# The Weathering of Brick: Causes, Assessment and Measurement

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# EXECUTIVE SUMMARY

This review discusses significant aspects of the problem of brick weathering.

## Review of brickmaking and masonry

The composition and processing of raw materials can effect both short- and long-term alteration. On exposure to moisture, brick raw materials rich in sodium and potassium expand more than materials rich in calcium, alumina, and magnesium. Mineral grains such as calcite, dolomite, pyrite, and siderite are associated with cracks, spalls, and pops in bricks, and some lime-rich Pleistocene materials develop complete friability unless treated with steam or water during cooling. Bricks made from illite-rich raw materials expand much more than those made from kaolinite-rich materials, but this greater expansion may be partly attributable to the fact that kaolinitic materials require greater firing temperature. Mortars can be made from several materials, but the preferred composition is Portland cement, quartz sand, and lime, in ratios depending on the strength required. If sulfate attack on the mortar is a likelihood, mortars low in sulfate and tricalcium aluminate should be used, and bricks with low sulfate content should be specified.

The firing of bricks is an essential determinant of brick durability and tendency to expand. Bricks fired at low temperatures expand much more, absorb more water, are less strong, and are more likely to deteriorate than are bricks fired at higher temperatures. Many brick materials have a relatively short vitrification range (the interval from under-fired to optimum firing and to over-fired due to bloating and/or melting). This short firing range, plus the high cost of fuel, makes temperature control a top priority in the production of brick. Firing to optimum levels seems to cause the crystallization of a series of high temperature phases, with corresponding increased strength and decreased water absorption and moisture expansion. Moisture expansion is thought to result from rehydroxylation of illite and other clay mineral anhydrides.

## Acid rain

Although the literature suggests that acid rain has not worsened dramatically in the past 25 years, several studies show that this problem is a very serious one that could increase in intensity in the future. The problem of sulfate and nitrate pollution is complicated by the fact that there are many forms in which the $SO_x$ and $NO_x$ can be transported and deposited, and by the fact that acid precipitation often results from the combined effects of several sources of pollution. These widespread phenomena essentially are outside current point source laws, and are not dealt with adequately in national or international law; however, almost everyone agrees that the effects of acid rain ought to be more extensively studied. Such research must deal with very complex phenomena and often the results show only subtle differences. In many cases the complexity of the natural setting can only be simulated by using outdoor situations and attempting to control as many variables as possible. The acid rain problem involves the effects of $SO_x$ and $NO_x$ deposition or absorption from rain, sleet, snow, fog, dust, and gaseous diffusion. It is clear that the amount of dry deposition cannot be reliably measured by current methods, and the full magnitude of the problem can only be estimated. The existence of crumbling monuments and acidified lakes does at least testify to the potential for great damage from atmospheric pollution.

## Weathering of building stones

Limestones, dolomites, and calcareous sandstones, which are often used for building stones, show the effects of sulfate attack very rapidly. In some cases of stone decay, the rate of deterioration has increased 40 times over normal rates during the last few years. Although erosion of rain-washed stone results in significant rates of loss, destruction of stone protected from direct precipitation is a much greater problem. Protected areas weather by the development of gypsum crusts (in some rare cases by recrystallization of calcite) and subsequent spalling and cracking of the stone. The crusts tend to hold moisture and promote deterioration by natural agents such as wet-dry and freeze-thaw phenomena. Studies of sulfate attack on a few other stones have shown essentially the same results, but no studies of the effects of $SO_x$ and $NO_x$ on brick masonry are known.

## Brick weathering

Bricks weather by spalling, cracking, and dusting. Moisture penetration along cracks or pore passageways often causes the damage, but mortar expansion due to sulfate attack causes failure of the bricks and mortar in some cases. It is difficult even with current test methods to predict the 5-year durability of a particular group of bricks. Failure of bricks and mortar is often associated with particular locations on a structure (such as at ground level or under sills). Some brick walls have fine cracks between brick and mortar that cause high permeability of the wall to water and air. Mortar often seems to decay faster than brick; in several cases the original brick has outlasted three generations of mortar.

## Methods of assessing weathering

Several approaches have been used in assessing masonry weathering. The most useful scheme includes a complete physical description, pH determinations, water absorption or permeability determination, hardness tests, measurement of sulfate and nitrate content, measurement of air and water penetration, and determination of weathering by indirect detection of hydroxyl or hydration water with infrared, visible, or microwave techniques. Sonic methods can be used to detect flaws and to estimate hardness. In order to detect surface zones of decay, it may be desirable to make several of the measurements on the surface and others at various depths within the wall.

## Restoration and preservation of brick

Restoration and preservation can be done by cleaning and coating the walls to increase their resistance to solution or penetration by atmospheric deposition. In future construction, optimum design, high-quality brick and mortar, and good workmanship should alleviate many problems. If sulfate attack is likely, the use of special materials may be justified, and coating of the structure may be warranted.

## Recommendations

It is suggested that future work on this problem focus on the study of several existing structures of known age in areas where probable pollution levels can be established. Laboratory testing should concentrate on measuring the interaction of freeze-thaw, wet-dry, hot-cold, pH, and biological factors on the deterioration of bricks and/or mortar, and on using multiple regression analysis. Further study of methods of restoration and preservation of existing buildings would also seem warranted. A study of existing buildings and a laboratory simulation should yield a determination of the extent of the acid rain problem on brick masonry structures.

# THE WEATHERING OF BRICK: CAUSES, ASSESSMENT, AND MEASUREMENT

by

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## Introduction

This report presents the results of a study of various factors related to weathering of bricks. A primary goal of the study was to compile an annotated bibliography on weathering (see appendix 1). Other goals included:

- assessment of the importance of human-induced pollutants--especially acid precipitation--in the weathering of bricks and similar materials.
- computerization of an existing file on research results dealing with moisture expansion in bricks differing widely in composition.
- investigation of regional brick weathering patterns and associations between brick type and degree of weathering (in order to compare our results with data from the literature).
- evaluation of several methods of studying the physical and chemical results of weathering.

The short- and long-term deterioration of brick and associated mortars is poorly understood and virtually unstudied. Concern for the long-term effects of acid rain on historic, modern, and future buildings prompted a study to evaluate the magnitude of the acid rain problem and to isolate the degree of brick deterioration due to anthropogenic versus "natural" weathering. A logical extension of the results of our study on the current state of deterioration was to evaluate the permanence of masonry structures under continued attack and to suggest methods of restoration and preservation of these materials and/or prevention of their deterioration.

Short-term reactions are examined first, because these phenomena are better understood than long-term reactions and provide an excellent model for longer-term reactions. Rehydration, recarbonation, and sulfate absorption are among the reactions that cause moisture expansion and various kinds of pops, cracks, and exfoliation in bricks. Mortar can also react with sulfate and possibly with other ions, resulting in expansion, erosion, and deterioration of structures. Many of these reactions are essentially complete within a few months to a few years. Since masonry structures have very long life expectancies, reactions associated with longer-term weathering can be expected. Limestone or marble often shows major deterioration from sulfate pollution within a few decades; the Athenian Acropolis has weathered more during the last fifty years of polluted rain than during the previous 2000 years of its existence (Gauri, 1982).

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The study of brick weathering is much more complicated than the study of limestone weathering. The composition and firing history of the bricks, the composition and production history of the mortar, the quality of construction, the location of the structure geographically, the details of design of the particular structure, and the various alterations during the life of a structure all lead to a multitude of variables to be isolated and examined in the study of masonry weathering. In our investigation we have (1) examined existing buildings to evaluate the range and total magnitude of brick deterioration, and (2) examined the effects of pollutants under controlled, laboratory conditions. Various methods of testing the physical and chemical effects of deterioration in the field and in the laboratory were evaluated.

## Review of Brick Making and Masonry

Detailed information on the raw materials used and the manufacturing techniques employed has been essential to these investigations, because during each step in the production and use of bricks a significant potential exists for enhanced deterioration. Only fired-clay bricks are considered in this study.

Although bricks are generally made from claystones, shales, or siltstones, wide variation in the composition of raw materials is common. In Illinois alone, bricks are produced from Pleistocene (ice age) materials rich in calcite and dolomite, from shales and siltstones of Pennsylvanian (coal-bearing age), and from mixtures of the two. Nearly every mineral present in a raw material affects the bricks produced from those materials. For instance, calcite, dolomite, siderite and pyrite often produce "pops" or disintegration after firing. An ideal raw material will contain enough clay for plasticity, just enough fluxes to produce sufficient glasses from some constituent minerals so that the bricks become steel-hard and impervious (without completely melting), and enough variation in refractoriness of the minerals to produce a wide temperature range over which fusion can take place. Various chemical and mineralogical methods can be used to evaluate and characterize different raw materials, and some comparisons between compositions of different materials can usually be made and used as a basis for predicting changes in properties. Yet one of the most difficult variables to test is the possible influence of raw material composition. The wide range of available raw materials in terms of composition allows an excellent discrimination of durability based on the different types of bricks.

After a raw material is chosen, bricks are commonly formed by three distinct methods. In a procedure not used extensively today, bricks were made as soft muds poured into molds and dried before firing (the soft mud method). A practice now commonly used today is the extrusion of plastic clay through a die, after which bricks are cut to size (the stiff mud method). Extrusion often causes planes of weakness within the brick called laminations. Several methods are used to retard or reduce lamination. Bricks are also formed by dry pressing (semi-dry or dry press method) into a mold. After the bricks are formed they must be thoroughly dried prior to firing, and should show no cracking or bending during drying. Several agents are added during forming to color the brick or inhibit efflorescences, and sometimes a surface coating and/or texture is added. Some raw materials are better suited to certain methods of forming and drying. Bricks are sometimes cored during forming to reduce their weight, aid in firing, improve oxidation, add insulation value, and increase mortar bonding.

The firing process is probably the most important step in determining the eventual strength, durability, permeability, color, and texture of a brick. The type of kiln is of primary importance. Three principal types of kilns have been used Illinois: scove, periodic, and tunnel. Scove kilns are made of stacks of unfired bricks that are then plastered on the exterior. Bricks in a scove kiln are stacked so that heat conduits are built into the base of the stacks and firing is by convection. Scove kilns were very commmon in earlier times and were often constructed and fired on the job site. Periodic kilns are dome-roofed kilns with fire boxes arranged around the exterior of the base of the wall. This type of kiln may be beehive, rectangular, or square in shape. Tunnel kilns are used in much of the fired-clay-products industry today, because they are labor and fuel efficient and because they give much more uniform heat distribution and thus produce a more uniform product. For all types of kilns the sequence, time, uniformity of temperature, and absolute temperature of firing are of great importance.

Bricks obtain their desirable physical properties as a result of firing in a relatively narrow temperature range. Differences of 50-100 degrees Celcius can often produce major differences in brick properties. Firing is accomplished by slowly raising the temperature and allowing various volatile products to completely escape and oxidation to take place before raising the temperature further. Generally, slow heating from 100° to 400°C removes any remaining water; heating from 400° to 800°C drives off the hydroxyl water from clays and causes oxidation; and heating from 800°C upward produces various high temperature phases and/or fusion products. Raw materials containing pyrite, sulfates, and/or organic constituents often must be fired for longer times to oxidize them to eliminate "black cores" and produce uniform, oxidized colors before vitrification begins. Firing usually results in some shrinkage. Excessive or erratic shrinkage can be a serious problem. The ideal level of firing is usually the point at which the brick is steel-hard and has very low water absorption. Firing beyond the ideal point will often cause bloating and/or melting (as well as wasting energy), and firing below the ideal point usually results in a product of low durability (as measured by sulfate intrusion or freeze-thaw tests, high water absorption, and high moisture expansion).

Although well-fired bricks have great strength, mortar is the key ingredient in holding a structure together. Masonry mortar is usually a mixture of Portland cement, sand (or other grit), and lime. Contrary to what might be assumed, mortar should be only as strong as required by the specific structure. Strength is primarily determined by the cement content. Aggregate is mostly present as an inert, nonshrinking filler, and lime gives mortar plasticity and acts in synergism with cement. Mortar plasticity can often accommodate some expansion by brick (Hughes, Bargh, and White, Appendix II) and is therefore desirable. Mortars also have different levels of tolerance to deleterious ions such as $SO_4^=$, $CO_3^=$, and $NO_3^-$--all important factors in atmospheric pollution. The other critical property of mortar is the degree to which it adheres to the brick and seals the wall. An impervious wall greatly reduces deterioration from external causes.

Permanence of masonry construction depends not only on the use of optimum brick and mortar, but also on proper design and workmanship. If there is potential for expansion, provision should be made to absorb this expansion. Interaction of other construction elements with the masonry must also be considered.

## Short-Term Deterioration

Although the distinction between short- and long-term alteration is somewhat arbitrary, short-term reactions in this report are viewed as being readjustments to low-temperature conditions and failure due to production flaws in the brick. After firing, bricks are completely out of equilibrium with standard conditions, and some readjustment can be expected. If the bricks are not impervious, they will often absorb water as both $H_2O$ and $OH^-$ (by breakdown of water). The latter ion is associated with moisture expansion in bricks. Moisture expansion often causes great damage because of the relatively rapid change in dimension. This expansion varies as the logarithm of time and can be partly compensated for by storing bricks for a few months before construction. If laminations and/or cracks are present, they will lead to failure by spalling, and further cracking. "Pops" are also associated with the expansive reabsorption of $OH^-$, $CO_3^=$, $SO_4^=$, and possibly $NO_3^-$ with oxides of mineral grains that were present before firing, such as calcite, pyrite, siderite, and dolomite. Such short-term changes in bricks are of major importance within the first few years after firing and are not produced by weathering in the fullest sense. This report summarizes the important factors in short-term reactions in brick; a thorough review can be found in Hughes, Bargh, and White (appendix II).

Several factors related to the composition of raw materials seem to have a significant effect on the degree of moisture expansion of a particular brick. Freeman (1966) observed that crystallization of calcium and magnesium-rich phases was associated with low levels of moisture expansion. He found that high $Al_2O_3:CaO + MgO$ ratios were correlated with high expansion. Cole (1975) showed the reduction of expansion of bricks with higher $CaO + MgO:Na_2O + K_2O$ ratios. Actually, his graph shows a boundary area where values below a certain ratio show very large expansion, and values above a critical ratio (higher $CaO + MgO:Na_2O + K_2O$ ratios) show equal amounts of expansion. Although Schurecht and Pole (1929) found that magnesite inhibited expansion, Cole's work seems to explain the lack of reduced expansion after MgO additions to certain bricks (including some of our experimental bricks); this lack of response to higher ratios clearly occurs in cases where the ratio is above the critical range. Goldfinch (1980) suggested that additions of MnO, ground basalt, and brown coal inhibit expansion. These inorganic additives have a similar divalent state and promote the formation of specific high-temperature phases--probably spinel, in this case. The beneficial effects of brown coal may be due to either the formation of $Fe^{+2}$ and $Fe^{+3}$ as magnetite, or to a change in texture of the fired product. The best model of the effects of divalent cations seems to be the reduction of nucleation temperature for spinel-type minerals and the promotion of the formation of those minerals.

Increases in the denominator of the $CaO + MgO:Na_2O + K_2O$ ratio are associated with high levels of moisture expansion, and higher alkali contents are associated with mica-type clay minerals. Hosking, White, and Parham (1966) described in detail the increase in moisture expansion associated with illite (see also Hughes, Bargh, and White, Appendix II).

Although the exact mechanism of moisture expansion is poorly understood, Holland and Stevens (1968) proved that bricks cooled in a vacuum did not expand until they were exposed to air. In further work Stevens and Holland (1972) found that bricks exposed only to methanol expanded similarly to those exposed to air, and they concluded that availability of the $OH^-$ ion was the most important factor in moisture expansion.

Grim and Bradley (1948) examined the resorption of $OH^-$ by illite fired at 600° and 800°C, and found that about a third of the hydroxyls had been resorbed after nine months. They also found that the amount of uptake of hydroxyl at 600° and 800°C was essentially equal, and that illite was especially prone to this resorption. Although maximum expansion of bricks usually occurs in the 850° to 1000°C temperature range, it seems quite likely that rehydroxylation of remnant-dehydrated illite may be the principal cause of moisture expansion of bricks. An experiment to test this hypothesis has been designed and will be pursued.

Morgan (1941) discovered both permanent expansion and a significant weight gain in bricks subjected to up to 200 wet-dry cycles. The percent weight gain and degree of expansion are strongly correlated, and loss of material from bricks fired at lower than optimum temperatures often results in large errors in measurements. In fact, wear from handling and repeated measurements of test bricks often causes apparent shrinkage or weight loss. The low levels of moisture expansion observed for bricks fired at 800 and 850°C usually result from wear, because the bricks are relatively soft at those temperatures.

At higher firing temperatures (1000°C and up) bricks show little moisture expansion because (1) this temperature range corresponds to the development of spinel and other high temperature phases at the expense of dehydrated clay minerals, and (2) increasing temperatures lead to a rapid decline in porosity and permeability. The more important factor of the two is probably the formation of high-temperature phases that do not take up hydroxyls. It would seem that even low permeability would lead to expansion after enough time in most environments where bricks are used.

"Pops" and spalling of brick commonly result from two causes. Bricks that have zones of high porosity or cracks due to lamination and similar flaws from forming, drying, and firing are quite susceptible to freeze-thaw or wet-dry failure. The water absorption test measures the uptake of cool water by a brick after soaking 24 hours. High water absorption values are usually associated with high rates of failure. Robinson, Holman, and Edwards (1977) investigated various specified properties of brick and the tendency of those bricks to fail in a freeze-thaw test. Their results show a clear association between low water penetration into the brick and low failure rates, but the correlation is imperfect and no reliable test methods were found to separate durable and nondurable brick. For instance, when using water absorption or strength tests as a control method, many bricks that were rejected as nondurable would have passed the freeze-thaw test. Some nonhomogeneity would seem to cause these inconsistencies. Isolated cracks or voids from burned out volatile materials will act as local sites of increased water absorption, but these isolated areas only add a small amount to the overall permeability of the brick. Therefore, bricks with homogeneous water penetration at a relatively low level (%) will resist failure under freeze-thaw tests or actual conditions, while bricks with isolated, high permeability zones and an overall water absorption at the same relatively low level will tend to fail.

Remnant oxides from mineral grains with volatile components also cause pops and spalls. Firing drives off $CO_2$ or $SO_2$ from mineral grains and these (or similar) ions are reabsorbed by the grains on contact with the atmosphere. In some raw materials, this phenomena can cause complete crumbling of bricks within a few days of firing. Apparently, several anions can substitute for the volatile anion, because steam treatment during cooling usually anneals bricks that would normally crumble. The smaller $OH^-$ ion may cause less expansion than the larger $CO_3^=$ or $SO_4^=$ ions do. Oxides from carbonates produced by firing this type of brick apparently inherit a preference for the larger ions from the original mineral. Unless saturated with $OH^-$ by steam treatment, these oxides will resorb $CO_3^=$ and/or $SO_4^=$ and cause failure.

Much of the tendency of a particular raw material to cause moisture expansion can be compensated for by the firing step: optimum firing can overcome all sorts of raw material problems. Most common and face bricks show a progressive increase in hardness and decrease in permeability as the level of firing temperature increases from 850° to 1100°C or higher temperatures. As previously mentioned, maximum expansion is observed at temperatures where the bricks first become steel-hard, yet are still relatively permeable. Usually, if the maximum temperature is raised 50° to 100°C, the hardness is increased, permeability is reduced, and moisture expansion will be reduced to insignificant levels. However optimum firing conditions are hard to maintain, because of temperature control difficulties in the kiln; changes in ideal temperature due to fluctuations in the composition of raw materials and forming techniques; the desirability of keeping fuel use at an adequate but minimum level; incomplete oxidation or a reducing atmosphere causing melting and bloating conditions; and inadequate monitoring or control tests.

Scove and beehive kilns can also cause firing problems. Even when the average or overall temperature of the kiln is at the correct level, these kilns have inherent zones of cooler- (and hotter-) than-average temperatures. Regions of the world where these kilns predominate will usually have a built-in moisture expansion problem, because each batch of brick contains some underfired bricks. Underfired bricks from the lower parts of the kiln are often kept in a group when the kiln is unloaded, and the problem is aggravated by this segregation.

Moisture expansion can be reduced by steaming bricks during their cooling cycle. Similar to the annealing action observed in the firing of carbonate-rich bricks, steam treatment seems to pre-expand and anneal the brick. However, the brick only partly expands with this treatment, and after a small lag time these bricks continue to expand to the same degree as untreated bricks of the same batch (McDowall and Birtwistle, 1971).

White (1964) further shows that brick stored outdoors expand at a faster rate than those stored in the laboratory. Davison and Sereda (1978) observed an irreversible expansion of bricks during freeze-thaw cycles. The first cycle usually accounted for most of the permanent expansion, while later cycles tended to maintain a fixed length. In their view, bricks with relatively large expansion values measured by freeze-thaw testing are not likely to be very durable.

To summarize, a number of preventative measures can be taken to prevent moisture expansion and short-term failures of brick:

- Select and/or process raw materials to avoid or remove deleterious components.
- Fire bricks to the optimum level, and control the optimum temperature level as carefully as possible.
- Use additives to reduce the optimum firing temperature and reduce moisture expansion if divalent cations are at a low level.
- Treat bricks with steam during cooling and age them in storage before construction.
- Seal the brick to provide protection, if a sealer is available with a life expectancy comparable to the masonry construction. (If not, expansion after sealer breakdown will probably lead to greater damage, because the mortar will have hardened to a greater extent.)
- Design the structure to allow for possible movement: this is often the most important means of insuring against failure of bricks.

