

DURABILIDAD DE LOS AGREGADOS Y DEL CONCRETO CONTROLADOS POR ADSORCION DE AGUA Y DE CATIONES Y POR OSMOSIS

por

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Sinopsis: La superficie interna de los sólidos porosos hacen que las paredes del poro y los agregados y del concreto jueguen un importante papel en la durabilidad de estos materiales bajo condiciones cíclicas de humedecimiento-secado y congelamiento-descongelamiento. Esto es especialmente verdadero si los poros son pequeños.

Este trabajo presenta tanto los argumentos teóricos como la evidencia experimental relacionando las características de la superficie del poro y el tamaño de este con la expansión y falla de los agregados y del concreto. La magnitud de las fuerzas (cargas) que la superficie son determinadas por el tipo de mineral que integra la superficie del poro, la estabilidad cristalina de la matriz y si la superficie es una superficie de cristal, hendiduras o fracturada. La magnitud en las cargas en la superficie determinan la cantidad de agua que es adsorbida de la superficie. Los iones en solución son preferiblemente adsorbidos a la superficie y aumentan la cantidad de agua retenida en ésta. El agua adsorbida tiene niveles menores de presión de vapor y si el poro es lo suficientemente pequeño para poder llenarse completamente con el agua adsorbida, la baja presión de vapor de agua actúa como un fluido osmótico, estableciendo fuerzas osmóticas y expansión. Los iones presentes en la superficie y en el agua en los poros aceleran el proceso.

Mientras mayor sea el área total de la superficie interna para un tamaño dado de sólido, menores serán los poros y mayor será el potencial osmótico. El área de superficie interna está directamente relacionada con el daño por congelamiento-descongelamiento. Se demuestra que el contenido de agua adsorbida está relacionada con la expansión isotérmica, con los ciclos de humedad-secado y por el daño por ciclos de congelamiento y descongelamiento. Además se demuestra que existe una relación entre la expansión por la reactividad alcalina y la expansión isotérmica al humedecer el concreto que no ha reaccionado.

Palabras Claves: Superficie interna, poros, adsorción, expansión isotérmica, humedecimiento y secado, congelamiento y descongelamiento, durabilidad, reactividad alcalina.

AGGREGATE AND CONCRETE DURABILITY AS CONTROLLED BY WATER AND CATION ADSORPTION AND OSMOSIS

by

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Synopsis: The internal surfaces of porous solids that make up the pore walls in aggregate and concrete play a significant role in the durability of those materials under cyclic conditions of wetting and drying and freezing and thawing. This is especially true if the pores are small.

The paper presents both theoretical arguments and experimental evidence linking the characteristics of the pore surface and pore size to expansion and failure of aggregates and concrete. The magnitude of surface forces (charges) are determined by the type of mineral making up the pore surface, its crystal matrix stability, and whether the surface is crystal, cleavage, or fracture surface. The magnitude of the surface charge determines the amount of water that is adsorbed to the surface. Ions in solutions are preferably adsorbed to the surface, and increase the amount of surface-held water. The adsorbed water has lower vapour pressure, and if the pore is small enough so that it is completely filled with adsorbed water, the low vapour pressure water acts as an osmotic fluid, setting up osmotic forces and expansion. Ions present on the surface and in the pore water exacerbate the process.

The larger the total internal surface area for a given size solid, the smaller the pores, and the larger the osmotic potential. Internal surface area is directly related to freeze-thaw damage. Adsorbed water content is shown to be related to isothermal expansion, wet-dry cycling, and freeze-thaw cycling damage. A relationship between alkali reactivity expansion and the isothermal expansion on wetting of the un-reacted concrete is also demonstrated.

Keywords: Internal surfaces, pores, adsorption, isothermal expansion, wetting and drying, freezing and thawing, durability, alkali reactivity.

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INTRODUCTION

The durability of porous inorganic construction materials (stone, aggregate, concrete, tile, brick, etc) can be defined as their resistance to natural deterioration due to weather and induced deterioration due to impact, wear, temperature extremes, and the use of deicing salts and other chemicals.

If the material remains in a dry state, the amount of deterioration is likely to be minor (excluding dry thermal expansion or contraction, which in some environments can be severe). Likewise, if the interior of the material is kept dry because it lacks pores because the pores are not connected, very little damage is likely to occur. Interconnected porosity (effective porosity) which provides access to the material's interior and moisture are necessary for deterioration to occur.

