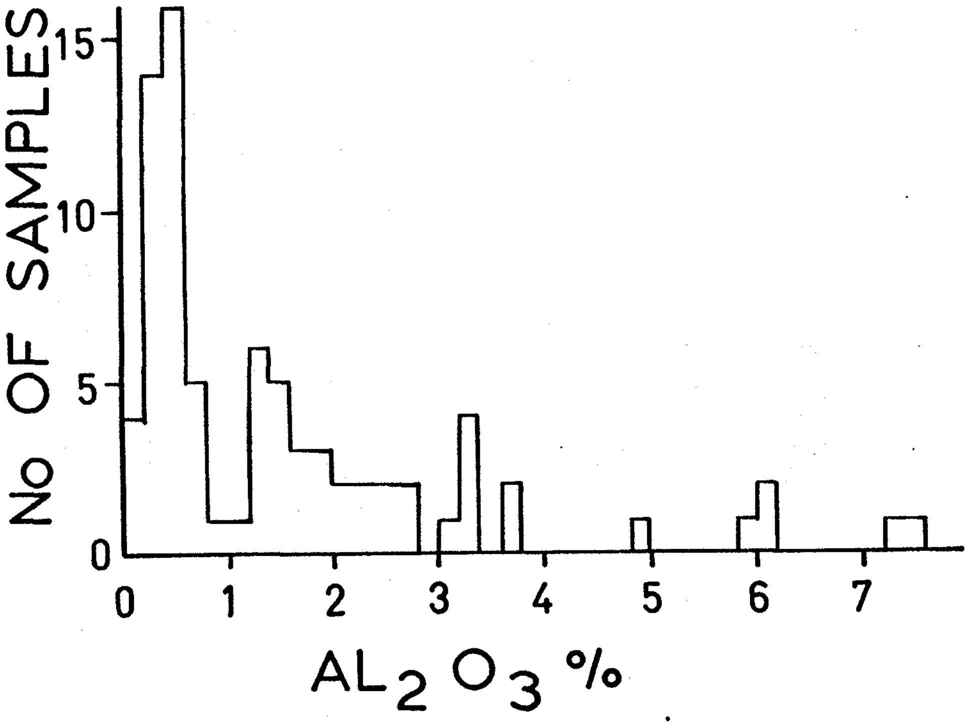


FIG 10. Incidence of alumina content in 75 carbonates.

HYGROSCOPIC NATURE OF SALTS

The results of the experiment desribed in Chapter 3 are presented in the Table 21 in Appendix A. Note that lithium, magnesium and calcium chloride all absorb appreciable quantities of water at 45% humidity while potassium and sodium chlorides do not. At 95% humidity the chlorides all take up more water than at 45%. The low values for potassium and sodium chlorides at 45% humidity may be due in part to the coarse grain sizes of these salts. The amount of water taken up is of the same relative order as that of the order of hydration of the cations in aqueous solution, i.e., $K^+ < Na^+ < Li^+ < Mg^{++} < Ca^{++}$. (Robinson and Stoakes 1959). At 45% humidity, lithium, magnesium and calcium chlorides were all observed to hydrate sufficiently to form concentrated solutions with no solid salt remaining.

ADSORPTION PHENOMENA IN CARBONATES

Table 4 shows the mean adsorbed water at 45% and 95% humidity for each group of carbonates. Note that the order of water adsorption by these rocks at 45% humidity is the same as the order observed for the free salts reported in Table 21. Because adsorption at 45% humidity is of the order of two molecular layers with no capillary condensation, the amount of adsorbed water should be proportional to the internal surface area of the sample, unless modified as discussed in Chapter 2 by the presence of exchangeable cations.

TABLE 4. MEAN ADSORBED WATER - ALL SAMPLES

SAMPLE GROUP	RELATIVE HUMIDITY	NUMBER OF SAMPLES	MEAN %	STANDARD DEVIATION OF THE MEAN
Unsalted	45%	80	.160	.170
Unsalted	95%	80	.358	.343
LiCl	45%	76	.232	.131
LiCl	95%	79	.563	.314
NaCl	45%	80	.171	.174
NaCl	95%	79	.590	.343
KCl	45%	68	.143	.141
KCl	95%	68	.392	.245
$MgCl_2$	45%	78	.270	.146
$MgCl_2$	95%	78	.620	.319
$CaCl_2$	45%	78	.361	.198
$CaCl_2$	95%	78	.770	.381
Calgon	45%	72	.150	.158
Calgon	95%	73	.356	.365

NOTE Only sedimentary carbonates have been included in the above analysis, sandstones, igneous and metamorphic rocks have been excluded.

Referring to Table 4 it will be seen that, at 95% humidity similar relationships are observed between the various sample groups as at 45% humidity, with the exception of lithium chloride. The fact that lithium chloride treated samples adsorb less water at 95% humidity than sodium chloride treated samples is surprising, in view of the experimental results reported in Table 21. The results suggest that lithium chloride should cause greater amounts of adsorbed water in rocks than sodium chloride. Lithium chloride has a high energy of hydration. Thus is is possible that oven drying at 110°C is not sufficient to remove all the hydrated water. This would account for the relatively low amount of adsorbed water compared with sodium chloride. Boon (personal communication) tried the same experiment but he performed the oven drying at 230°C. He found similar amounts of adsorbed water as were found in this series of determinations. Thus oven drying at 110°C appears to be sufficient to drive off all the hydrated water.

In carbonate rocks the clays are the only minerals present in any significant quantity to contribute alumina to an analysis. Thus alumina content should be a good quantative measure of the clay content. Lamar (1967) advocated the use of alumina content, multiplied by a suitable factor, to determine clay content in sedimentary carbonates. Adsorbed water, at low humidities, will depend largely on the internal surface area which, in turn, will be governed by clay mineral content, as discussed in Chapter 2. Table 6 shows the mean adsorbed water content of the unsalted group and various subgroups within the group. Note, that, for a given quantity of alumina, limestones adsorb significantly greater quantities of water than dolomites.

TABLE 5. CORRELATION OF ALUMINA vs ADSORPTION - ALL GROUPS

SAMPLE GROUP	RELATIVE HUMIDITY	NUMBER OF SAMPLES	COEFFICIENT OF CORRELATION 'r'	SLOPE	ALUMINA INTERCEPT
Unsalted	45%	76	.880	10.12	.09
Unsalted	95%	76	.861	5.03	-.07
LiCl	45%	76	.786	11.87	-1.02
LiCl	95%	73	.750	4.91	-1.07
NaCl	45%	76	.886	9.29	.08
NaCl	95%	75	.823	4.80	-1.09
KCl	45%	69	.894	12.15	-.02
KCl	95%	68	.883	6.20	-.88
$MgCl_2$	45%	74	.782	10.24	-1.18
$MgCl_2$	95%	74	.745	4.39	-1.07
$CaCl_2$	45%	75	.728	7.26	-.88
$CaCl_2$	95%	73	.670	3.50	-1.01
Calgon	45%	69	.879	11.29	.07
Calgon	95%	68	.889	4.84	-.02

TABLE 6. MEAN ADSORBED WATER @ 45% R.H. - UNSALTED SAMPLES

SAMPLE GROUP	NUMBER OF SAMPLES	% ADSORBED WATER BY WEIGHT AT 45% R.H.		PERCENTAGE ALUMINA	
		MEAN	STD DEV	MEAN	STD DEV
Whole	77	.160	.170	1.52	1.69
High Al_2O_3	36	.251	.145	-	-
Low Al_2O_3	41	.046	.033	-	-
Dolomites	45	.122	.140	1.63	1.98
High Al_2O_3	18	.247	.142	3.39	2.04
Low Al_2O_3	27	.037	.028	.45	.20
Limestones	32	.172	.148	1.39	1.15
High Al_2O_3	18	.254	.152	2.06	1.14
Low Al_2O_3	14	.066	.032	.53	.12

TABLE 7. CORRELATION OF ALUMINA AGAINST ADSORBED WATER - UNSALTED SAMPLES

SUBGROUP	RELATIVE HUMIDIY	NUMBER OF SAMPLES	COEFFICIENT OF CORRELATION 'r'	SLOPE	ALUMINA INTERCEPT
High Al_2O_3	45%	36	.781	9.50	.34
Low Al_2O_3	45%	40	.520	2.76	.34
Limestones	45%	32	.866	6.69	.24
Dolomites	45%	44	.979	13.72	-.03
High Al_2O_3	95%	35	.783	5.30	-.12
Low Al_2O_3	95%	40	.543	.82	.36
Limestones	95%	31	.846	3.48	.15
Dolomites	95%	43	.919	6.29	-.22

Note also, that the high alumina groups ($Al_2O_3 > 1\%$) adsorb greater quantities of water than the low alumina groups. Table 7 shown the correlation obtained between alumina and adsorbed water for the unsalted sample group when divided into various subgroups. The correlation coefficient 'r' is lower for both the low and high alumina groups compared with that of the group as a whole in Table 7. This suggests that a single population is present despite the bimodal appearance seen in Figure 10. When the group is divided into limestones and dolomites a better correlation is obtained for the dolomites (r = 0.979) as compared with the whole group. The degree of significance of this correlation coefficient and others may be found by referring to Table 18 at the end of this chapter. The highly significant correlation between alumina (clay) and adsorbed water demonstrates the dependence of adsorption on the clay content of carbonate rocks. Lower correlations are obtained at 95% humidity, as might be expected. A certain amount of capillary condensation takes place and thus adsorption is affected by the pore size distribution which is not necessarily dependent on the quantity of alumina (clay) in the rock.

In Figure 11 alumina has been plotted against percent adsorbed water for limestones and dolomites at 45% humidity. Note that limestones, as indicated by the mean adsorptions in Table 6, adsorb significantly greater amounts of water, for given amounts of alumina, than the dolomites. Thus it appears that the effect of the clays in limestones and dolomites on the adsorption of water is distinctly different.

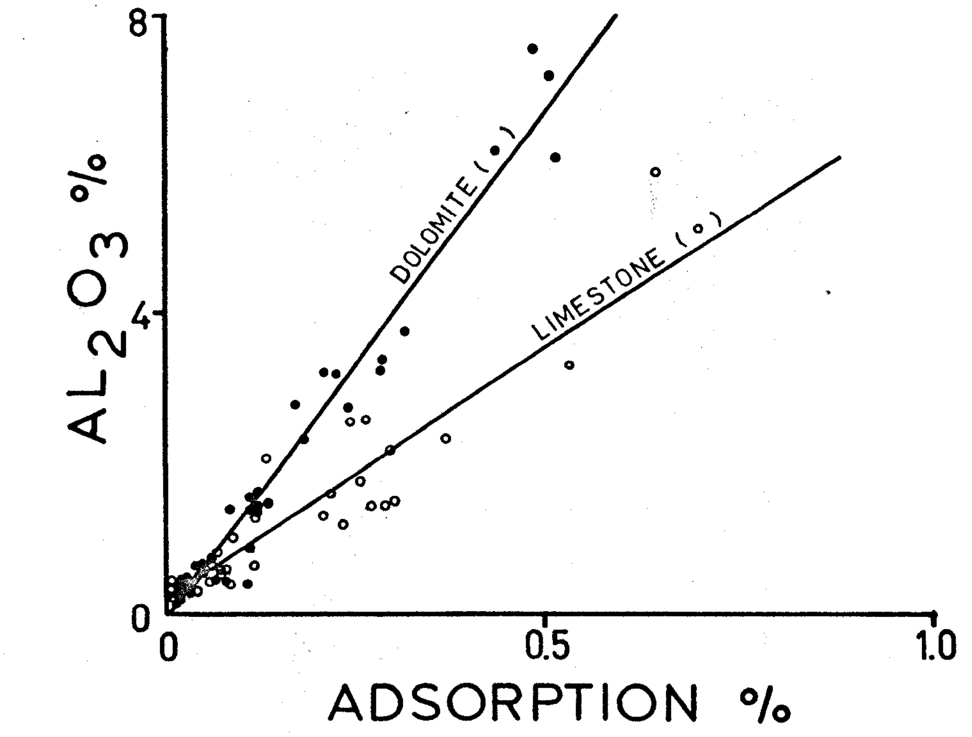


FIG 11. A plot of alumina content against % adsorbed water (by wt) for unsalted samples at 45% R.H. (see table 8).

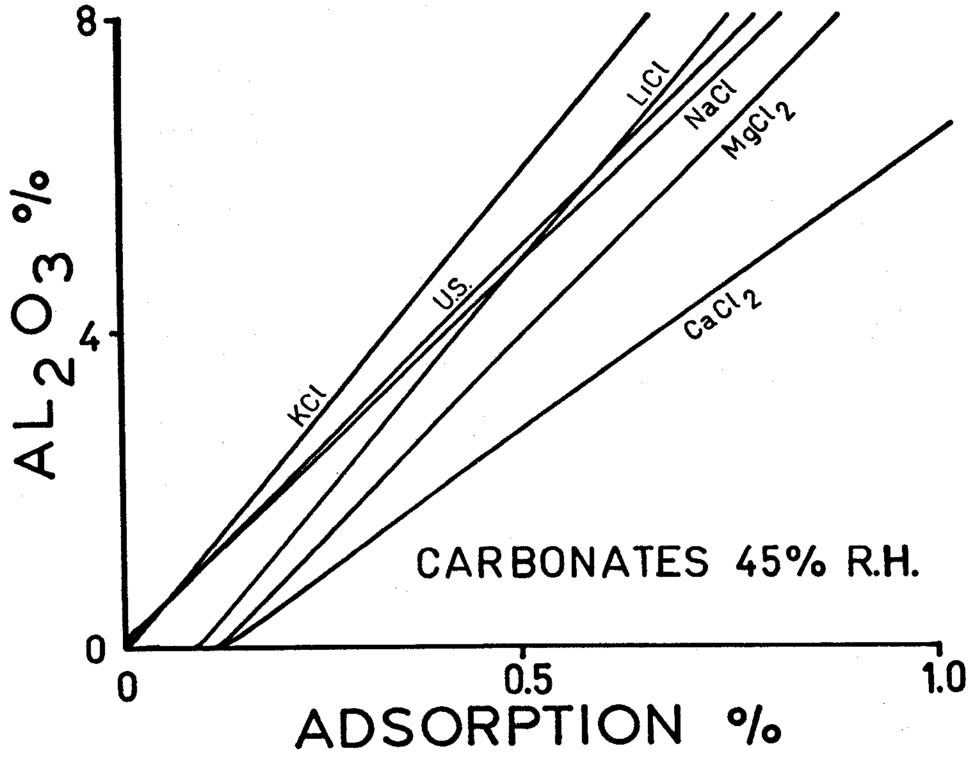


FIG 12. A plot of alumina content against % adsorbed water (by wt) for carbonates at 45% R.H. (see table 8). U.S.= unsalted.

TABLE 8. CORRELATION OF ALUMINA AGAINST ADSORBED WATER SUB-GROUPS AT 45% R.H.