## Acid Rain

In our assessment of the effects of natural and human-induced agents of alteration on bricks, only atmospheric pollution is considered, and this category includes deposition of pollutants as particulates, rain, sleet, snow, gaseous diffusion, and fogs (aerosol). Natural sources of atmospheric deposition include sea spray, plant and animal emanations, volcanic eruptions, and fumaroles or hot springs. Man-made pollutants that cause acid rain are produced by burning fossil fuels and smelting various sulfide ores. Nitrogen-based pollutants are generated from all combustion, while $SO_x$ is produced mainly from utilities and heavy industry in which coal, oil, and gas with significant sulfur contents are used. A full review of the literature suggests that the characterization of "acid rain" and related phenomena is one of the most complex problems facing science.

A recent news report quotes EPA Director Ann Gorsuch as saying that the evidence of the seriousness of acid rain is far from convincing, and that more research is required before stringent controls can be justified (The News Gazette, Oct. 7, 1982). In another recent news report, a large group of independent experts find that coal burning utilities and industries are the source of continuing and worsening acid precipitation in eastern Canada and eastern United States (The Chicago Tribune, Nov. 1, 1982). Carter (1979) has suggested several means of reducing $SO_x$ emissions without imposing new controls. The main problem in controlling acid rain is the wide regional extent of the phenomena. Current laws define and set standards on point-source pollution that has an easily definable, local environmental impact; however, the deposition of acid rain often takes place at a great distance from the original source of pollution. Taller smoke stacks exacerbate the problem by shifting local phenomena to regional problems. Budiansky (1980) suggested that acid rain may require a catalyst and will vary according to several complexities of cloud physics and chemistry; therefore, the greatest difficulty in controlling emissions may be in coming up with a precise legal definition of acid, atmospheric deposition. Legal difficulties of this sort make it even more important to expand our understanding of the causes and effects of acid deposition.

At least one report attributed most or all of the acid rain phenomena to either natural sources of the materials, or to natural variations in precipitation (Poundstone, 1980). This point-of-view holds that atmospheric concentrations of $SO_x$, and $NO_x$ (and perhaps $CO_2$) result mainly from volcanic activity and related, natural phenomena; that these ions show long-term variation; and that the present problem with acid rain is associated with a cycle of relatively low pH. An extension of the argument says that no harm has ever been reliably associated with acid rain, and that all point sources of pollution are within justifiable standards. Semonin (1981) recently pointed out some of the possible errors that have often led to dramatic indications of the magnitude of the acid rain problem. Semonin shows that comparison of recent rain chemistry with the results of earlier studies by Junge and Werby (1958) leads to several erroneous conclusions. As Junge and Werby were aware, the atmospheric chemistries that they measured across the continent during 1956-1957 included particulates from several dust storms in the southwest that were common in that period. Likens et al (1979) calculated 1956-1957 pH levels, based on the earlier study, and found dramatic indications of a major drop in pH in 20 years. Semonin (1981) shows that dust particles rich in calcium and magnesium effectively raised the pH above expected values. When he corrected for the anomolous dust particles, the contour maps of recent rain pH and of 1956-1957 were essentially alike. His conclusions are that the problem has not become much worse in the last 25 years, and that the acidity has been essentially uniform over that period.

Studies by Glass et al. (1982) and Glass, Glass, and Rennie (1980) have surveyed the extent of possible damage associated with acid deposition. They also point out several factors that lead to complexities in the study of the effects of acid rain. The evidence seems to suggest that most systems (lakes, soils, etc.) have a reserve of alkalinity which allows neutralization of a certain level of acidity from atmospheric deposition, but beyond some critical point, small additional imputs of acidity cause severe damage. Hileman (1981) estimates that rain in the eastern United States is 40 times as acid as unpolluted rain, and that deposition by rain may represent only 50 percent of the $SO_x$ loading on the earth's surface, with dry deposition of several types making up the other half. She estimates human $SO_x$ production at 100 times the natural level, and $NO_x$ production about equal from human and natural sources. She further points out that the earliest snow melting has the greatest toxicity and acidity caused by the depressed freezing point of polluted snow. Early meltwater contains high aluminum contents, and often includes much of the winter's dry deposition of $SO_x$ and $NO_x$. Indeed, aluminum and other ions solubilized by acidity often cause greater toxicity than the acidity level itself (Johnson, 1979; Hileman, 1981; and Glass et. al, 1982).

Soils are especially complex with respect to atmospheric deposition of sulfates and nitrates. If present at moderate levels, these ions are usually beneficial to plant growth, but higher levels cause various types of plant damage. The vegetation canopy, surface litter, and various soil zones all modify incoming wet and dry acid deposition in very complicated reaction series. Budiansky (1980) points out that it is of little importance whether atmospheric ammonia neutralizes $SO_4^=$, because the ammonia will be immediately taken up by plants in the soil, and it will have the same result as acid deposition. A recent note in Chemical and Engineering News (1982) suggests complete neutralization of nitric acid deposition by biologic mechanisms.

The complexity of these systems requires controlled experiments in natural settings, especially in the study of plant growth. Most of the literature relating acid rain to plant growth mentions the lack of transference of laboratory results to natural systems, primarily because it is impossible in laboratory experiments to include all the interactions and complexities of the natural setting. Successful experiments usually are designed so that only rain and/or atmospheric deposition are varied, while all other factors are held equal. Precipitation shows wide variability in pH. Budiansky (1981) suggests that rains associated with cold fronts, summer, and thunderstorms are more acid than average. A note in Science 82 announces the discovery of fog in Los Angeles as acid as lemon juice. The note suggests greater danger from fog than from the well-known smog. The consensus of the scientific literature is that acid precipitation is a serious environmental hazard and the problem is of at least regional scale.

Two recent articles review the complex chemistry of the earth's atmosphere. Chameides and Davies (1982) discuss the progress that has been made in understanding the troposphere and point out the areas of confusion or disagreement about particular effects. Their general model involves production of reduced materials from terrestrial sources such as methane, carbon monoxide, and sulfur dioxide. Photochemical oxidation of these reduced species, by very complicated reactions, generates several oxidized species--some of which are stable enough to be mixed throughout one or both hemispheres or to be "washed out" as rain or dry deposition. The lifetime of various species controls their distribution: methane, which has a long residence life in the atmosphere, has a uniform global distribution, and carbon monoxide (CO) lasts only long enough to be mixed throughout the northern hemisphere, where it is produced in great quantities. The lifetime of sulfur dioxide is less than that of CO, and the effects of $SO_2$ are therefore regional rather than hemispheric. The human production of $SO_2$ rivals or exceeds production by natural sources in many areas. Tropospheric reactions also influence the relative production of species that cause the greenhouse effect. Baum (1982) reviewed the state of knowledge of the stratosphere and the estimates of human-induced alterations. Both studies emphasize the critical importance of understanding the interactions of the atmosphere. When measured levels of some species vary by orders of magnitude from levels predicted by current models, significant differences must exist between the model and nature. As Chameides and Davies (1982) point out, the atmosphere must have great stability to have sustained life throughout geologic time. The limits on atmospheric resiliency are among the most important questions of the present time.

## Weathering of Building Stones

A fairly extensive literature exists on the weathering of building stones, and since the reactions that cause weathering of stones by man-made agents are often similar to those associated with brick masonry, as Gauri (1980) points out, these studies are pertinent to our background investigation. Hydration, carbonation, and sulfation are very common reactions. The formation of oxides, hydroxides, hydrates, carbonates, and sulfates often causes a volumetric expansion, and expansion from salt or ice crystallization can lead to further mechanical breakdown. It is well known that the first minerals to crystallize from a magma, according to Bowen's reaction series, are more susceptible to weathering. Abrasion pH can also be used as an index of tendency to weather and of degree of alteration (Grant, 1969; Stevens and Carron, 1948). The effects of acids on calcareous rocks are of special importance in the weathering of building stones. Essentially weathering is an adjustment of a rock (or other material) to the conditions at or near the surface of the earth and in a particular environment. Often a rock will have been formed under much different chemical and temperature conditions from those common at the earth's surface or at its current location. Even distilled water is a corrosive weathering agent to most rocks, because the rock will tend to lose ions to the water until the water and solid are in equilibrium. Large differences in equilibrium pH provide increased driving force for weathering reactions.

When exposed to acid precipitation, limestone, dolomite, and marble can react in two ways: (1) the carbonate may dissolve directly, or (2) the anion in the rain ($SO_4^=$, $Cl^-$, $NO_3^-$) may react with calcium and/or magnesium to form a new mineral. If gypsum ($CaSO_4.2H_2O$) or epsomite ($MgSO_4.6H_2O$) form, the new mineral can cause severe mechanical damage by expansion, which furthers weathering of stone. Winkler (1966); Winkler (1973); Fassini, Lazzarini, and Biscontin (1976); Frediani, Malesani, and Vanucci (1976); Hoke (1976); Hoffman, Schimmelwitz, and Rooss (1976); Efes and Luckat (1976); Longinelli and Bartelloni (1978); and Gauri (1980) examined many examples of gypsum formation as crusts on calcareous building stones. Winkler (1966) was chiefly concerned with the effects of $SO_x$ dissolved in water, while Fassina, Lazzarini, and Biscontin (1976) observed that particulates were higher than rain in $SO_4^=$ and that most crusts on Venetian marble were gypsum. Winkler (1973) illustrated several examples of accelerated weathering due to atmospheric $SO_x$ and the increased solubility of the sulfates as compared to the calcareous materials from which they formed. A study of Florentine stone by Frediani, Malesani, and Vannucci (1976) compared chemical, gravimetric, and x-ray diffraction techniques as a means of quantifying gypsum in crusts, and a transcript of a discussion after their talk suggests that barium chloranilate is an excellent colorimetric means of evaluating low levels of sulfate contamination. Hoke (1976) mapped the ionic concentrations of encrusted and cleaned marbles and found sulfur clearly associated with crusts. Hoffmann, Schimmelwitz, and Rooss (1976) found gypsum, $CaSO_3.\frac{1}{2}H_2O$, and $MgSO_4.6H_2O$ as reaction products of lime plaster exposed to $SO_2$. They also showed that when oxides and hydroxides in plaster were converted to carbonates, the plaster had more resistance to sulfate attack.

Efes and Luckat (1976) studied corrosion of a sandstone, and they found the corrosion mostly due to $SO_x$ attack on the calcite cement of the stone and the subsequent gypsum deposition. Using isotopic methods to discriminate source ions causing stone corrosion in Venice, Longinelli and Battelloni (1978) were able to trace the sulfate in stone crusts to man-made $SO_x$ rather than to local sea spray. In an extensive review article, Gauri (1980) illustrated the complex factors that cause decay of limestone and marble and the unexpected result that stone protected from rain is usually weathered more severely than rain-washed areas of a structure. Although he and Winkler (1966) found solution weathering of exposed stone in the Midwest to amount to a millimeter or two in 50 to 70 years, exfoliation of gypsum crusts in protected environments is shown to result in much faster weathering. Gauri (1980) illustrates the synergism between the opening of pores and entrapment of water by crystallization of gypsum crusts and greater freeze-thaw effects. He also suggests that continuous aerosol and gaseous deposition partly account for the greater damage in locations protected from rain. An analysis of crusts from statuary at the Field Museum in Chicago shows calcium enriched 50 times, sulfate enriched 200 times and several associated cations enriched when compared with the unaltered stone (Gauri, 1980).

Gauri's (1980) study of the Athenian Acropolis revealed the potential for damage due to corrosion of iron anchors holding stone, and the fact that restoration in this case led to increased weathering because lead coated iron bars in the original structure were replaced with uncoated iron. The new iron rusted rapidly and caused severe pops and cracks due to expansion pressure from the rust. Straps and anchors used in masonry and terra cotta may show the same deterioriation.

Arnold (1976) and Rossi-Manaresi (1976) describe the effects of the attack of stone by soluble salts such as NaCl and $Na_2SO_4.xH_2O$. In some cases the hydration of salts will change in response to humidity and temperature, adding to the forces driving the decay. In a discussion included with Arnold's (1976) paper, the question was raised whether hydration caused more damage than the original salt crystallization; it was concluded that both mechanisms cause great damage. Gauri (1980) described a case of extensive damage to street-level granite due to the penetration and crystallization of salt used for de-icing streets.

Rodrigues (1976) drew a correlation between clay content of stone and a tendency for that stone to deteriorate. He used moisture determination to measure clay content, and found that other factors were also involved in stone decay. Gauri (1980) associated clay with sites of gypsum formation and with hydration. Winkler (1973) also found several examples of stone failure that could be traced to clay zones.

The effects of bacteria and algae in Etruscan tombs were shown by Vero, Bettini, and Sila (1976) to be quite severe. Damage was greater when light penetration promoted the growth of algae. Winkler (1966) noted the acid character of many organisms that extract nutrients from surrounding rocks. The reactions he discusses are essentially acid exchange reactions, although oxidation-reduction reactions are also promoted by some microorganisms.

Two studies (Winkler, 1973; and Gauri, 1980) mention the use of Shore hardness measurements to study weathering rinds that are often only a few millimeters thick. The test measures the rebound of a small hammer after impact with the test surface. Sleater (1977) used abrasion-induced weight loss to measure the strength of surface material before and after treatment with various types of preservatives.

Stone Preservation. Several studies have been made of the efficacy of cleaning and preserving stone. Gauri and colleagues in a series of articles attempt to evaluate various treatments for preservation and to set standards on performance of treatments (Gauri, Hagerty, and Ullrich, 1972; Gauri, Gwinn, and Popli, 1976; and Gauri, 1978). Treatments are shown to be of three basic types: (1) a soluble barium salt is added to precipitate ions such as sulfates and to coat pore surfaces with less reactive $BaCO_3$ or $BaCa(CO_3)_2$; (2) various silicone agents are used to seal the stone; and (3) several organic polymers are used as coatings (Gauri, Gwinn, and Popli, 1976). Some polymers are discolored and destroyed by ultraviolet light and each coating imparts different degrees of improvement. Sleater (1977) evaluated about 50 preservatives and found none that filled all the requirements of stone preservation. He tested strength, water and water vapor movement, abrasion resistance, UV resistance, wet-dry cycles, acid attack, salt attack, and discoloration of coated specimens. Gauri (1978) suggests that mechanical cleaning is safer than chemical methods, and shows that treating stone involves trade-offs. An example would be the desirability of sealing the stone to water, without retarding water vapor movement through the stone. Gauri (in a lecture, 1982) reviewed an example of impregnating a statue by evacuating the surface moisture and then carrying out the silicone treatment under the evacuation tent. In some cases the silicone was found to have penetrated the stone for two inches. It is clear that much remains to be done in the field of stone preservation, and the estimates of rapidly accelerating decay caused by acid precipitation add great urgency to this work.

## Brick Weathering

Bricks respond to weathering forces in essentially the same manner as do similar materials. The most permeable bricks are not as open as sandstone, and the most impervious probably rank with tightly crystallized rocks of several types. Bricks will weather and are observed to do so. The difficult question in a given case of brick alteration is the cause of the decay. Bricks have been observed to crumble or spall only at ground level, or only below sills in a building. In the first case, wet-dry and freeze-thaw effects seem to be principal factors. Severe weathering below sills, which sometimes makes it necessary to replace all the brick below sills in a building, often seems to result from rain penetration into the brickwork. Bricks under sills and overhangs are often discolored, suggesting deposition of atmospheric particulates, but it is unclear whether this staining and the failure of masonry are directly related.

Robinson, Holman, and Edwards (1977) showed that the best test of brick durability was to expose the brick in the appropriate environment for five years, essentially testing brick by placing them in use. The next most reliable test was 50 cycles of freeze-thaw tests--but this test requires a couple of months and is a relatively involved, prolonged procedure for a high-volume, low-cost building material. Although their final test specifications still cannot totally discriminate between durable and nondurable bricks, Robinson, Holman, and Edwards propose a series of indirect tests to define acceptability. If a group of bricks averages below 8.2% water absorption, or if their saturation coefficient (ratio of 5-hour, boiling-water absorption to 24-hour, cool-water absorption) is less than .74, or if the bricks have an initial water absorption rate of less than 22 g/min, or if they have compression strengths in excess of 12,000 psi, the bricks will be considered durable. Bricks that meet more than one of these criteria will be considered durable, with a high level of confidence. Robinson, Holman, and Edwards (1977) also suggest a sulfate soundness test (5 cycles) as an alternative way to test brick durability.

The potential for penetration of atmospheric rain and dry deposition into or through a wall is of great importance to the durability of a wall. Newman and Whiteside (1981) studied the movement of air and water through various walls. They investigated a wide range of brick grades and wall types, and found a surprisingly high level of penetration of rain--even without a pressure differential--and greater penetration when differential pressure was applied on the exterior wall. The cause of the water flow was eximated as: 6 percent from flow through bricks, 40 percent from flow through horizontal cracks between mortar and brick, and 54 percent due to vertical cracks at the brick-mortar interface (no flow occurred through mortar). They estimated that the cracks were about 0.1 mm wide, and found evidence for a "siphon" pressure or force acting on water flow. There is always some chance, of course, that their bricks were particularly porous, and that the cracks resulted from excessive dewatering of the mortar by absorption into the bricks. They also found an excellent correlation between air and water permeability and suggested air flow as a means of testing walls (Newman and Whiteside, 1981). If their work is representative even of the magnitude of water penetration in a general case, brick masonry should be regarded as much more open to agents of weathering than might be assumed.

Freeze-thaw testing is of interest because it provides a measure of a prime agent of weathering in many parts of the world. West (1970) reviews the methods used and some conclusions about the weathering of clay products. He mentions two tests: (1) soaking for 24 hours and freezing for 24 hours, or (2) boiling for 5 hours, soaking for 24 hours and freezing for 24 hours. These two schedules should differentiate freezing of pores that are easily accessible (penetration by 24 hours in cool water) from freezing of the water in pores which are penetrated only by boiling water. West also suggests that failure of brick walls by vertical expansion is most likely due to concrete shrinkage and not moisture expansion of brick. In a related study of freeze-thaw testing, Bessey and Harrison (1969) reviewed the results of 20 to 30 years of exposure of calcium silicate bricks to outdoor conditions and burial. They found an excellent correlation between bricks that were graded high by compressive strength and brick durability as measured by exposure or freeze-thaw testing. They associate high compressive strength with low water absorption and assume that durability results from low permeability.

Gauri (1980) mentions very common gypsum efflorescences on brick as a particularly detrimental agent of deterioration. In most cases these salt "blooms" are assumed to have originated from sulfate within the brick, but he suggests that gypsum dry wall on interior walls is a very important source of sulfate in the alteration of exterior wall materials. Adding to the confusion in tracing the cause of sulfate deterioration is the fact that mortar often contains sulfate as an aid in set-up. Gilardi (1966) studied the removal of atmospheric $SO_2$ by bricks, and found that after very high initial rates of removal, $SO_2$ removal stabilized at 5.5 µg $SO_2$/min $ft^2$ when the atmosphere contained 2.7 mg $SO_2/M^3$. Buildings are known to be a sink for both wet and dry $SO_x$, but studies of the results of sulfate pollution on bricks are essentially nonexistent.

Two studies of sulfate alteration of mortar have suggested a large potential for damage from this cause. A 1968 study by the Building Research Board of Britain illustrated the severe damage that can result from this form of alteration. They show a sequence of events that occurs from the formation of ettringite (synethetic $Ca_6Al_2(SO_4)_3(OH)_{12}.25H_2O$ formula, or naturally as $Ca\text{-}Al\text{-}SO\text{-}SiO\text{-}CO\text{-}OH.H_2O$ with variable composition) by the reaction of tri-calcium aluminate in mortar with sulfate from brick and water from the atmosphere. This alteration can cause cracks on interior walls, bowing and expansion of long walls, cracking of mortar, chalking and spalling of mortar, almost complete loss of mortar strength, and sometimes spalling of the brick. The expansion is often of the order of .2 percent (and may exceed 2 percent) and the damage can obviously be great. In a follow-up study, Harrison (1981) sets standards for avoiding sulfate-mortar interactions. The reaction requires sulfate, tri-calcium aluminate, and water; therefore, reduction of any of these sources will reduce the effect. He assumes that sulfate comes only from brick, and calcium aluminate only from mortar. It is possible to control ettringite formation by using low-sulfur bricks, using low-calcium aluminate mortars, and restricting moisture penetration of the wall. Harrison assumes that acid rain may erode the face of mortar joints, but he does not think that sulfate from the atmosphere will cause sulfate-mortar reactions. He also says that it is possible to distinguish wall expansion caused by brick from that caused by mortar, because mortar-sulfate reactions require two years or more, while brick expansion is generally evident in the first year after construction. This phenomena deserves further study. During the examination of a house built in the first decade of this century, it was noted that the bricks were of uniform color and appeared unaltered, but at least three generations of mortar were present, having been redone according to degree of exposure to precipitation.

## Preliminary Observations and Experiments

We have observed examples of brick that spall or become so friable that they begin to crumble. We have also seen face bricks in downtown Chicago that appear unaffected by a hundred years of exposure. Several factors seem to lead to increased decay of bricks. If the bricks are exposed to moisture and agents of decay, they will probably deteriorate at some point. Even the design and use of the brick is optimum, decay of the mortar will still be a potential problem. Environmental factors that can significantly alter masonry are freeze-thaw and wet-dry cycles, cold-hot, rainfall amount, atmospheric pollution level, and amount of attack by organisms.

Several types of bricks have been studied by x-ray diffraction. In a few instances of very severely deteriorated bricks, X-ray diffraction indicated a possibility of either underfiring, or reformation of clay-like materials. As a general rule, however, x-ray diffraction is useful only when a well-crystallized alteration product (such as gypsum) is present, or when test bricks are fired at comparatively high temperatures and for long times to develop high-temperature phases to a degree that allows detection by x-ray diffraction. Microscopic study of bricks is similarly hampered by the difficulty of detecting very fine crystal nuclei in bricks. Tests of pH were made on brick powders, and the range of results suggests the efficacy of this testing. Abrasion pH clearly reveals the degree to which a particular brick is out of equilibrium with acid rain and its tendency to weather.