Moisture in the form of water or ionic solution and a porous, permeable solid are required before any deterioration takes place. The total porosity, effective porosity, pore size distribution, along with the degree of saturation by moisture are among the major factors in the durability of porous solids. Pore size is especially important. For given porosity, the material with the smaller pore size is more likely to fail.

INTERNAL PORE SURFACES, ADSORPTION, AND PORE SIZE

Nature of Surfaces

Surface is a zone of discontinuity between the solid and either air or solution. A surface possesses a residual charge due to partially satisfied bonding. The magnitude and polarity of the charge is a function of the nature of the surface. Four types of internal pore surfaces can be recognized in minerals and materials of a given building material:

1. Surface on amorphous solid
2. Crystal face surface
3. Cleavage surface
4. Fracture surface

All pore walls are lined with one of the types of surfaces listed above. Diagrams illustrating the nature of the surfaces are given in Figures 1 and 2. The strength of the surface force is indicated by the thickness of the band in both figures.

Amorphous solids are minerals that have not crystallized, that is, that have no or incomplete arrangement of internal elements (atoms). Examples of these are chert, opal or flint, and quickly chilled melt, such as glass, slag, and volcanic rock. Surfaces on these solids are very active, since few of the elements (atoms or ions) in the solid are bonded to other surrounding elements, and the unsatisfied bonds are reflected in high surface charges. This is reflected in the random orientation of the elements as shown in Figure 1.

Crystal face surfaces are the least charged, since the atoms making up the solid are bound to other internal atoms, usually by ionic or covalent bonding, and occasionally by Van der Waals bonds. Because the atoms bond by sharing electrons, only residual surface charges remain at the surface of the crystal. An illustration is given in the left upper diagram of Figure 2.

Cleavage surfaces of minerals in rocks and cement paste represent a relative plane of weakness along which the mineral preferentially fails when subjected to stress. The cleavage is a plane along which the bonds are relatively weak. When cleaved, the bond that held the two sides of the cleaved plane together now becomes a surface charge. The more difficult it is to cleave the surface, the higher the surface charge. The best example of this type of surface is a clay mineral, which cleaves easily along its basal plane; pure clay with a stable lattice such as kaolinite has a relatively weak residual surface charge. Calcite and feldspar respectively have progressively higher surface charges along their cleavage planes.

Fracture surfaces have the largest surface charges, even exceeding those of an amorphous solid. The break along a fracture surface takes place in a random direction across the solid, because the solid does not have a weak bond plane or direction. An example of a fracture surface would be that of quartz or garnet.

The charge on most crystal and cleavage surfaces is negative, but the charge at fracture surfaces can be positive. The surface charge in natural and artificial (hydrated cement) minerals is affected by the lattice imperfections in the crystal due to atomic substitution by elements similar to the principal element comprising the lattice - such as the substitution of Mg for Ca in calcite. The substitution may strain the lattice and significantly increase the surface charge of crystal, cleavage, or fracture surfaces.

Leaching of the lattice due to weathering will likewise increase surface charges. Leaching partially and selectively removes certain cations without changing the crystal lattice. The lattice remains that of the original mineral until a sufficient number of cations (and anions) are removed to make it totally unstable, at which point it recrystallizes into a new form stable under the given conditions. Thus, in the first instance, fresh chert changes to its weathered equivalent which is more active, and in the second instance, the feldspar of igneous rocks recrystallizes into clay, which may be more or less surface active, depending on the degree of 'perfectness' of its lattice.

Surface Activities of Hydrated Cement Paste and Aggregate

Hydrated cement -- Hydration of cement in the presence of water is basic crystallization of di- and tri-calcium silicates, tricalcium aluminate, and tetracalcium aluminoferrite (1). The result is a micro-crystalline mass of the above 'minerals'. The porosity and permeability of the hardened paste is governed largely by the water-cement ratio, all other conditions being equal. The surface activity of a paste pore is governed by the cement composition and any additives that may have been used. It is therefore highly controllable and relatively constant. Since the paste crystallizes under ambient climate conditions, it is inherently more stable than minerals of aggregates that usually form under significantly different conditions of temperature, pressure, and moisture. The minerals of the paste are hydrates, and as such in equilibrium with the ambient moisture conditions. Adequate curing allows the minerals to develop stable lattices with relatively low surface energies.