SAMPLE GROUP	SUB-GROUP	NUMBER OF SAMPLES	COEFFICIENT OF CORRELATION 'r'	SLOPE	ALUMINA INTERCEPT
Unsalted	Limestone	32	.866	6.69	.24
Unsalted	Dolomite	44	.979	13.72	-.03
LiCl	Limestone	31	.842	8.53	-.35
LiCl	Dolomite	43	.798	15.27	-1.76
NaCl	Limestone	32	.878	6.21	.23
NaCl	Dolomite	44	.981	12.52	-.04
KCl	Limestone	29	.884	8.28	.11
KCl	Dolomite	40	.982	15.84	-.10
$MgCl_2$	Limestone	30	.853	6.10	-.21
$MgCl_2$	Dolomite	44	.816	12.56	-1.76
$CaCl_2$	Limestone	31	.775	5.00	-.14
$CaCl_2$	Dolomite	44	.734	9.29	-1.72
Calgon	Limestone	29	.885	7.51	.18
Calgon	Dolomite	41	.985	15.65	-.06

TABLE 9. CORRELATION OF ALUMINA AGAINST ADSORBED WATER SUB-GROUPS AT 95% R.H.

SAMPLE GROUP	SUB-GROUP	NUMBER OF SAMPLES	COEFFICIENT OF CORRELATION 'r'	SLOPE	ALUMINA INTERCEPT
Unsalted	Limestone	31	.846	3.48	.15
Unsalted	Dolomite	43	.919	6.29	-.22
LiCl	Limestone	31	.840	3.80	-.45
LiCl	Dolomite	42	.745	5.83	-1.64
NaCl	Limestone	32	.854	3.43	-.35
NaCl	Dolomite	43	.845	5.83	-1.70
KCl	Limestone	29	.870	3.99	-.23
KCl	Dolomite	40	.949	8.03	-1.39
$MgCl_2$	Limestone	31	.839	3.25	-.40
$MgCl_2$	Dolomite	44	.738	5.50	-1.87
$CaCl_2$	Limestone	30	.810	2.97	-.47
$CaCl_2$	Dolomite	43	.646	4.20	-1.71
Calgon	Limestone	28	.867	3.40	.05
Calgon	Dolomite	39	.981	6.55	-.21

Why are limestones able to adsorb greater quantities of water, for given amounts of alumina, than dolomites? Using data from Table 6, it is possible to calculate the amount of water adsorbed for 1% Al_2O_3 in a carbonate:

$$\text{Water adsorbed by 1\% } Al_2O_3 = \frac{\text{Mean amount of adsorbed water}}{\text{Mean alumina content}}$$

Thus: Water adsorbed by 1% Al_2O_3 for dolomites = 0.075% by wt

Water adsorbed by 1% Al_2O_3 for limestones = 0.124% by wt

Therefore the limestones studied adsorb 65% more water for equal amounts of alumina than the dolomites.

There appear to be three possible solutions to explain the differences in adsorption observed between dolomites and limestones.

1. Clays in dolomites are magnesium rich while those in limestones are calcium rich (P.P.Hudec, personal communication). It is possible that, as discussed in Chapter 2, the calcium rich clays adsorb much more water than the magnesium rich clays. In Figure 6 the amount of water adsorbed by calcium and magnesium montmorillonite at various humidities is shown. The calcium montmorillonite only adsorbs about 20% more water than the magnesium rich clay at 0.4 relative pressure of water. It does not seem likely that this mechanism can completely explain the differences between limestones and dolomites.
2. Tooker (1962) in a study of sedimentary carbonates of Pennsylvanian age, found that the clay mineral assemblage depended on the nature of the rock in which they were

found. He found that illite and chlorite commonly occurred in limestones. Dolomitic limestones had an assemblage of chlorite, illite and a mixed layer clay of montmorillonitic material. Dolomites in general contained chlorite or a mixed layer clay or both. These differences, in clay mineral assemblage, are unlikely to account for substantial variations in the thickness of the adsorbed water layer since, in the view of Anderson et at (1973), the interaction between clay and water falls off with distance, in the same manner and to the same degree for all alumino-silicate surfaces. However, it is possible that the different clays have different particle sizes and hence different surface areas. Thus, in the carbonates studied, the limestones may have clay minerals of a smaller particle size than the dolomites. This may account in part for differences in adsorbed water.

3. Dunn and Hudec (1972) formulated a 'rejection texture' hypothesis in which they postulated that growing dolomite crystals exclude clay minerals from their lattice and 'push' the clays toward their crystal boundaries. This results in concentration of clay minerals at the dolomite crystal boundaries and 'clear' dolomite crystals. This is not an uncommon phenomenon. Roy et al (1955) noticed that dolomite crystals in the carbonate rocks they studied were noteably free of inclusions while calcite crystals were commonly cloudy and discoloured. Hadley (1964) showed photomicrographs of dark areas of clay surrounding clear secondary dolomite crystals which

had excluded clay from the crystal lattice of the dolomite.

Gillott(1975) considered the mechanism of disruption in the alkali-carbonate reaction in concrete. Dolomitic limestones with secondary dolomite rhombs are those rocks that are susceptible to this reaction. These dolomite crystals typically show the rejection phenomenon described above. Gillott considered that pressure during induration had dried the rejected clay minerals that were clustered around the dolomite crystals and compacted them so that they could not adsorb water. He concluded that dedolomitisation accompanying the alkali-carbonate reaction opened channels enabling water to be adsorbed on clay mineral surfaces which resulted in the generation of swelling pressure and expansion of the rock. In view of his conclusion, it is possible to explain the observed differences in adsorption of water between limestones and dolomites. The greater water adsorption by limestones may be attributed to the fabric of the rock allowing moisture to migrate and be adsorbed on the clay minerals. In dolomites 'clustering' of clays as a result of dolomitisation may impede migration of water to the adsorption sites. Subsequently, dedolomitisation or thermal shock may open channels and increase adsorption.

It is unlikely that the solution is simple; all the above explanations may contribute to the observed differences in adsorption displayed by limestones and dolomites.

THE EFFECT OF ADSORBED CATIONS ON WATER ADSORPTION IN ROCKS

The addition of a deicing agent to a carbonate rock may influence the water adsorption by the operation of two processes:

1. Modification of the adsorptive properties of the clay.
2. Hydration of free salt in open pores increasing the water 'adsorbed'. Thus: Total adsorption = Adsorption on clay surfaces + Hygroscopic adsorption of water. The relative importance of each will depend on the prevailing humidity and the nature of the salt.

Evaporation of salt solution, following saturation in the experimental procedure, resulted in the deposition of salt on the surface of the rock particles and in the rock pores. In Table 20 it will be seen that potassium and sodium chloride do not hydrate significantly at 45% humidity and thus hygroscopic water cannot contribute toward adsorption. In Figure 12 it will be seen that the lines of best fit for these salts go nearly through the origin, in a similar manner to the unsalted sample group. The lines of best fit for samples treated with LiCl, $CaCl_2$ and $MgCl_2$ intersect the adsorption axis at about 0.1% by weight This value represents the contribution due to the adsorption by the salts which were precipitated on and in the rock in the drying process. All the salts appear to modify the sorptive properties of the clays to a greater or lesser extent. The slope of the lines of best fit for each group vary according to the nature of the salt. The steeper slopes shown by lithium and potassium chloride, as compared with the unsalted group, indicate that these salts decrease the sorptive power of the clay. The more gentle slopes shown by sodium, magnesium and calcium chloride suggest that these salts increase the

TABLE 10. MEAN ADSORBED WATER FOR LEACHING EXPERIMENT

SALT GROUP	MEAN ADSORBED WATER @ 45% RELATIVE HUMIDITY		
	UNSALTED	SALTED	LEACHED
NaCl	.224	.277	.226
LiCl	.224	.269	.193
$CaCl_2$	.158	.324	.169

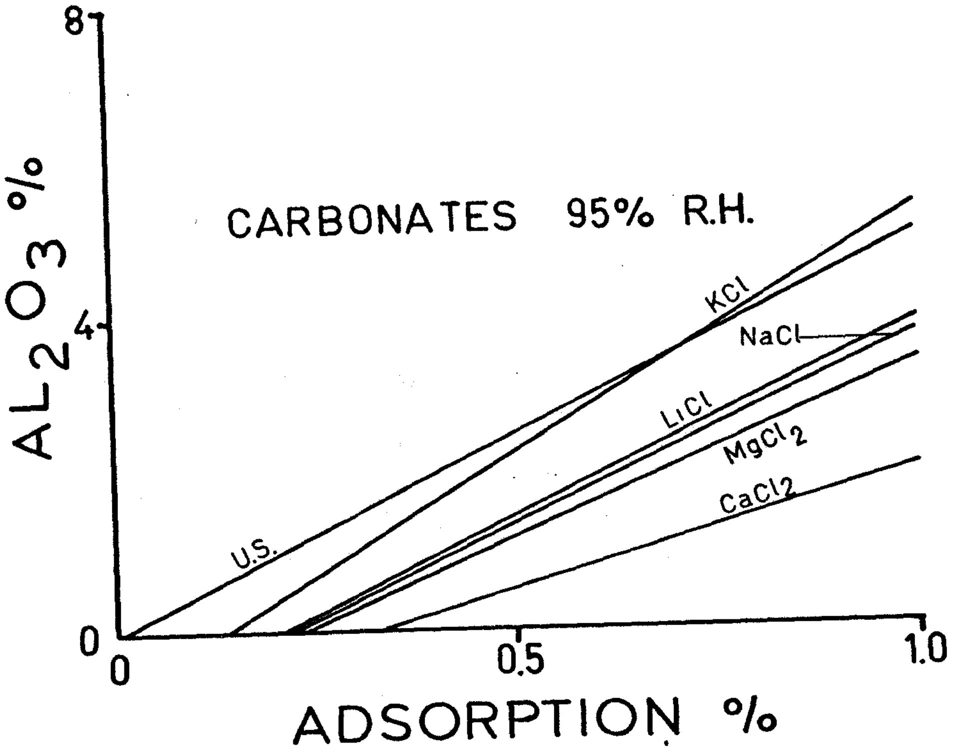


FIG 13. A plot of alumina content against % adsorbed water (by wt) for carbonates @ 95% R.H. U.S. = unsalted group (see table 8).

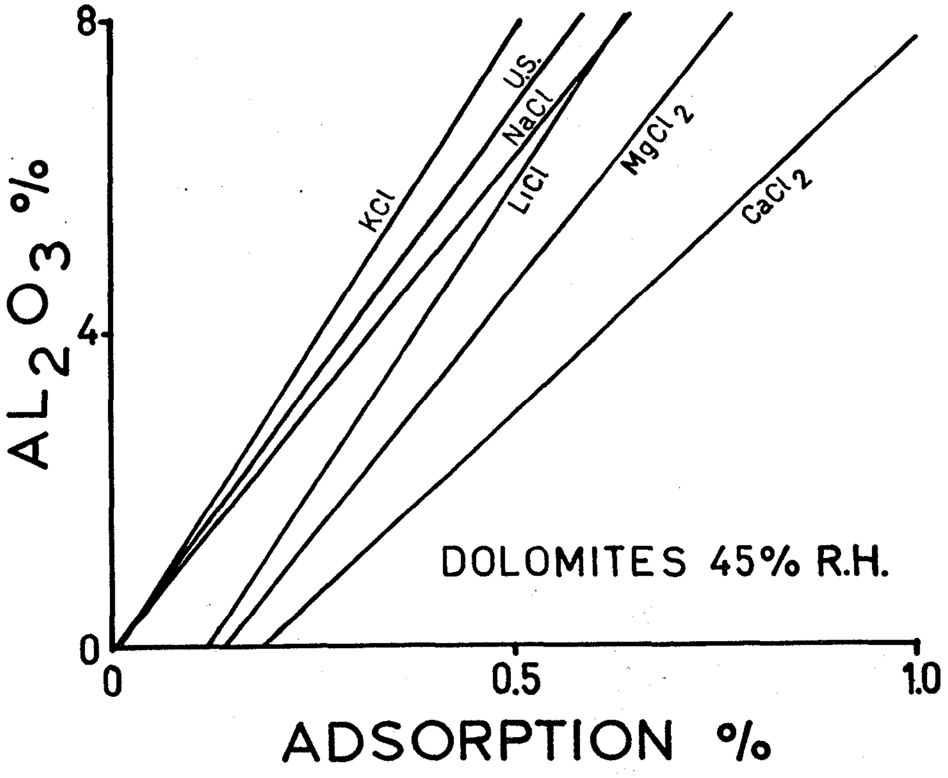


FIG 14. A plot of alumina content against adsorbed water (% by wt) for dolomites at 45% R.H., U.S. = unsalted group (see table 9).

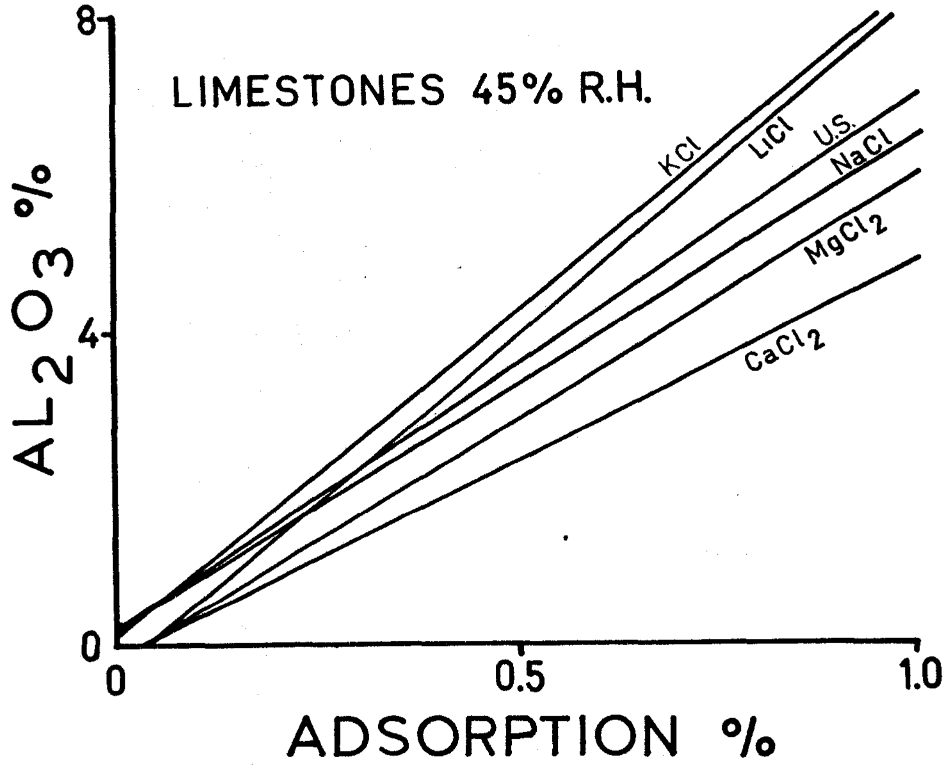


FIG 15. A plot of alumina content against adsorbed water (% by wt) for limestones at 45% R.H., U.S. = unsalted group (see table 9).

