THE MIGRATION AND PRECIPITATION OF WATER-SOLUBLE IONS IN CONCRETE

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Field observations from the Middle-East are reported which show that water-soluble ions, such as alkalies, sulphate, and chloride, migrate through concretes and become concentrated in particular groundwater-concrete domains. Crystallization of compounds containing these ions leads to the destruction of concrete at rates which can be estimated and where the rate reflects the specific domain into which the concrete is placed. Five separate domains are recognised, each showing different mechanisms for the transport and precipitation of ionic species. Field data are used in an attempt to quantify this deleterious process which in extreme cases can lead to the removal of external concrete at a rate in excess of one centimetre per annum. Experiments have been conducted to investigate the mechanisms by which the necessary high ion concentrations can be reached, where the solutions are initially dilute, and the results of these experiments are described. The process of concrete decomposition derived from both reactions between soluble ions and the concrete and from the direct precipitation of salt from aqueous solution. The mechanism by which these processes bring about decompositon is discussed.

1. INTRODUCTION

In the Middle East, damage to concrete structures is widespread and serious. It is rare, however, to encounter deleterious changes that reflect alkali-aggregate reactivity. In the United Arab Emirates it has been suggested that serpentinite may be reactive in the alkaline cement-paste environment but there is no evidence to support this contention. Disintegration due to reinforcement corrosion is widespread and this can usually be attributed to salts within the aggregates used to make the concrete. Most commonly these salts are chlorides and sulphates derived from either the aggregate sources or the ground of the constructional area. Salts may also cause chemical damage below the ground surface as in the orthodox sulphate attack.

Concrete placed in or on sabkha deposits, or on any similar bedrock with a potentially saline groundwater, is commonly progressively decomposed. In some instances the changes can be explained as a relatively straightforward chemical sulphate attack but damage may occur even where sulphate levels are low. It is also notable that the greatest alteration occurs when the concrete is out of direct contact with the saline solutions and in this the changes are strictly analogous with rock weathering which is widespread under these conditions. The most profound attack occurs for up to 50 cm above the ground surface and the magnitude of the alteration is dependent on several factors. These include the salinity of the water and composition of dissolved ions, the position and stability of the water table, the capillarity of foundation rocks and soils, the design and manufactured qualities of the concrete, and cyclicity in wetting and drying and in humidity variations. This paper is concerned with the relative influence of these various factors, with the mechanism by which rocks, concretes and cement paste are dissociated and with the rate of decomposition.

Examples of the behaviour of concretes in aggressive environments are widespread and some have been given, for example, by Fookes and Collis (1975). Here only a few illustrations are cited of very many occurences of damage seen in the field, but some broad generalizations are made from the larger body of data. All the examples quoted are taken from sabkha environments in the Middle East because these provide the clearest 'model' conditions permitting analysis of the factors promoting decay.

Following description of these samples, experiments are described which attempted to simulate the field conditions as realistically as possible and, for example, avoided the use of saturated salt solutions as are used in the well known soundness test. The results of these tests show that it is not necessary to use saturated solutions to cause the growth of crystalline phases. They also show that the structure of certain rocks and concretes is such that they can create concentration gradients of dissolved ions within themselves. Crystalline phases have been grown within and on rocks and concretes from initially dilute solutions and these have led to minor *mechanical* damage to the materials in a matter of weeks without *chemical* reaction taking place. The field evidence suggests that chemical reaction may accompany this mechanical damage in the real system.

2. FIELD OBSERVATIONS

a) Concrete within sabkha, Bahrain.

A series of concrete blocks, initially, about 70 cm square were placed in sabkha to support a pipe-line. Their upper surfaces were at various levels with respect to the sabkha surface. The sabkha consists of a silty sand which is impregnated with gypsum and sodium chloride and the groundwater varies slightly in level because of tides and intermittent rainfall. In some places the surface is permanently wet but generally a dry crust of a mixture of gypsum and sodium chloride is present. This softens and dissolves when wetted with fresh water but rapidly develops again on drying. The redeveloped crust envelopes objects left on the sabkha surface and may coat vegetation as well as mineral substances. In general the salt grows as polygonally distributed ridges with hollows between.