A small series of tests was run during our study to determine the effects of four anions on clay pellets made from a Pleistocene, high-lime material. Several pellets were fired at optimum temperature (about 980°C). Two control pellets were cooled in air, and two pellets each were cooled from 400°C in distilled water,.1N $Na_2SO_4$, .1N $Na_2CO_3$, and .1N $NaNO_3$ solutions. All the pellets cooled in solutions were subjected to 50 cycles of soak and dry tests to determine if particular anions lead to failure, and at this point in the test the two control pellets each have a lime "pop." It would seem that exposure to water during cooling is beneficial regardless of salt content, although all the pellets in salt solutions show evidence of surface salt caking during drying cycles.

A future goal of our project is to determine the mineralogy of bricks in our sample collection of representative compositions fired to several different temperatures, and an investigation of the mineralogy of the raw materials in this collection. These studies seem appropriate, because as shown by abrasion pH, moisture expansion and tendency to weather are directly related to composition.

## Restoration and Preservation of Brick

Since building materials in general and brick masonry in particular are expected to have great permanence under very harsh conditions, some attention should be given to restoration and preservation of existing buildings and prevention of deterioration in future structures. Restoration often requires cleaning and replacement of some wall elements. Gauri (1978) defined several criteria for the evaluation of treatments to be used on stone, and he suggested mechanical treatment in preference to chemical methods. Harrison (1968) recommended reconstruction of as much of the building as possible whenever sulfate-induced expansion of masonry was present; he points out that remortaring will probably only cause a recurrence of the problem. Clark, Campbell, and Frohnsdorff (1975) evaluated several coatings and test methods for waterproofing masonry walls. They tested ultraviolet resistance, water absorption, wet-dry cycles, water vapor transmission, efflorescence, effects of humidity, changes after outdoor exposure and aging, wind-driven rain, hydrostatic pressure effects, and the effect of the method of application. They also evaluated about 50 substances and found that the effectiveness of various coatings varied widely. Gauri (1978) shows that ideal methods of preservation are not yet available.

## Recommendations for Durable Masonry

In new construction, emphasis can be placed on prevention of future problems:

- Proper design of a structure can reduce exposure of the structure to agents of decay: large overhangs, few horizontal surfaces, competent sills and other inserts should greatly reduce future problems.

- Thorough firing of bricks can greatly enhance their resistance to agents of decay.
- The use of brick with low water absorption and high strength will often return higher initial cost with time.
- The type of mortar should be selected to meet the strength requirements for an individual building in a specific environment, and only recommended mortar compositions should be used.
- The use of the appropriate, high-quality construction methods is essential in creating structures that will resist decay to the greatest extent possible.

## Test Methods

An important mandate of this study was the design and evaluation of test methods. Since the studies reviewed in this report indicate that many methods could be used to examine the existence or potential for deterioration of brick. We need to set priorities for our project. Nondestructive methods seem especially useful for studying existing buildings. Tests should require a reasonable amount of time, and only in rare cases should a small sample of part of a structure require protracted analysis. A complete analysis of a structure would include some or all of the following steps:

- Physical description of the type of brick, uniformity of brick and mortar, occurrence of replacements, cracking, spalling, compass orientation, organic growths, and florescences (in situ).
- Determination of pH of (1) water from soaked surfaces, by pH indicator tape on wet bricks, and of (2) scrapings and borings, as an abrasion pH (in situ or laboratory).
- Hardness measurement by "ring" of impact, by Shore hardness, or perhaps by sonic methods (in situ).
- Permeability determination by water loss, wick effects, or dye absorption (in situ).
- Determination of deleterious anions by dyes, selective ion electrodes, or wet chemistry of samples (in situ or laboratory).
- Assessment of degree of weathering by infrared and visible spectroscopy, and in some cases by microwave attenuation (in situ).
- Determination of wall penetrability by air flow and/or water loss through the structure (in situ).

It might be useful to abrade the brick or mortar and measure several of the properties as a function of depth: determination of pH, hardness, and anion content would be particularly interesting as a function of distance from the exposed surface. These tests would also give some information on the original properties of the brick.

The physical description of a structure is a very important means of getting an overview of the building. It is sometimes possible to determine whether the bricks were formed by extrusion or molds, and to determine the approximate grade of the brick. If signs of deterioration are present, the distribution of sound and altered brick is of central importance in determining cause. Features such as cracks, organic growths, and florescences should also be described in terms of their structural location.

A measure of abrasion pH is very useful, because it defines the present degree of alteration of the surface (as compared to the interior) and measures the continuing tendency to weather. The most reliable way to measure pH is to determine the actual abrasion pH by repeated grinding steps and pH determinations until equilibrium is reached. An alternative method that gives adequate results is to soak a brick surface in water and record the pH of the water. The pH of a dampened surface of the brick can also be measured with pH indicator tape.

The determination of hardness is of considerable interest, because it indicates the soundness of the material and correlates with strength and water absorption. The Shore hardness test is probably the best method, but may require removal of samples for the test. A frequently used quality control test is to listen to the ring of bricks when two of them are tapped together. A well-fired brick should give a clear ring. A qualitative test using impact sound may be the best available means. It is possible that a test using sonic instrumental analysis could be developed to quantify relative hardness.

Analysis of the occurrence and distribution of sulfate and similar pollutant ions such as $NO_3^-$ and $Cl^-$ is the most direct method of finding and proving effects due to acid precipation. As already noted, barium chloranilate can be used as an analytical technique to detect and quantify sulfate ions in extracts from masonry materials. Selective ion electrodes can also be used for these determinations. A number of standard determinations should be made to certify the detection and error limits of these methods.

Hydroxyl and adsorbed water in minerals often give a strong absorption peak in near visible and infrared radiation. These spectroscopic effects should make it possible to inventory large structures and to locate areas of maximum alteration characterized by high water absorption of weathered areas and by structural water in gypsum, ettringite, or clays. It may even be possible to isolate the spectrum of a particular mineral. If feasible, this method would provide the speed and detail required in assessing the general state of large structures and relatively small details on an individual structure.

A reliable measure of the ease of passage of atmospheric pollutants and rain into and through a wall would be of great value in these investigations. It seems possible to measure wall permeability by either air or water penetration. Any type of test used must be carefully designed to establish its reliability as a measure of penetration. Wherever possible, the nature of the wall cavity and the composition of interior walls should also be determined.

Several other experiments seem worth pursuing. Some measure of the interrelationship of freeze-thaw, wet-dry, and water acidity would greatly facilitate the evaluation of the magnitude of the acid rain problem; multiple regression could be used to evaluate this set of variables as functions of water absorption, expansion, or physical decay of the material. The experiment should probably include brick and mortar. A range of compositions of raw materials should certainly be tested, and some allowance for biological effects should be made.

At this point in our study we need to evaluate several existing structures by the methods outlined here. A set of several existing buildings with a known range of decay could be used to evaluate various test methods and provide some assessment of the rate of decay of brick masonry structures. Retrospective studies of a number of buildings exposed to low and high levels of pollution would make it possible to isolate the effects of acid precipitation.

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# APPENDIX I

Anonymous, 1982, L.A.'s acid fog: Science 82, v. 3, no. 7, p. 7-8.

Annotation

Los Angeles' fog is acidic, and at times has a pH equivalent to that of lemon juice. Every sample taken during a 6-month study by Caltech was determined to be acidic. This acidic fog is potentially more dangerous than acidic rain because of its higher level of acidity, concentrations near the earth's surface in populated areas, and of its potential formation during humid conditions in any polluted area.

Anonymous, 1968, Sulphate attack on brickwork: Building Research Station Digest 89, Second Series, 6 p.

Annotation

The reaction of tricalcium aluminate, a constituent of Portland cements, and sulphates in solution causes the formation of calcium sulphoaluminate (ettringite), accompanied by expansion. The soluble salts in bricks are a source of the necessary sulphates. When the reaction occurs in brickwork, the result is an overall expansion of the brickwork and subsequent disintegration of the mortar joints in extreme cases. Sulphate attack can be differentiated from moisture expansion by a factor of time: moisture expansion occurs in the first few months after construction, and sulphate attack on brickwork takes about two years to develop.

Tricalcium aluminate, soluble sulphates, and water must be present for sulphate attack to occur. The amount of water movement through the brickwork is important. Sulphate attack in new work can be prevented by using low sulphate bricks, increasing the resistance of mortars (decreasing the tricalcium aluminate content), and limiting the extent to which brickwork becomes and remains wet. Improving design by providing generous overhangs and eliminating parapets and free standing walls may help remedy existing sulphate attack as well as preventing it in new work.

Arnold, A., 1976, Behavior of some soluble salts in stone deterioration: Second International Symposium on the Deterioration of Building Stones, Athens, Greece, p. 27-35.

Annotation

The reactions of soluble salts that cause stone deterioration in buildings are studied. Salts of alkali and alkaline earth metals with sulfates, nitrates, chlorides, and carbonates are the most common causes of deterioration. Observable as efflorescences, soluble salts move in and out of porous stone surfaces and also migrate along them. Seasonal variations in temperature and humidity and atmospheric conditons govern the appearance of efflorescences of soluble salts, which occur in the winter but not in the summer--they appear when conditions are cold and humid and disappear when conditions are warm and dry.

Elimination of all sources of soluble salts is necessary to halt the deterioration. But because there are so many possible sources of salts (cement mortars, cleaning and sealing materials containing alkaline matter or salts of alkali metals, biological agents, ground moisture, pollutants in the air and even the stone itself) their elimination is nearly impossible.

Asmus, J. F., 1978, Properties of laser-cleaned carrara marble surfaces: Geological Society of America, Engineering Geology Case Histories No. 11, p. 81-88.

Abstract

The outdoor statuary of the city of Venice is being lost at the rate of approximately 5% per year. As in most areas of the industrialized world, this phenomenon stems from accelerated weathering of stone caused by air pollution. In the conservation of these artistic works, it is usually necessary to remove the surface encrustation that forms during the deterioration process; this procedure is required for both aesthetic appearance and physical-chemical stability. Unfortunately, much of the Renaissance statuary of Venice is exceedingly friable and highly soluble, so encrustation divestment has been largely a tedious manual effort.

Experiments are described here in which pulsed laser radiation was used to selectively evaporate black encrustations from highly altered Carrara marble statuary. Scanning electron microscopy was employed to determine thresholds for microcracking of the calcium carbonate grains as a function of laser-beam energy. Long-pulse xenon flash-lamp radiation and the air-abrasive technique are found to induce considerably more surface damage than optimum laser cleaning. However, limitations of laser technology suggest that at present it will be impractical to clean marble at a rate greater than a few square metres per day. On the other hand, xenon flash-lamp banks may be readily scaled to rates of tens or hundreds of square metres per day.

Associated Press, 1982, Acid rain theories challenged: The Champaign-Urbana News Gazette, p. A10.

Annotation

Anne Gorsuch, Environmental Protection Agency administrator, questioned the validity of current theories concerning the problem of acid rain. She urged that no legislative or regulative measures be undertaken until the problem is better understood and claims of environmental damage and long distance transport of pollutants substantiated.

Bell, K. E., 1965, Influence of lime on the thermal expansion of clay: Journal of the Canadian Ceramic Society, v. 34, p. 21-27.

Abstract

The dilatometric behavior of high-lime clays and shales is illustrated. Two types of crack appearing on the bricks are shown to be related to stresses arising from dimensional changes during heating. The effect on expansion of adding lime to clay is shown quantitatively for artifical mixtures heated at temperatures below 1000$^{\circ}$. The influence of the form of lime added, i.e. calcite, dolomite, hydrated lime, is illustrated. Additions of certain materials are shown to reduce the extent and severity of the dimensional changes.

Bessey, G. E., and W. H. Harrison, 1969, Some results of exposure tests on durability of calcium silicate bricks: Building Science, v. 4, no. 2, p. 63-77.

Abstract

Batches of calcium silicate bricks from over 25 different brickworks and ranging in compressive strength from 7 to 35 N/mm$^2$, have been exposed in shallow trays and on concrete slabs for periods up to 30 years. The results of annual inspection have been correlated with the original compressive strength according to the classes used in the current British Standard Specification No. 187 : 1967. Transverse strength, accelerated freezing and water absorption tests are reported on a proportion of the sample batches.

Also, eleven larger sample batches of bricks from nine different brickworks were used in burial tests, in which individual bricks were exposed in both completely buried and half-buried conditions in a heavy, wet clay soil. Determinations of compressive strength and chemical analysis were made on some bricks of each batch excavated at various ages up to 20 years. Some decrease in strength was found under these severe conditions, coupled with substantial carbonation of calcium silicate material.

Small free-standing panels and retaining walls were built from four of the batches of bricks used in the burial tests. These also were inspected at intervals of up to 20 years.

The results of these long term exposure tests are compatible with present British Standard classification of calcium silicate bricks and the recommendations for their use in British Standard Codes of Practice.

Birkeland, O., and S. D. Svendsen, 1963, Norwegian test methods for rain penetration through masonry walls: Proceedings of the 65th ASTM Annual Meeting, Symposium on Masonry Testing, p. 3-15.

Abstract

The Norwegian Building Research Institute has developed methods for laboratory testing of masonry walls, in which wall panels are exposed to artificial rain and a pressure difference. Laboratory results have been compared with results from test houses and field experience to determine the validity of the laboratory results.

Budiansky, S., 1981, Understanding acid rain: Environmental Science and Technology, v. 15, no. 6, p. 623-624.

Annotation

The weather is an important factor in determining the character of acid rain. Meteorological conditions can affect the amount of acid rain deposition and the concentrations of chemicals in the rain. The precipitation associated with cold fronts has been found to contain the highest concentrations of $H^+$ ions and sulfates while that associated with warm fronts contains the lowest.

Only recently has a systematic sampling network begun operations; therefore, historical data is lacking. The existing data--modern and historical--are suspect, because of flaws in sampling methodology and lack of suitable analytical methods.

Budiansky, S., 1980, Acid rain and the missing link: Environmental Science and Technology, v. 14, no. 10, p. 1172-1173.

Annotation

The reaction pathways for the production of $SO_2$ and $NO_x$ in the atmosphere are currently unknown but available evidence indicates many different pathways. Neither the gas-phase photochemical oxidation reaction nor the liquid-phase reactions can account for the abundance or seasonal variations in $SO_2$ production. Evaluation of $NO_x$ is hampered by the difficulty of measuring ammonium nitrate, the common particle form of nitrate, in the atmosphere. Future experiments should be on a smaller scale in order to determine the chemical reactions that occur in a raindrop.

Butterworth, B., 1964, Laboratory tests and the durability of bricks. II. The recording, comparison, and use of outdoor exposure tests: Transactions of the British Ceramic Society, v. 63, no. 11, p. 615-628.

Abstract

Long-period exposure tests are necessary as a check on laboratory tests that purport to indicate the durability of bricks; they have formed part of the programme of the Building Research Station since about 1926. The present paper introduces a series of papers which aim to give a definite account of the results of this programme, both the exposure tests and the associated laboratory tests. The brick-cemetery and tray-tests are described, the problems of recording and comparing the results of exposure tests are considered, and the significance of the results is discussed. It is concluded that: (1) the cemetery and tray tests are similar in severity. The latter is the more convenient form of test as it avoids the labor of weeding. (2) The results of the cemetery and tray tests indicate the probable durability of bricks only in situations where they may be frozen whilst saturated, e.g. parapets, free-standing walls, and retaining walls. In the British climate normal external walls of buildings do not come in this category. The cemetery and tray tests cannot therefore be used as a guide to the durability of bricks in normal external walls. It is possible, however, that bricks that decay very rapidly in these tests may be damaged whilst stacked on a building site or exposed in unfinished brickwork in winter. With facing bricks, too, the choice of bricks for many buildings may be governed by the need to withstand the conditions in parapets and retaining walls, since an architect would not wish to use one brick in main walls and another for parapets and other places where exposure is more severe.

Butterworth, B., 1964, Laboratory tests and the durability of bricks. IV. The indirect appraisal of durability: Transactions of the British Ceramic Society, v. 63, no. 11, p. 639-646.

Abstract

The average compressive strength, water absorption and saturation coefficients of bricks exposed in a brick cemetery are compared with their average durability in the latter test. The analysis of the results presented here is that which led, in 1937, to the conclusion that the combination of limits for water absorption and saturation coefficient, as used in the A.S.T.M. standard for bricks, was the best method available at that time for judging durability. It was recognized, however, that an investigation of the durability of bricks of individually known properties was required.

Butterworth, B., and L. W. Baldwin, 1964, Laboratory tests and the durability of bricks. V. The indirect appraisal of durability: Transactions of the British Ceramic Society, v. 63, no. 11, p. 647-661.

Abstract

The results of tray exposure tests on many bricks tested individually for water absorption and saturation coefficient before exposure are described. In one series of tests, exposure walls were also built, and the behavior of bricks in the tray test and in the copings of parapets and retaining walls is compared. It is shown that the correlation between water absorption and saturation coefficient and resistance to exposure in these tests is far too poor to justify using these properties as a guide to durability. The American work which led to an A.S.T.M. specification being based on these properties is re-examined; it appears on close examination that the results were not substantially different from those here reported.

Butterworth, B., and J. W. Skeen, 1962, Experiments on the rain penetration of brickwork: Transactions of the British Ceramic Society, v. 61, no. 9, p. 487-519.

Abstract

A rain machine of the pressure-box type is described which possesses two unusual features, the use of intermittent spraying, controlled by a time switch, to limit the amount of water applied to the test wall, and the use of time-lapse photography to provide a continuous record of the condition of the back of the wall. The results of preliminary tests on 9-in. solid brick walls, 9-in. divided-joint walls built with perforated double bricks, and an 11-in. cavity wall, are reported. The significance and the limitations of this type of test are discussed.

Annotation

Walls were tested for rain penetration with and without the use of air pressure. When air pressure was used, the area of dampness on the back of the wall increased at a slightly faster rate. The time to initial penetration showed little or no dependence on air pressure, suggesting that penetration may be controlled by capillary forces. Porous bricks were shown to provide an important leakage path.

Carter, L. J., 1979, Uncontrolled $SO_2$ emissions bring acid rain: Science, v. 204, no. 11, p. 1179-1182.

Annotation

Politics hampers efforts to regulate and reduce $SO_2$ emissions from coal-fired power plants. EPA regulations now require new power plants to cut $SO_2$ emissions to half of what was previously allowed, but existing coal-burning power plants are excluded from compliance. $SO_2$ is a precursor to acid rain, a problem which is no longer viewed as an isolated regional event. Congress is loath to act, possibly due to pressure not to burden the utility companies with the additional costs necessary to comply with stiffer laws and regulations. Meanwhile, $SO_2$ levels in the atmosphere are expected to increase by nearly two million tons over the next fifteen years.

Churchill, W. M., C. Brough, and H.W.H. West, 1972, 'Peacocking': A blue discoloration of blue bricks exposed to rain: Transactions and Journal of the British Ceramic Society, v. 71, no. 7, p. 211-215.

Abstract

'Peacocking' of blue bricks is a common phenomenon which has recently come into prominence due to the increasing use of such bricks for facing brickwork. The defect is described and illustrated. EPMA and optical microscopy techniques were used to identify the discoloration as being due to silica. It was also reproduced in the laboratory and experiments were conducted to check the ease of its removal. Masonry silicone-treated blue bricks failed to develop the fault and an obliterating paint has been made to cover up the discoloration. It is suggested that anorthite, a mineral developed near the surface of blue bricks, is responsible for providing the silica causing the discoloration.

Clark, E. J., P. G. Campbell, and G. Frohnsdorff, 1975, Waterproofing materials for masonry: National Bureau of Standards Technical Note 883, 78 p.

Abstract

The initial effectiveness and durability characteristics of fifty-five clear masonry waterproofing materials were evaluated using laboratory tests. This report contains the results of initial performance tests including water absorption, water vapor transmission, resistance to efflorescence and change in appearance. Durability tests, including periodic measurement of water absorption after exposures to accelerated weathering and outdoor exposures, were also conducted. Based on test results, performance criteria for clear waterproofing materials were developed. In addition, recommendations for the application of waterproofing materials were formulated. Finally, the report contains a summary of a survey concerning field experiences with waterproofing and a brief theoretical discussion of waterflow.

Cogbill, C. V., 1976, The history and character of acid precipitation in eastern North America: Water, Air, and Soil Pollution, v. 6, nos. 2-4, p. 407-413.

Abstract

The history and present distribution of precipitation acidity in eastern North America are reviewed. Precipitation chemistry from the 1920's indicates heavy ionic deposition, but low acidity (calculated) in Tennessee (pH 7.4) and New York (pH 6.15). However, high acidity was apparently widespread over northeast North America by 1955-56 and measured pH's below 4.5 were observed earlier. The geographic distribution of acid precipitation has spread through the present. Yearly average pH values for 1972-73 are not significantly different in New York and New Hampshire, indicating a regional consistency in acid (pH 4.10) deposition. Summer acidity is currently lower in Tennessee than in the Northeast. Precipitation chemistry of individual storms reveals some local variation even within a 3 km range, but a storm in central New York is generally homogenous over 70 km.

Cole, W. F., 1980, Fundamental causes of moisture expansion: Proceedings of the Ninth Australian Ceramic Conference, Sydney, Australia, by the Australian Ceramic Society.

Annotation

An investigation into the causes of moisture expansion reviews previous works in the field. The maximum moisture expansion is found to occur between 900-1100°C firing temperature. The lower moisture expansion at higher temperatures indicates that the presence of a glass phase contributes little to moisture expansion, at least in natural expansion. The kinetics and activation energy of moisture expansion are briefly discussed, as is the relationship between moisture expansion and internal surface areas.

Cole, W. F., 1975, Predictions on moisture expansion from chemical data: Journal of the Australian Ceramic Society, v. 11, no. 1, p. 20-21.