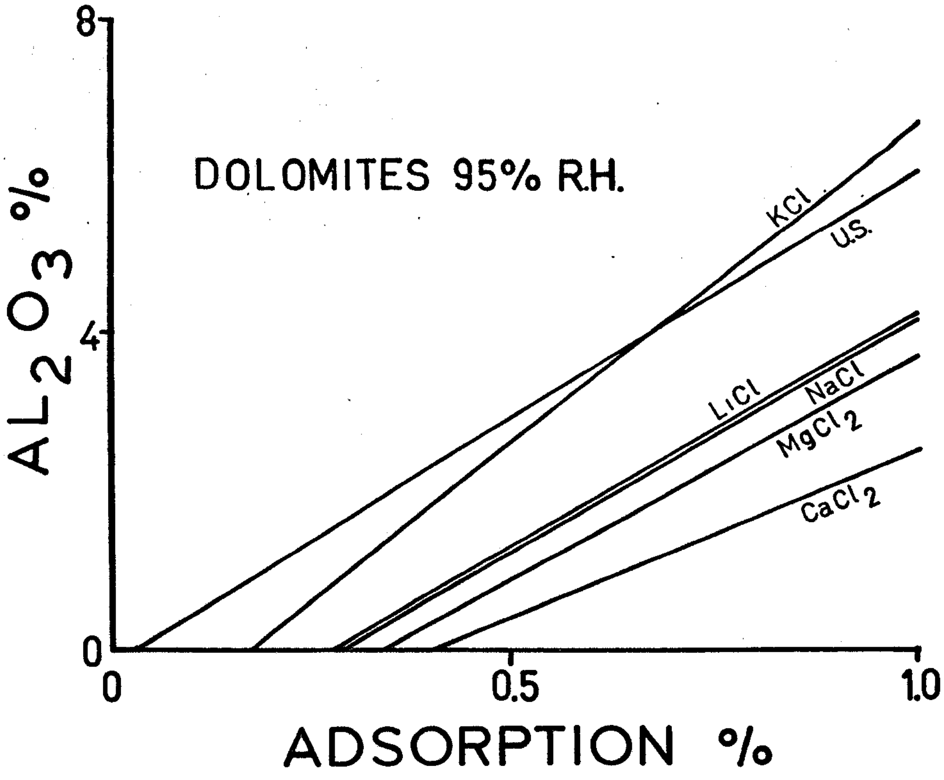


FIG 16. A plot of alumina content against adsorbed water (% by wt) for dolomites @ 95% R.H., U.S. = unsalted group (see table 10).

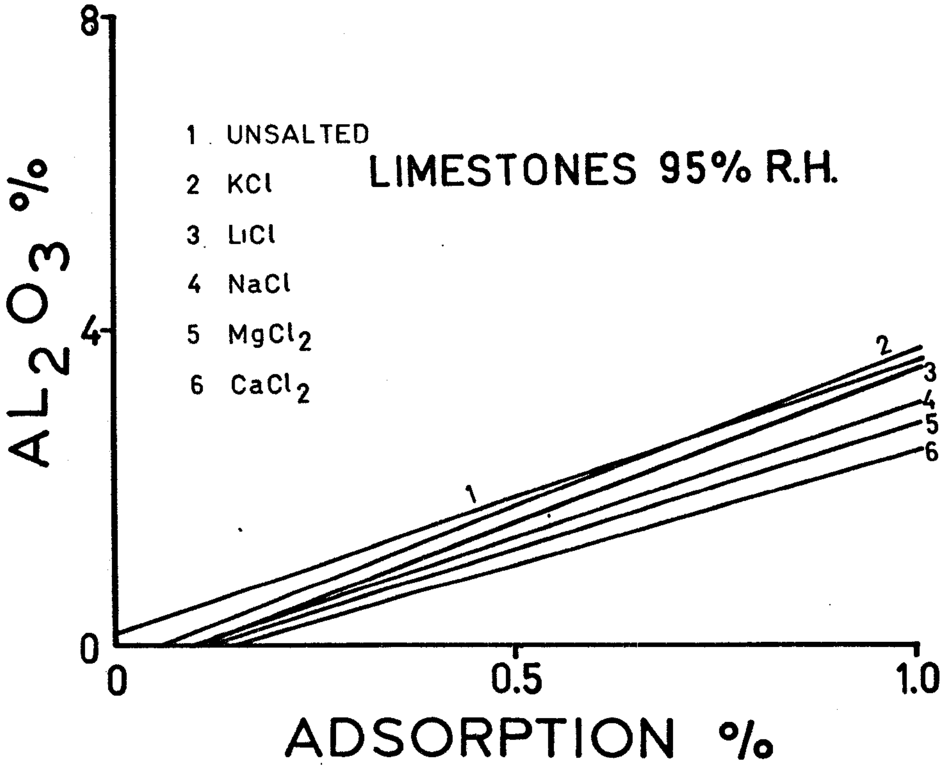


FIG 17. A plot of alumina content against adsorbed water (% by wt) for limestones @ 95% R.H., U.S. = unsalted group (see table 10).

sorptive powers of the clay. This relationship holds at both 45% and 95% humidity for the carbonates as a whole and also the limestone and dolomite subgroups (Figures 12-17).

The decrease in sorptive power of clay caused by the action of lithium chloride is rather surprising in view of its strong hygroscopic properties. Of further interest is the behaviour of carbonates originally saturated in lithium chloride and subsequently leached by distilled water. Figure 18 shows the slope of lines of best fit of alumina versus adsorption before and after leaching. The similar slopes obtained for lithium chloride suggest that the clay surface sorption is not affected. There is only a shift of the line, presumably a result of removal of salt trapped in the pores of the rocks.

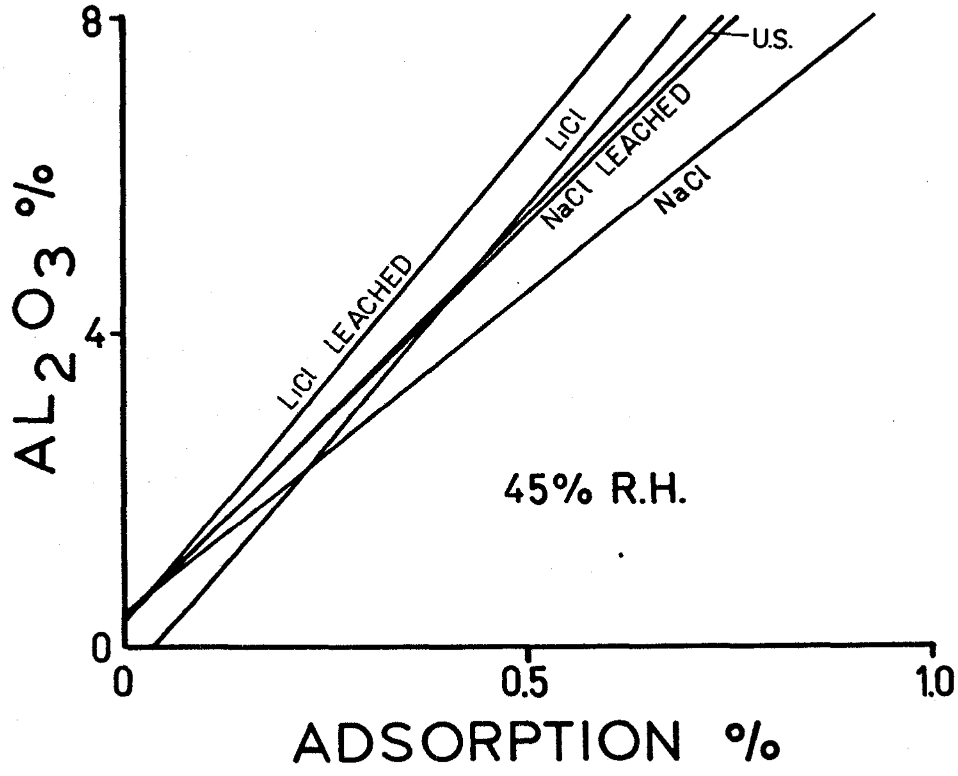


FIG 18. A plot of alumina content against % adsorbed water (by wt) for leached and unleached carbonates at 45% R.H. U.S. = unsalted group. (see table 7).

TABLE 11. CORRELATION OF ALUMINA AGAINST ADSORBED WATER FOR LEACHED SAMPLES AT 45% R.H.

SAMPLE GROUP	NUMBER OF SAMPLES	COEFFICIENT OF CORRELATION 'r'	SLOPE	ALUMINA INTERCEPT
Unsalted	9	.841	10.27	.34
NaCl	9	.792	8.13	.38
NaCl leached	9	.857	10.00	.37
LiCl	9	.803	12.07	-.48
LiCl leached	9	.833	12.14	.30

By consideration of Figures 12,14 and 15 it will be seen that the slopes obtained for lithium and potassium chloride are always greater than those obtained for the unsalted sample groups at 45% humidity. This suggests that these salts act in such a way as to decrease the sorptive properties of the clay. Conversely, the other salts; sodium, magnesium and calcium chloride generally increase the sorptive properties of the clay compared with the unsalted sample group at 95% humidity. At 45% humidity, the line for samples treated with magnesium chloride shows a slope very similar to that of the unsalted sample group, but sodium and calcium chloride both increase the sorptive properties of the clay. How can the addition of certain salts (KCl and LiCl) decrease the adsorption of clays and other salts increase it? Venkata-Raman and Jackson (1963) in a study of the influence of the interlayer cation on vermiculite surface morphology found that the effect of K^+ and NH_4^+ ions contrasted sharply with that of Li^+ or Na^+ ions. Soaking in solutions of lithium or sodium ions resulted in an increase in surface irregularities due to slow exchange with K^+ ions held in the interlayer positions. The edges of the clay plates curled and formed rolls and scrolls with a resultant increase in surface area. This process may be reversed by the addition of K^+ or NH_4^+ ions which results in unrolling and gives a relatively smooth surface. There is an excellent diagram of this effect in Bear (1964 p.92). The former authors considered that this curling due to the removal of K^+ ions may have been caused by a number of processes, principal among them being that the introduction of hydrated cations of a larger size results in sheet strain which is compensated by curling of the layers. They also thought that this process may result in the trapping of water and the resultant exfoliation observed on heating vermiculite. Illite clays are similar to vermiculites and thus the same phenomena may well occur in them. Since most of the clay in carbonates is probably illite (Dunn 1963), the foregoing discussion appears to explain the decrease in the sorptive powers of clays observed after treatment with KCl solution compared with the unsalted group. It would also account for the increase in adsorptive power shown after treatment with NaCl solution. Lithium, it appears however, should also result in an increase in surface area as a result of curling. This should result in an increase in adsorbed water due to the larger surface area, but this was not observed.

The adsorption on alumino-silicate surfaces at any particular humidity is not only a function of the hydration status of the cation as discussed in chapter 2 but also may be caused by changes in the surface area of the clay particles due to curling and uncurling. Whether this process of curling and uncurling may actually occur in argillaceous carbonates must depend on the space available around clay particles. It seems unlikely that there is sufficient space available to allow curling to significantly increase the surface area of the clays. The same argument cannot be used to argue against uncurling and reduction in clay particle net surface area. Thus it is possible that in this case, the action of potassium chloride may decrease clay surface area. An interesting and useful test would be the observation of the effect on adsorption of prior treatment of rocks with NH_4Cl solution. This should result in similar adsorption phenomena to that observed for KCl as predicted by the work of Venkata-Raman and Jackson (1963). It should be noted that the samples treated with KCl had been previously soaked in sodium hexametaphosphate (calgon) which may have altered the sorptive properties of the clay surfaces.

In fig 18 it will be seen that the slope of the sodium chloride treated samples is less than that of the untreated samples. The almost identical intercept with the alumina axis of the unsalted and sodium chloride treated sample groups suggests that unlike lithium, and presumably calcium chloride there is no water adsorbed by the rock due to the hygroscopic nature of discreet salt particles at 45% humidity. On leaching sodium chloride out of the samples, the adsorption characteristics very nearly revert to those shown by the untreated samples. Had the increased adsorption been due to an increase in net surface area by curling, as the observations of Venkata-Raman and Jackson (1963) predict, leaching would not be expected to affect surface area, since K^+ or NH_4^+ ions are required to cause uncurling. Thus removal of NaCl and a subsequent decrease in sorptive properties may be taken to indicate that increases in surface area due to curling do not take place to any measurable degree, if at all, with this salt.

From the above discussion it seems reasonable to argue that increases in adsorbed water compared with the unsalted group shown in Figures 13 - 18 are due to direct hydration of cations on or near clay surfaces, and also the hygroscopic nature of certain salts. In the anomalous behaviour shown by KCl, a mechanism by which this salt could cause decreases in adsorbed water on clay surfaces is clear. It is uncertain, however, if this particular mechanism (uncurling) is acting here. Further experimental work may resolve this question.

From consideration of the data presented in Figures 12 - 17, the effect upon adsorption of the various chlorides may be determined. At 45% humidity, carbonate rock adsorption is increased in the order: KCl< Untreated< NaCl < LiCl< $MgCl_2$< $CaCl_2$. At 95% humidity the order of increasing adsorption is: Untreated< KCl< LiCl< NaCl< $MgCl_2$< $CaCl_2$. These results are in agreement with those expected as a result of consideration of the work reviewed in Chapter 2.

THE EFFECT OF SODIUM HEXAMETAPHOSPHATE ON WATER ADSORPTION

The mean adsorption at 45% humidity obtained for carbonates previously immersed in a solution of 5g per litre of sodium hexametaphosphate (calgon) is 0.150% by weight (Table 4). This is a reduction of about 0.01% by weight as compared with the unsalted sample group. At 95% humidity the results obtained are similar to those of the unsalted sample group (sodium hexametaphosphate = 0.356%, unsalted = 0.358%). When a correlation of alumina against adsorption is considered (Table 5), results very similar to those of the unsalted sample group are obtained. In Table 8 the slope of the lines of best fit for both the sodium hexametaphosphate treated limestones and dolomites suggests that the clay is not as efficient at adsorbing water as the unsalted sample group. Note, however, that the correlation coefficients between alumina content and adsorption are the highest of any group (0.855 for limestones and 0.985 for dolomites).

Sodium hexametaphosphate is probably not hexameric but rather a polymer containing between 15 - 30 PO_3 groups (Van Olphen 1950). This chemical is used in the stabilisation of clay sols. It prevents flocculation of such suspensions by preventing edge to face association of clay particles. The polyvalent hexametaphosphate anions are adsorbed at the positively charged edges of clay miscelles to produce a net negative charge which hinders and prevents edge to face bonding of clay particles (Norrish and Rausell-Colom 1961). The same effect may be produced by increasing the pH of the suspension which reduces and reverses the edge charge. Since the activity of Na^+ ions of sodium hexametaphosphate is generally low, they do not induce flocculation. At high concentrations, however, the activity of the sodium ions may be sufficient to cause flocculation of the clay particles in the same manner in which a solution of an electolyte such as sodium chloride may do so.

The effect of sodium hexametaphosphate on the adsorption of the samples under investigation is not sufficiently different from that of the unsalted sample group to require further explanation or discussion.

MAGNESIUM SULPHATE RESULTS

The results of tests performed by the Ontario Ministry of Transportation and Communications are presented in Table 26 in Appendix A. Loss is expressed as a percentage of dry weight of the sample tested. It will be seen that two results are given for each sample tested. The first is the percentage passing a #4 sieve and is that used by the Ministry in determining compliance with specifications. The second result is the ASTM loss which is the percentage passing a #5 sieve. In the statistical analysis, both values were used where appropriate. In all instances the degree of correlation obtained with alumina or adsorption against magnesium sulphate loss was always less when the ASTM result was used.