The concrete blocks set so that their surfaces are level with the sabkha surface have over some 20 years become decomposed with virtually the complete elimination of paste so that only a sandy gravel now remains. The concrete has been broken down to a depth of up to 10 cm and damage has been most marked on the corners and edges of the blocks which have become rounded. The gravel produced has become coated with the salt crust of the surrounding sabkha. The underlying still coherent concrete is friable to a depth of a further 5 cm.

Where the concrete has been placed so that its upper surface is some 20 cm above the sabkha, similar damage has been produced but is confined to a zone at the sabkha surface and several centimetres thick. Concretes set at levels between these two extremes show intermediate decomposition.

Excavation showed that the main damage was confined to the upper parts of the blocks and become progressively less downwards. It is a common observation that concrete actually buried in the sabkha shows less damage than that near or on the surface.

b) <u>Concrete Anchors, Bahrain</u>.

A second set of concrete supports set in sabkha extend for some 70 cm above the sabkha surface and are 150 cm square. These were found to be altered for up to 40 cm above the sabkha surface. They remained coherent and strong within the sabkha. Here the sabkha materials are in the capillary fringe but the ground surface is only just damp and there is a comparatively thin and powdery salt crust. The maximum damage occurs for some 10 cm above the sabkha surface and in this zone concrete has spalled to a depth of two or three centimetres. The level to which the sabkha becomes intermittently saturated with groundwater is some 70 cm below the present ground surface.

c) Concrete blocks placed on sabkha, Bahrain.

Near the blocks described in section 'a.' above are concrete blocks standing some 80 cm above the ground surface and about 50 cm across. These are decomposed for up to 35 cm from the ground and at the point of maximum penetration the concrete has been removed to a depth of about 10 cm. Each concrete block is now surrounded by a gravel cone derived from the concrete.

d) Walls of rendered concrete blocks, Bahrain.

Here concrete walling blocks have remained comparatively stable but their rendering has been completely decomposed for some 40 cm above the ground surface. A crust of sodium chloride has been developed for a few centimetres above the upper limit of the spalling.

e) Concrete fencing posts.

In many parts of the Middle East, concrete fencing posts provide good indicators of aggressive ground conditions. Commonly it is possible to map out these changing conditions by following lines of such posts. In dry soils or rock platforms little damage accrues and posts may be serviceable for many years. In the most active zones the concrete spalls for up to 40 cm from the ground surface and within a very few years the posts may collapse. The most aggressive ground conditions indicated by these occurrences appear to be where the concrete is placed in soils which are in the capillary fringe and where the groundwater is saline. It is usually obvious that concrete placed in the ground to hold the posts in place shows much less damage than the posts themselves.

f) Concretes in Sharjah (U.A.E.)

In one area in Sharjah it is possible to find concretes of up to 40 years in age, placed in and on sabkha, and showing various degrees of damage. At one place a dense concrete apron ten years old sits directly upon sabkha but, though the sabkha surface is within the capillary fringe, there is no sign of decomposition whatsoever. Nearby, fencing posts need to be replaced every other year or so. In some 40-year old concrete the paste is decomposed and spalling occurs for up to 7 m from the ground. This, however, appears to relate to defective starting materials rather than the aggressive ground conditions. On the other hand, a four year old mosque built on the same sabkha has both aggregate and ground problems and has become unsafe to use. The worst damage results from the influence of the aggressive ground conditions and pillars and walls are decomposed for up to 40 cm above the ground surface.

g) Influence of aggregate type.

In most of the situations where damage occurs, it is the paste which decomposes and the aggregate remains coherent. Some aggregates may, however, facilitate the mechanical decomposition process. These are the more porous aggregates and may accelerate damage when used in concrete, bituminous roads, or as rip-rap or armouring (Fookes and French, 1977). These materials act mainly by transmitting salt solutions but sometimes cause added weakness because of their own mechanical instability.

3. GENERALIZATIONS FROM FIELD OBSERVATIONS

a) Shape of concrete.

Whatever the ground conditions, it seems evident that the maximum damage results when the concrete has the minimum cross sectional area. Large slabs are scarcely altered, even when placed directly onto sabkha, if the concrete is made to a good specification. Conversely, even vibrated concrete, if of very small cross-section, will begin to decompose rapidly. It is also noticeable that the alteration takes place higher in the structure if the cross-sectional area is small. It seems likely that this may be due in part to the rapidity with which water and, hence, soluble ions, are introduced into the concrete. The smaller the cross-section, the greater the evaporative transfer of water into the concrete is likely to be.

b) Ground Conditions.