Annotation

The potential moisture expansion of a fired clay body can be determined from the molecular ratio $(CaO + MgO)/(K_2O + Na_2O)$ of the unfired clay. The equation $y = 15.25-7.91x$, with y = maximum moisture expansion of bricks after 4 years of a natural exposure $(x10^{-2}\%)$ and $x = \log (CaO + zMgO)/(K_2O + NA_2O)$ with $z = 1$, is said to predict the moisture expansion of ceramic bodies. This claim is based on the premise that chemical composition is more important in determining moisture expansion than is initial mineralogy of the clay. The firing temperature of the predicted moisture expansion peak of the clay can be calculated by the equation $t = 1067-12.29w$ with $t$ = firing temperature for the moisture expansion peak ($^{o}C$) and $w$ = loss on ignition (%).

Cole, W. F., 1968, Some relationships between mineralogical and chemical composition and moisture expansion of fired clay bodies: Journal Australian Ceramic Society, v. 4, no. 1, p. 5-9.

Annotation

An attempt is made to reconcile conflicting conclusions by various investigators studying the influence of mineralogical and chemical composition of the original clay in the determination of the moisture expansion of the fired body. A linear relationship is shown to exist between maximum moisture expansion and the content of kaolinite or mica in quartz-kaolinite-mica clays. A linear relationship also exists between maximum moisture expansion and the molecular ratio $Al_2O_3/(K_2O+Na_2O)$ for the same type clays when no additional fluxing agents are present. Maximum moisture expansion depends on chemical composition when additional fluxing agents are present.

Cole, W. F., 1967, Changes in a 50m mural tape standardizing base: The Engineer, v. 223, no. 5809, p. 769-770.

Annotation

The expansion of a long mural base used in the standardization of precision measuring tapes was studied. Fifty-eight years after construction, the wall was still expanding at a rate of slightly less than 0.2 mm per year, proving that brickwork of fired clay products will continue to expand for long periods of time. The results of the study were used to formulate a linear regression equation which would predict expansion. The equation was based on the assumption that the natural expansion of fired clay products is linear with a function of time.

Cole, W. F., and R. Birtwistle, 1969, Kinetics of moisture expansion of ceramic bodies: Bulletin of the American Ceramic Society, v. 48, no. 12, p. 1128-1132.

Summary

Where accurate measurements establish that ceramic bodies expand with time the kinetics law followed is very well represented by a linear log-time function. This function involves an adjustable parameter $k_1$ and the physical interpretation to be given to this parameter is considered from calculations made on the authors' data and data from the literature for a variety of exposure conditions. The same data are also fitted to a second-order growth curve and the coefficients are compared with those derived for the log-time function. The log-time function is preferred over the growth curve for explaining the kinetics of moisture expansion, because it is usually a better fit to the data and has proved more accurate in predicting future expansions in those cases where measurements have shown expansions to be maintained for a considerable time (10 years or more).

Cole, W. F., and D. N. Crook, 1968, High-temperature reactions of clay mineral mixtures and their ceramic properties: IV. Dimensional and weight changes on refiring and the pore-size distribution of fired kaolinite-muscovite-quartz mixtures with 25% weight quartz: Journal of the American Ceramic Society, v. 51, p. 79-84.

Abstract

Dimensional and weight changes on refiring of clay mineral mixtures were used as a measure of moisture expansion and moisture uptake, respectively. Pore-size distributions were measured by the mercury penetration method. With specimens containing more than 15% muscovite, the moisture expansion had a peak value when fired 1000° and 1050°C. At 1050° the magnitude of moisture expansion and moisture uptake was approximately linear with the muscovite content. For specimens with less than 15% muscovite, the variation of moisture expansion with mica content was complex and this was ascribed to the fact that muscovite particles coated with kaolinite behaved differently from bulk mica in the original firing treatment and on subsequent exposure to moisture. The volume percentage of pores greater than 0.2μ in diameter increased as the muscovite content and firing temperature increased, and reached a maximum when moisture expansion was at a maximum. The volume percentage of pores less than 0.2μ in diameter decreased under the same conditions but increased slightly in specimens of low muscovite content because the kaolinite reacted on firing with the mica which it coated.

Davies, T. D., 1974, Dissolved sulphur dioxide and sulphate in urban and rural precipitation: Atmospheric Environment, v. 13, no. 9, p. 1275-1285.

Abstract

Sulphur dioxide washout and total sulphate scavenging by precipitation at a rural and urban site have been measured in Norfolk (easternmost part of U.K.) over a period of one year. The basic sampling period was one day although, on occasions, more intensive sampling was undertaken. Estimates have been made of the role of sulphur dioxide washout in the total sulphur removal process. Because the "same" rainfall was collected in the urban and rural locations, attempts have been made to compare city and rural sulphur dioxide washout and sulphate scavenging rates in relation to precipitation amount, intensity, atmospheric sulphur dioxide, rainfall pH and weather-type. There is a greater difference between urban and rural sulphur dioxide washout levels than between the respective precipitation sulphate levels. The field measurements of sulphur dioxide solubilities agree reasonably well with some previous theoretical work.

Davison, J. I., and P. J. Sereda, 1978, Measurement of linear expansion in bricks due to freezing: Journal of Testing and Evaluation, v. 6, no. 2, p. 144-147.

Abstract

A linear extensometer is described that can be used to measure expansions resulting from freezing in saturated porous inorganic building materials. Typical freezing curves illustrate reversible and irreversible expansions. The procedure may have application as a simple test method for assessing the durability of bricks or other porous inorganic building materials.

Demediuk, T., and W. F. Cole, 1960, Contribution to the study of moisture expansion in ceramic materials: Journal of the American Ceramic Society, v. 43, no. 7, p. 359-367.

Abstract

Measurements were made of the expansions produced by autoclaving coprecipitated and mixed gels of silica and alumina fired over the temperature range 850° to 1200°. The effect of adding soda to gels of kaolinite composition was investigated and the compositions of the phases were determined. The results show that amorphous silica has a limited influence and must be modified by alumina or by soda and alumina to produce expansions comparable with those of ceramic bodies. The active material is an amorphous alkali aluminosilicate, to be distinguished from permutites and glass. Formation of glass and crystalline compounds reduces moisture expansion. At low firing temperatures (below 950°C) the hydration of $\gamma$-$Al_2O_3$ to boehmite produces high moisture expansions, but $\gamma$-$Al_2O_3$ modified by silica (silicon spinel) has only a limited influence. Some observations are made on the nature of cristobalite developed during the firing of pure amorphous silica and amorphous silica into which additives were introduced.

Annotation

The literature on moisture expansion in ceramic materials is reviewed and an extensive bibliography of papers up to 1959 compiled.

Drufuca, G., and M. Giugliano, 1977, The duration of high $SO_2$ concentrations in an urban atmosphere: Atmospheric Environment, v. 11, p. 729-735.

Abstract

$SO_2$ concentrations have been continuously measured in the urban area of Milan at three stations and for three winter semesters from 1972 to 1974. The nine time series have been processed statistically with particular regard to the duration of the events for which the concentration exceeded some levels of interest. It has been found that all the statistics of interest are strongly dependent upon the six-month-average concentration, this value being easy to determine. Simple and accurate descriptive models have been formulated and verified.

Dukes, W. H., 1972, Conservation of stone: Chemical treatments: The Architects' Journal, v. 156, no. 34, p. 433-438.

Annotation

Deterioration and conservation of stone was studied by the Commonwealth War Graves Commission, beginning in the early 1900s. Water proofers, water repellents, consolidants, and treatments containing algicidal and fungicidal additives to destroy biological growth were the types of chemical treatments tested. In the initial study, begun in 1918, the preservative treatment accelerated the rate of deterioration of the headstones. Further testing of headstones in sites presenting natural, mechanical, industrial, underground and external damp weathering conditions was begun in 1956. Headstones were treated with silicone-based water repellents and consolidants. Half of the trials were abandoned within two years. The results led to recommendations that the preservatives tests not be used on any materials containing large quantities of soluble salts or in contact with any such materials. The mechanism of the failure was examined and examples given.

The surface treatments greatly increased the risk of frost damage because they inhibited the escape of water.

The type of treatment used, supply of soluble salts, composition of stone and water, and the frequency of the capillary cycle controlled the speed of failure.

Efes, Y., and S. Luckat, 1976, Relations between corrosion of sandstones and uptake rates of air pollutants at the Cologne Cathedral: Second International Symposium on the Deterioration of Building Stones, Athens, Greece, p. 193-200.

Annotation

The cause of the accelerated corrosion of the sandstones used on the Cologne Cathedral was determined to be the increased atmospheric pollution. Chemical analysis of the deteriorated stone revealed a decrease in $SiO_2$, $Al_2O_3$, and MgO content and an increase in CaO, $SO_3$, and $Fe_2O_3$ content. Dolomite and calcite cements were important factors contributing to the corrosion. When the carbonate cement reacted with the $SO_2$ from the atmosphere, gypsum was formed and the rock was damaged.

Areas with high uptake rates of $SO_2$ from pollutants in the atmosphere were found to have a high sulphate content in the layers of corrosion.

Fassina, V., L. Lazzarini, and G. Biscontin, 1976, Effects of atmospheric pollutants on the composition of black crusts deposited on Venetian marbles and stones: Second International Symposium on The Deterioration of Building Stones, Athens, Greece, p. 201-211.

Summary

On the basis of the considerations described above and from the data obtained, the first important observation regarding the relatively large amount of iron present either on the filter papers or in the scabs confirms both hypotheses of $SO_2$ catalytic oxidation in the aerosols and on the stone and marble surfaces exposed.

This mechanism has been confirmed by the presence of high sulphate concentrations in correspondence to high iron levels.

The contribution to the total amount of atmospheric sulphate, which is very abundant in the black scabs, may be ascribed partly to atmospheric sources (primary pollutants), and partly to secondary pollutants produced by reactions in situ. To date it is almost impossible for us to distinguish the source of the sulphate present in the black scabs.

Some diffractometric analyses on scab samples carried out till now have emphasized that sulphates are present as gypsum, but other analyses carried out on efflorescence of salts in the interior of buildings have shown the presence of thenardite ($Na_2SO_4$). This compound can confirm the reaction between sulphuric acid and sodium chloride forming the hydrochloric acid and sodium sulphate.

Instead from the chloride data reported above, there should be the presence of sodium chloride, but the results from the analyses by x-ray diffractometry showed the constant absence of sodium chloride and in some cases the presence of antarcticite ($CaCl_2.6H_2O$) reported by Lazzarini and Begolli in their paper to this Symposium. This could confirm reactions between hydrochloric acid and limestone or between the same acid and gypsum.

The notable amount of carbon, estimated by means of microscopic examination of the filter papers and with greater precision in scabs, increases the possibility of catalytic reactions which can form sulphuric acid.

A quantitative determination of carbon and the analyses of V, Cr, Mn could be extended to filter papers, as well as scabs in order to clarify the main processes which cause the chemical alteration of marble and stone.

Fishburn, C. C., 1940, Effects of wetting and drying on the permeability of masonry walls: National Bureau of Standards, Building Materials and Structures Report BMS55, 6 p.

Abstract

Since the volume changes resulting from the wetting and drying of masonry units and mortars are unequal, changes in the moisture content of a masonry wall may produce differential volume changes between the units and the mortar, resulting in the formation or enlargement of cracks in the joints. The effects of changes in the moisture content of 8 small masonry walls were studied by measuring the permeability of the walls during each of about 12 cycles of wetting and drying. The walls were wetted by applying water to the exposed face simulating an exposure to a wind-driven rain. The specimens were not subjected to freezing during wetting or drying. Five of the walls were of all-brick construction, one was a stucco-faced wall, and two were faced with brick and backed with hollow units. There was no significant change in the permeability of the walls resulting from the exposure to wetting and drying.

Forrest, J., R. Garber, and L. Newman, 1979, Formation of sulfate, ammonium and nitrate in an oil-fired power plant plume: Atmospheric Environment, v. 13, p. 1287-1297.

Abstract

A series of experiments were performed at the oil-fired Anclote Power Plant of the Florida Power Corp., Tarpon Springs, Florida. Plume samples at varying downwind locations were obtained by means of a high-volume filter pack. Operational oxygen levels during fuel combustion were varied experimentally; particulate sulfate and sulfuric acid concentrations in both flue gas and plumes increased directly with excess $O_2$ levels. Plume dropout of particulate sulfate was found to occur during some experiments. A generalized trend toward increasing ammonium content of plume particulates with time was observed. Particulate nitrate formation did not indicate a similar trend. Oxidation of $SO_2$ to sulfate within a time frame of up to 100 min. and 50 km ranged within 1-3%, with but two runs exceeding 3%. No correlation was found between any individual meteorological parameter and extent of oxidation. A significant difference between conversions during summer and winter runs was observed, conceivably attributable to differences in the vanadium content of the fuel oils and to some extent the combination of higher temperature, relative humidity, water partial pressure and unstable weather during the summer.

Frediani, P., P. G. Malesani, S. Vannucci, 1976, Weathering of Florentine stones: Sulfation and its determination: Second International Symposium on the Deterioration of Building Stones, Athens, Greece, p. 117-118.

Annotation

Chemical, diffraction, and gravimetric methods were used to analyze the gypsum ($SO_4$) content in deterioration crusts. The gypsum is not a primary cause of the deterioration of the building materials but may act to increase the rate of natural decay. Deterioration occurs in three stages and gypsum is present only in the advanced stages. Sulfur dioxide pollution in the atmosphere and calcium sulfate contained in preservatives previously applied to the stone are possible sources of the gypsum.

Freeman, I. L., 1966, Moisture expansion of structural ceramics. II. The influence of composition: Transactions of the Tenth International Ceramic Congress, Stockholm, Sweden, p. 141-153.

Summary

The moisture expansion, in normal atmospheric conditions, of some typical structural ceramics is compared with selected features of the raw material and fired body compositions.

Earlier work, described in Part I, had shown that the curve of moisture expansion with time could be divided into two parts: 1) an initial stage of very rapid expansion, generally completed within the first 24 hours, and 2) a slower, regularly diminishing later expansion. The two stages in the expansion were not closely related. Since it is the expansion in the later stage which is of interest to the user of structural ceramics, the index of moisture expansion adopted for comparison purposes was based on the expansion in closely controlled conditions, between the second and 128th days after firing.

For the ten materials studied, porosity is shown to have a dominating effect on the expansion index, tending to obscure other effects. The phases developed in the fired bodies correlate broadly with the expansion index, in that crystallization of Ca- and Mg-bearing phases tends to be associated with moderate or very low expansions, and is little affected by changes in firing temperature; absence of such phases is associated with high expansions at low firing temperatures, which can be greatly reduced by harder firing. This relationship is confirmed by a correlation found between the chemical analyses of the raw materials and expansion indices: A high ratio of $Al_2O_3$ to CaO-MgO (say >2) gave high expansions, whilst lower ratios usually gave low, or very low expansions. This relationship held for only one specific firing temperature, probably because of the porosity effect. The clay mineralogy of the raw material appears to influence expansion only through its effect on the total analysis.

Freeman, I. L., and R. G. Smith, 1967, Moisture expansion of structural ceramics I. Unrestrained expansion: Transactions of the British Ceramic Society, v. 66, no. 1, p. 13-35.

Abstract

Describes the moisture expansion of ceramic bodies made from ten typical British raw materials, each fired at four different temperatures. Expansion occurring in the first day after firing is large, and not closely related to subsequent expansion. Rate of expansion diminishes progressively and fairly predictably after the first day. The humidity of the storage atmosphere significantly affects the degree of expansion. A moisture index is derived and is used to compare the expansions of the ten materials. Steam treatment at atmospheric pressure is suggested as a possible test for natural expansion. Pre-treatment with steam, either at low or high pressure, markedly reduces subsequent natural expansion.

Gauri, K. L., 1980, Deterioration of architectural structures and monuments: In Polluted Rain, T. Y. Toribara, M. W. Miller, and P. E. Morrow editors . New York: Plenum Press, p. 125-144.

Abstract

Natural stone, concrete, and mortar are the common materials exposed at the facade of architectural structures. Carbonate and silicate minerals are the essential constituents of these materials. These minerals are susceptible to attack by atmospheric $CO_2$. The weathering of these minerals has increased at an alarming rate in the industrial countries due to $NO_2$ and $SO_2$ emanations.

The $SO_2$ attack has produced sulfate crusts on ancient buildings. The continued reactivity behind these crusts has resulted in the removal of stone in layers obliterating the original sculptural details and causing serious damage to the structures.

Most ancient buildings and monuments contain florescences. Evaporation of water at the surface tends to accumulate the florescences in the subsurface regions of the stone; their migration is facilitated by increased ionic concentration resulting from atmospheric pollution. Repeated dissolution and crystallization of the florescences in subsurface regions and the accelerated oxidation of reinforcing metals generate stresses which disintegrate the stone. Weathering also changes the physical properties such that the stone becomes more susceptible to atmospheric attack. These properties relate to mechanical strength, water absorption, and permeability of the stone. Design of conservation treatment should include regeneration of these properties so that the stone performs as though it had been reestablished anew in the existing environment.

Gauri, K. L., 1978, The preservation of stone: Scientific American, v. 241, p. 126-136.

Annotation

This article explores the processes of weathering, cleaning, consolidating and restoring weathered objects, the development of replacement structures, and the development of performance criteria for preservative treatments.

The rate of stone deterioration is increasing in urban atmospheres because of increasing concentrations of sulfur and nitrogen oxides. Mechanical weathering is largely responsible for structural damage; the effects of chemical weathering are concentrated near the stone's surface. The chemistry of the stone should be considered when choosing a method of cleaning the deteriorating stone so as to lose as little of the stone as possible. Mechanical methods should be attempted first.

Crumbling stone can be consolidated by replacing certain constituents of the stone, precipitating chemically resistant materials in the pore spaces, or by the impregnating the stone with organic monomers and polymers. The design of consolidation treatments should consider the desired rate of capillary water movement, permeability, compressive strength, and chemical reactivity of the treated stone.

Any preservative treatment should be carefully tested and monitored, because treatment can result in an increase in the rate of deterioration.

Gauri, K. L., 1974, Decay and its prevention in natural stone: Transactions of the Kentucky Academy of Science, v. 35, nos. 1-2, p. 29-36.

Abstract

In our studies on a variety of natural building stones, we have observed two basic types of profiles of weathering. In highly compact rocks such as marble, the zone of weathering is characterized by a reduced specific gravity and augmented capillarity. Here, the texture of the zone of weathering is quite distinct relative to the texture of the parental material. In less compact rocks such as limestone, the pore space in the zone of weathering becomes plugged due to the recrystallization of salts obtained by the solution of the parent rock. The effect of continued weathering of all these stones is the surface reduction of objects which leads to destruction of ornamentation and surface relief. Using industrial polymers, methods of impregnation have been given which, by reducing water transport into the stone, have greatly minimized the effect of weathering agents.

Gauri, K. L., 1970, Improved impregnation technique for the preservation of stone statuary: Nature, v. 228, p. 882.

Annotation

A preservation technique developed for use on marble but suitable for most porous materials is discussed. The stone is immersed in mixtures of acetone and water, then saturated with mixtures of resin and water prior to impregnation by resin.

Gauri, K. L., and M. V. Appa Rao, 1978, Certain epoxies, fluorocarbon-acrylics, and silicones as stone preservatives: Geological Society of America, Engineering Geology Case Histories No. 11, p. 73-79.

Abstract

The sample for this study consisted of Indiana limestone and several marble varieties. The treatment varied from surface coatings to in-depth impregnation. The chemical tests included exposure to $SO_2$-enriched dynamic atmospheres and immersion in carbonic and sulfurous acid solutions. The $SO_2$ reactions were studied as a function of the formation of calcium sulfite determined by X-ray diffraction. The acid reactions were studied on leached $Ca^{2+}$ determined by EDTA titration and atomic absorption. The physical tests included the soundness test based on hydration of $Na_2SO_4$ in the pore space of the stone.

Chemically, certain epoxies and silicones increased the reaction relative to controls. The epoxies did so by absorption of gases, the silicones by probably acting as semipermeable membranes. The reactivity of immersed specimens was greater than that of specimens in a gaseous environment. The resin films during 20 to 40 hr of reaction, necessary for steady state, were not discolored or damaged.

In soundness tests, in-depth impregnations produced far better results than surface treatments. All silicone treatments highly reduced water and water-vapor absorption but did not proportionally increase the soundness. The soundness was improved in fluorocarbon-acrylic copolymers, but here the chemical improvement was at its best. The maximum improvement of soundness was experienced by epoxy-treated specimens.

An absolute prediction of the long-range behavior of preservative treatments in a natural environment seems to be difficult. Above tests only indicate the relative merits and permit identification of materials that may actually accelerate the weathering process.

Gauri, K. L., and A. C. Sarma, 1973, Controlled weathering of marble in a dynamic $SO_2$ atmosphere: Proceedings of the 3rd Annual Environmental Engineering and Science Conference, University of Louisville, Louisville, Kentucky, p. 209-218.

## Abstract

Specimens representing several textural varieties of marble were reacted with dynamic $SO_2$-atmospheres at ambient temperatures but with variable conditions of flow rate, humidity and $SO_2$ concentrations. The products of reaction of marble with such atmospheres were quantitatively determined by x-ray diffraction. The study reveals that $CaSO_3.2H_2O$ is the main product formed under normal humidity conditions. In high humidity the first product of reaction is still calcium sulfite but it oxidized to $CaSO_4.2H_2O$ progressively with increasing time of exposure. The study also reveals that the rate of reaction is directly related to $SO_2$ concentration and inversely related to the rate of flow of the dynamic atmosphere. These results permit a tentative correlation of the laboratory data on stone deterioration with the weathering of stone due to $SO_2$ in natural conditions.