In Table 12 the absorption percentage by weight after 24 hours has been correlated against magnesium sulphate test loss. In all cases but two the correlation is insignificant at the 5% level. The exception is for the low alumina dolomites on both the #4 and #5 sieves. The performance of dolomites of low alumina (clay) content in the magnesium sulphate test is thus related in some degree to absorption. This is not so in the case of the other groups studied. Harvey _et al_ (1974), in a similar study of absorption versus sodium sulphate soundness test loss, found relatively good correlations both with their whole carbonate group ($r = 0.59$) and for low alumina carbonates (limestones $r = 0.81$, dolomites $r = 0.88$). For the high alumina carbonates they

TABLE 12. CORRELATION OF 24 HOUR ABSORPTION AGAINST MAGNESIUM SULPHATE SOUNDNESS TEST LOSS

GROUP	SUB-GROUP	NUMBER OF SAMPLES	SIEVE SIZE	COEFFICIENT OF CORRELATION 'r'	SLOPE	ABS INTERCEPT
Dolomite	Whole	40	#4	-.060	-.003	2.92
Limestone	Whole	27	#4	.284	.010	1.11
Dolomite	High Al_2O_3	19	#4	-.185	.006	2.97
Limestone	High Al_2O_3	16	#4	.221	.009	1.16
Dolomite	Low Al_2O_3	22	#4	.467	.049	2.42
Dolomite	Low Al_2O_3	22	#5	.423	.046	2.72
Limestone	Low Al_2O_3	11	#4	-.194	-.026	1.40
Limestone	Low Al_2O_3	11	#5	-.130	-.024	1.45

TABLE 13. CORRELATION OF ALUMINA CONTENT AGAINST MAGNESIUM SULPHATE SOUNDNESS TEST LOSS

GROUP	NUMBER OF SAMPLES	SIEVE SIZE	COEFFICIENT OF CORRELATION 'r'	SLOPE	ALUMINA INTERCEPT
Whole	72	#4	.816	.05	.19
Dolomite	43	#4	.837	.04	.32
Limestone	29	#4	.824	.05	.16

found poor correlations (limestones r= 0.40, dolomite r = 0.07). These results show that at low clay concentrations soundness is related significantly to absorption, but not at high concentrations of clay.

Why are the correlations obtained by Harvey et al (1974) much better than the correlations obtained in this series of experiments? First, they were using sodium rather than magnesium sulphate. The correlations between results obtained using the different sulphate salts has been reported to be significant but not excellent (r = 0.645, P.P.Hudec personal communication). Secondly, as reported in chapter 3, the absorption results obtained are not very reliable due to uncertain dry specific gravity determinations.

In Table 13 a correlation of alumina content against magnesium sulphate test results is presented. The degree of correlation is high, both for the group as a whole (r =0.816) and when the limestones (r = .824) and dolomites (r =0.837) are treated seperately. This result is somewhat surprising since Harvey et al (1974) found a very poor correlation (r = 0.14) for the same comparison although they were using sodium sulphate salt. Their study was of a larger number of samples (122) than in this present study (72), also the range of alumina content was smaller (maximum 3.6%) than in the present work. In an earlier study, Baxter and Harvey (1969) found a much higher degree of correlation (r = 0.79), but they attributed this result to the fact that the samples studied were of a 'fairly restricted type of limestone lithology'. They concluded that the clay content had very little direct effect on soundness loss. The present study shows that in this group of samples, soundness loss is directly related to clay content expressed as alumina.

Harvey et al (1974) argued that the poor correlation obtained by them in a comparison of alumina against sulphate test loss was due in some measure to the wide variety of samples in their study. In this study it will be seen that here also is a wide variety of carbonates. The range in alumina contents suggests that the range in this analysis is in fact wider than in the carbonates used by Harvey et al.

In Table 14 and Figures 19 and 20, the correlation of adsorption against magnesium sulphate test results is presented. The correlations obtained are marginally better than those obtained in the correlation with alumina in Table 13, both for the groups as a whole and when divided into limestones (r =0.93) and dolomites (r =0.85). The results of Table 13 show the dependence of soundness test losses on clay content and hence internal surface area. Adsorption at 45% humidity is a more sophisticated measure of surface area and hence the improved correlations in this case suggest that performance in the soundness test is significantly related to internal surface area. The correlation obtained for the limestones is particularly good. Note that the correlation coefficients for the low alumina limestones and dolomites are much lower, especially the latter, than the high alumina sub groups. This may be due to the generally low magnesium sulphate losses for low alumina dolomites. Discrimination between the different rocks is thus low, with the result that, the correlation obtained should be somewhat lower than should ideally be the case. This should apply to both the low alumina limestones and dolomites. It also seems possible that the lower correlation of adsorption against sulphate test loss obtained for the low alumina dolomites is due, in part, to the dependence of the test loss of the low alumina dolomites on absorption as discussed above.

TABLE 14. CORRELATION OF ADSORBED WATER AGAINST LOSS IN MAGNESIUM SULPHATE TEST

GROUP	NUMBER OF SAMPLES	R.H.	SIEVE SIZE	'r'	SLOPE	ADSORPTION INTERCEPT
Whole	72	95%	#5	.84	.009	.12
Whole	72	95%	#4	.85	.009	.09
Whole	72	45%	#4	.85	.004	.02
Dolomites	43	45%	#4	.84	.004	.01
Limestones	29	45%	#4	.93	.005	.03
High Al_2O_3 dolomites	20	45%	4	.80	n.r.	n.r.
Low Al_2O_3 limestones	17	45%	#4	.38	n.r.	n.r
Low Al_2O_3 dolomites	23	45%	#4	.05	n.r.	n.r.
High Al_2O_3limestones	12	45%	#4	.79	n.r.	n.r.

Note. n.r. = not recorded.

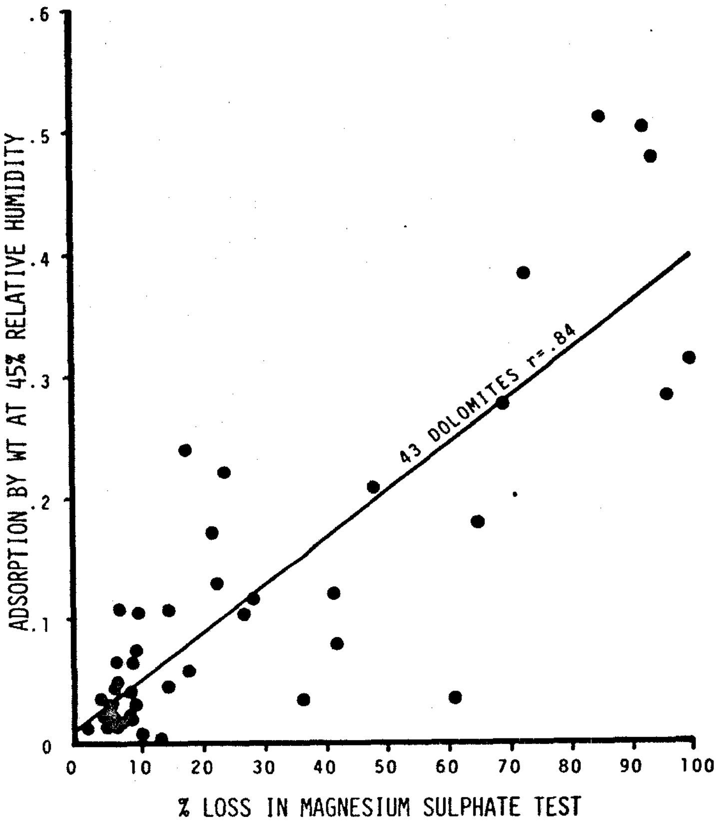


FIG 19. Plot of adsorption against magnesium sulphate test loss.

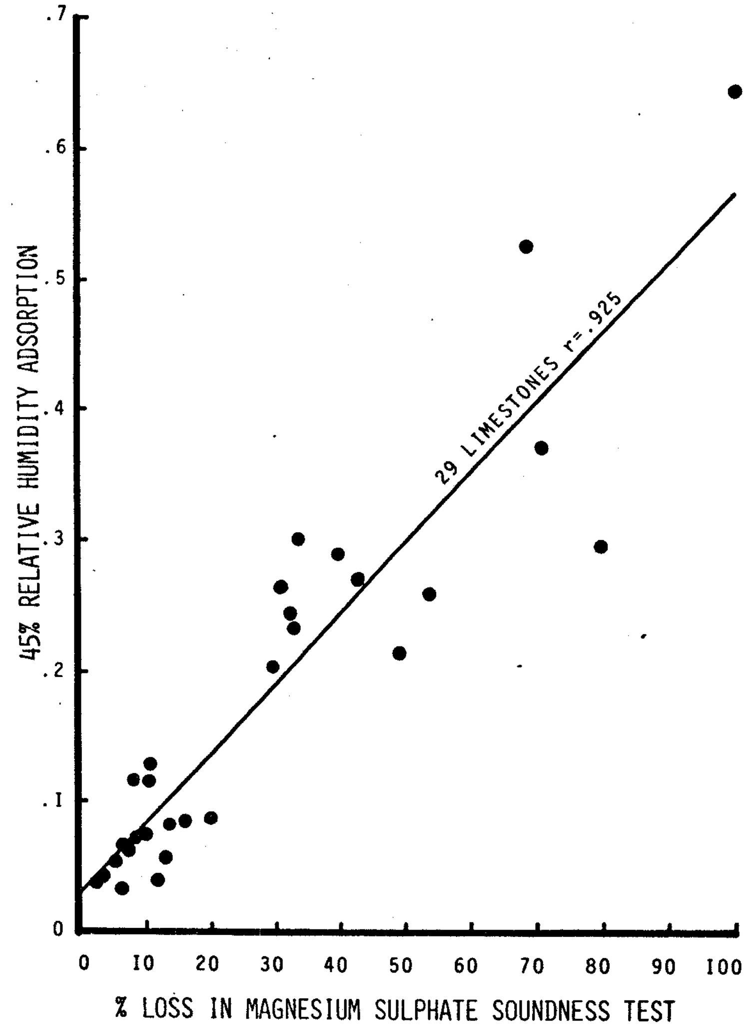


FIG 20. Plot of adsorption against magnesium sulphate test loss.

In the limestone samples studied, it is possible to say that water adsorption is probably one of the main factors influencing performance in the magnesium sulphate soundness test. In the case of the dolomites, adsorption is not such an important factor. In the low alumina dolomite group, adsorption does not seem to be important.

From consideration of the above conclusions, it is possible to propose that there are two separate mechanisms. involved in the deterioration of aggregates in the magnesium sulphate test.

1. In the case of the high alumina limestones and dolomites,

deterioration is caused by a process of shrinking and swelling as a result of the wetting and drying procedure in the magnesium sulphate test. The greater the internal surface area and, hence, adsorption, the lower the durability of the rock being tested.

2. In the case of the low alumina dolomites, some other mechanism related to water absorption is operating. Low alumina, and hence low clay, rocks have a small internal surface area and thus the first mechanism has little opportunity of operating. It seems possible that the creation of destructive pressures, as result of salt crystallisation in pores, is causing the deterioration. This is the classical explanation of the mechanism of deterioration in this test. Low alumina carbonates generally have low sulphate losses (there are exceptions) and thus it may be argued that correlation is bound to be poor due to restricted range of results.

It is likely that these two mechanisms should both operate to a greater or lesser extent in any carbonate rock. The actual proportion contributed by each will probably depend on subtle variations in pore size distribution. It is probable that determination of the pore size distribution of the samples tested would permit more sophisticated analysis. Unfortunately, as explained earlier, there is some doubt as to the accuracy of the absorption results. Thus a detailed analysis of rather imperfect data, to gain some idea of pore size distribution, seems inappropriate. When better absorption data are obtained it should be possible to approach the problem of causes of deterioration in the soundness test rather more realistically.

TABLE 15. CORRELATION OF 45% HUMIDITY ADSORPTION AGAINST PERCENT VOIDS REMAINING ON 24 HOUR SATURATION

GROUP	NUMBER OF SAMPLES	COEFFICIENT OF CORRELATION 'r'	SLOPE	ADSORPTION INTERCEPT
Dolomite	39	-.611	-.009	.23
Limestone	27	-.225	-.008	.22

TABLE 16. CORRELATION OF ALUMINA CONTENT AGAINST PERCENT VOIDS REMAINING ON 24 HOUR SATURATION

GROUP	NUMBER OF SAMPLES	COEFFICIENT OF CORRELATION 'r'	SLOPE	ADSORPTION INTERCEPT
Dolomite	41	-.608	-.127	3.08
Limestone	27	-.187	-.046	1.49

TABLE 17 CORRELATION OF 45% HUMIDITY ADSORPTION AGAINST LENGTH CHANGE ON WETTING

GROUP	NUMBER OF SAMPLES	COEFFICIENT OF CORRELATION 'r'	SLOPE	ADSORPTION INTERCEPT
Carbonates	22	.285	.0001	.14
Limestone	11	.025	.0019	-1.82
Dolomite	11	.249	.0001	.17

PERCENTAGE VOIDS AFTER 24 HOUR SATURATION

In Table 15 and 16 the results of correlation of adsorption and alumina content with percentage voids remaining after a 24 hour saturation period are presented. The results obtained for the dolomites are significant at the 1% level but not for the limestones, where a much lower correlation has been onbtained. Note that the values obtained for voids remaining unfilled after 24 hour saturation are not dependent on the dry specific gravity and, hence, the potential error introduced as a result of uncertain values, for the volume determination is not present. It is interesting to note that, as in correlations with soundness test results, slightly better correlations are obtained when adsorption rather than alumina content is considered. The former is a more sophisticated measure of internal surface area.

The negative slopes of the line of best fit for the dolomites show that the greater the alumina content, the greater is the degree of saturation. Immersing a rock in water results in capillary filling. The smaller capillaries will fill first, which will result in air being trapped in the larger pores (Honeyborne and Harris 1958). Thus material consisting of widely different pore sizes would be expected to be only partly saturated after 24 hours' immersion in water. Conversely, a material of uniform pore size would not be expected to trap air on immersion in water. For the dolomites studied it is possible that a higher alumina content results in a more uniform pore size. This causes a greater degree of saturation on immersion in water.

SORPTION EXPANSIVITY

In an attempt to ascertain if the results of length change on wetting, obtained by Sitar (Hudec and Sitar 1975), were related to internal surface area, the adsorption at 45% humidity, for the samples used by Sitar, was determined. The results of initial length change on wetting were correlated with adsorption and are presented in Table 17. The general lack of correlation is probably due to inadequate sample size and little significance should be attached to it.

Work by Amberg and McIntosh (1952) suggests that adsorption of water on rigid adsorbents should result in uniform linear expansion until a coverage of two molecular layers is obtained at about a humidity of 50%. Thereafter spontaneous condensation in capillaries, according to the Cohan mechanism, results in two opposing effects which prevent net expansion. These effects are:

1. Further decrease in free surface energy and lowering of surface tension with resultant expansion.
2. Capillary filling with resultant negative pressure under the concave menisci resulting in contraction.