It is evident that the greatest damage is caused to concrete placed in or above the capillary fringe. Where the ground is permanently saturated with water, salts are not precipitated in the concrete. This is presumably because saturation of the solution in soluble ions cannot be attained. Damage here more often takes place through reaction with the paste or aggregate and this chemical change may be much slower than the mechanical effect. It may also be self limiting in that a barrier of reaction product may be established between saline groundwater and fresh concrete.

4. INFLUENCE OF GROUNDWATER CONDITIONS

Five different groundwater zones can be recognized and the behaviour of the concrete varies with these zones.

a) Zone 1.

This is that volume of rock or soil which is permanently saturated with water and has water above it. There is often a tendency for compounds to be precipitated at the water-solid interface. Concretes in this situation are not especially liable to damage providing they do not become contaminated on placement and providing they are impermeable. If the concrete is sufficiently porous to carry moisture by capillarity then precipitation of compounds and mechanical disintegration may follow.

b) Zone 2.

This zone is also permanently saturated with water but is overlain by soil or rock. Here again damage is not likely except at the water surface where crystallization may occur. Geologically, nodules, concretions or hardpans may appear at this level and similar chemical changes induced in concrete may not be deleterious. Groundwater in this zone may be capable of flow and if so it is likely that transference of material will be greatly accelerated and the growth of new crystalline phases will speed up by an order of magnitude. The flow in these circumstances is usually slow and therefore lamellar and this both speeds growth and produces regularly shaped concretions or other growth forms. The numerical treatment of these relationships has been given by Neilson (1961) and Berger (1968 and 1971). There are numerous descriptions of the influence of such processes in saline soils such as sabkhas. Here carbonate sands are often replaced by dolomite and gypsum and secondary silica may be produced. Conversely, dolomites may be dedeolomitized according to their situation and the nature of the groundwater. Concrete in this situation should remain stable but may become the locus for the collection of particular phases, particularly where Ca-rich phases are likely to be precipitated. Precipitation is liable to be by replacement reactions and the formation of cementitious phases filling cavities and making overgrowths on existing phases. Most such changes are likely to be advantageous. The maximum growth is likely to occur where concentration gradients are highest and this means at the solvent surface.

c) Zone 3.

This zone occurs above Zone 2. It is thin and defined by the upper and lower positions of the water-table. Here the rocks or soils are intermittently saturated and if this wetting and drying cycle operates on a short term basis, it might be expected to produce direct growth of crystalline phases within porous systems. The conditions correspond closely with those of the conventional soundness test for aggregates and it has been shown that many rocks are disrupted by this treatment

(Goudie et.al. (1970), Minty (1965) and Minty and Monk (1966). Cooke (in press) has carried out numerous experiments on the conditions operating in this zone and shown that the wetting and drying cycle coupled with temperature variations greatly reduces the particle size of fragmented materials. The materials most likely to be damaged are those with high microporosity and where the crystalline phases are of low strength, such as carbonates. It is well know that if saturated solutions are used then sulphates are most effective in breaking down porous rocks. Whether this is because of the force of crystallization of the sulphate or the energy changes involved on recrystallization by hydration and dehydration is not yet understood, but it is shown later that it is not necessary to introduce saturated solution or thermal variations to promote crystallization.

Concrete in this environment will behave in the same way as rock; it will be decomposed at a rate consonant with its porosity and mechanical strength and, more importantly, with the properties of its coarse and fine aggregate. An important difference between the experimental soundness test and natural systems is that in nature drying is not likely to be complete but a moisture concentration gradient will be produced. In most laboratory systems this is not so, the material is dried uniformly for a long period before re-immersion in saturated solutions.

d) Zone 4.