Aggregates -- Coarse and fine aggregates together make up approximately 75% of finished concrete. Thus, the pore surface characteristics of the aggregate in so far as they affect its durability will have a major impact on the durability of concrete. The surface activity of aggregate pore walls is a function of the minerals making up the aggregate, and the nature of the porosity. In most fresh igneous rock aggregate, the pore walls consist of crystal faces (Figure 2). Pure chemical precipitates (limestone and dolostone) are commonly also crystalline and micro-crystalline in texture, and pore walls behave similarly to igneous rocks. However, limestone and dolostone are seldom pure, and may contain clay as impurities. Clay minerals, depending on type, have very active external and internal surfaces, and even in small amounts exert undue influence on the pore properties of the rock. Shale, consisting mostly of clay minerals, is of course undesirable as an aggregate. Sandstone and siltstone, depending on the grain type, size, type of impurities, and the cement type, present a variety of pore surfaces, ranging from relatively inactive to very active.

The degree of weathering of aggregate greatly affects its properties. During weathering, the minerals undergo a variety of chemical alterations. The weathering process results in a gradual change of the original minerals through lattice substitution and recrystallization into minerals most stable at the earth's surface - clay, iron hydroxide, calcite, gypsum, etc. In general, there is a decrease in density and an increase in porosity. The character of the pore walls change as the mineral composition changes. In the initial stages, leaching of and substitution of different elements in the mineral lattice strains and increases its surface energy. The end product minerals are often smaller in size than the originals, decreasing the pore size. Also, the end product minerals are often more surface active than their parents.

EFFECT OF GRAIN SIZE ON PORE SIZE AND ON THE TOTAL INTERNAL SURFACE AREA OF AGGREGATES

The chapters in most introductory texts dealing with the physical weathering of rocks give an example relating the importance of an increase in surface area to the decrease of particle size for the same weight of material. Thus, a one centimetre cube of solid has a surface area of 6 cm². If this 1 cm³ cube were divided into 1000 1 mm³ cubes, the surface area would increase to 6000 cm². The relationship of grain size to surface area is given in Table 1. A rock containing smaller particle size is likely to have a significantly larger internal surface area than an equivalent coarser grained rock, all other conditions being equal. The relationship of internal surface area to freeze-thaw durability on a variety of building materials - rock, brick, and concrete is given in Fig 3 (after Blaine et al, (2)). The internal surface area determined by the BET nitrogen method gives an excellent correlation with durability - the larger the surface area, the lower the durability, as expressed in freeze-thaw cycles to failure (cracking).

The internal surface area bears a relationship to pore size. Pore size is in turn determined by the grain size of aggregate. Consider spheres of 1 cm diameter packed into a 10 cm per side cube. Assuming cubic packing, the pore size would be:

$$\text{pore diameter} = 1 \text{ cm}^3 - (4/3 \pi 0.5^3)$$

or 0.476 cm³. For 0.01 cm³ diameter spheres, the maximum pore size would be 0.4764 cm³. The relationship is shown in Table 2. The relationship between durability of carbonate aggregates (as expressed by freezing and thawing tests) and their estimated grain size is shown in Figure 4 (3). The grain size of a variety of aggregate rock types has been estimated by assigning the small grain size a category one, intermediate category 2, and the large grain size a category 3. Although the relationship is a general one, a trend is indicated: the smaller the grain size, the lower the resistance to freezing and thawing. The wide range of freeze-thaw failure in the small grain size may be due to the fact that some larger pores may be present which are not related to grain size.

WATER AND ION ADSORPTION ON INTERNAL PORE SURFACES

Water Adsorption

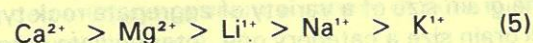
Water is a di-polar fluid, and as such is attracted to the charged internal surfaces of the paste and aggregate. The polarity of water is due to the uneven distribution of hydrogen ions in the molecule. The shape of the molecule can be thought of as a 'Mickey Mouse Head' - a round face (oxygen) with two big ears (hydrogens) - Figure 5.