Thus a good correlation should be expected between adsorption and length change up to a humidity of about 50%, thereafter capillary condensation will cause complications which should result in a relatively poor correlation. The length changes, observed by Sitar were obtained by wetting a dry sample of rock so that it became saturated. Thus capillary effects should be expected to result in the poor correlation obtained. The foregoing argument does not imply that length change of rocks does not take place due to wetting and drying, with resultant destruction. Consideration of the work of Amberg and McIntosh (1952) suggests that such expansion is related to pore size distribution and resultant capillary effects of a complicated nature.

TABLE 18.

VALUES OF CORRELATION COEFFICIENT FOR DIFFERENT LEVELS OF SIGNIFICANCE

Number of degrees of freedom	0.1% level of significance for two variables
1	1.000
2	.999
3	.991
4	.974
5	.951
6	.925
7	.898
8	.872
9	.847
10	.823
15	.725
20	.652
25	.597
30	.554
40	.490
50	.443
60	.408
70	.380
80	.357
90	.337

CHAPTER 5

CONCLUSIONS

1. The amount of water taken up by chlorides of the following cations, at any particular humidity, is of the same relative order as the order of degree of hydration of the cations in aqueous solution: i.e., $K^+ < Na^+ < Li^+ < Mg^{++} < Ca^{++}$.
2. The correlation coefficient of alumina content against adsorption at 45% humidity is excellent for 44 dolomites ($r = 0.979$) and is good for 32 limestones ($r = 0.866$). This demonstrates the dependence of adsorption on the clay content of carbonates. It follows that alumina determinations may be used to gain some idea of the internal surface area of carbonates, or, alternatively, adsorption may be used to find the quantity of clay in a carbonate.
3. For equal amounts of clay, limestones adsorb about 65% more water than dolomites.
4. Treatment of rocks with equimolar solutions of chlorides results in a relative order of adsorption of: Untreated < K < Li < Na < Mg < Ca at 95% humidity. At 45% humidity the order observed changes due to the hygroscopic nature of discreet particles of the salts LiCl, $MgCl_2$ and $CaCl_2$ resulting in an order of increased adsorption: K< untreated < Na < Li < Mg < Ca
5. Sodium hexametaphosphate (calgon) does not appear to alter, to any great extent, the sorptive properties of carbonates.
6. There is a high degree of correlation between magnesium

sulphate soundness test results and alumina (clay) content, for 29 limestones (r = .824) and 43 dolomites (r = .837). There is also a good correlation between adsorption at 45% humidity and magnesium sulphate test results, 29 limestones (r = .93) and 43 dolomites (r = .85).

7. In the limestone samples studied, it is possible to conclude that degree of water adsorption is probably one of the main factors influencing performance in the magnesium soundness test. In high alumina dolomites, adsorption is also an important factor influencing performance in the test. In the low alumina dolomites, the correlation found between magnesium sulphate test results and absorption (r = .467 for 22 samples), suggests that in this group, absorption has an influence on performance in the soundness test.

8. As a result of the positive slope of the regression of adsorption and magnesium sulphate test loss, any factor that increases the adsorption of a rock will also result in an increase in deterioration in the magnesium sulphate test. The action of deicing agents such as sodium and calcium chloride is to increase adsorption. This increase in adsorption following the application of deicing agents will cause a decrease in durability.

9. Dolomites show a significant correlation between voids remaining after 24 hour saturation and adsorption. The grea~~te~~r the alumina (clay) content, adsorption and hence internal surface area, the more likely dolomites are to be completely saturated after 24 hour saturation.

APPENDIX A

EXPERIMENTAL RESULTS

Table 19.

ADSORBED WATER AT 45% RELATIVE HUMIDITY, % OF DRY WEIGHT.

SAMPLE NO	SAMPLE GROUP						
	NO SALT	NaCl	LiCl	$CaCl_2$	$MgCl_2$	CALGON	KCl
6.01	.315	.325	.000	.539	.414	.282	.271
6.02	.285	.343	.333	.567	.411	.247	.238
6.03	.063	.075	.291	.474	.303	.076	.071
6.04	.278	.282	.311	.514	.376	.245	.230
6.05	.385	.407	.347	.530	.433	.343	.320
6.06	.107	.114	.184	.321	.218	.107	.105
19.01	.114	.122	.230	.295	.246	.105	.113
19.02	.058	.063	.214	.294	.217	.055	.055
19.03	.108	.140	.177	.277	.201	.108	.108
19.04	.223	.245	.231	.342	.277	.197	.187
19.05	.035	.020	.250	.392	.257	.024	.031
20.01	.295	.313	.307	.400	.382	.291	.275
20.02	.050	.051	.108	.117	.106	.053	.054
20.03	.071	.057	.132	.170	.133	.062	.061
20.04	.261	.260	.270	.370	.312	.219	.210
27.01	.513	.542	.473	.631	.579	.429	.429
27.02	.120	.141	.285	.474	.318	.114	.115
27.03	.045	.047	.258	.395	.269	.045	.043
27.04	.048	.041	.229	.308	.228	.036	.036
27.05	.504	.588	.499	.780	.647	.484	.513
27.06	.022	.028	.177	.359	.282	.026	.031
27.07	.131	.160	.251	.364	.280	.128	.130
27.08	.064	.081	.209	.325	.259	.066	.069
53.01	.021	.015	.100	.245	.156	.014	.017
53.02	.015	.013	.087	.134	.090	.012	.018
56.02	.022	.027	.209	.422	.301	.020	.025
56.03	.208	.242	.283	.511	.364	.000	.000
56.04	.019	.029	.165	.363	.213	.025	.032
56.05	.011	.023	.246	.387	.313	.021	.024
56.06	.034	.050	.326	.529	.414	.044	.050
56.07	.081	.158	.263	.429	.279	.070	.078
56.08	.106	.083	.211	.246	.191	.086	.086
56.09	.117	.130	.218	.348	.274	.085	.090
56.10	.179	.196	.252	.468	.319	.153	.158
56.11	.200	.191	.370	.638	.441	.164	.174
56.12	.286	.277	.487	.804	.000	.000	.000
56.13	.670	.559	.520	.766	.625	.527	.475
56.14	.793	.751	.706	1.071	.851	.796	.000
62.01	.041	.048	.117	.192	.146	.039	.043
62.02	.172	.197	.226	.308	.282	.153	.152
62.03	.034	.027	.156	.261	.198	.026	.027
62.04	.043	.041	.172	.321	.247	.035	.043

Table 19. continued

ADSORBED WATER AT 45% RELATIVE HUMIDITY, % OF DRY WEIGHT.

SAMPLE NO	SAMPLE GROUP						
	NO SALT	NaCl	LiCl	$CaCl_2$	$MgCl_2$	CALGON	KCl
63.01	.083	.067	.135	.265	.167	.059	.063
63.02	.204	.224	.176	.354	.281	.195	.193
63.03	.116	.118	.138	.266	.206	.109	.113
63.04	.288	.291	.243	.428	.325	.237	.225
63.05	.215	.246	.216	.321	.276	.202	.199
63.06	.371	.399	.362	.476	.463	.333	.316
63.07	.053	.053	.110	.201	.151	.046	.049
64.01	.527	.535	.498	.768	.554	.513	.461
64.02	.030	.044	.083	.134	.098	.037	.039
78.01	.016	.035	.137	.283	.205	.029	.033
78.02	.029	.038	.095	.169	.137	.000	.000
78.03	.001	.019	.196	.308	.190	.017	.018
80.01	.035	.041	.114	.197	.147	.038	.045
80.02	.039	.037	.129	.200	.157	.034	.035
87.01	.010	.025	.122	.158	.186	.018	.023
87.02	.239	.204	.237	.354	.283	.167	.162
87.03	.482	.533	.429	.640	.538	.423	.413
87.04	.105	.028	.142	.243	.162	.030	.035
87.05	.075	.023	.178	.300	.261	.021	.026
87.06	.027	.023	.190	.404	.271	.018	.023
88.01	.644	.690	.574	.899	.000	.555	.509
88.02	.270	.275	.247	.384	.325	.225	.211
88.03	.301	.303	.279	.125	.387	.264	.246
88.04	.069	.065	.140	.243	.160	.065	.063
88.05	.232	.231	.212	.349	.290	.191	.179
91.01	.130	.217	.195	.259	.229	.190	.176
91.02	.086	.103	.125	.144	.135	.102	.094
91.03	.263	.205	.252	.350	.341	.255	.245
92.01	.077	.089	.117	.153	.130	.074	.071
92.02	.037	.045	.075	.103	.084	.042	.040
98.01	.117	.124	.000	.000	.000	.000	.000
98.02	.243	.473	.231	.343	.282	.000	.000
98.03	.141	.142	.131	.245	.160	.000	.000
98.04	.031	.119	.065	.082	.073	.000	.000
98.05	.004	.006	.055	.092	.046	.000	.000
98.06	.006	.001	.039	.089	.059	.009	.014
98.07	.011	.014	.048	.101	.227	.014	.019

Table 19. continued

ADSORBED WATER AT 45% RELATIVE HUMIDITY, % OF DRY WEIGHT.

SAMPLE NO	SAMPLE GROUP						
	NO SALT	NaCl	LiCl	$CaCl_2$	$MgCl_2$	CALGON	KCl
103.01	.123	.109	.000	.000	.000	.000	.000
103.02	.122	.134	.000	.000	.000	.000	.000
106.01	.072	.095	.000	.000	.000	.000	.000
106.02	.162	.164	.000	.000	.000	.000	.000
112.01	.000	.061	.000	.000	.000	.000	.000
115.01	.130	.110	.000	.000	.000	.000	.000
115.02	.193	.222	.000	.000	.000	.000	.000
201.01	.008	.016	.000	.000	.000	.000	.000
202.01	.089	.134	.000	.000	.000	.000	.000
203.01	.037	.048	.000	.000	.000	.000	.000
204.01	.065	.025	.000	.000	.000	.000	.000
205.01	.056	.021	.000	.000	.000	.000	.000
206.01	.079	.071	.000	.000	.000	.000	.000
210.01	.057	.058	.101	.143	.124	.059	.063

Table 20.

ADSORBED WATER AT 95% RELATIVE HUMIDITY, % OF DRY WEIGHT.

SAMPLE NO	SAMPLE GROUP NO SALT	NaCl	LiCl	$CaCl_2$	$MgCl_2$	CALGON	KCl
6.01	.693	.986	.000	1.265	.966	.691	.709
6.02	.676	.870	.909	1.306	.894	.635	.666
6.03	.141	.847	.689	1.069	.761	.167	.318
6.04	.604	1.021	.880	1.124	.893	.586	.624
6.05	.707	.882	.814	.998	.853	.782	.696
6.06	.281	.524	.506	.772	.520	.278	.348
19.01	.313	.600	.631	.699	.651	.298	.440
19.02	.160	.508	.617	.660	.545	.177	.307
19.03	.281	.491	.453	.646	.496	.298	.351
19.04	.495	.762	.610	.726	.637	.504	.439
19.05	.065	.620	.636	.891	.652	.081	.253
20.01	.582	.670	.691	.760	.754	.632	.583
20.02	.115	.221	.299	.297	.271	.210	.135
20.03	.146	.242	.344	.405	.339	.055	.211
20.04	.526	.565	.623	.739	.629	.503	.497
27.01	1.015	1.265	1.173	1.339	1.230	1.078	1.017
27.02	.374	.679	.701	1.072	.739	.339	.479
27.03	.697	.448	.643	.922	.644	.132	.294
27.04	.112	.379	.536	.770	.613	.104	.217
27.05	1.062	1.300	1.139	1.431	1.293	1.120	1.042
27.06	.075	.406	.456	.809	.702	.075	.199
27.07	.387	.804	.627	.877	.663	.396	.506
27.08	.186	.436	.543	.760	.696	.174	.320
53.01	.035	.445	.265	.571	.385	.034	.166
53.02	.037	.271	.231	.357	.239	.037	.143
56.02	.058	.411	.556	.907	.725	.061	.231
56.03	.497	.744	.722	1.146	.876	.000	.000
56.04	.067	.371	.404	.799	.524	.073	.223
56.05	.057	.525	.587	.834	.185	.063	.235
56.06	.151	.618	.782	1.093	1.018	.143	.334
56.07	.257	.614	.670	.911	.658	.235	.414
56.08	.258	.366	.506	.548	.473	.231	.353
56.09	.317	.633	.559	.764	.673	.228	.334
56.10	.458	.679	.659	.945	.772	.452	.574
56.11	.502	1.078	.900	1.299	1.138	.523	.764
56.12	.727	1.253	1.466	1.754	.000	.000	.000
56.13	1.246	1.384	1.258	1.539	1.437	1.384	1.137
56.14	1.823	1.872	1.746	2.035	1.000	1.647	1.506
62.01	.112	.304	.312	.446	.399	.116	.230
62.02	.451	.593	.179	.650	.668	.441	.469
62.03	.069	.395	.401	.501	.526	.072	.206
62.04	.104	.532	.434	.703	.647	.101	.266

Table 20. continued.

ADSORBED WATER AT 95% RELATIVE HUMIDITY, % OF DRY WEIGHT.

SAMPLE NO	SAMPLE GROUP						
	NO SALT	NaCl	LiCl	$CaCl_2$	$MgCl_2$	CALGON	KCl
63.01	.098	.329	.387	.641	.472	.153	.270
63.02	.450	.677	.565	.688	.591	.480	.499
63.03	.293	.464	.390	.642	.503	.300	.379
63.04	.600	.637	.597	.802	.661	.564	.544
63.05	.451	.598	.505	.610	.558	.449	.456
63.06	.757	.883	.785	.949	.891	.755	.708
63.07	.154	.308	.283	.481	.394	.117	.228
64.01	1.035	1.275	1.081	1.368	1.255	1.185	1.025
64.02	.089	.270	.220	.301	.243	.092	.170
78.01	.071	.415	.393	.638	.527	.064	.198
78.02	.081	.272	.275	.415	.382	.000	.000
78.03	.038	.549	.556	.689	.531	.045	.188
80.01	.100	.362	.310	.483	.374	.113	.247
80.02	.111	.344	.348	.486	.383	.103	.204
87.01	.136	.310	.343	.504	.456	.046	.188
87.02	.468	.645	.615	.816	.677	.455	.492
87.03	.946	1.177	1.090	1.209	1.125	1.038	.940
87.04	.151	.360	.396	.566	.455	.088	.245
87.05	.025	.365	.464	.682	.722	.059	.191
87.06	.056	.393	.495	1.001	.669	.057	.244
88.01	1.160	1.424	1.354	1.797	1.602	1.398	1.235
88.02	.544	.650	.606	.728	.650	.516	.506
88.03	.639	.686	.676	.487	.800	.607	.586
88.04	.197	.348	.357	.577	.409	.181	.264
88.05	.488	.560	.537	.635	.660	.460	.445
91.01	.333	.427	.392	.453	.429	.349	.349
91.02	.194	.271	.284	.316	.312	.191	.252
91.03	.472	.608	.483	.000	.594	.471	.461
92.01	.184	.320	.307	.378	.314	.181	.220
92.02	.092	.210	.187	.263	.228	.087	.148
98.01	.234	.295	.000	.000	.000	.000	.000
98.02	.543	.605	.567	.675	.608	.000	.000
98.03	.223	.354	.256	.362	.274	.000	.000
98.04	.072	.148	.164	.192	.191	.000	.000
98.05	.021	.122	.164	.228	.113	.000	.000
98.06	.011	.118	.127	.203	.181	.018	.079
98.07	.025	.248	.149	.251	.192	.027	.093

Table 20. continued.