This is the capillary fringe and occurs above Zone 3. It may be several tens of centimetres thick and, where this is so, the chance of total dessication in Zone 3 is minimal. Transference of water to the surface by evaporative pumping, or other forms of abstraction such as transpiration, may lead to the establishment of a slow, almost steady, state, vertical flow of moisture through the capillary zone. Migration of a solvent through a capillary system is directly analogous with certain chromatographic processes and can lead to the production of steep concentration gradients and layers or 'fronts' of extreme composition. The distribution coefficient for soluble ions between the aqueous mobile phase and the static portion of the sediment is such that high concentrations of salt will develop in the mobile phase. Motion of this solution will enhance the concentration of the solution and produce concentration maxima for each ionic species. In the zone of capillaries it is therefore possible for the solutions to become saturated locally and for particular salts to be precipitated. Those ions which have the greatest solubility in the brine will be carried to the highest in the capillary fringe. Precipitation may be direct with, for example, the formation of sodium chloride crystals directly from the solution. However, it is common to find that sulphates grow by reaction and that the transport of the sulphate ion into calcareous sediments can lead to the growth of gypsum. The growth of sulphate in these circumstances may be very rapid and desert rose type gypsum can be grown in a matter of weeks in piles of loose sand placed upon ground with saline groundwater.

If the ground surface corresponds with the level of intermittent saturation, it is common to find crusts of evaporite materials developed which are typically two or three centimetres thick. Generally gypsum is abundant and forms polygonal ridges over flat areas. Between the ridges it is common to find sodium chloride deposited. Hummocks of sand above this level, i.e. in the capillary zone are impregnated with salt and there is usually a zone in which the salts are concentrated some 30 to 50 centimetres above the top of Zone 3. Gypsum crystals tend to grow in the outermost part of the capillary fringe where in fact the soils appear superficially dry.

Changes such as these have also been found to occur in soils around concrete and road structures placed on saline soils, and sulphate and chloride are drawn towards these small artificial protruberances.

e) Zone 5.

Zone 5 occurs above the capillary fringe. It is moistened only during wet weather or periods of high humidity. Relatively trivial concentrations of deleterious ions may be built up here. Commonly, rainfall will wash out most of the salt content but this may be only temporary and the salts return by motion along grain surfaces.

5. EXPERIMENTAL STUDIES

In order to analyse the factors influencing the transference of ions into and through cement paste and aggregate materials, a series of medium term experiments were set up. These consisted of prisms of rock of various dimensions set in and protruding from a bed of sand. Mortar made of cement and fine aggregate was moulded into cylindrical blocks and these were also set in the sand bed. A salt solution was added to the sand bed and this was then kept damp by feeding it with distilled water under a constant small head. The temperature was not specially controlled but the position of the experiments ensured an ambient temperature of between 22 and 25°C. No attempt was made to create the thermal variations encountered in the field since this would have increased the number of variables.

A number of rock types were studied but chalk was chosen for the largest number of experiments. This was selected because Goudie et.al. (1970) have shown that chalk is among the rocks that are most rapidly disintegrated by salt weathering and it is well known to be thoroughly unsound. The rock is also extremely porous and has a high capacity to hold water in its pores. All these features were expected to allow processes to take place rapidly in chalk that might be very much slower in other rocks and hence allow results to be obtained much more quickly than would otherwise be possible.

A large block of chalk was selected for its uniformity and cut into a series of prisms measuring up to 15 cm in length and 3 cm by 3 cm in cross section. The residue of rock was broken into angular coarse aggregate with the pieces all greater than 2 cm in estimated mean diameter. The prisms were set vertically in a bed made of British Standard sand such that the lowest two centimetres of the prisms were embedded in the sand. The coarse aggregate was piled onto the surface of the sand. The sand bed was wetted with 4% $^{w}/_{v}$ NaCl, 0.4% $^{w}/_{v}$ Mg_2SO_4 solution so that all the space was filled but that no solution remained on the surface. Distilled water was added at a constant rate to compensate for evaporation and to maintain a constant moisture gradient in the sand bed. The chalk was initially dried for three days at 90°C. It was then immersed in distilled water and it was found that 25% of the volume of the rock could be filled with water.

Within a few days of standing the prisms in the sand a salt deposit began to form on the chalk. This developed into a ring beginning about 4 cm above the sand bed and in three weeks a coarsely crystalline salt overgrowth had developed some 4 to 5 cm above the sand with a much thinner more continuous crust appearing above this. After a month no further obvious growth of salt took place. In detail, the form of the salt ring was spherical with the centre of the sphere at the lower end of the prism.