Further, a few specimens were treated with polymers to enchance their capability to resist $SO_2$ attack. Specimens treated with a variety of epoxy resins reveal a variable degree of "protection." While certain epoxies enhanced the reactivity, others suppressed it as much as 7 percent as compared with 100 percent reactivity of an untreated specimen.

Gauri, K. L., J. A. Gwinn, R. K. Popli, 1976, Performance criteria for stone treatment: Second International Symposium on the Deterioration of Building Stones, Athens, Greece, p. 143-151.

## Annotation

The function of a preservation treatment is to decrease the vulnerability of stone that is subject to weathering by modifying its properties. Weathering occurs despite treatment, primarily because of continued access of atmospheric gases such as $CO_2$ and $SO_2$ to the stone. Also, the preservatives themselves are vulnerable to weathering processes. Polymers used in stone preservation are degraded by UV radiation, but the degree of degradation depends on the amount of radiation absorbed and certain characteristics of the polymers. Performance criteria developed for polymers used in stone preservation assess the transparency of the polymer to UV radiation of wave length longer than 290 NM. Because of the long exposure time necessary to produce symptoms of deterioration, polymers that absorb ambient UV radiation must be evaluated in accelerated decay conditions. UV spectrophotometry and contact angle measurement are efficient methods of detecting decay by UV radiation.

Performance specifications are given as measures of permeability and compressive strength of the stone for specimens treated against weathering due to $CO_2$, $SO_2$, $SO_2$ gas, and transport of water through the stone.

The weathering of stone due to $CO_2$ occurs only in the presence of a $CO_2$-water solution, whereas $SO_2$ reacts with stone in dry as well as rainy periods.

Gauri, K. L., D. J. Hagerty, and C. R. Ullrich, 1972, Comparative physical properties of weathered impregnated and unimpregnated marble: Engineering Geology, v 6, p. 235-250.

Abstract

Chemical weathering of marbles has greatly increased during the past decades. The gaseous pollutants generated mainly by combustion of automobile, domestic, and industrial fuels have contributed significantly towards this increase. The weathering affects marble gradationally from outside inwards, producing three distinct zones. The success of a technique developed to provide cohesion to reduced and dislodged calcite crystals in the zone of weathering, by impregnation with resins which even permeate the inter-crystalline boundaries in the non-weathered region, is tested. As these weathered layers are quite thin and easily destructible, direct measurement of compressive strength is impossible. This property is, therefore, determined indirectly via Shore scleroscope hardness and specific gravity.

The impregnation increased the strength of the weathered zone up to 59 percent and of the unweathered region up to 24 percent. Corresponding values for permeability and capillarity, relative to untreated specimens, change inversely to strength changes as the pores receive relatively larger amounts of resin in the outer weathered region than in the unweathered region in depth. This phenomenon is substantiated by scanning electron microscopy (S.E.M.).

Gauri, K. L., P. Tanjaruphan, M. Appa Rao, and T. Lipscomb, 1977, Reactivity of treated and untreated marble in carbon dioxide atmospheres: Transactions of the Kentucky Academy of Science, v. 38, nos. 1-2, p. 38-44.

Abstract

Marble specimens were impregnated with certain epoxies and fluorocarbon-acrylic copolymers. The treated and untreated specimens were exposed to, while immersed in deionized water, 0.983, 6.2, 8.28, and 11.02 percent $PCO_2$ at 20°C in a dynamic system. The concentration of leached $Ca^{2+}$ in the water was determined by EDTA titrations and atomic absorption. The values obtained by those methods were nearly identical. The rate of reaction was based on the increment in $Ca^{2+}$ concentration as a function of time. The equilibrium constant K, calculated from the experimental data, had a value of $1.49 \times 10^{-6}$, and compared well with the value of $1.58 \times 10^{-6}$ given by Garrels and McKenzie (1971). Specimens treated with fluorocarbon-acrylic compounds revealed only one-half reactivity relative to untreated specimens in the initial phases of reaction. Certain epoxies provided protection, other epoxies actually enhanced the rate of reaction. It is proposed that pertinent data generated in the course of this study be used as a basis for quantitative performance criteria for stone and concrete preservation treatments.

Gilardi, E. F., 1966, Absorption of atmospheric sulphur dioxide by clay brick and other building materials--Ph.D Thesis: Rutgers State University, 151 p.

Abstract

Clay building bricks were exposed to atmospheres containing 1 to 10 mg $SO_2/m^3$ in flow-through systems for periods up to 5 days. Experiments were carried out at 35 to 85% R. H. Wet bricks removed a greater fraction of the applied $SO_2$ than dry bricks. An increase in R. H. prolonged the time that the $SO_2$ removal rate of the initially wet brick was higher than that of the initially dry brick. This was due to the slower drying rate of the wet brick at the higher R. H. No conclusive effect of high R. H. on the % $SO_2$ removed by dry brick was noted. A rapid decrease in $SO_2$ removal was noted during the initial 5 to 10 H of exposure of wet or dry bricks. An increase in flow rate resulted in a decrease in the fraction of applied $SO_2$ removed by brick. The percent $SO_2$ removed by wet brick was inversely related to the applied $SO_2$ concentration. No conclusive effect of $SO_2$ concentration on its percent removal by dry brick was demonstrated. The removal of $SO_2$ on a weight basis (after the initial rapid decrease in removal) by brick whose surface was saturated, varied with concentration as described by the equation $A = kC^a$. In this expression, A is the weight of $SO_2$ removed per minute per unit brick surface area, and C is the $SO_2$ concentration. The $SO_2$ removal rate of a 2 inch brick cube exposed in a 4 L. chamber to an atmosphere of 2.7 mg $SO_2/M^3$ at a flow rate of 1.11/min. was calculated to be 5.5 µg $SO_2$/min. ft.$^2$. Studies on the mechanism of removal of $SO_2$ by brick were carried out by investigating the interaction of crushed brick with dilute $H_2SO_4$ and $H_2SO_4$. Crushed brick and the solutions present in the interstices of whole brick perfused with 0.1N $H_2SO_4$ catalyzed the oxidation of $H_2SO_3$ to $H_2SO_4$. The rate of oxidation in the presence of 0.1N $H_2SO_4$ extract of brick was correlated with the concentration of Fe in the oxidizing solution. Removal of total sulphite from $H_2SO_3$ solution (35 mg $SO_2$/L) by crushed brick was found to be not significant at concentrations up to 45,500 mg brick/L.

Glass, N. R., D. E. Arnold, J. N. Galloway, G. R. Hendrey, J. J. Lee, W. M. McFee, S. A. Norton, C. F. Powers, D. L. Rambo, and C. L. Schofield, 1982, Effects of acid precipitation: Environmental Science and Technology, v. 16, no. 3, p. 162-169.

Annotation

All states east of the Mississippi are now affected to some degree by acid precipitation. In order to determine the long-term effects, a short-term study was commissioned by the EPA on the ecology and geology of areas in the eastern U.S. to determine the extent of the effects of acid rain. Surface water sensitivity of lakes and streams, crop sensitivity and forest leaching effects were determined and historical changes in acidity were analyzed. Bedrock geology was studied to determine its reliability as a predictor of the sensitivity of an area to acid deposition. Soil and bedrock geology were mapped according to their sensitivity to acid precipitation. Bedrock containing high concentrations of calcium or calcium and magnesium, such as limestones or dolomites, had a very high buffering capacity while bedrock with low calcium concentrations, such as granites and granitic gneisses, had little or no buffering capacity.

Glass, N. R., G. E. Glass, and P. J. Rennie, 1980, Effects of acid precipitation in North America: Environment International, v. 4, p. 443-452.

Abstract

Recent evidence indicates that acid rain is a growing environmental phenomenon of potentially far reaching consequences and increasing geographical extent in North America. Acid rain is but one aspect of the broader problem of atmospheric deposition which includes snow, fog, and dry deposition of material. First noticed and studied in the Scandinavian countries, acid precipitation has now been well documented in the United States, first in the northeast and more recently throughout much of the United States east of the Mississippi River. Numerous streams and lakes in regions with poorly buffered soils have become devoid of fish, have an impoverished aquatic flora and fauna, and are changing toward conditions of low aquatic productivity. Evidence also indicates that acid precipitation may cause damage to forest growth, crop production, wildlife, and man-made materials such as buildings, metals, paints, and statuary.

Goldfinch, W., 1980, A brickmaker's approach to moisture expansion: Proceedings of the Ninth Australian Ceramic Conference, The Australian Ceramic Society, Sydney, Australia.

Annotation

Moisture expansion in bricks can be controlled to a certain extent. First the long-term (5 year) unrestrained moisture expansion must be determined. Accelerated weathering tests of the bricks made and the clays used in brick manufacture produce results from which long-term expansion can be predicted. The accuracy of these predictions can be tested by comparison with the results of a five-year natural exposure test of expansion. Uniformity of clay proportioning, harder firing of the bricks to reduce moisture expansion, and uniformity of firing are measures that can be taken during production to control long-term moisture expansion in the finished products. Suggestions for reducing moisture expansion are: substitution of low expanding clays for high expanding clays; addition of other materials such as lime, glass, manganese dioxide and basalt fines to help reduce expansion; and grassing the bricks for longer periods of time prior to delivery and use.

Goudie, A. S., 1977, Sodium sulphate weathering and the disintegration of Mohenjo-Daro, Pakistan: Earth Surface Processes, v. 2, no. 1, p. 75-86.

Summary

In Pakistan, various brick building structures are currently disintegrating in the Indus Valley. These include the Harappan site of Mohenjo-Daro. The environment of this site is described, the nature and speed of the disintegration problem is outlined, and the cause of disintegration is discussed. Weathering occurs in association with the development of salt efflorescences and some bricks disintegrate only a few years after being laid down. Chemical and x-ray diffraction analyses show that the predominant salt is the sodium sulphate mineral thenardite. The reasons for its effectiveness are discussed. They include its high solubility, the rapid change with temperature, and its hydration characteristics.

Grant, W. H., 1969, Abrasion pH, an index of chemical weathering: Clays and Clay Minerals, v. 17, no. 3, p. 151-155.

Abstract

If a series of rock samples with granitic composition in various stages of chemical weathering is ground in a mortar with distilled water and the pH of the slurry produced is determined, it will be evident that the pH declines as the weathering increases. This relationship can be made useful by plotting abrasion pH against some other index of weathering such as the percentage of clay mineral or the bulk density of the weathered rock. Factors controlling abrasion pH are the cations such as K, Na, Ca, and Mg and the amount of clay mineral present.

Grim, R. E., and W. F. Bradley, 1948, Rehydration and dehydration of the clay minerals: The American Mineralogist, v. 33, nos. 1-2, p. 50-59.

Abstract

Certain clay minerals, particularly the illites and montmorillonites, regain some hydroxyl water as well as absorbed water on standing at room temperature after being dehydrated by heating to temperatures as high as 800°C. The removal of the recombined hydroxyl water may take place at slightly lower temperature than the original hydroxyl water.

Experimental data are presented showing the rehydration and loss again of the rehydration water together with a discussion of the structural significance of the rehydration.

Annotation

Many common minerals share a structural arrangement of oxygen and hydroxyl ions coordinated about combinations of cations. Fundamental structural units are able to survive extraction of hydroxyl water with moderate readjustment. In the better crystallized examples, hydroxyl water is not easily removed by firing.

Hales, J. M., and M. T. Dana, 1979, Regional-scale deposition of sulfur dioxide by precipitation scavenging: Atmospheric Environment, v. 13, p. 1121-1132.

Abstract

Although sulfate ion is usually the predominant sulfur species found in natural precipitation, dissolved sulfur dioxide often appears as an important constituent as well. Despite this importance, however, relatively few measurements of sulfur dioxide in precipitation are available, owing primarily to difficulties involved in the sampling and preservation of this material.

This paper describes sampling procedures for obtaining valid measurements of precipitation-borne sulfur dioxide, and presents a method for estimating regional wet deposition rates. Trial calculations using this method are compared with observed values for the northeastern United States, and these considerations are utilized to project future trends of total sulfur deposition.

Harrison, W. H., 1981, Conditions for sulphate attack on brickwork: Chemistry and Industry, v. 19, p. 636-639.

Annotation

The expansion and disruption of brickwork can result from the reaction of sulphates in solution with hydrated tricalcium aluminate. Calcium sulphoaluminate (ettringite) is formed and the accompanying expansion inside the mortar joints and accelerated surficial weathering of the mortar are the principal problems of sulphate attack on brickwork. The sulphates can be derived from the bricks and the tricalcium aluminate is a constituent of most Portland cements. Sulphate from the atmosphere is also a viable source and though not considered a serious threat at this time, sulphuric acid in rainwater is thought to cause gradual erosion of the face of the mortar.

Certain conditions are necessary for sulphate attack on brickwork. The mortar must be permeable, contain above 8 percent tricalcium aluminate and remain wet for long periods of time. There must be water movement between brick and mortar and the bricks must contain above 0.5 percent sulphate. All of these conditions must be fulfilled for a serious failure of brickwork due to sulphate attack to occur.

A great deal of research has been done on the effect of sulphate on concrete and the conclusions drawn were considered applicable to the problem of sulphate attack on brickwork. However, significant differences in the effect of sulphate on concrete and brickwork may be caused by the higher porosity of most mortars used in brickwork.

Haynie, R. H., J. W. Spence, and J. B. Upham, 1976, Effects of gaseous pollutants on materials--A chamber study: Environmental Sciences Research Lab, Environmental Protection Agency, Research Triangle Park, NC (EPA/600/3-76/015), 98 p.

Abstract

This document describes a comprehensive laboratory study using specially designed controlled environment exposure chambers to assess the effects of gaseous air pollutants (sulfur dioxide, nitrogen dioxide, and ozone) on a variety of materials. Materials included weathering steel, galvanized steel, aluminum alloy, paints, drapery fabrics, white sidewall tire rubber, vinyl house siding, and marble. The exposure experiment was statistically designed using a two-level factorial arrangement to identify the environmental factors or combination of factors, or both, that cause materials damage. Over 200 different direct and synergistic effects were examined. The study revealed that only 22 of the possible effects were statistically significant at better than a 95 percent confidence level. Sulfur dioxide, relative humidity, and the interaction between them, were the main factors causing effects. A number of empirical functions were developed that relate materials effects to various factors causing the effects. An exceptionally good relationship was obtained for the corrosion of weathering steel.

The lack of statistical significance that was found for the large majority of effects that were studied is equally as important as the significant effects. As a result a large number of materials-pollutant combinations may be excluded from further detailed study.

Annotation

A strong relationship was also found for the attack of pollutants on marble.

Hileman, B., 1981, Acid precipitation: Environmental Science and Technology, v. 15, no. 10, p. 1119-1124.

Annotation

The causes and environmental effects of acid precipitation are discussed. Although the pH of "normal" rainfall is 5.6, the pH of natural rainfall varies. Precipitation with a pH of less than 5.6 is said to be acidic. Some areas of Canada and the eastern U.S. receive precipitation measured to be about forty times more acidic than "normal" rain.

Acid precipitation causes the corrosion of marble and stone work. In Europe, it accelerates the deterioration of historical buildings and monuments. However, because the effects of acid precipitation are similar to the effects of $SO_2$ and other pollutants, culpability is difficult to assess.

Hoffmann, D., P. Schimmelwitz, and H. Rooss, 1976, Interactions of sulfur dioxide with lime plasters: Second International Symposium on the Deterioration of Building Stones, Athens, Greece, p. 37-42.

Annotation

The hardening and weathering of lime plasters used to protect and preserve monuments were studied. Test results indicated complex reaction mechanisms of $SO_2$ attack on lime plasters.

The rate of deterioration decreased due to the formation of carbonates from oxide and hydroxide cement phases. Carbonates are less susceptible to $SO_2$ attack.

Gypsum and $CaSO_3.\frac{1}{2}H_2O$ were found to be weathering products of lime plaster while $MgSO_3.6H_2O$ was formed from the weathering of dolomitic lime plasters.

Hoke, E., 1976, Microprobe investigations on incrusted as well as cleaned marble specimens: Second International Symposium on the Deterioration of Building Stones, Athens, Greece, p. 119-125.

Annotation

The electron microprobe is useful in determining the chemical composition of corrosion crusts. Once the composition is known, the most effective cleaning process can be chosen and applied.

Cleaning pastes containing EDTA are effective against some sulphate crusts. The paste converts salts such as $CaSO_4$ into water soluble compounds. However, there are limitations to any treatment. Pastes containing EDTA do not work well on hydrophobic substances or on non-EDTA-soluble silicates.

Impregnation of the cleaned stone surface is necessary to prevent further atmospheric attack.

Holland, A. E., and T. J. Stevens, 1968, Effect of vacuum on moisture expansion of a fired clay: Claycraft and Structural Ceramics, v. 41, no. 10, p. 341.

Annotation

An apparatus is decribed in which a clay body can be fired, cooled, and remain for observation for any length of time while being continuously measured and in vacuum. After firing and cooling the specimens did not expand more than $10^{-4}$ inches while in vacuum; but when air was admitted to the chamber an expansion of $4 \times 10^{-4}$ inches occurred.$_4$ Those specimens that were not fired in vacuum expanded up to $10 \times 10^{-4}$ inches. The reducing conditions present during firing in vacuum produced the smallest moisture expansion. An atmospheric component, probably water, is responsible for moisture expansion in fired clay bodies.

Hosking, J. S., 1979, Ceramic bodies and their chemically sorbed water: Journal of the Australian Ceramic Society, v. 15, no. 1, p. 1-4.

Annotation

Chemical sorption of water by fired clay bodies was studied by examining the behavior of clay bodies made from clays of differing chemical and mineralogical composition and fired at different temperatures. Some of the bodies were exposed to laboratory conditions while comparable bodies were exposed out of doors. The fired clay bodies were tested periodically to determine their chemically sorbed and physically sorbed water content. The moisture content of the laboratory bodies increased with increased exposure time and decreased as the initial firing temperature increased. The outdoor specimens' moisture content showed no distinct relationship with either exposure time or initial firing temperature. The amount of water chemically sorbed was roughly comparable for both indoor and outdoor exposure conditions. The chemically sorbed water content for both exposure conditions increased with time and decreased as the initial firing temperature increased; the relationship between the physically sorbed water, firing temperature, and exposure time depended on the ambient exposure conditions. The total water content was found to be closely related to the chemically sorbed water content of the brick, independent of the initial firing temperature. The physical condition and internal surface properties were more important in determining the amount of water chemically sorbed by fired clay bodies than the original chemical and mineralogical composition.

Hosking, J. S., and H. V. Hueber, 1963, Dimensional changes due to moisture in bricks and brickwork: American Society for Testing Materials, Special Technical Publication 320, Proceedings of the 65th ASTM Annual Meeting, Symposium on Masonry Testing, p. 107-126.

Abstract

A detailed seven-year study has been made of the moisture expansion of clay products, with special emphasis on bricks and the consequent damage to brickwork. Methods have been developed for measuring the expansion of bricks and brickwork under varying conditions of exposure. These methods are described, and the results are briefly discussed with reference to the influence of various factors on the rates and magnitude of expansion. Finally, the possible causes and kinetics of expansion are considered and estimates made of the likely maximum expansion of brickwork. Results have shown that bricks expand on leaving the kiln, and expansion of brickwork in buildings can reach more than 2 in. per 100 ft.

Hosking, J. S., H. V. Hueber, and A. E. Holland, 1965, Long-term expansion and contraction of clay products: Nature, v. 206, no. 4987, p. 888-890.

Annotation

Results of long-term moisture expansion tests indicate that in some cases expansion is followed by contraction of the brick. A steady state is not achieved after maximum expansion is reached as was previously believed. The implications of this discovery are discussed. (Further study revealed equipment error was responsible for the apparent contraction. No actual contraction occurred. An explanation is given in Stevens, Holland, and Hosking, 1965.)

Hosking, J. S., W. A. White, and W. E. Parham, 1966, Long-term dimensional changes in Illinois bricks and other clay products: Illinois State Geological Survey Circular 405, 44 p.

Abstract

A four-year study has been made of the long-term dimensional changes in Illinois clay bricks and in laboratory test bars made from clays used in various ceramic products manufactured in Illinois. Results have been compared with those for Australian bricks and laboratory test bars that have been studied for up to ten years.

The Illinois bricks, like those in Australia, expanded when exposed to the atmosphere, after leaving the kiln, and this expansion has continued for the four years of exposure. A number of the Illinois bricks, however, have shown little change for some time, and none has reached the stage of continuous contraction after earlier expansion now shown by most of the Australian bricks.

General behavior patterns of the Illinois and Australian laboratory test bars are similar when expansions are considered in relation to the temperatures of firing. The expansions of the three varieties of Illinois brick--common, red-facing, and buff-facing--are low compared to the Australian bricks. The low expansions of the common bricks correspond with the relatively low expansion of their clays at all temperatures of firing, and in this respect the common bricks resemble the low-expanding red bricks from Adelaide, South Australia. The low expansions of the red- and buff-facing brick, compared with those in Australia, are explained on the basis of their higher industrial firing temperatures. The magnitudes of expansion of the Illinois ceramic bodies are related to the contents of kaolinite and illite as well as to those of other components of the clays.

A lower incidence of damage in Illinois brickwork, compared with that in parts of Australia, has been attributed partly to the higher firing temperatures and the consequently lower expansion of the bricks, and partly to the more general practices of using lime-rich mortars, of allowing movement joints in the brickwork, and, in some cases, to long distance haulages that allow some expansion in the bricks before use.

Hosking, J. S., H. V. Hueber, E. H. Waters, and R. E. Lewis, 1959, The permanent moisture expansion of clay products. I. Bricks: Division of Building Research Technical Paper No. 6, Commonwealth Scientific and Industrial Research Organization, Australia, 56 p.