ADSORBED WATER AT 95% RELATIVE HUMIDITY, % OF DRY WEIGHT.

SAMPLE NO	SAMPLE GROUP						
	NO SALT	NaCl	LiCl	$CaCl_2$	$MgCl_2$	CALGON	KCl
103.01	.224	.715	.000	.000	.000	.000	.000
103.02	.329	.706	.000	.000	.000	.000	.000
106.01	.214	.477	.000	.000	.000	.000	.000
106.02	.397	.680	.000	.000	.000	.000	.000
112.01	.145	.570	.000	.000	.000	.000	.000
115.01	.278	.683	.000	.000	.000	.000	.000
115.02	.464	.687	.000	.000	.000	.000	.000
201.01	.040	.215	.000	.000	.000	.000	.000
202.01	.123	.213	.000	.000	.000	.000	.000
203.01	.079	.257	.000	.000	.000	.000	.000
204.01	.078	.318	.000	.000	.000	.000	.000
205.01	.083	.233	.000	.000	.000	.000	.000
206.01	.124	.181	.000	.000	.000	.000	.000
210.01	.145	.218	.272	.353	.315	.152	.210

TABLE 21. AMOUNT OF WATER TAKEN UP BY SALTS

The amount of water taken up by 1 gram mole wt of a salt under either 45% or 95% relative humidity conditions in 72 hours is presented. Results are expressed in grams.

SALT	HUMIDITY	WATER IN GRAMS PER 1 GRAM MOLE
KCl	45%	.14
KCl	95%	.21
NaCl	45%	.1
NaCl	95%	4.6
LiCl	45%	30.1
LiCl	95%	92.0
$CaCl_2$	45%	128.0
$CaCl_2$	95%	224.0
$MgCl_2$	45%	52.0
$MgCl_2$	95%	138.5

Table 22.

LEACHING EXPERIMENTS

ADSORBED WATER AT 45% RELATIVE HUMIDITY, % OF DRY WEIGHT

SAMPLE NO	SAMPLE GROUP		
	LEACHED	.5M NaCl	NO SALT
6.04	.279	.282	.278
20.01	.293	.313	.295
27.05	.534	.588	.504
56.07	.076	.158	.081
62.02	.175	.197	.172
63.06	.380	.399	.371
78.02	.033	.038	.029
80.02	.040	.037	.039
98.02	.223	.478	.243

SAMPLE NO	SAMPLE GROUP		
	LEACHED	.5M LiCl	NO SALT
6.04	.228	.311	.278
20.01	.255	.307	.295
27.05	.430	.499	.504
56.07	.061	.263	.031
62.02	.132	.226	.172
63.06	.321	.362	.371
78.02	.031	.095	.029
80.02	.060	.129	.039
98.02	.216	**.231**	.243

SAMPLE NO	SAMPLE GROUP		
	LEACHED	.5M $CaCl_2$	NO SALT
6.05	.393	.530	.365
80.02	.037	.200	.039
88.04	.079	.243	.069

Table 23.

LEACHING EXPERIMENTS

ADSORBED WATER AT 95% RELATIVE HUMIDITY, % OF DRY WEIGHT.

SAMPLE NO	SAMPLE GROUP		
	LEACHED	.5M NaCl	NO SALT
6.04	.621	.986	.693
20.01	.577	.670	.582
27.05	1.109	1.300	1.062
56.07	.210	.614	.257
62.02	.428	.593	.451
63.06	.745	.833	.757
78.02	.063	.272	.081
80.02	.084	.344	.111
98.02	.487	.605	.543

SAMPLE NO	SAMPLE GROUP		
	LEACHED	.5M LiCl	NO SALT
6.04	.562	.880	.693
20.01	.566	.691	.582
27.05	1.036	1.139	1.062
56.07	.186	.670	.257
62.02	.387	.179	.451
63.06	.710	.785	.757
78.02	.067	.275	.081
80.02	.160	.348	.111
98.02	.511	.567	.543

SAMPLE NO	SAMPLE GROUP		
	LEACHED	.5M $CaCl_2$	NO SALT
6.05	.795	.814	.707
80.02	.062	.348	.111
88.04	.182	.357	.197

Table 24. Absorption results.

SAMPLE No	DRY S.G.	24Hr AB S.G.	VAC SAT S.G.	24 Hr % AB WATER	VAC SAT % AB WATER	UNFILLED VOIDS @ 24 Hr.
6.01	2.598	2.808	2.808	3.111	3.111	.00
6.02	2.533	2.806	2.806	4.254	4.254	.00
6.03	2.544	2.778	2.824	3.615	4.326	16.42
6.04	2.680	2.822	2.829	1.977	2.074	4.69
6.05	2.700	2.795	2.801	1.303	1.385	5.94
6.06	2.662	2.821	2.839	2.243	2.497	10.16
19.01	2.543	2.689	2.694	2.257	2.334	3.31
19.02	2.611	2.826	2.840	3.153	3.359	6.11
19.03	2.754	3.026	3.026	3.586	3.586	.00
19.04	2.624	2.809	2.809	2.686	2.686	.00
19.05	2.623	2.816	2.833	2.805	3.052	8.09
20.01	2.678	2.714	2.714	.501	.501	.00
20.02	2.645	2.717	2.717	1.029	.971	-5.88
20.03	2.668	2.706	2.707	.533	.547	2.56
20.04	2.608	2.715	2.715	1.573	1.573	.00
27.01	2.656	2.800	2.800	2.041	2.027	-.69
27.02	2.572	2.847	2.866	4.157	4.444	6.46
27.03	2.634	2.993	3.034	5.246	5.765	8.99
27.04	-					
27.05	2.667	2.737	2.738	1.687	1.701	.82
27.06	2.618	2.783	2.814	2.407	2.859	15.81
27.07	2.626	2.831	2.832	2.972	2.987	.48
27.08	2.619	2.661	2.675	.612	.816	25.00
53.01	2.440	2.798	2.831	6.013	6.567	8.43
53.02	2.550	2.803	2.814	3.890	4.059	4.16
56.02	2.586	2.781	2.819	2.915	3.484	16.30
56.03	2.567	2.796	2.803	3.475	3.581	2.96
56.04	2.642	2.791	2.818	2.134	2.521	15.34
56.05	2.525	2.759	2.855	3.670	4.595	20.13
56.06	2.458	2.814	2.894	5.892	6.570	10.32
56.07	2.610	2.873	2.873	3.860	4.169	7.39
56.08	2.600	2.861	2.870	3.860	4.112	6.11
56.09	2.666	2.849	2.826	2.574	2.870	10.29
56.10	2.680	2.824	2.629	2.004	2.032	1.36
56.11	2.366	2.612	2.660	4.394	4.698	6.46
56.12	2.306	2.620	2.700	5.904	6.657	11.29
56.13	2.399	2.700	2.712	5.230	5.230	.00
56.14	2.412	2.708	2.712	5.037	5.156	1.33
62.01	2.728	2.812	2.826	1.128	1.316	14.28
62.02	2.700	2.825	2.830	1.714	1.783	3.84
62.03	2.586	2.778	2.806	2.871	3.289	12.72
62.04	2.652	2.812	2.833	2.274	2.573	11.60

Table 24. Absorption results.

SAMPLE No	DRY S.G.	24 Hr AB S.G.	VAC SAT S.G.	24 Hr % AB WATER	VAC SAT % AB WATER	UNFILLED VOIDS @ 24 Hr.
63.01	2.623	2.716	2.718	1.351	1.380	2.10
63.02	2.594	2.720	2.720	1.872	1.872	.00
63.03	-					
63.04	2.650	2.714	2.714	.911	.911	.00
63.05	2.655	2.716	2.716	.865	.865	.00
63.06	2.660	2.719	2.719	.833	.833	.00
63.07	2.653	2.714	2.715	.866	.880	1.61
64.01	2.566	2.721	2.721	2.354	2.354	.00
64.02	2.691	2.725	2.727	.469	.497	5.55
78.01	2.610	2.794	2.843	2.701	3.420	21.03
78.02	2.750	2.813	2.836	.833	1.137	26.74
78.03	2.588	2.780	2.828	2.866	3.583	19.99
80.01	2.622	2.717	2.718	1.381	1.396	1.04
80.02	2.562	2.730	2.733	2.559	2.605	1.75
87.01	2.681	2.790	2.827	1.516	2.031	25.34
87.02	2.740	2.827	2.827	1.158	1.158	.00
87.03	2.719	2.824	2.824	1.420	1.420	.00
87.04	2.605	2.727	2.761	1.797	2.298	21.79
87.05	2.536	2.772	2.874	3.669	5.255	30.17
87.06	2.564	2.746	2.853	2.768	4.396	37.02
88.01	2.480	2.720	2.720	3.902	3.902	.00
88.02	2.685	2.713	2.715	.388	.416	6.66
88.03	2.542	2.715	2.715	2.677	2.677	.00
88.04	2.701	2.806	2.808	1.439	1.466	1.86
88.05	2.562	2.713	2.713	2.300	2.300	.00
91.01	2.644	2.715	2.717	1.015	1.044	2.73
91.02	2.690	2.713	2.713	.317	.317	.00
91.03	2.534	2.716	2.722	2.834	2.927	3.19
92.01	2.645	2.720	2.723	1.072	1.114	3.84
92.02	2.604	2.708	2.708	1.533	1.533	.00
98.01	2.715	2.720	2.721	.067	.081	16.66
98.02	2.690	2.725	2.728	.483	.525	7.39
98.03	2.527	2.596	2.596	1.080	1.080	.00
98.04	2.790	2.796	2.796	.077	.077	.00
98.05	2.810	2.858	2.861	.607	.645	5.88
98.06	2.834	2.840	2.840	.074	.074	.00
103.01	2.397	2.620	2.658	3.881	4.542	14.55
103.02	2.377	2.611	2.682	4.141	5.398	23.27
106.01	2.451	2.598	2.639	2.446	3.129	21.80
106.02	2.625	2.824	2.840	2.887	3.120	7.44
112.01	2.330	2.539	2.613	3.849	5.212	26.14
115.01	2.484	2.575	2.667	1.474	2.965	50.27
115.02	2.609	2.791	2.816	2.673	3.041	12.07

Table 24. Absorption results.

SAMPLE No	Dry S.G.	24 Hr Ab S.G.	VAC SAT S.G.	24 Hr % Ab WATER	VAC SAT% Ab WATER	% UNFILLED VOIDS @ 24 Hr
201.01	2.619	2.632	2.632	.189	.189	.00
202.01	-					
203.01	2.562	2.638	2.642	1.157	1.218	4.99
204.01	2.631	2.672	2.675	.592	.635	6.81
205.01	2.712	2.765	2.768	.720	.761	5.35
206.01	2.842	2.933	2.934	1.126	1.139	1.08
210.01	2.691	2.753	2.755	.856	.883	3.12

Table 25.

CHEMICAL ANALYSIS.

SAMPLE NO	Al_2O_3% by wt	SiO_2% by wt	CaO:MgO
6.01	3.8	18.3	1.40:1
6.02	3.4	19.8	1.40:1
6.03	.5	4.9	1.59:1
6.04	3.3	15.0	1.47:1
6.05	6.1	16.8	1.40:1
6.06	.9	3.6	1.48:1
19.01	1.4	30.0	3.50:1
19.02	.8	3.2	1.53:1
19.03	1.6	10.4	1.40:1
19.04	3.2	14.4	1.40:1
19.05	.3	1.3	1.53:1
20.01	2.2	6.9	27.2:1
20.02	.4	1.8	41.2:1
20.03	.6	2.1	27.8:1
20.04	1.8	5.6	34.4:1
27.01	6.1	22.0	1.40:1
27.02	1.5	6.2	1.42:1
27.03	.7	3.5	1.55:1
27.04	.6	3.2	1.51:1
27.05	7.3	23.5	1.40:1
27.06	.5	2.2	1.54:1
27.07	1.5	6.1	1.49:1
27.08	.8	16.3	16.5:1
53.01	.2	.8	1.54:1
53.02	.2	.6	1.52:1
56.02	.3	2.2	1.52:1
56.03	3.2	11.8	1.40:1
56.04	.4	2.3	1.50:1
56.05	.2	1.4	1.54:1
56.06	.6	4.4	1.54:1
56.07	1.4	7.0	1.40:1
56.08	1.4	4.9	1.40:1
56.09	1.7	8.9	1.40:1
56.10	2.4	10.1	1.40:1
62.01	.6	2.6	1.59:1
62.02	2.8	11.8	1.40:1
62.03	.3	1.6	1.59:1
62.04	.5	2.6	1.56:1

Table 25. continued.

CHEMICAL ANALYSIS.

SAMPLE NO	Al_2O_3% by wt	SiO_2% by wt	CaO:MgO
63.01	.4	1.9	40.0:1
63.02	1.3	4.5	17.4:1
63.03	.7	2.7	11.7:1
63.04	1.5	4.6	24.8:1
63.05	1.6	5.6	24.9:1
63.06	2.3	7.5	31.2:1
63.07	.4	1.7	80.0:1
64.01	3.3	2.8	23.5:1
64.02	.5	3.0	64.5:1
78.01	.3	1.0	1.61:1
78.02	.4	1.1	1.59:1
78.03	.1	.6	1.55:1
80.01	.5	8.5	17.0:1
80.02	.5	3.8	13.7:1
87.01	.3	2.5	1.62:1
87.02	2.8	13.6	1.70:1
87.03	7.6	20.6	1.64:1
87.04	.4	1.5	4.82:1
87.05	.4	1.4	1.74:1
87.06	.4	1.4	1.66:1
88.01	5.9	37.1	2.56:1
88.02	1.4	5.0	33.7:1
88.03	1.5	5.1	36.8:1
88.04	.6	2.9	4.05:1
88.05	1.2	4.0	56.5:1
91.01	2.1	7.6	35.3:1
91.02	1.0	3.9	48.8:1
91.03	2.6	8.7	31.3:1
92.01	.6	2.6	57.1:1
92.02	.3	1.7	66.5:1
98.01	1.3	4.4	21.7:1
98.02	2.6	12.0	10.0:1
98.03	.5	2.0	8.34:1
98.04	.5	14.7	1.40:1
98.05	.6	1.3	1.66:1
98.06	.5	8.3	1.59:1
98.07	2.0	8.6	61.3:1
210.01	.7	2.8	10.4:1

Table 26.

MAGNESIUM SULPHATE TEST RESULTS.