Some of the prisms were removed and dried. Each lost close to 11% of its total moist weight. Two prisms were than analysed chemically. Firstly the crust was removed in narrow horizontal zones, weighed and examined by infrared absorption spectroscopy and chemical analyses. Then the prism itself was cut, dry, into 'horizontal' slices each about

10 mm thick. These slices were analysed for Na^+, Cl^-, Mg^{++} and SO_4^{--}. The salt crust proved to be halite and minor gypsum formed in the lower part of the ring.

The total mass of salt found within each prism exceeded 8% of the damp weight and this means that the concentration of salt throughout the pore fluid was close to saturation. The conditions were maintained in the sand bed for a further several weeks. During that time the rings moved slightly up the prisms at a rate of about 1 mm in 10 days. After several months the bed was allowed to dry out. A thin salt crust developed on the sand bed but analysis of the dried sand showed only a very low concentration of soluble ions. Calculations of the total salt content of the prisms showed that virtually all the soluble ions added to the water had been transferred into the prisms.

The prisms themselves remained mainly intact throughout the experiment but two split along joint surfaces and minor spalling occurred at the junction with the sand bed, particularly on the edges of the prisms. Chalk aggregate left on the sand bed also transmitted salt and moisture and the collected aggregate pieces behave in much the same way as the chalk prisms with salt crust developing a few centimetres above the sand bed.

Other rocks treated in the same way showed variously different results. Crystalline limestones of low porosity showed virtually no growth of salt. Sandstones varied in their behaviour and some samples with microporosity transmitted salt to form a thin ring analagous with that made on the chalk. However, porous serpentinite did not transmit salt even when left for several months on the sand bed. This presumably reflects the nature of the pores which are rather larger in the serpentinite than they are in the chalk.

The chemical profile of a salt impregnated prism is shown in Fig.1.

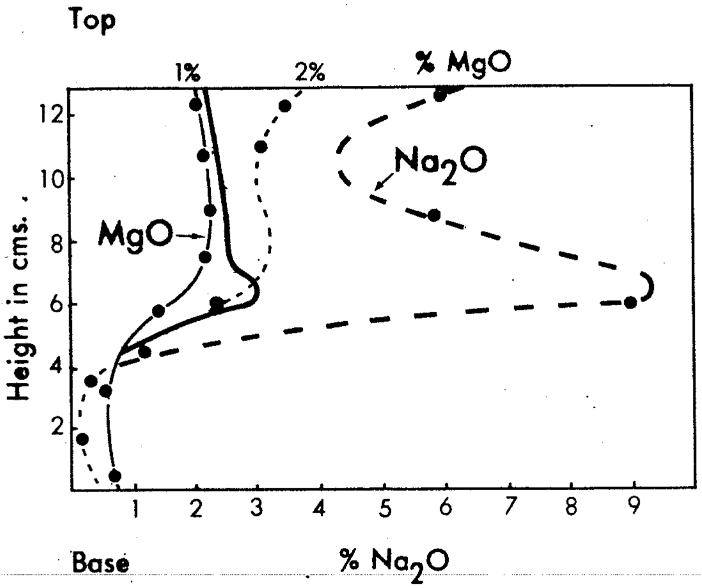

Fig. 1. Chemical variations through a typical chalk prism after 5 weeks on a moist saline sand bed. The left of each pair of lines represents the concentration inside the chalk prism, the right hand line is the total concentration including the salt crust.

From this it is apparent that a concentration band is produced within the chalk and that the crust is merely the surface expression of this zone of maximum salt precipitation. Both sodium and magnesium show the same concentration profile. Analysis of the data for several prisms shows that the ratio of the cross sectional area of the prism to the amount of salt and water transferred is effectively a constant. This is shown by the plot of the ratio of prism weight to height against weight gain (Fig.2).

Some of the chalk prisms were treated with a second pulse of salt solution and in this case further salt was added to each prism with movement of the first ring further up the column and the development of a second less well-defined ring at the site of the original crust. This, taken together with the form of the concentration bands, is typical of a chromatographic process.

6. EXPERIMENTS ON CONCRETE

The columns of concrete measured up to 12 cm in length by 5 cm diameter with the thinnest being of 2 cm diameter. On all these columns salt developed as it had on the chalk and a ring was produced from about 2 cm above the sane bed. The form of the crust was generally broader and flatter than it was on the chalk and more salt appeared higher on the columns. When treated with two pulses of salt solution again two salt rings were produced. The typical profile of the mass of salt deposited on the concrete by a single pulse of salt solution is shown in Fig.3.