Abstract

It has been found that clay bricks start to expand permanently as soon as they are exposed to the atmosphere after leaving the kiln. This expansion is sufficient to account for much of the cracking of brick-work structures previously considered to be due to other causes.

Measurements of expansion have been made on some 500 bricks representing the raw materials and types used in Melbourne and Sydney, following their exposure to air both in an air conditioned laboratory and out of doors, to cycles of soaking and drying, and to saturated steam at 200°C. The expansion of and damage to brick-work in experimental brick walls and many actual buildings have also been investigated.

The raw material, temperature of firing, and possibly the method of manufacture all affect the rate and extent of expansion, and the influence of each and the causes of expansion are discussed.

From the expansions of individual bricks and experimental brick walls the extent to which brick-work may be expected to expand in practice has been estimated for the various types and varieties of brick examined. These expansions have been discussed in relation to the movement and damage in actual buildings. To prevent damage through expansion it is recommended that (1) only well-burnt bricks be used, (2) all bricks be allowed to stand as long as possible before use, (3) lime-rich mortars be used instead of strong cement mortars, and (4) efficient movement joints be provided at sufficiently frequent intervals to take up expansion of the bricks.

Houston, J. T., and C. T. Grimm, 1973, Field quality control test for wetting brick in masonry construction: Journal of the Construction Division, American Society of Civil Engineers, v. 99, no. CO1, Proc. Paper 9839, p. 5-10.

Abstract

Obtaining desired water tightness and adequate bond strength of brick masonry may require the prewetting of brick. An inexpensive and convenient field test is suggested for determining the necessity of prewetting: Select a representative sample of five brick specimens. With a wax pencil draw two 1-in. diameter circles on a bed area of each brick--; with a medicine dropper place 20 drops of water within each circle in 10 ± 2 sec--do not overflow the circle; average the time from the placement of the last drop for all the water to be absorbed for each of the five bricks; and if the average time is less than 10 min. wet the brick prior to laying; if not, wetting is not required.

Howden, M. G., 1977, Activation energy of moisture expansion of some fired clay bricks: Transactions and Journal of the British Ceramic Society, v. 76, no. 2, p. 27-30.

Abstract

A relationship between the rate of moisture expansion of fired clay bricks in an atmosphere saturated with water vapor as a function of the activation energy and the absolute temperature is given. The activation energy of the expansion of two brick clays was determined. It was found that the value of the activation energy was not constant; however, on average the value was around 70 to 75 kJ $\text{mole}^{-1}$. This paper demonstrates that an autoclave may be used to predict the expansion that will take place at ambient temperatures.

Hudec, P., 1978, Rock weathering on the molecular level: Geological Society of America, Engineering Geology Case Histories No.11, p. 47-51.

Abstract

The major causes of weathering can be ascribed to two factors: water and temperature. The classical concepts of weathering call upon water (1) to freeze in pores and cracks of rock, and by its volume expansion, cause the rock to break--so-called physical weathering; and (2) to dissolve, hydrate, and leach the rock--chemical weathering. The above concepts explain the end products but do not explain the actual process of weathering in both categories.

Weathering of rock under all climatic conditions begins with the interaction of the water molecule and the mineral surface. Water, a highly polar fluid, is attracted to the mineral surface by residual Van der Waal's forces, and forms the extension of that surface. Such water has lower vapor pressure, is unfreezable, and possesses certain "rigidity" and force of "crystallization."

The statistical relationship is obtained between the internal surface area of 26 rock specimens and their various physical properties. It is seen that the internal surface area has a significant direct and/or indirect effect on most of the rock properties considered.

Annotation

The interesting correlation is made between percentage of water frozen and percentage of water freezable, and both parameters are tested for several aggregate samples. These determinations are of special interest because water in very small pores has been shown to be structured and therefore unfreezable. Effects often assumed to be due to freeze-thaw apparently are properly caused by pore-water interactions.

Hueber, H. V., and A. A. Milne, 1955, Expansion and deterioration of ceramic bodies: Nature, v. 176, p. 509.

Annotation

Irreversible expansion of kiln fresh bricks occurred on exposure of the bricks to the atmosphere or to moisture. A linear expansion of from 0.04 to 0.8 percent was observed when the bricks were soaked in water. Although bricks fired at lower temperatures showed a greater rate of expansion, the degree of expansion depended more on the composition of the raw material than on the firing temperature.

The authors concluded that the formation of zeolites, mainly permulites, was the cause of expansion on rehydration of ceramic bodies burnt above 950°C.

Hughes, R. E., B. L. Bargh, and W. A. White, 1981, Expansion and weathering of brick: Proceedings of the 18th Forum on the Geology of Industrial Minerals, Bloomington, Indiana (in press). See Appendix II.

Abstract

This paper reviews research on alteration of brick by expansion and summarizes preliminary results of a new study of the weathering of bricks. Damage caused by moisture expansion of brick, including the rate and absolute amount of expansion, is illustrated in a series of photographs and graphs. Graphs of expansion through time show that the following factors are significant: kiln design (underfired brick from cooler areas of a beehive kiln expand more than brick fired in other parts of the kiln); clay content (illite-rich bricks expand greatly at certain temperatures, whereas kaolinite-rich bricks show less expansion); environment, especially conditions of exposure (bricks stored outdoors expand at a greater rate than similar ones stored in the lab); mineral composition and/or additives (MgO and fluorite additions reduce expansion while $K_2O$ additions increase it); and preventive measures (steam treatment during cooling of brick causes pre-expansion and reduces subsequent expansion during usage).

A background study on weathering of bricks was prompted both by the specific concern about the effects of acid rain on historic, present, and future brick structures and by the general need for basic information on the alteration of bricks--whatever the mechanism.

Husar, R. B., J. P. Lodge, D. J. Moore eds. , 1977, Sulfur in the atmosphere: Proceedings of the International Symposium at Dubrovnik, Yugoslavia, Atmospheric Environment, v. 12, 796 p.

Annotation

This proceedings presents a wide range of papers dealing with every aspect of sulfur in the atmosphere. Actual measurements, laboratory simulations, and results of computer modeling show the complexity of the $SO_x$ problem. An article by J. A. Garland (Dry and wet removal of sulphur from the atmosphere, p. 349-362) suggests that about one half of emitted $SO_2$ is removed from the atmosphere as dry deposition and about one half as sulfate in precipitation. Garland also estimates the average residence time of sulfur in the atmosphere to be about 5 days.

Hyvert, G., 1978, Weathering and restoration of Borobudur Temple, Indonesia: Geological Society of America, Engineering Geology Case Histories No. 11, p. 95-100. (Note: This manuscript was prepared by E. M. Winkler from lecture notes of Giselle Hyvert.)

Summary

The purpose in choosing work techniques was to stop the alterations and to give back to the stones a homogeneity of color without removing the natural patina. Modification of the actual aspect of the monument was not intended, and the use of chemicals on the outer stones will be severely restricted.

The outer surface contains 240,000 blocks of stone. The reliefs of the walls represent 33,100 blocks plus 30% from the balustrades. To this average must be added the 482 statues of Buddha to be cleaned and restored. Of these, 258 are headless; there are 54 heads for which so far only 15 corresponding bodies have been found (Fig. 6). The duration of the work on stone conservation will be around 5 1/2 years with a 42-hour work week for 150 workers and 52 specialists.

The important search program and the trials in the field have been possible because all specialists, Indonesians or foreigners, have followed the same working plan for the fundamental research. All work has always been done in excellent team spirit.

Johnson, N. M., 1979, Acid rain: neutralization within the Hubbard Brook ecosystem and regional implications: Science, v. 204, p. 497-499.

Abstract

The neutralization of strong acids from precipitation is largely accomplished (75 percent) in the soil zone by rapid reaction with basic aluminum salts and biologic matter. On a regional basis, acidified and aluminum-rich lakes and streams in New England are confined mainly to low-order watersheds.

Judeikis, H. S., and T. B. Steward, 1976, Laboratory measurement of $SO_2$ deposition velocities on selected building materials and soils: Atmospheric Environment, v. 10, p. 769-776.

### Abstract

Measurements of $SO_4$ deposition velocities have been carried out in the laboratory utilizing a cylindrical flow reactor. Analysis of data from these experiments was carried out using models that specifically account for diffusive transport in the system. Consequently, the resulting deposition velocities were independent of diffusion processes and represent the maximum removal rates that would be encountered in the environment under turbulent atmospheric conditions. The measured values range from 0.04 cm $s^{-1}$ for asphalt to 2.5 $cm^{-1}$ for cement, and were found to be independent of $SO_2$ and oxygen concentrations, as well as relative humidity and total pressure.

Prolonged exposure to $SO_2$ eventually destroyed the ability of the various solids to remove this species. Overall capacities were found to increase significantly at moderate relative humidities yielding values of 0.4-2.8 g $SO_2$ $m^{-2}$ of solid in moist systems. Several experiments indicated that the reactivity of a solid subjected to prolonged $SO_2$ exposures could be restored by washing the surface with distilled water or exposing the spent solid to ammonia. Some implications of these findings with regard to the environment are discussed.

Judeikis, H. S., and A. G. Wren, 1978, Laboratory measurements of NO and $NO_2$ depositions onto soil and cement surfaces: Atmospheric Environment, v. 12, p. 2315-2319.

### Abstract

Laboratory measurements have been made of the deposition of NO and $NO_2$ onto selected soil and cement surfaces. Experimental results yielded deposition velocities of 0.1-0.2 cm $S^{-1}$ for NO and 0.3-0.8 cm $S^{-1}$ for $NO_2$ over freshly prepared surfaces. Deposition was largely irreversible and decreased with time (exposure to NO or $NO_2$). The latter observations indicate a finite capacity of these surfaces for removal of the gaseouos species. However, additional experiments carried out in this study suggest that surface activity in the environment can be regenerated, in the case of $NO_2$, but not NO, by interaction with atmospheric ammonia. The results further suggest, that for both NO and $NO_2$, surfaces can be reactivated by precipitation washing away soluble surface reaction products. The lower deposition rates and capacities, and more limited regeneration of surface activity observed for NO, relative $NO_2$, suggest that uptake of NO by ground level surfaces in the environment will be considerably less important than that of $NO_2$.

Junge, C. E., and R. T. Werby, 1958, The concentration of chloride, sodium, potassium, calcium, and sulfate in rain water over the United States: Journal of Meteorology, v. 15, no. 5, p. 417-425.

Abstract

The distribution of yearly averages of the concentration of various inorganic ions in rain water over the United States is discussed. The major source of $Cl^-$ is the ocean. The $Cl^-/Na^+$ ratio, however, is considerably less than that in sea water. It is very likely that this is caused by excess $Na^+$ from the soil. A similar distribution of excess material from the soil is observed with $K^+$. In contrast to $Na^+$ and $K^+$, which are rather uniformly distributed over the United States, $Ca^{++}$ shows highest values over the Southwest, in agreement with the occurrence of dust storms.

Most of the $SO_4^{--}$ over the ocean originates from sea spray. The source of additional $SO_4^{--}$ is the land. Budget considerations indicate that about 30 percent of this additional $SO_4^{--}$ on a global scale is due to human activities.

On the basis of the data presented, the average global residence time of $SO_2$ is estimated to be 40 days. This value is compared with available data on residence times of other constituents which are also primarily controlled by washout.

Keller, W. D., 1978, Progress and problems in rock weathering related to stone decay: Geological Society of America, Engineering Geology Case Histories No. 11, p. 37-46.

Annotation

This article reviews general principles of weathering and evaluates the various agents that are active in stone decay. Examples are given of the complex geochemical reactions that occur during weathering. Keller emphasizes the important rule of weathering that is summarized in the following quote: "Weathering obeys the so-called law of stability of rocks and minerals; namely, that a rock or mineral is stable so long as it remains in the environment of its formation, but if the environment of residence changes, the rock or mineral tends to change to a new form stable under the new environment."

Likens, G. E., and F. H. Bormann, 1974, Acid rain: a serious regional environmental problem: Science, v. 184, p. 1176-1179.

Abstract

At present, acid rain or snow is falling on most of the northeastern United States. The annual acidity value averages about pH 4, but values between pH 2.1 and 5 have been recorded for individual storms. The acidity of precipitation in this region apparently increased about 20 years ago, and the increase may have been associated with the augmented use of natural gas and with the installation of particle-removal devices in tall smokestacks. Only some of the ecological and economic effects of

this widespread introduction of strong acids into natural systems are known at present, but clearly they must be considered in proposals for new energy sources and in the development of air quality emission standards.

Likens, G. E, R. F. Wright, J. N. Galloway, and T. J. Butler, 1979, Acid rain: Scientific American, v. 241, no 4, p. 43-51.

Annotation

This article illustrates the profound increases in acidity that the authors suggest occurred in the past twenty years or so in both the eastern U.S. and Europe. Their data from Europe are reliable and suggest recognizable correlations between sources of $SO_x$ and acid precipitation. The relationships shown for the eastern U.S. are thought to have been affected by dust storms in 1955-1956 (see Semonin, 1981).

Estimates of current and future $SO_x$ emissions are given in this paper for both the U.S. and Europe. The authors also point to emissions from tall smoke stacks as transforming a local problem into a regional one. Plots of hydrogen ion versus time for various cities and comparisons of precipitation chemistry in polluted versus unpolluted areas in Europe clearly suggest $SO_x$ and $NO_x$ as causes of the acidity; available evidence also suggests a strong correlation between acidity and time.

Plans to expand the use of coal without increased control of emissions are seen by the authors as leading to great potential for continued environmental harm. This work also outlines the areas where bedrock geology creates sensitivity to acid rain.

Llewellyn, H. M., and B. Butterworth, 1964, Laboratory tests and the durability of bricks. III. Some conventional laboratory freezing tests: Transactions of the British Ceramic Society, v. 63, no. 11, p. 629-637.

Abstract

The results of a simple form of laboratory freezing test on bricks are reported and compared with those of outdoor exposure tests. The work was done in 1932-33. Some of the laboratory tests gave results inconsistent with those of outdoor exposure, and these anomalies led the Building Research Station to abandon routine freezing tests in favor of indirect methods of assessing frost resistance until further progress had been made in understanding the mechanism of frost action.

Longinelli, A., and M. Bartelloni, 1978, Atmospheric pollution in Venice, Italy, as indicated by isotopic analyses: Water, Air, and Soil Pollution, v. 10, p. 335-341.

Abstract

Rainwater samples collected in Venice over a period of about 1 year were studied along with stone samples collected from buildings and monuments. Isotopic measurements of O, S, and C were carried out on rainwater, rainwater dissolved sulfate, carbonate in stone, and sulfate present in altered limetone, with the purpose of proving that atmospheric pollution is mainly responsible for the deterioration of monuments and buildings. The results obtained lead to the conclusion that, in spite of the geographic position of the city, atmospheric sulfate in Venice is basically tied to the emission of anthropogenic $SO_2$ and that only minor contribution can be expected from seawater spray and aerosols. The measurements carried out on stone samples clearly indicate that stonework is damaged by the interaction between limestone and S-bearing atmospheric pollutants.

McDowall, I. C., and R. Birtwistle, 1971, Predicting the long-term moisture expansion of fired clay products: Proceedings of the Second International Brick Masonry Conference, published by the British Ceramic Research Association Stoke-on-Trent, 5 p.

Abstract

The literature on moisture expansion of fired clay bodies is briefly reviewed. Details are given of a method for accelerating the rate of expansion, which can be completed in 24 hours or less, and gives results which correlate well with the behavior of similar bricks exposed to ambient conditions for periods up to 4 years. Correlation of accelerated and natural expansion is based on 1479 observations of 378 pairs of bricks drawn from all over Australia, and the results are used to provide a basis for predicting the long-term size change of bricks. Sources of variability in the results are investigated and confidence limits are established for the predictions of long-term growth. The methods developed are thought to be valid for measurements made at or near sea level, on Australian bricks which have a range of moisture expansion from zero to 0.25% in 5 years' exposure to ambient conditions. Some modification to the conversion factors used may be needed in other localities.

The practical implications of the work for brick manufacturers and for designers of brick buildings are briefly outlined.

Meierding, T. C., 1981, Marble tombstone weathering rates: A Transect of The United States (unpublished report): Geography Department, University of Delaware, Newark, Delaware, 20 p.

Abstract

Mean weathering rates measured on marble tombstones appear to vary linearly with mean annual rainfall at locations along the 10°C mean annual isotherm in the United States. Chemically induced granular weathering is the dominant mechanism. Weathering is most rapid on upper portions of stone faces, which recede at about 1mm/1,000 yrs where mean annual rainfall is 200mm/yr and 16mm/1,000 yrs when rainfall is 1,000mm/yr. These rates are about fifty percent greater than on central inscribed portions of vertical faces and on upward-facing horizontal slabs. Weathering rates on marble tombstones are perhaps one-quarter of those reported for limestone denudation in locations with similar climates and about one-half of the rates on marble tombstones in heavily polluted environments. Preliminary work in a high mountain environment with a mean annual temperature of 2°C indicates that marble weathering rates are an order of magnitude greater than at 10°C, probably because of frost weathering. Where sprinkler irrigation is used in semi-arid localities, tombstones show mechanical spalling, exfoliation and pitting, and weathering rates are one to two orders of magnitude greater than where sprinkling is not used.

Morgan, W. R., 1941, Effect of repeated wetting and drying on physical properties of a clay body: Journal of the American Ceramic Society, v. 24, no. 3, p. 84-88.

Abstract

Specimens of fine-grained, red-firing clay, which had been fired to temperatures corresponding to various stages of vitrification, were subjected to 200 cycles each of wetting at 100°F. and 60% of relative humidity. This treatment, simulating weathering in mild climates, caused (1) a permanent gain in weight which was greater for the softer specimens; (2) a moisture expansion for the softer specimens but none for those near vitrification; (3) a fairly uniform decrease in modulus of elasticity for all specimens; and (4) a decrease in modulus of rupture for the softer specimens but an increase in strength for those that were completely vitrified. The data indicate that moisture expansion and a decrease in strength of soft-fired clay bodies, caused by repeated wetting and drying, may be eliminated by proper vitrification.

Newman, A. J., and D. Whiteside, 1981, Water and air penetration through brick walls--a theoretical and experimental study: Transactions and Journal of the British Ceramic Society, v. 80, p. 17-26.

Abstract

This paper investigates the penetration of water through 100 mm single-leaf brickwork, such as that found in the outer leaf of external cavity walling. Small panels, built to a standard typical of that found in practice, were wetted on their external face at a rate corresponding to severe storm conditions. Several pressure differences were imposed across the walls to imitate different wind speeds. Measurements were also made of air leakages through the same walls.

It was shown that after saturation a high proportion of the applied water was able to pass through wall panels which from visual inspection of their external face would be said to be "well built." This applied even when there was no pressure difference across the wall, although imposed pressures did increase penetration. It was confirmed that leakage occurs primarily through cracks between brick and mortar at their interface. Measurements of air leakage indicated that these cracks were on average 0.1 mm across.

A mechanism is proposed for water transfer through brickwork in terms of simple hydrodynamic theory. The leakage to water was considerably lower than that which one would expect from corresponding measurements of air leakage. Experiments indicate that this is at least partly due to air entrainment and movement of brickwork with varying moisture content. However, these processes appear to be well ordered and reproducible, so that a good correlation existed between water and air leakage. This suggests that a method of assessment based on the latter property could be developed.

Nriagu, Jerome O., ed. , 1978, Sulfur in the environment. Part II: Ecological impacts. New York: John Wiley and Sons, 482 p.

Annotation

Part II summarizes the presence and effects of sulfur compounds in the environment. The occurrence and results of air- and water-born pollution are summarized, and specific effects on materials, plants, and animals are illustrated. In the first chapter, Nriagu evaluates the effect of acid deposition on metals, building stone, paint, paper, and wood. He has an especially interesting section on metal corrosion, and clearly shows the potential for rapid loss of metals in polluted areas.

Palmer, L. A., 1931, Volume change in brick masonry materials: National Bureau of Standards Research Paper, RP321, Journal of Research, v. 6, p. 1003-1026.

Abstract

Volume changes in bricks and mortars attending variations in moisture content and temperaure have been studied. There were included in the study 21 cements (both Portland and masonry), 7 limes, and 8 makes of brick received from various sections of the United States. The shrinkage of mortars during hardening and the alternate expansion on wetting and shrinkage on drying occurring subsequent to hardening have been measured. Varying the moisture content produced far smaller volume changes in well-burned brick than in most of the mortars. Under-burned brick expanded appreciably on wetting. It is indicated that differential volume changes between brick and mortar caused by variation in moisture content are apt to be greater than those produced by normal temperature variations. Volume changes in hardened mortars were least in the case of straight lime-sand mortars.

Annotation

The thermal coefficients of the bricks ranged from a low of 0.36 x $10^{-5}$ per °C for the fireclay bricks to a high of 0.85 x $10^{-5}$ per °C for the most porous bricks. Under-burned bricks exhibited the greatest expansion during prolonged soaking. Expansion that occurred during prolonged immersion in water was relatiely uneffected when the specimens were dried for one week at approximately 150°C.

When the bricks were kept well-saturated during freezing and thawing cycles there was a small increase in apparent porosity. This was accompanied by a small and relatively slow expansion of the bricks though the expansion was rapid for under-burned bricks.

Poundstone, W. N., 1981, Let's get the facts on acid rain: Mining Congress Journal, v. 66, no. 7, p. 45-47.

Annotation

The degree to which the acidity of recent precipitation is due to man-made or natural sources is undetermined. It is known that more than 70% of the total atmospheric sulfates come from natural sources and natural atmospheric nitrates contribute more than 90% of the nitrates in the atmosphere. Though Eastern rain is acid there has been no change in it in two decades of sampling. There is no evidence of environmental damage caused by acid rain. During the last twenty-five years acid rainfall has supposedly been increasing while the total sulfur dioxide emitted by coal-burning power plants has only increased slightly.