SAMPLE NO	M.of T&C.	ASTM
6.01	99.7	99.4
6.02	96.1	95.4
6.03	8.8	4.9
6.04	68.7	59.6
6.05	72.6	58.8
6.06	14.5	10.9
19.01	10.8	7.0
19.02	17.9	12.7
19.03	6.8	2.7
19.04	23.4	17.3
19.05	36.3	34.6
20.01	79.6	62.2
20.02	5.5	2.2
20.03	10.1	6.2
20.04	53.6	42.5
27.01	85.0	80.1
27.02	40.7	30.5
27.03	14.6	10.4
27.04	3.3	2.6
27.05	92.2	87.7
27.06	4.2	1.3
27.07	22.3	13.9
27.08	6.2	2.9
53.01	8.5	5.6
53.02	7.1	1.5
56.02	8.6	3.6
56.03	47.7	33.9
56.04	5.8	2.3
56.05	6.6	2.6
56.06	61.0	49.7
56.07	41.5	31.4
56.08	26.9	21.7
56.90	28.2	22.7
56.10	64.7	54.4
56.11	28.6	13.7
56.12	46.8	26.9
56.13	93.5	90.8
56.14	94.4	91.8
62.01	8.4	4.9
62.02	22.1	13.7
62.03	3.9	1.6
62.04	6.1	2.9
63.01	15.8	13.0
63.02	29.1	23.6
63.03	7.7	3.9
63.04	39.7	30.9
63.05	48.8	34.8
63.06	70.6	62.6
63.07	13.0	8.8
64.01	68.3	63.1
64.02	6.1	4.2
78.01	5.5	3.6
78.02	9.5	5.6
78.03	13.4	9.8
80.01	2.3	1.3
80.20	3.6	2.0
87.01	2.0	1.3
87.02	17.3	14.0
87.03	93.4	89.2
87.04	9.8	7.8
87.05	9.1	7.8
87.06	5.3	2.4
88.01	100.0	100.0
88.02	42.9	35.8
88.03	33.2	26.4
88.04	8.5	5.2
88.05	32.5	26.9
91.01	10.4	5.5
91.02	19.9	12.4
91.03	30.2	21.8
92.01	13.6	4.3
92.02	11.8	8.8
98.02	32.1	25.9
98.06	10.5	7.8
98.07	4.6	2.6
103.01	35.0	31.0
106.02	51.6	44.2
112.01	46.6	41.2
115.01	96.4	95.8
115.02	59.7	54.2
201.01	3.9	3.1
204.01	3.7	2.3
205.01	3.9	3.2
210.01	7.0	2.9

NOTE Loss expressed as a percentage of dry weight.

Table 27. 45% R.H. adsorption for Sitars' samples.

SAMPLE No.	Wt % ADSORBED WATER @ 45% R.H.
IA2	.041
CL1	.019
CL2	.023
IA1	.011
IH1	.020
CCS3	.018
PT05	.446
CCS2	.o19
CH1	.085
CYBA4	.243
CND1	.015
PT03	.686
BDT1	.435
DW A	.263
DW B	.579
WG	.100
CIBA2	.179
DW 1	.302
IH2	.090
LK1	.066
SWPC4	.078
LK3	.058

Samples from Sitar (1973)

APPENDIX B

SAMPLE DESCRIPTIONS AND LOCATIONS

SAMPLE DESCRIPTION AND LOCATIONS

SAMPLE NO & LOCATION NO.	DESCRIPTION
6	Armstrong brothers Vinemount quarry, Saltfleet Twp, Wentworth Cty, Niagara Penn. Not used as concrete aggregate.
6.1	Dolomite, argillaceous, medium brown/grey, aphanitic, medium bedded, microporous, Decew dolomite.
6.2	A/A, weathers slightly better in outcrop.
6.3	Dolomite, calcitic, med grey/lt grey, aphanitic, medium bedded, macroporous, chert nodules, Ancaster chert beds of the Goat Island dolomite.
6.4	Dolomite, argillaceous, cherty, dk brown/med grey, medium bedded, laminated, microporous, Goat Island dolomite.
6.5	Dolomite, argillaceous, cherty, med grey, aphanitic, thin bedded, laminated, easily weathered, microporous, Vinemount shaly dolomite beds of the Eramosa dolomite.
6.6	Dolomite, med brown, lt brown weathering, medium bedded, vuggy, macro/micro porous, Eramosa dolomite.
19	George Cambell Ridgemount quarry, Bertie Twp, Welland Cty, Niagara Penn.
19.1	Dolomitic limestone, cherty, Med/lt grey, lt grey weathering, aphanitic to fine crystalline, thin irregular bedding, glauconitic in part, laminated, fossiliferous, Bois Blanc formation.
19.2	Dolomite, mottled lt brown, buff weathering, aphanitic, medium bedded, microporous, Bertie-Akron formation.
19.3	Dolomite, cherty, medium brown, buff weathering aphanitic, medium bedded, microporous, Bertie-Akron formation.

19.4	Dolomite, argillaceous, medium brown with dk grey shaly partings, aphanitic, laminated, thin to med bedded, laminated, microporous, Bertie-Akron formation.
19.5	Dolomite, med brown/lt grey, aphanitic, stylolites, medium bedded, microporous, very similar to 62.3, Bertie-Akron formation.
20	M. Cambell quarry, Sebright, Rama Twp, Ontario Cty.
20.1	Limestone, argillaceous, lt grey, lithographic with dk shaly leafs, laminated, thin to medium bedded, microporous, this rock weathers easily, Gull River formation.
20.2	Limestone, lt grey, lithographic, stylolites, thin to medium bedded, microporous, Gull River formation.
20.3	Limestone, lt brown- lithographic, thin to medium bedded, microporous, Gull River formation.
20.4	Limestone, lt grey, lithographic, pyrite, laminated, thin bedded, microporous. Bobcaygeon formation.
27	Cayuga quarries, N. Cayuga Twp, Haldimand Cty.
27.1	Dolomite, argillaceous, blue grey, aphanitic, laminated, thin to medium bedded, microporous, Bertie-Akron formation.
27.2	Dolomite, mottled lt grey/med grey, aphanitic, medium bedded, microporous, similar to 56.7, Bertie-Akron formation.
27.3	Dolomite, lt/med grey, aphanitic, aphanitic, thin to medium bedded, microporous, Bertie-Akron formation.
27.4	Dolomite, med brown, aphanitic, laminated, medium to thin bedded, microporous, Bertie-Akron formation.
27.5	Dolomite, argillaceous, med/dk brown, aphanitic, partly laminated, medium to thin bedded, weathers easily, microporous, Bertie-Akron formation.

27.6	Dolomite, lt grey/lt brown, partly laminated, aphanitic to fine crystalline, medium to thin bedded, microporous, Bertie-Akron formation. Similar to 56.4.
27.7	Dolomite, lt grey, mottled, aphanitic, medium bedded, microporous, Bertie-Akron formation.
27.8	Limestone, cherty, med to lt grey, medium crystalline, to aphanitic, stylolitic, glauconitic, quartz sand medium crystalline, microporous, Bois Blanc formation.
53	James D. Gray and Son, W. Flamborough Twp, Wentworth Cty.
53.1	Dolomite, lt brown/grey, fine crystalline, macroporous, thin evenly bedded, Guelph formation.
53.2	Dolomite, med brown, fine crystalline to aphanitic, medium to thin bedded, macro/microporous, top of Eramosa formation?
56	Haldimand quarries Ltd, Hagersville, Walpole Twp, Haldimand Cty. 56.11 to 56.14 are not used as concrete aggregate.
56.2	Dolomite, lt brown, aphanitic to microcrystalline, medium bedded, brecciated, microporous, Bertie-Akron formation.
56.3	Dolomite, argillaceous, med brown/grey, microcrystalline laminated, thin bedded, microporous, weathered, Bertie-Akron formation.
56.4	Dolomite, lt grey/brown, aphanitic, laminated, medium bedded, microporous, Bertie-Akron formation. Similar to 27.6.
56.5	Dolomite, lt brown/grey, aphanitic to fine crystalline, massive to thick bedded, microporous, Bertie Akron formation.
56.6	Dolomite, lt grey/brown, aphanitic to microcrystalline, medium bedded, microporous, Bertie Akron formation.

56.7	Dolomite, mottled lt grey/med grey, aphanitic, medium bedded, microporous, Bertie Akron formation.
56.8	Dolomite, argillaceous, med brown/grey, dk grey shaly laminations, aphanitic, medium to thin bedded, microporous, Bertie Akron formation.
56.9	Dolomite, med brown, fine crystalline to aphanitic, medium to thick bedded, mixture of shaly base and clastic calcarenite, microporous, Bertie Akron formation.
56.10	Dolomite, argillaceous, blue grey, aphanitic, rapid weathering, microporous, Bertie Akron formation, from quarry floor.
56.11	Limy glauconitic siltstone, lt grey, aphanitic to medium crystalline, thin irregularly bedded, microporous, Bois Blanc formation.
56.12	Limy glauconitic siltstone, lt grey, aphanitic to microcrystalline, medium bedded, microporous, Bois Blanc formation.
56.13	Limy glauconitic siltstone, spotted dk grey lt grey, medium bedded microporous, Bois Blanc formation.
56.14	A/A, but more fissile and slightly darker colour.
62	R.E. Law Crushed Stone Ltd, Port Colborne, Wainfleet Twp, Welland Cty, Niagara Penn.
62.1	Dolomite, lt brown/grey, aphanitic to microcrystalline, medium bedded, microporous, Bois Blanc formation.
62.2	Dolomite, argillaceous, med brown, aphanitic, thin bedded, microporous, Bois Blanc formation.
62.3	Dolomite, med brown, aphanitic, stylolitic in part, laminated, thick bedded, microporous, Bertie Akron formation.

62.4	Dolomite, med brown/lt brown, aphanitic to microcrystalline, laminated, thick bedded, microporous, Bertie Akron formation.
63	Limestone Products Ltd, Uhthoff, Orillia Twp, Simcoe Cty.
63.1	Limestone, lt brown/grey mottled, medium crystalline to aphanitic, pyrite, microcrystalline, medium bedded, microporous Gull River formation.
63.2	Limestone, dolomitic, med brown, lithographic, shaly laminations, medium bedded, microporous, Gull River formation.
63.3	Limestone, dolomitic, lt/med brown mottled, medium crystalline to aphanitic, traces dk brown siderite, microporous, Gull River formation.
63.4	Limestone, dolomitic, lt brown/med grey mottled, shale laminations, micro crystalline to lithographic, microporous, Gull River formation.
63.5	Limestone, dolomitic, lt brown, lithographic, easily weathered, thin bedded, laminated, microporous, traces pyrite, Gull River formation.
63.6	Limestone, dolomitic, lt brown/green, aphanitic to microcrystalline, thin to medium bedded, laminated, fissile, microporous, traces pyrite, Gull River formation.
63.7	Limestone, brown coquinoid calcarenite, thin bedded, fossiliferous, medium crystalline to aphanitic, macroporous, Lower Bobcaygeon formation.
64	Mc Carthy Brothers quarry, Gamebridge, Thorah Twp, Ontario Cty. Notused as concrete aggregate..
64.1	Limestone, argillaceous, med brown/grey, aphanitic to microcrystalline, shaly partings, thin to medium bedded, microporous, Verulam formation.

64.2	Limestone, lt/med grey, brown weathering, medium crystalline, fossiliferous, medium bedded, macroporous, Verulam formation.
78.	Milton Quarries Ltd, Milton, Nassagaweya Twp, Halton Cty.
78.1	Dolomite, calcitic, grey/brown, aphanitic to medium crystalline, medium to thick bedded, macroporous, traces dk brown siderite, Amabel formation.
78.2	Dolomite, calcitic, blue/grey, buff weathering, fine to medium crystalline, medium to thick bedded, macroporous, Reynales formation.
78.3	Dolomite, calcitic, lt buff/grey, porous, fine Crystalline, fossiliferous, thick bedded, macroporous, Reynales formation.
80.	Norfolk Quarry Company, Port Dover, Woodhouse Twp, Norfolk Cty.
80.1	Limestone, dolomitic, cherty, lt grey/brown, fine crystalline to aphanitic, stylolites, thick bedded, macroporous, Dundee formation.
80.2	Limestone, dolomitic, fine crystalline to aphanitic, thick bedded, macroporous, Dundee formation.
87	Queenston Quarries Ltd, Queenston, Stamford Twp, Welland Cty.
87.1	Dolomite, calcitic, lt grey, medium crystalline, massive bedded, crinoidal, stylolites, macroporous, Gasport Dolomite of Lockport formation. Similar to 87.4.
87.2	Dolomite, calcitic, argillaceous, med/dk brown, aphanitic, medium bedded, laminated, microporous, Decew Dolomite.
87.3	Dolomite, calcitic, argillaceous, dk grey, aphanitic, laminated, rapid weathering, microporous, Decew Dolomite.

87.4	Dolomite, calcitic, lt grey, medium crystalline, thick to massive bedded, macroporous, Gasport Dolomite of the Lockport formation. Similar to 87.1 but not as porous.
87.5	Dolomite, calcitic, lt brown, buff weathering, aphanitic to medium crystalline, porous, macroporous, Goat Island Dolomite of Lockport formation.
87.6	Dolomite, calcitic, lt grey, medium crystalline, macroporous, Gasport Dolomite of Lockport formation.
88.	Rama Township Quarry, Ontario Cty. Not used as concrete aggregate.
88.1	Calcareous shaly siltstone, lt green, aphanitic to fine crystalline, shale laminations, rapid weathering, soft, microporous, Shadow Lake formation of the Black River.
88.2	Limestone, argillaceous, lt/med grey, aphanitic, medium to thin bedded, rapid weathering, laminated microporous, Gull River formation of the Black River.
88.3	Limestone, argillaceous, grey/brown mottled dk grey, medium bedded, aphanitic, laminated microporous, Gull River formation of the Black River.
88.4	Limestone, dolomitic, lt brown, aphanitic, macroporous, thin to medium bedded, Gull River formation of the Black River.
88.5	Limestone, lt grey, aphanitic, fossiliferous, rapid weathering, microporous, Gull River formation of the Black River.
91.	Roblindale Quarries Ltd, Roblindale, Camden East Twp, Lennox and Addington Cty.
91.1	Limestone, argillaceous, dk grey, laminated, medium bedded, microporous, Gull River formation (upper) of Black River.

91.2	Limestone, med grey, lt grey weathering, aphanitic to medium crystalline, calcarenite, macroporous, Gull River formation of the Black River formation.
91.3	Limestone, argillaceous, med/dk grey, aphanitic to fine crystalline, laminated, rapid weathering, microporous, Gull River formation of the Black River.
92.	Kirkfield Crushed Stone, Kirkfield, Carden Twp, Victoria Cty.
92.1	Limestone, lt to med grey, aphanitic to medium crystalline, calcarenite, thin to medium bedded, macroporous, Lower Trenton or Upper Bobcaygeon of the Trenton limestone.
92.2	Limestone, lt grey, medium to coarse crystalline, calcarenite, thin bedded, macroporous, Middle Trenton or Verulam of the Trenton limestone.
98.	Stoklosar Marble Quarries, Madoc Twp, Hastings Cty.
98.1	Limestone, argillaceous, med brown, aphanitic, microporous.
98.2	Limestone, argillaceous, dk brown, aphanitic, quartz 2mm to .01mm 20%, microporous.
	Note. samples 98.1 and 2 constitute a single sample as received. Reported $MgSO_4$ test results were 1.98% loss. This differs radically from MTC test result on 98.2 of 25.2% loss. 98.2 constituted 80% of the sample as received. This rock when used in a Terrazzo floor at York University reportedly failed, after a winter in which shoes covered with salt from the outside had added salt to the floor, since it was inside, presumably with out the action of frost.
98.3	Limestone, white, aphanitic, to fine crystalline, macroporous, Marble.
98.4	Dolomite, lt green, fine crystalline, macroporous, Marble.