It is evidently more difficult to make as complete an analysis of concretes as it is of chalk, but the concrete was broken into horizontal slices and the pieces were crushed and analysed by extracting water solubles. The results show that there is significant addition of both sodium and magnesium throughout the column and that where two pulses of salt solution were used, two concentration maxima were found within the columns.

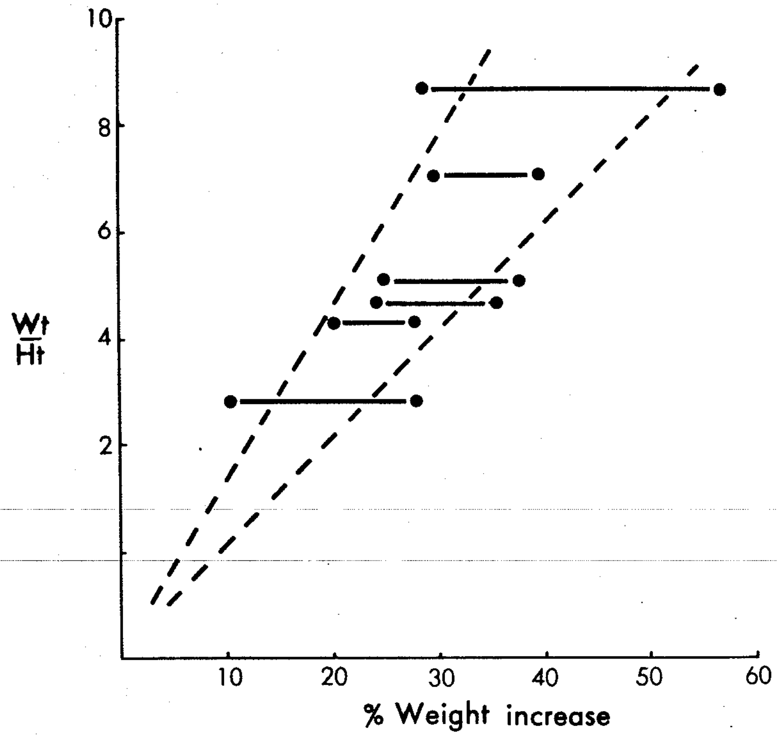

Fig. 2. The initial weight of chalk prisms divided by their height and plotted against the percentage gained. The left hand point of each pair refers to the weight of salt, the right hand point refers to the weight of water and salt.