Riederer, J., 1978, Recent advances in stone conservation in Germany: Geological Society of America, Engineering Geology Case Histories No. 11, p. 89-94. (Note: This manuscript was prepared by E. M. Winkler from lecture notes of Josef Riederer.)

Summary

The development of new products based on synthetic resins or ethyl silicate is the result of continuous research by universities and industry. More indicative of progress in stone conservation is the fact that the people responsible for the preservation of monuments now are aware that these monuments, sculptures, and buildings cannot be preserved by a single treatment but need regular maintenance. One of the main reasons for the rapid stone decay in our time is that objects treated 20 and 30 years ago were left untended. Therefore, weathering started again after some time and continues inflicting damage at an even higher rate than before. The trend now is to develop products that can be reapplied after a certain time, so that continuous protection is possible. The change in attitude of the people responsible for stone conservation, together with the progress in various fields of protection techniques, gives us hope that our cultural heritage can be preserved with greater efficiency.

Ritchie, T., 1966, The influence of efflorescence on decay and expansion of mortar: Journal of the Canadian Ceramic Society, v. 35, p. 92-95.

Abstract

A particular case of cracking and spalling of masonry mortar was attributed to the migration of soluble salts from the brick to the mortars and showed that their expansion was influenced by soluble salts in bricks. Efflorescence is therefore considered to be more than a problem of aesthetics; it may affect the dimensional stability and durability of masonry.

Ritchie, T., and J. I. Davison, 1963, Factors affecting bond strength and resistance to moisture penetration of brick masonry: American Society for Testing and Materials, Special Technical Publication 320, Proceedings of the 65th ASTM Annual Meeting, Symposium on Masonry Testing, p. 16-30.

Summary

The resistance of brick masonry to moisture penetration and the strength of bond between brick and mortar primarily depend on the properties of the materials used and the manner in which brick and mortar are brought together to form masonry. Leakage may take place through the brick, depending on its permeability, but more usually it occurs through channels at the brick-mortar interface. In this connection the extent of bond between brick and mortar is critical and depends largely on the condition of the upper surface of the mortar bed when a brick is laid in it.

Factors affecting the condition of the mortar at the time of bricklaying include the rate of water absorption of the bricks on which the mortar is spread, the inherent resistance of the fresh mortar to loss of moisture (water retention value) and the amount of water in the fresh mortar, the thickness of the mortar bed, the length of time that elapses before a brick is placed in the mortar, and the energy used to bed a brick.

The strength of bond between brick and mortar also depends on the nature of the bond between the two. A particular brick and mortar combination may, however, have a complete extent of bond at interface and have relatively low strength of bond, whereas another combination may have a "patchy" or incomplete extent of bond with greater strength. The extent of contact between brick and mortar and the tensile strength of the mortar appear to influence the bond strength.

A selection of typical test results involving almost 1000 panels illustrates the effects of various factors on the properties of masonry. The extent of these effects is frequently difficult to assess because the factors are interdependent. A certain factor may be important under one set of conditions and have little significance when these conditions are varied by using materials having different properties or by altering bricklaying techniques.

In practice, deficiencies in the properties of materials may be recognized and partially compensated for by the bricklayer. For example, he may call for a very fluid mortar to offset high suction of the brick being used, or he may shorten the "string-out" of a mortar bed to compensate for its low water retention properties. Inconsistent results in some tests, however, indicate that there are unrecognized factors, or combination of factors, affecting properties of masonry.

Robinson, G. C., J. R. Holman, and J. F. Edwards, 1977, Relation between physical properties and durability of commercially marketed brick: American Ceramic Society Bulletin, v. 56, no. 2, p. 1071-1079.

Abstract

The relation between strength and absorption properties and the resistance to freezing and thawing of 5,217 commercial brick was analyzed. Statistical analysis showed no acceptable relation between individual properties or combinations of properties and the resistance of the brick to freezing and thawing. The present specification for brick is inadequate because it may accept as many as 22.8% nondurable brick and, at the same time, reject as many as 31.5% durable brick. The saturation coefficient is the only specification that presently discriminates between durable and nondurable brick. The use of <8% absorption as a waiver for the saturation coefficient was found to be valid, but the use of >8,000 psi strength was found to be an unacceptable waiver. A sequential property specification is proposed as a replacement for the present specification.

Rodrigues, J. D., 1976, Estimation of the content of clay minerals and its significance in stone decay: Second International Symposium on the Deterioration of Building Stones, Athens, Greece, p. 105-108.

Annotation

The deterioration of stone may be accelerated by a high content of expandable clay minerals. Direct and indirect methods of estimating clay mineral content are considered. The moisture absorption of the stone could be used to estimate the clay mineral content as water retention is thought to be mainly due to the presence of clay minerals in pores. Of the rock types tested, basic rocks exhibited the greatest moisture expansion. No single method tested is useful for all types of rocks.

Ross, C. W., 1941, Thermal expansion of clay building bricks: National Bureau of Standards Research Paper, RP1414, Journal of Research, v. 27, p. 197-216.

Abstract

The coefficients of thermal expansion of 139 bricks were measured over the range -10° to +40°C (14° to 104°F). These bricks included 1 sample of sand-lime, 9 of fire-clay, and 61 of clay and shale bricks. The clay and shale bricks represented a wide range in properties and included samples from various districts in the United States.

The coefficients of 87 percent of the clay and shale bricks were between 5 and 7 millionths per °C (2.8 to 3.9 per °F). The average coefficient of the clay bricks was 6.0 (3.3), of the shale bricks 6.1 (3.4), and of the fire clay bricks 3.9 millionths per °C (2.2 per °F). No relation was observed between the thermal expansion and the other physical properties of the bricks.

Rossi-Manaresi, R., 1976, Causes of decay and conservation treatments of the Tuff of Castel Dell'Ovo in Naples: Second International Symposium on the Deterioration of Building Stones, Athens, Greece, p. 233-247.

Annotation

Results of accelerated weathering tests confirmed that the deterioration was due mainly to physical weathering processes. Moisture expansion and repeated wetting and drying cycles, during which seawater containing chloride was absorbed by the tuff, contributed to the decay. The crystallization of salts from solution during the drying cycles weakened the structure of the rocks.

Five different impregnation products were tested. Only one treatment proved to be an effective preservation treatment.

Schaffer, R. J., 1932, The weathering of natural building stones: Great Britain Department of Scientific and Industrial Research, London, Building Research Board, Special Report No. 18, 149 p.

Annotation

A detailed assessment of natural and anthropogenic-induced weathering is given in this report. This study gives early recognition to the formation of gypsum crusts in areas sheltered from rain and shows the tremendous potential for damage from "acid gases." Some early attempts at restoration and preservation are presented, and the potential for accelerated weathering after restoration is shown. The interesting phenomena of decay of stone as a result of placement of dissimilar rock types in contact in a structure is illustrated. The report includes a discussion of virtually every agent of weathering: temperature change, moisture expansion, frost, erosion, evaporation, capillary effects, florescences, crystallization forces and effects, and the effect of living organisms. Tables on pages 59 and 60 show that the compositions of florescences on bricks, terra-cotta, and stone are largely sulfates. Methods to test durability of building materials are illustrated, and the last chapter attempts to distinguish between artificial and natural weathering. This report is an excellent reference to the field of building stone decay.

Segnit, E. R., 1970, Moisture expansion and formation of glass in fired clay products: Journal of the Australian Ceramic Society, v. 6, no. 1, p. 25-28.

Annotation

The effect of glass in fired clay bodies for which the moisture expansion is already known is examined. The glass is derived from a liquid phase formed during firing. Experiments on American, Australian, and English clays are studied and considered, and the results indicate that the glass phase in a fired clay body is not a major contributor to the degree of moisture expansion. It is shown that as the glass content of a fired clay body increases, the moisture expansion decreases, partly due to the decrease in surface area and porosity resulting from the increasing vitrification of the clay body.

Semonin, R. G., 1981, Acid rain: Is it a recent problem?: Proceedings of the Illinois Mining Institute, Springfield, Illinois, p. 19-29.

Abstract

A reassessment of data on chemistry of Illinois precipitation for 1953-1954 revealed excessively high values, as compared to current measurements, of the elements calcium and magnesium. This feature was also found in the 1955-1956 data for the United States. The most likely explanation for this feature is that much of the U.S. experienced a severe drought with accompanying duststorms during the 1950's. The precipitation events during the drought partially scavenged the high ambient loadings of crustal dust leading to high concentrations of calcium and magnesium. The pH of 1953-1956 precipitation samples, calculated by an ion-balance equation, is shown to be very sensitive to the concentration of these cations as well as the pollutant-related sulfate and nitrate anions. In an attempt to depict the non-drought acid rain distribution in the 1955-1956 period, a reduction of the calcium and magnesium concentrations was made and pH values recalculated. The resulting pattern of pH for 1955-1956 shows a much larger areal extent of acid rain in the eastern U.S. and conforms relatively well to currently observed values. These results suggest that the downward pH trend since the mid-1950's due to the increase of acid-forming emissions is much smaller than previously estimated. The basic influence on the precipitation chemistry of a major drought was not considered previously. The drought-corrected pH trend is small and may well be within the errors of the total measurement and analysis system.

Shriner, D. S., C. R. Richmond, and S. E. Lindberg, 1980, Atmospheric sulfur deposition--environmental impact and health effects: Proceedings of Second Life Sciences Symposium on Potential Environmental Impact and Health Effects of Atmospheric Sulfur Deposition in Gatlinburg, Tennessee, in 1979. Ann Arbor, Michigan: Ann Arbor Science Publishers, 568 p.

Annotation

An extensive compilation of papers presents views on: (a) environmental versus control costs, (b) natural and anthropogenic sources, (c) human health effects, (d) atmospheric transformation, (e) air mass/landscape interactions, (f) process level effects, (g) ecosystem level effects, and (h) regional scale studies. The symposium was sponsored by the Oak Ridge National Laboratory, the Department of Energy, the U.S. Environmental Protection Agency, and the Tennessee Valley Authority. In addition to papers on the science of sulfur in the environment, articles on the cost-benefit of $SO_2$ emissions controls and on communication or organizational problems are included. An overall view suggests great difficulties in efficiently gathering scientific information, translating science into costs, transferring information from scientists to social and political groups, and establishing and maintaining organizations to transform information into decisions.

Sleater, G., 1978, Development of performance criteria for the selection of stone preservatives: Geological Society of America, Engineering Geology Case Histories No. 11, p. 65-71.

Annotation

Susceptibility of various stone preservatives to weathering is measured by weight loss, appearance, water absorption, permeability, abrasion, and hardness after numerous cycles of accelerated weathering by several agents.

Sleater, G. A., 1977, Stone preservatives: Methods of laboratory testing and preliminary performance criteria: National Bureau of Standards Technical Note 941, 79 p.

Abstract

Although numerous materials have been proposed as preservatives for stone in historic buildings and monuments, their efficacy is difficult to establish. In the work described here, a laboratory research program of accelerated simulated stone decay was used to obtain data on stone preservatives and to suggest criteria for their selection. Over 50 materials usable as stone preservatives were tested.

Tests to simulate stone decay were of two types:

1. exposure to combined weathering factors using a special test chamber for accelerated decay (CAD), in which chemical attack, salt and water action, and thermal effects were simulated in one operation;
2. exposure to single causes of stone decay using sulfurous acid fog, sodium chloride fog, water condensation/evaporation cycling, sodium sulfate penetration and crystallization, and ultraviolet radiation.

Methods for measuring the effects of the exposures are given together with the test data; these have been used to set limits of acceptable performance in preliminary performance criteria for the selection of stone preservatives. The behavior of each stone preservative tested in meeting these criteria is given. No one stone preservative met all criteria.

Smith, A. N., 1955, Investigations on the moisture expansion of porous ceramic bodies: Transactions of the British Ceramic Society, v. 54, no. 5, p. 300-315.

Abstract

The moisture expansions caused by different steam pressures are compared. The mechanism of moisture expansion is postulated and the contributions of the crystalline, amorphous, and glassy constituents of a body are described. The attack and alteration of the glassy material in a body is demonstrated.

The release of moisture expansion and the loss in weight on heating of specimens that have previously undergone moisture expansion are investigated. The pressure of adsorption of water vapour on a broken silicate surface is calculated and the rates of loss of water found approximately from such surfaces are compared with the calculated rates of loss for pores of different diameters.

Smith, R. G., 1973, Moisture expansion of structural ceramics III. Long-term unrestrained expansion of test bricks: Transactions of the British Ceramic Society, v. 72, no. 1, p. 1-5.

Abstract

Ceramic specimens, made from 10 British raw materials, have been allowed to expand in air for a period of approximately 7 1/2 years since firing. Generally, the expansions observed have been proportional to the logarithm of the period of exposure to the atmosphere but, in a few cases, the expansions have been slightly greater than would have been predicted from preliminary results given in Part I, especially with materials fired to the higher temperatures.

Spicer, C. W., 1982, Nitrogen oxide reactions in the urban plume of Boston: Science, v. 215, no. 4536, p. 1095-1096.

Abstract

The rate of removal or conversion of nitrogen oxides has been determined from airborne measurements in the urban plume of Boston. The average pseudo-first-order rate constant for removal was 0.18 per hour, with a range of 0.14 to 0.24 per hour under daylight conditions for four study days. The removal process is dominated by chemical conversion to nitric acid and organic nitrates. The removal rate suggests an atmospheric lifetime for nitrogen oxides of about 5 to 6 hours in urban air.

Stevens, R. E., and M. K. Carron, 1948, Simple field test for distinguishing minerals by abrasion pH: The American Mineralogist, v. 33, nos. 1-2, p. 31-49.

Abstract

A simple field test is described for distinguishing minerals by estimating the pH of suspensions made by grinding them in water. The term abrasion pH is proposed to designate the pH values obtained by this grinding technique, which may differ from pH values obtained by shaking previously ground minerals in water. Soft minerals are scratched in one or two drops of water on a streak plate for about a minute to form a milky suspension and the resulting pH of the solution estimated with indicator papers. Hard minerals and those that absorb water are ground with a few drops of water in an agate mortar for about a minute. Abrasion pH values are given for about 280 mineral species, many of them confirmed repeatedly by determinations on specimens from different localities. Abrasion pH values of minerals range from 1 to 12. Many minerals whose compositions vary because of isomorphous replacements yield a range of values that reflect the varying content of alkali- or acid-forming materials, whereas minerals similar in appearance but differing in composition are easily distinguishable by the abrasion pH test, for example calcite from dolomite or magnesite, talc from pyrophyllite, and muscovite from phlogopite.

Stevens, T. J., and A. E. Holland, 1972, Moisture expansion of fired clay: Experiments in controlled environments: Journal of the Australian Ceramic Society, v. 8, no. 1, p. 1-5.

Summary

Water in the atmosphere is shown to cause expansion and increase in weight in fired clay products, and it is suggested that this phenomenon may occur in four steps, beginning measurably at about 400°C during cooling. Expansion occurs at very low water vapor pressures and can be recovered by heating, but not readily by applying vacuum.

Annotation

The four steps theorized by which expansion and weight increase occur are: (1) weight increase without length increase--possibly due to absorption of water at the surface, (2) further penetration of water--causing maximum expansion, (3) continued adsorption of water--mostly physically bonded, and (4) physical equilibrium with the environment.

Experiments using nonaqueous vapors indicate that expansion similar to that caused by water may be produced by atmospheres containing OH ions.

Stevens, T. J., A. E. Holland, and J. S. Hosking, 1969, A reconsideration of 'contraction' following moisture expansion of clay products: Claycraft and Structural Ceramics, v. 42, p. 192-193.

Annotation

Previously reported contraction of some clay products following a period of moisture expansion was found to be erroneous. The contradictory behavior of small laboratory prepared specimens when compared to the industrial bricks measured first indicated the possibility of error. Examination of the procedures and equipment used revealed that the comparator used to measure the length of specimens relative to a reference bar had suffered wear in its basal cup. The error was estimated and when taken into account all specimens conformed to the original pattern of rapid growth followed by a much slower growth rate.

Thiemecke, H., 1944, Notes on moisture expansion: Journal of the American Ceramic Society, v. 27, no. 12, p. 355-358.

Abstract

Moisture-expansion determinations were made over a period of more than three years on bisque and glazed specimens of two types of semivitreous bodies (having approximately the same absorption) that were exposed to four different atmospheric conditions. The data indicate the cone 6 talc-pyrophyllite body to expand less under all conditions of exposure than the cone 9 clay-flint-feldspar body. Glazed specimens of both bodies expanded more than the bisque specimens and a possible explanation is given. From mathematical considerations, a three-year storage period appears to be sufficient to permit moisture expansion that closely approaches the ultimate which might be expected in the types of bodies investigated. The autoclave treatment gave the highest expansion values and should serve as an index of the service performance as to delayed crazing of ware so tested.

Thiemecke, H., 1943, Thermal and moisture expansion of ball clays and bodies fired to different temperatures: Journal of the American Ceramic Society, v. 26, no. 6, p. 173-179.

Abstract

Thermal and moisture expansion determinations were made on ten ball clays of the Kentucky, Tennessee, and English types alone and on typical semivitreous and vitreous bodies in which each of these ball clays was incorporated. The clays and bodies were fired at cones 6, 9, and 11. The data indicate that the ball clays fall into five distinct groups. Although none of the clays showed a direct relation between its expansion and that of the bodies in which it was incorporated, a majority possessed characteristics sufficiently similar to permit their classification into groups in which the behavior of the clays alone is indicative of their influence on the bodies. When several ball clays were jointly incorporated into bodies, they showed additive thermal and moisture expansion values.

Thiemecke, H., 1941, Thermal and moisture expansion of kaolins and bodies fired to different temperatures: Journal of the American Ceramic Society, v. 24, no 2, p. 69-75.

Abstract

Thermal-expansion and moisture-expansion determinations were made on four kaolins of the Georgia, Florida, North Carolina, and English types alone and on typical semivitreous, hotel china, and electrical porcelain bodies embodying each of these kaolins after being fired at cones 6, 9, and 11. The Georgia and Florida kaolins and bodies showed surprisingly similar expansion characteristics. The general order of decreasing thermal expansion and increasing moisture expansion of the kaolins at all three firing treatments was Georgia, Florida, North Carolina, and English china. The semivitreous bodies at cones 6 and 9 showed the same order of expansion as the kaolins alone, but at cone 11 the thermal expansion of the English china clay body was the highest and the North Carolina kaolin body next in order. Moisture expansion of the bodies at cone 11 was found to be a function of the absorption, regardless of the kaolin used, with no expansion obtaining at zero absorption. Mixtures of clay, flint, and feldspar, given an autoclave treatment after being fired to cones 6 and 9, showed that feldspar additions increased moisture expansion. When these mixtures were dehydrated at different temperatures, the data obtained were insufficient to confirm any theory on the nature of moisture expansion in a porous ceramic body.

Thomas, A., 1971, Moisture expansion in brickwork: Transactions of the British Ceramic Society, v. 70, no. 1, p. 35-38.

Abstract

The moisture expansion is described of walls 40 feet long built of a clay brick and a shale brick, respectively, both kiln-fresh and after having been stored for two weeks. The walls of kiln-fresh bricks gave high initial rates of expansion; the rates of expansion for the clay-brick walls subsequently reduced more rapidly. The walls built with the stored bricks had high initial expansion which, however, was less than that of the kiln-fresh walls. For the comparison, moisture expansion was measured on individual bricks from the same batches, but there was little correlation. Variation in the ambient temperature considerably affected the readings; variation in humidity had little effect. It is recommended that future experiments be carried out in an outdoor environment.

Thorton, Jr., H. T., 1978, Acid attack on concrete caused by sulfur bacteria action: American Concrete Institute Journal, v. 75, p. 577-584.

Summary

The concrete in two artificial lakes decomposed to a "mush" consistency to depths up to 1 1/4 in. (approximately 32 mm) over a period of about 5 years. The program of investigation includes a literature review, sample collection, and physical, chemical, and bacteriological tests. It is concluded that the deterioration is due to acid attack and is the final stage of a corrosive process caused by sulfur bacteria action. Immediate and long range remedial measures are suggested for consideration for implementation at both sites. Attention is drawn to the fact that undetected deterioration of other concrete structures may be in progress.

Vaughan, F., and A. Dinsdale, 1962, Moisture Expansion: Transactions of the British Ceramic Society, v. 61, no. 1, p. 1-18.

Abstract

The view that the moisture expansion of a ceramic body is produced by the penetration of moisture into the glassy phase is discussed, and supporting evidence is presented. The problem of predicting from an accelerated test the moisture expansion likely to occur in service is considered. The value of an accelerated test in steam is questioned, and evidence is given to show that steam-tests are not a reliable guide to moisture expansion in service. The implications of this in connection with autoclave crazing-tests are briefly considered. Finally, the significance of moisture expansion in different types of ceramic ware is discussed.

Annotation

The continued expansion of ceramic bodies in service is caused by the continuous penetration of moisture into the glassy phase. This argument is supported by the results of tests on moisture penetration of glass, structural changes of glass caused by moisture penetration, the difficulty of removing adsorbed moisture, the degree to which moisture expansion is effected by changes in composition and is dependent on the amount of glass in a ceramic body.

The validity of the autoclaving test of moisture expansion is based on the assumption that the processes causing moisture expansion of a ceramic body in the autoclave are identical to those causing it in service. Testing has revealed that the attack of water on glass at room temperature differs significantly from the attack by steam under pressure and at a higher temperature.

Vero, L. B., C. Bettini, and M. M. Sila, 1976, Chemo-autotrophic micro-organisms in semi-insulated environment: Second International Symposium on the Deterioration of Building Stones, Athens, Greece, p. 61-65.