98.5	Dolomite, calcitic, lt buff, fine to medium crystalline, macroporous, Marble.
98.6	Dolomite, calcitic, lt grey/blue, aphanitic, macroporous, Marble.
98.7	Limestone, very dark grey, medium to fine crystalline, colour due to inclusions of dark particles in clear calcite crystals, microporous Marble.
103.	Rice and McHarg Quarry, Esquesing Twp, Halton Cty, (P. 23 Building stones of Ontario, Sandstone).
103.1	Sandstone, lt grey, fine grained quartz 98%, thin laminations mica and green glauconite? macroporous Medina Sst.
103.2	Sandstone, A/A, some mineralisation present, pyrite, calcite and chalcopyrite, macroporous, Medina Sst.
106.	Structural Sandstone Quarry, Glen Williams, Esquesing Twp, Halton Cty. (P. 26 Building Stones of Ontario, Sandstone).
106.1	Sandstone, grey buff, fine grained, macroporous, Medina Sst.
106.2	Sandstone, lt grey/brown, fine grained, 50% dolomite, microporous from a horizon twenty feet above Medina Sst.
112.	Norrie Quarry, Inglewood, Caledon Twp, Halton Cty. (P. 33 Building Stones of Ontario, Sandstone).
112.1	Sandstone, buff grey, porous, fine grained, macroporous Medina Sst.
115	Wilsons Quarry, Inglewood, Caledon Twp, Halton Cty. (P. 36 Building Stones of Ontario, Sandstone).
115.1	Sandstone, red, fine grained, poorly cemented, friable macroporous, Medina Sst.

115.2	Sandstone, dolomitic, mottled grey, shaly, medium crystalline to aphanitic, porous macroporous, from a horizon fifteen feet above Medina Sst.
201.1	Halley quarry, Monmouth Twp, Haliburton Cty. Granite, red, 40% quartz, 40% orthoclase, 10% boitite, 10% plagioclase, grains from 2mm to .5mm, microporous. (P. 20 Building Stones of Ontario, Granites).
202.1	Test Site, Lot 23 Con 4, Glamorgan Twp, Haliburton Cty. Gabbro, black, Ca plagioclase 1. to 1.5 cm 70%, pyroxene 30%, Extremely hard, microporous. (P. 21 Building Stone of Ontario, Granites).
203.1	Test Site, On 507 S 50 yards N of Trappers Inn, Cavendish Twp, Peterborough Cty. Granite, red, 50% quartz, 2mm, 10% biotite 2mm, 40% pink orthoclase 2mm, microporous. (P. 22 Building Stones of Ontario, Granites).
204.1	Test Site, 2 miles north of Westport on Bolingbroke rd at the top of a hill. N. Crosby Twp, Leeds Cty. Granite, red, 10% Quartz .5 cms, Pink Orthoclase 70% .5 to 1.5 cms, 20% biotite .5 cms, Trace amounts of pyrite, microporous.
205.1	Road Cut, Highway 7, Elzevir Twp, Hastings Cty. Micaceous gneiss, dk grey/black, 50% biotite 1mm, 50% quartz 1mm, microporous.
206.1	Road Cut, Highway 7, Elzevir Twp, Hastings Cty. Mica schist, dk grey, 70% biotite .5mm, 30% quartz .5mm, Microporous.
210.1	Road Cut, Pittsburgh Twp, Fontenac Cty. Limestone, med grey, lt grey weathering, fine crystalline to aphanitic, thin bedded, macroporous, Trenton/Black River.

REFERENCES

Adams,F.S., 1973, Highway salt; social and environmental concerns; Highway Research Record, #425.

Adamson,A.W., 1960, Physical chemistry of surfaces.

Amberg,C.H., R.McIntosh, 1952, A study of adsorption hysterisis by means of length changes of a rod of porous glass: Can. J. of Chem., v.30,p.1012.

Amfelt,H., 1943, Damage on concrete pavements by wintertime salt treatment: Statens Vaeginst. (Swed.), Medd.,#66.

Anderson,D.W., P.F.Low, 1958, The density of water adsorbed on Li, Na and K bentonite: Soil Sci. Soc. of Amer. Proc., v.22, p.99.

Anderson,D.W., P.Hockstra, 1965, Migration of interlamellar water during freezing and thawing of Wyoming bentonite: Soil Sci. Soc. of Amer. Proc., v.29, p.498.

Anderson,D.W., 1967, The interface between ice and silicate surfaces: Jour. of Colloid and Interface Sci., v.25, p.174-191.

Anderson,D.W., A.R.Tice, 1971, Low-temperature phase of interfacial water in clay-water systems: Soil Sci. Soc. of Amer. Proc., v.35, p.47-54.

Anderson,D.W., 1972, Ionic migration of frozen antarctic soil: Antarctic Jour. v.7, p.112-113.

Anderson,D.W., A.R.Tice, A.Baun, 1973, Water-ice phase composition of clay-water systems: Soil Sci. Soc. of Amer. Proc., v.37, p.819.

Andrews,D.E., P.W.Schmidt, H.Van Olphen, 1967, X-ray study of the interactions between montmorillonite platelets: 15th Nat. Conf. on Clays, p.321.

Baxter,J.W., R.D.Harvey, 1969, Alumina content of carbonate rocks as an index to sodium sulphate soundness: Illinois Geol. Survey, Industrial Minerals Note 39.

Bear,E.F., 1964, The chemsitry of the soil, Reinhold, New York.

Boyd,K.A., 1971, A theoretical approach to adsorption of water on mineral surfaces. Unpublished MS thesis, Rensselaer Polytechnic Institute, Troy, New York.

Browne,F.P., P.D.Cady, 1975, Deicer scaling mechanisms in concrete: Durability of Concrete, ACI Special Pub. #47, p.101-119.

Deer,W.A., R.A.Howie, J.Zussman, 1966, An introduction to the rock forming minerals, Longmans, London.

Dolar-Mantuani,L., R.Laakso, 1974, Results of ethylene glycol swelling test on argillaceous limestone: Can. Jour. Earth Sci., v.11, p.430-436.

Dunn,J.R., 1963, Characteristics of various aggregate producing formations in New York state: Bureau of Physical Reasearch Pub.

Dunn,J.R., P.P.Hudec, 1965, The influence of clays on water and ice in rock pores: Bureau of Physical Reseach Pub. 65.5.

Dunn.J.R., P.P.Hudec, 1972, Frost and sorption effects in argillaceous rocks: Highway Reseach Record #393, p.66-78.

Evans,I.S., 1969, Salt crystallisation and rock weathering, a review: Rev. Geomorphologie Dynamic, #4, XIX, p.153-177.

Faust,S.D., J.V.Hunter, 1967, Principles and application of water chemistry: New York.

Fisher,L.A., 1972, The influence of electrolyte on the surface forces of a mineral: Unpublished MS thesis, Rensselaer Polytechnic Institute, Troy, New York.

Folman,M., D.J.C.Yates, 1958, Expansion-contraction effects in rigid adsorbents at low coverages: Trans. Faraday Soc. #423, v.54 Pt.3.

Gillott,J.E., 1968, Clay in engineering geology: Elsevier, New York.

Gillott,J.E., 1975, Alkali-aggregate reactions in concrete, Eng. Geol., v.9, p.303-326.

Graham,J. et al, 1964, Nuclear magnetic resonance study of interlayer water in hydrated layer silicates: Jour. Chem. Physics, v.40, p.540-550.

Grim,R.E., 1962, Applied clay mineralogy: McGraw-Hill, New York.

Hadley,D.W., 1964, Alkali reactivity of dolomitic carbonate rocks: Highway Research Record #45, p.1-20.

Harvey,R.D., G.S.Frazer, J.W.Baxter,1974, Properties of carbonate rocks affecting soundness of aggregate: Illinois Geol. Survey, Industrial Minerals Note 54.

Hendricks,S.B., 1940, Jour. Amer. Chem. Soc., v.62, p.1457.

Hewitt,D.F., 1960, The limestone industries of Ontario: Ont. Dept of Mines, Industrial Mineral Circular #5.

Hewitt,D.F., 1964, Building stones of Ontario: Ont. Dept of Mines, Industrial Mineral Reports 14,15,17 and 19.

Hewitt,D.F. M.A.Vos, 1972, The limestone industries of Ontario: Ontario Division of Mines, Industrial Mineral Report #39.

Hockstra,P., et al, 1967, Mobility of water molecules in the transition layer between ice and solid surface: Jour. of Colloid and Interface Sci. v.25, p.166-173.

Honeyborne,D.B., P.B.Harris, 1958, The structure of porous building stone and its relation to weathering: Proc. Tenth

Horne,R.A., 1970, Sea water: Advan. Hydrosci. v.6, p.107-140.

Horne,R.A., 1972, Water and aqueous solutions, structure, thermodynamics and transport processes: Wiley, New York.

Hudec,P.P., N.Sitar, 1975, Effect of water sorption on carbonate rock expansivity: Can. Geotech. Jour. v.12, p.179-186.

Keyser,J.H., 1973, Deicing chemicals and abrasives, state of the art: Highway Research Record #425.

Lahav,N., _et al_, 1973, Exchangeable cation-structural parameter relatioships in montmorillonite: Clays and Clay Minerals, v.21, p.249.

Lahav,N., D.H.Anderson, 1973, Montmorillonite-bensidine reactions in frozen and dry states: Clays and Clay Minerals, v.21, p.137-139.

Lamar,J.E., 1967, Handbook on limestone and dolomite for Illinois quarry operators: Illinois State Geol. Survey, Bull. 91.

Litvan,G.G., 1972, Phase transitions of adsorbates IV, mechanism of frost action in cement paste: Jour. Amer. Ceramic Soc., v.55, p.38-42.

Litvan,G.G., 1973a, Pore structure and frost susceptibility of building materials: Nat. Res. Council Canada, Division of Building Res., Research Paper #584.

Litvan,G.G., 1973b, Frost action in cement paste: Mater. Constr. Mater. Struct., v.6, p.293-298.

Litvan,G.G., 1973c, Phase transitions of adsorbates V: Jour. of Colloid and Interface Sci., v.45, p.154-169.

Litvan,G.G., 1975, Phase transitions of adsorbates VI, effect of deicing agents on cement paste: Jour. of Amer. Ceramic Soc., v.58, p.26-30.

MacInnis,C., E.C.Lau, 1971, Maximum size effect on frost resistance of concrete: ACI Jour. v.68, p.144-149.

MacInnis,C., J.J.Beaudoin, 1972, Mechanism of frost damage in hardened cement paste: Cem. Conc. Res., v.4, p.225.

Murrman,R.D., P.Hockstra, R.C.Bialkowski, 1968, Self diffusion of sodium ions in frozen Wyoming bentontite-water paste: Soil Sci. Soc. of Amer. Proc., v.32, p.501.

Neville,A.M., 1972, Properties of concrete: Pitman, London.

Nielsen,D.R., 1972, Soil Water: Amer.Soc. of Agronomy.

Norrish,K., J.A.Rausell-Colom, 1961, Low angle X-ray diffraction studies of the swelling of montmorillonite and vermiculite: 10th Nat. Conf. on Clays, p.123, Pergamon Press, London.

Oster,J.D., P.F.Low, 1963, Activation energy for ion movement in thin water films on montmorillonite: Soil Sci. of Amer. Proc., v.27, p.369.

Powers,T.C, 1945, A working hypothesis for the further studies of frost resistance of concrete: ACI Jour. Proc., v41, p.245-272.

Powers,T.C., R.A.Helmuth, 1953, Theory of volume changes in hardened portland cement pastes during freezing: Proc. Highway Research Board, v.32, p.285-292.

Powers,T.C., 1955, Basic considerations pertaining to freeze/ thaw tests: ASTM Proc., v.55, p.1132.

Powers,T.C., 1968, The properties of fresh concrete: Wiley, New York.

Powers,T.C., 1975, Freezing effects in concrete: ACI Special 47, The deterioration of concrete. p.1-11.

Ravina,A.I., P.F.Low, 1972, Relation between swelling, water properties and b dimensions in montmorillonite-water systems: Clays and Clay Minerals, v.20, p.109-123

Rigbey,S., 1975, The effect of sodium chloride upon water adsorption characteristics of rock aggregates: Unpublished BS Thesis, University of Windsor, Ontario.

Robbins,C., W.D.Keller, 1952, Clay and other non-carbonate minerals in some limestones: Jour. Sed. Petrol., v.22, p.146-152.

Robinson,R.A., Stoakes, 1959, Electrolytic solutions.

Roy,C.J., L.A.Thomas, R.C.Weissmann, R.C.Schneider, 1955, Geologic factors related to quality of limestone aggregates: Highway Res. Bd. Proc., v.34, p.400-412.

Sanioilov,O.Ya., 1972, Residence times of ionic hydration: In Horne 1972.

Shainberg,I., W.D.Kemper, 1966, Hydration status of adsorbed cations Li, Na and K on bentonite: Soil Soc. of Amer. Proc., v.30 p.707.

Sherard,J.L., et al, Piping in earth dams of dispersive clay: Not known, copy obtained from P.P.Hudec.

Sposito,G., 1973, Volume changes in swelling clays: Soil Sci., v.115, p.315.

Spry,A., 1968, Metamorphic textures: Pergamon Press, London.

Tooker,E.W., 1962, Clay minerals in rocks of the lower part of the Oquirrh formation, Utah: 9th International Conf. on Clays and Clay Minerals, p.355-364.

Van Olphen,H., 1950, Stabilisation of montmorillonite sols by chemical treatment: Rec. Trav. Chem. Pays. Bas., v.69, p.1308-1322.

Van Olphen,H., 1961, Unit layer interaction in hydrous montmorillonite systems: Shell Development Co. Expl. and Prod. Res. Div. Pub. 273, p.1-14.

Venkata-Raman,K.V., M.L.Jackson, 1963, Curling of clay layers by exchange of Na ions for K ions at the mica cleavage surface as revealed by electron microscope: 12th Conf. Clays and Clay Minerals, p.423-429.

Verbeck,G.J., P.Klieger, 1957, Studies of salt scaling of concrete: Highway Research Board Bull. #150, p.1-17.

Verbeck,G.J., R.Landgren, 1960, Influence of physical characteristics of aggregates on the frost resistance of concrete: ASTM Proc., v.60, p.1063-1079.

Vos,B.H., E.Tammes, 1969, Moisture and moisture transfer in porous materials: Rept. No.B 1-69-96, Inst. TNO for building materials, Delft, Holland, 54p.

Wayman,C.H., 1967, Adsorption on clay mineral surfaces: In Faust, S.D. and J.V.Hunter, 1967.

Whiting,J.D., 1974, The frost resistance of concrete subjected to a deicing agent: Unpublished MS Thesis, University of Windsor, Ontario.

Winkler,E.M., 1975, Stone: properties, durability in mans environment: 2nd Ed., Springer-Verlag, New York.

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