Because the internal surfaces are statically charged, water dipole molecules are attracted to the surface and may cover it to a depth of several layers. These are termed 'adsorbed' water layers. The strength of the charge on the surface determines the amount of water that will be adsorbed, the thickness of the adsorbed layer, and the 'rigidity' of the adsorbed water. The latter refers to the opposition to water flow within the adsorbed layers. The thickness of the double layer at different surfaces is proportional to the mineral's surface charge - the larger the charge, the thicker the adsorbed layer. In Figure 1 and 2, the thickness of the adsorbed water layer can be substituted for the section labelled 'surface force'.

Pore sizes in rock and concrete can be classified according to the dominant water type that they contain - whether adsorbed, capillary, or normal (bulk) water. If a pore is small enough, all of it will be occupied by adsorbed water. The pore size classification is shown in a diagrammatic form in Figure 6 (4). The **critical pore** size in terms of durability can be considered that which is filled with adsorbed water at near 100% relative humidity. The pore size contains both adsorbed and capillary water, both of which have lower vapour pressure than normal water.

Ion Adsorption

Any dissolved ions in the water, especially cations, have a profound effect on the adsorbed layer water thickness. The cations, being more strongly charged than the water dipole, are preferentially adsorbed to the internal surfaces. The stronger charge of the cation attracts more water molecules, and the thickness of the layer increases. This is illustrated in Figure 7. The affinity of water for the cation is a function of its charge/size ratio, and is given in the series below, where the first mentioned ion has the greatest affinity for water than the following:



Divalent ions such as calcium have a greater hydration potential than monovalent ions. Calcium is an abundant ion in cement paste, and thus has a dominant influence on 'critical pore size'. As will be seen later, the proportion of pores in the critical pore size range determine the material's durability.

The effect of ions on the critical pore size is shown in Figure 8. Comparing Figure 8a to Figure 8b, the net effect of the presence of ions is to fill a greater proportion of pores with adsorbed water and thus to increase the critical pore size - that is, place more of the pores in the material in the critical category.

A. Vapour pressure in pores.

Vapour pressure in pores is a function of the surface tension of the solution, the temperature, and the pore radius and is expressed by Kelvin's equation:

$$\ln(p/p_0) = -2 \sigma M / \rho R T r \quad (\text{Eq 1})$$

where: p/p_0 = relative vapour pressure
 p = pressure over concave surface
 p_0 = pressure over plane surface
 σ = surface tension of solution
 M = molecular weight of the solution
 ρ = density of the solution
 R = the Gas Constant
 T = absolute temperature
 r = radius of the pore

Because large changes (in orders of magnitude) of radius are possible, the radius is the main factor in determining the relative (and absolute) vapour pressure existing over the meniscus of the fluid in the pore. As the radius of the pore decreases, the vapour pressure over its meniscus also decreases. The vapour pressure of the fluid in the small pore can be significantly lower than the vapour pressure of fluid in a larger pore, or the vapour pressure outside the porous material (ie, if the porous material finds itself in a higher humidity environment or submerged in water).

Vapour pressure is also affected by the dissolved ion content, but to a lesser degree than that due to the pore radius. It is well known that the vapour pressure of a solution is a function of its molality - that is, the number of moles of the solute dissolved in one liter of the solvent, which in this case is water. As molality increases, vapour pressure of the solution decreases. The solute in the pore solutions of concrete paste is derived from the hydration reaction, and is mostly calcium hydroxide. The pore fluid in aggregates can contain a variety of soluble ions, the most common being the alkalies Na, K, and Ca.

OSMOTIC PRESSURE AND EXPANSION

Whenever two fluids of different concentration are brought in proximity, they seek to establish equilibrium, ie, common concentration through exchange of their dissolved ions. The equilibrium can be established by transfer of water molecules through the vapour phase, through a semi-permeable membrane, or directly by diffusion. The driving force to establish equilibrium is osmosis (greek for *push*). Osmosis is defined as the spontaneous flow of solvent into a solution, or a flow from a more dilute to a more concentrated solution.

Nature of osmotic forces

In porous, permeable solids, if the pore is full of high concentration solution, the flow of the lower concentration solution from other pores is resisted. This resistance is known as osmotic pressure. The semi-permeable membrane in paste and aggregate are the small