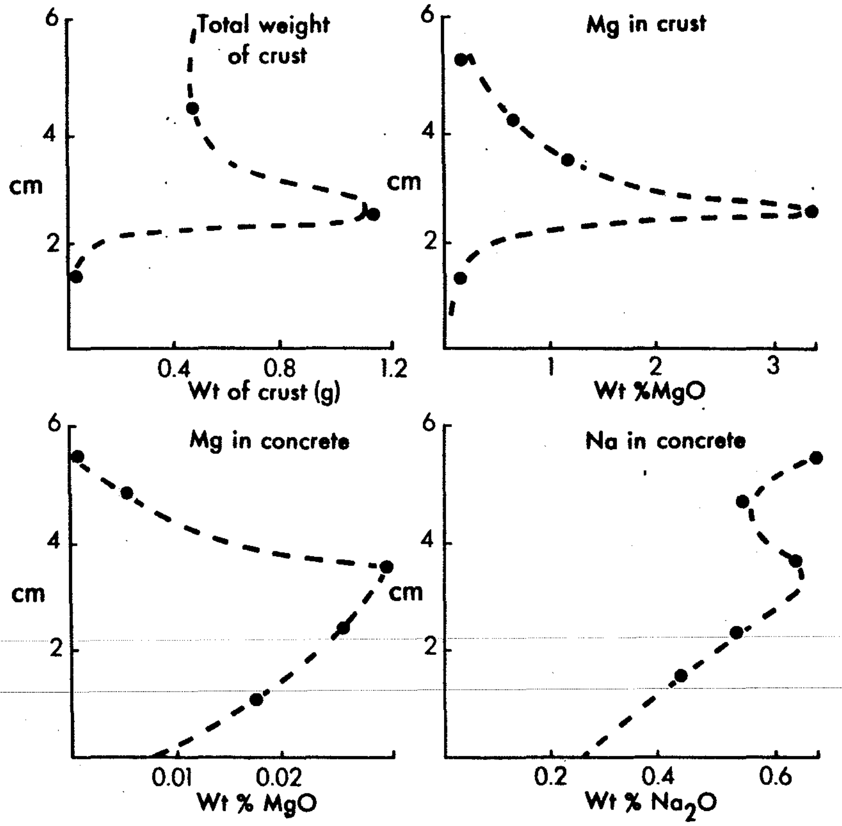

Fig. 3. Profile through a concrete cylinder of 6 centimeters in height. Analyses are of salts scraped from the surface and of the water soluble extract from crushed concrete.

Over several months there was only a little spalling or other decomposition of the concrete. Hence it seems that the direct precipitation of salts in both rock and concrete produce relatively little damage and this is so even when sufficient salt is precipitated to form a crust and to fill available cavities.

Conversely, in the experiments conducted by Goudie et.al. (1970) and by Cooke (in press) it is common for rocks to break down rapidly - principally porous friable rocks such as chalk which are destroyed in a few cycles of wetting and drying. The present work suggests that crystallization of salts alone is not likely to cause disruption, but that alternation of conditions coupled with crystallization is necessary.

7. FACTORS CONTROLLING DISRUPTION

The disruption of rocks and concretes by growing crystals can be visualized by considering the pressure exerted by the environment on the growing crystal. The free energy of the growth of the crystalline phase is then equal to the maximum mechanical energy exerted on the growing crystal. For disruption to occur, the energy available for growth, particularly the surface energy, must exceed the mechanical energy of the rock or concrete. Gibbs showed long ago (see Turner and Verhoogen, 1954) that if a_i is the area of any growing facet and s_i is the corresponding surface energy, then $\sum a_i s_i$ is a minimum at equilibrium for a given volume. If the surface energy is the same for all faces then the crystal must approach a sphere, but if particular faces have greater energy then the 'force of crystallization' will be greatest in that direction. This, however, means that the pressure of the environment on the growing crystal will also be non-hydrostatic and a proper study of the interplay of crystal growth and deformation of the environment becomes very difficult.

If hydrostatic pressure is assumed, for simplicity, then the hydrostatic pressure acting upon a growing crystal is the mean of three orthogonal pressures

$$-p = (X_1 + X_2 + X_3)/3$$

If at constant temperature the free energy of growth is set equal to the mechanical energy of deformation then

$$\Delta G = V\Delta P$$

Hence the molar free energy of formation gives an indication of the total maximum pressure which needs to be applied by the environment to prevent growth. If the growth is undirectional then the force exerted in the direction of growth is three times as great as if the growth were uniform in all directions. The growth of sodium sulphate may exert a maximum unidirectional pressure of several hundred atmospheres if grown in a confined space and the pressure generated by hydration of anhydrous sodium sulphate would be of similar magnitude. It is therefore to be expected that thermal oscillations will cause rapid pressure changes. Temperature variations, however, will invalidate the expression given above for then an expression for $S\Delta T$ must be added to the free energy and hence the effective pressure change could be enhanced.

8. CONCLUSIONS

From the field evidence it is apparent that the precipitation of salts within concrete paste and aggregate can induce the spalling and disintegration of both the paste and the aggregate. In general the smaller the cross-section of the concrete, the greater the damage that may result. Sections of only a few square centimetres cross-section may disintegrate in a year or two but larger masses may lose as little as 1 cm a year or less.

The experimental work shows that even good quality concretes may have sufficient porosity to transmit water and to build up saturated solutions within them. Rocks and concretes transmitting these solutions are effectively chromatographic materials and the transmission of the salts if effected by evaporative transference of the solvent into and through the porous medium. Taken together with previous work on the lines of the soundness test, the present work suggests that thermal effects are a prime factor in causing destructive crystallization of salts and this is especially true where acicular crystal forms result. The prevention of such mechanical damage may therefore derive from two sources:-

a) the prevention of chromatographic transfer by the impregnation of concrete or rocks with a decapillary medium, and,

b) the creation of peripheral surface concrete around pillars and piles or other structures of small cross-sectional area so that the effective cross-sectional area is increased.

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