Annotation

A study of the importance of biologic processses in the alteration of stone was carried out in two Etruscan tombs. Soluble salts of sulfates and nitrates, important contributors to the alteration of stone, can be produced by enzymatic reactions of specific microorganisms. This work examines the success of sulfur and nitrogren cycle bacteria in semi-insultated environments compared to those in open air environments, the relationship between heterotrophic and autotrophic microflora, and the importance of the tomb itself in determining the type of biological colonization. In one tomb, with a metal door facing south and no protection against sunlight, algae were spread uniformly on the walls while heterotrophic and autotrophic microflora were concentated towards the floor with decreasing concentrations upwards along the walls. Algae were found to be the primary colonizer, sunlight favoring its growth. The second tomb contained a limited but evenly distributed growth of ammonifying and heterotrophic bacteria. Algae are absent due to the absence of light in the tomb.

Sulphur bacteria was found in smaller quantities in semi-insulated environments compared to open air environments.

Vos, M. A., and D. A. Moddle, 1976, Repetitive wetting and drying as a test of weathering resistance: CIM Bulletin (Canadian Institute of Mining and Metallurgy), v. 69, no. 766, p. 103-108.

Abstract

Wetting and drying is an integral part of normal weathering conditions. During wetting, the capillary action and an air hammer effect, implosion, cause widening and deepening of existing pores and the opening of new fractures leading, when repeated many times, to structural failure. To test samples of aggregate, a turntable was designed so that material was alternately wetted by spray and dried by heat lamps. A number of test runs were carried out on various materials which showed different disintegration rates. Further work may lead to the development of a test for the weathering resistance of mineral aggregates and building materials and to a definition of quantitative standards.

Walters, H. V., and P. B. Adams, 1982, Predicting the resistance of inorganic architectural materials to appearance degradation in natural and polluted environments: Bulletin of America Ceramic Society, v. 61, no. 11, p. 1224-1227.

Abstract

Various glass and ceramic architectural products were studied to define accelerated chemical durability tests that would predict long-term performance outdoors. Tests in the laboratory and on industrial pollution sites were compared. Evaluation of visual appearance change gave a good correlation for 90 percent of the material-test combinations. It is concluded that short-term laboratory tests based on appearance evaluation can predict with reasonable confidence the service life of nonstructural building components in various environments.

Watson, A., 1964, Laboratory tests and the durability of bricks. VII. Frost dilatometry as a routine test: Transactions of the British Ceramic Society, v. 63, no. 11, p. 681-695.

Abstract

A relatively simple form of frost dilatometry test has been developed in which the specimens used are half-bricks, cut lengthwise. The test has been applied to samples from 38 batches of bricks of durability known from their behavior in the copings of experimental walls. The correlation between the permanent set (or residual distension), after five cycles of freezing to -3°C and thawing at room temperature, and behavior on exposure was reasonably good, though there were a few anomalous results, some of which could be explained. It is concluded that the conditions of the test were a little too severe and that the work should be continued with a modified method.

Watson, A., 1964, Laboratory tests and the durability of bricks. VI. The mechanism of frost action on bricks: Transactions of the British Ceramic Society, v. 63, no. 11, p. 663-680.

Abstract

The changes in dimensions that are caused by freezing 10 x 4 x 1 cm slices cut from clay building bricks have been measured. Five varieties of bricks, of differing degrees of frost resistance, have been measured at temperatures down to -5°C. when fully saturated. The results show that the physical mechanism of freezing is essentially the same as that described by W. N. Thomas on the basis of his pioneer studies of the freezing of natural building stones, although some of the observed results cannot at present be fully explained. It is also shown that measurements of the distention of the saturated bricks correlated well enough with what is known of their durability to justify a fuller investigation of the method.

West, H.W.H., 1967, Moisture movement of bricks and brickwork: Transactions of the British Ceramic Society, v. 66, no. 4, p. 137-159.

Abstract

The work of the Heavy Clay Division, British Ceramic Research Association, on the moisture movement of bricks and brickwork is described. Methods of measurement are given and sources of error indicated. The magnitude of the moisture movement, which is often an expansion but may be a contraction, is difficult to replicate, and the phenomenon is complex. The size and orientation of the specimen in the measuring-rig are important. While laboratory experiments on single specimens have shed light on the mechanism of moisture movement, the expansion of brickwork appears to be complicated by other factors.

Annotation

Maximum moisture expansion for most clays occurs at a firing-temperature between 900° and 1000°C.

High pressure steam treatment, while accelerating moisture expansion, is not reliable enough to use as a moisture expansion test base.

The determination of moisture expansion in brickwork is complicated by the interaction between the bricks and mortar.

West, H.W.H., and H. R. Hodgkinson, 1968, The performance of walls built of wirecut bricks with and without perforations. III. Tests of rain penetration: Transactions of the British Ceramic Society, v. 67, no. 10, p. 461-472.

Abstract

Tests were carried out on 4 1/2-in. single-leaf walls in a replica of the Building Research Station's rain penetration apparatus. The penetration of dampness was recorded photographically. In addition, the walls were suspended from a steelyard and their changes in weight were recorded periodically. Within any particular brick category the rate of absorption appeared to be related in a general way to the water absorption and suction rate of the bricks, but not to the presence or absence of perforations. Examinations of the walls, dismantled course by course, gave no evidence of water in the perforations.

White, W. A., 1964, Permanent expansion in bricks: Illinois State Geological Survey Industrial Mineral Notes, no. 18, 5 p.

Abstract

Bricks produced in Illinois and the clays from which they are made were tested to determine whether they were subject to sufficient expansion to cause structural damage when used in construction.

Sample bricks were taken from all Illinois brick plants, and test bars were made from the raw clays used by the manufacturers. The bars were fired at various temperatures. Both bricks and test bars were measured at intervals for 3 1/2 years. Bricks stored in a controlled atmosphere were compared with bricks from the same kilns that had been kept outdoors.

Data indicate that expansion behavior depends on the type of clay used and on the temperature of firing; that expansion takes place rapidly in the first week after firing and diminishes thereafter; and that bricks fired at low temperatures expand most.

Expansion was not found to be an acute problem in Illinois-made bricks when proper precautions were taken by manufacturer and builder.

Annotation

Bricks stored outdoors expanded more rapidly and to a greater absolute amount than those stored indoors.

Winkler, E. M., 1978, Decay and preservation of stone: Geological Society of America, Engineering Geology Case Histories No. 11, 103 p.

Annotation

Fifteen articles grouped into three main sections: Stone properties and testing, Stone weathering, and Stone preservation. A few of the articles are individually cited elsewhere in this bibliography. The first section of the study describes test procedures and results on some rocks. The middle set of papers deals with stone weathering. W. D. Keller reviews weathering in general, and P. P. Hudec discusses fine details of weathering at the molecular level. E. M. Winkler reports on a study of stone decay in urban atmospheres and gives a literature review of stone weathering. The final section of the report contains several articles on testing, types of chemical agents, and results of various treatments to restore and preserve stone. J. Riederer reviews preservation in Germany and illustrates potentially damaging preservatives that ultimately exacerbate the problem. An article by G. Hyvert shows an interesting example of silica-rich florescences formed on a temple in Indonesia.

Winkler, E. M., 1978, Stone decay in urban atmospheres: Geological Society of America, Engineering Geology Case Histories No. 11, p. 53-61.

Annotation

This paper gives several examples of accelerated decay in the modern, urban environment. Winkler points out that capillary movement of moisture may equal 10 m vertically and 20 m horizontally. He shows the strong effect of dissolved salt ($NaCl$) on the hygroscopic moisture absorption of brick. Spring and fall rains are shown to be especially corrosive, because pollution levels are higher during the heating season. Winter snows are not as corrosive, because snow contains less dissolved $SO_2$ and $CO_2$. This article illustrates the tremendous pressure that can be generated by insolation--merely heating pore-filling water. If de-icing salts were not used and buildings were sealed from moisture, much of the present-day damage could be avoided, but $CO_2$ and $SO_2$ pollution can be expected to accelerate weathering in rural and urban areas.

Winkler, E. M., 1973, Stone: Properties, Durability in Man's Environment, New York: Springer-Verlag, 230 p.

Annotation

The properties of igneous, metamorphic, and sedimentary rocks are examined. Natural deformation of stone occurs by brittle rock fracture, plastic deformation and active rock pressures in quarries. Stone is also damaged by blasting, bombing, and other quarrying operations which can cause microfracturing. Overall color of stone depends on mineral colors and on rock texture and structure.

The atmosphere and rainwater are the most important weathering agents of stone. The atmosphere contains aggressive impurities which are removed from the atmosphere mainly through washout by precipitation. The solvent action of water and its dissolved impurities is the main cause of chemical attack on stone. Dry deposition, reaction with airborn dust and escape into outer space remove a smaller portion of atmosphere pollutants. The combustion of fossil fuels produces the major supply of $CO_2$, $SO_2$ in the atmosphere. Autombile exhaust contributes much of the $NO_2$ to the atmosphere. The increased output of pollutants due to increased industrial activity during the last 100 years has led to a rapid acceleration in the decay of stone.

Sulfate is the strongest of the corrosive pollutants. It attacks carbonate rocks in two ways: (1) solution by action of sulfuric or sulfurous acid, or (2) the conversion of carbonates to either calcium sulfite or calcium sulfate.

The effect of moisture and salts in stone is discussed. Moisture is important as it provides transport for salts and can be a disruptive force by itself. Salt may come from a number of sources: ground moisture, stone weathering or pollutants in the atmosphere.

Chemical weathering is the most powerful mechanism in the decay of stone. It can occur by solution as with carbonates or gypsum. Solution rates depend on temperature of the solvent, flow velocity and $CO_2$ content for carbonates. High $CO_2$ concentrations in urban atmospheres can double or triple the weathering (solution) rates of limestone, dolomite, and marble.

Solubilization of ions from silicate rocks and minerals removes ions and exposes the gaps remaining in the crystal lattices to hydration. Ca, Mg, and Na are leached faster than Al. The weathering rates of silicate rocks are generally slower than the weathering rates of carbonates. Stone decay by plants and animals, natural rust, and frost are discussed along with the fire resistance of rocks and minerals.

The conservation of stone on buildings and monuments is very important. Modern impregnation treatments have two jobs: to impregnate and harden the rock. Water tight surface sealants are no longer used, as the moisture trapped inside may damage the stone. Impregnation treatments should be applied after the removal of water soluble salts. The response of a stone to a chemical treatment is very difficult to predict, so great care should be taken in choosing a preservation treatment. An unwise choice can do more harm than good.

Winkler, E. M., 1966, Important agents of weathering for building and monumental stone: Engineering Geology, v. 1, no. 5, p. 381-400.

Summary

The atmosphere has little corrosive effect on stone without the presence of water. Washout of aggressive ingredients from the atmosphere by rainwater, however, increases corrosion and solution of stone. Dissolved $CO_2$, $SO_2$, $SO_3$, and Cl are the most effective corrodents. The urban atmosphere supplies much more $CO_2$ and sulfates through the combustion of fossil fuels than does the atmosphere of rural areas; thus stone decay in urban areas is very much accelerated. Water with few ions in solution may be as corrosive as $CO_2$ and $SO_4$ charged water, as it attempts to reach equilibrium with the stone. Silicate rocks can resist exposure to rainwater successfully for a long time.

Exposure of facing stone and concrete aggregate to soft or acid running water or lake waters causes damage primarily to carbonate rocks. Resistant silicate rocks should be selected.

Primitive animals and plants may inhabit bare stone surfaces, paving the way to more extensive destruction through the production of organic acids along the root system. All rocks are subject to attack by low animals.

Boring sponges, sea shells, and sea urchins may develop a dense network of pock marks near the waterline in different rock types; occasionally also in concrete.

Wren, H., and B. Butterworth, 1949, A note on the effect of chlorides on the sulphate content of bricks: Transactions of the British Ceramic Society, v. 48, no. 10, p. 412-416.

Abstract

Previous work on the effect of chlorides on the sulphate content of bricks is reviewed. Tests on two German clays had shown that small additions of sodium chloride caused a marked reduction in the sulfate content of the clays after firing. The results of similar tests on a gypsiferous Keuper marl from a brickworks in Belfast are reported. There was a reduction in sulphate content, but it was not so marked as in the German work, and was not large enough to justify the general introduction of sodium chloride at the works. Further investigation would be worthwhile.

Zsembery, S., 1980, Developments in the determination of moisture expansion clay bricks: Proceedings of the Ninth Australian Ceramic Society Conference, The Australian Ceramic Society, Sydney, Australia.

Annotation

The long term expansion of bricks can be predicted from the results of an accelerated, steam-induced-expansion process with equations formulated for both kiln-fresh and nonkiln-fresh bricks. Tentative results from tests in progress indicate that a reasonably accurate estimate of residual expansion can be made for bricks whose ages are known to within ± 1 month.

APPENDIX II

# EXPANSION AND WEATHERING OF BRICK

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## ABSTRACT

This paper reviews research on alteration of brick by expansion and summarizes preliminary results of a new study of the weathering of bricks. Damage caused by moisture expansion of brick, including the rate and absolute amount of expansion, is illustrated in a series of photographs and graphs. Graphs of expansion through time show that the following factors are significant: kiln design (underfired brick from cooler areas of a beehive kiln expand more than brick fired in other parts of the kiln); clay content (illite-rich bricks expand greatly at certain temperatures, whereas kaolinite-rich bricks show less expansion); environment, especially conditions of exposure (bricks stored outdoors expand at a greater rate than similar ones stored in the lab); mineral composition and/or additives (MgO and fluorite additions reduce expansion while $K_2O$ additions increase it); and preventive measures (steam treatment during cooling of brick causes pre-expansion and reduces subsequent expansion during usage).

A background study on weathering of bricks was prompted both by the specific concern about the effects of acid rain on historic, present, and future brick structures and by the general need for basic information on the alteration of bricks—whatever the mechanism.

## INTRODUCTION

Masonry buildings of all types, and brick structures in particular, have always been symbols of permanence. Although adobe and cement bricks shore the name and shape, bricks commonly used for residential and commercial buildings are formed from clay-rich materials and fired to a temperature between 800° and 1100°C. In this report, bricks are defined as the fired product. In most cases, bricks and similar fired wares have great strength and durability; however, some bricks expand and show the effects of weathering. This report reviews past studies of brick expansion and weathering and presents some preliminary results of continuing studies at the Illinois State Geological Survey. The goal of our current work is to isolate factors that cause expansion or deterioration of brick and to suggest solutions as well as directions for future research.

In the United States, work with glazes led to the recognition of the expansion of ceramic products (Merritt and Peters, 1926; Schurecht, 1928; Schurecht and Pole, 1929). Much of the subsequent literature on expansion of brick and similar structural products is based on work conducted in Australia where structural damage to buildings prompted J. S. Hosking of the Australian CSIRO to look at long-term expansion and contraction of clay products (Hosking and Hueber, 1959; Hosking, Hueber, and Holland, 1965). Similar investigations of Illinois products were initiated in 1959 at the Illinois State Geological Survey by W. Arthur White, W. E. Parham, and J. S. Hosking while the latter was at the Survey for this purpose.

## THE PROBLEMS

Figures 1, 2, and 3 show the potentially severe problems caused by moisture expansion encountered in the Midwest—an area considered to have relatively well-fired bricks. Obviously, such expansion produces great economic and aesthetic damage. Figure 1 shows rotational shear of a door unit resulting from variations in window openings along an expanding wall. Figure 2 illustrates how the situation is aggravated as shrinking concrete causes additional separation between wall and foundation units. Figure 3 shows the possible magnitude of movement when a longwall (left of the photo) breaks away from the foundation and moves freely. One solution—to cut expansion joints and absorb further expansion—is illustrated in figure 4, but this solution cannot correct damage that has already occurred and certainly will do nothing to prevent future deterioration of the brick due to weathering. Bricks that tend to expand may also tend to weather at high rates. If brick structures are intended to last for centuries, potential problems such as expansion and weathering will have to be understood and, insofar as possible, avoided. In some cases, the problem of expansion can be solved inexpensively during production, specifically at the time of firing. At the least, builders should be aware of the long-term results of choices made about the design of a structure and the type of brick used.

Additional problems, imposed by weathering phenomena, may or may not be related to expansion. Deterioration may be the result of wet-dry and freeze-thaw cycles, thermal

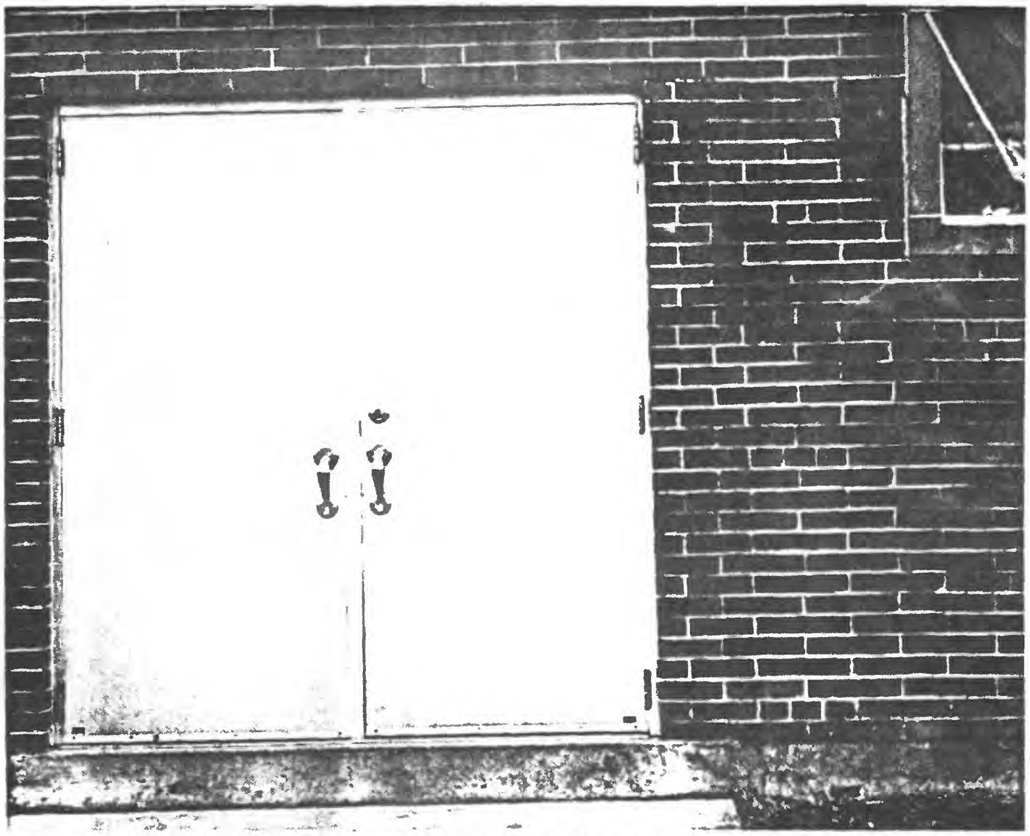

**Figure 1.** Rotational distortion of doors due to placement of wall openings. (Note level of door handles and space above left door.)

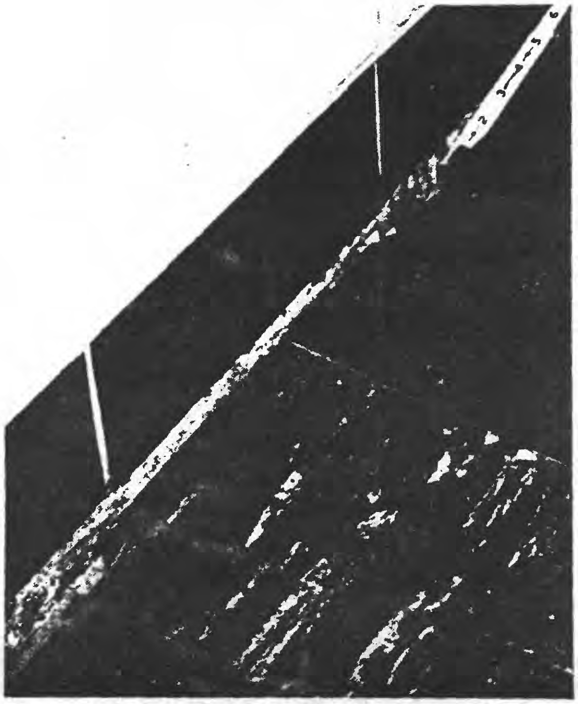

**Figure 2.** Separation of wall and floor, possibly exacerbated by concrete shrinkage.

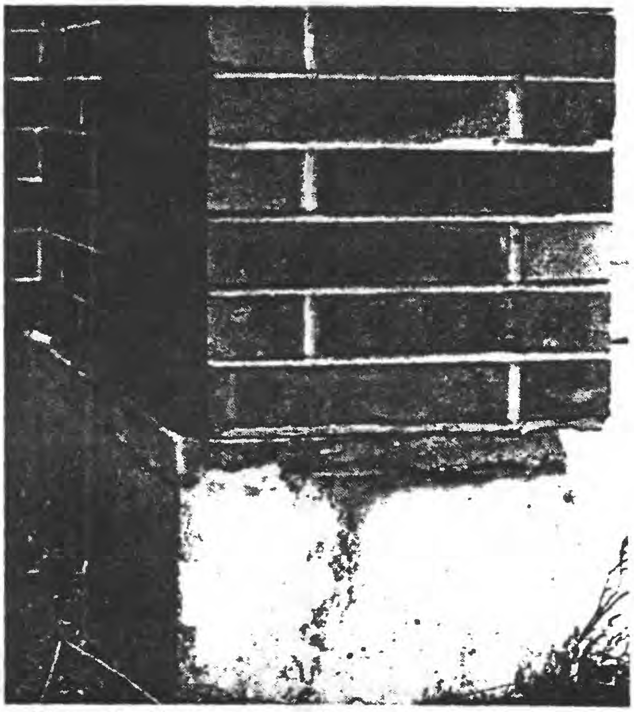

**Figure 3.** Movement of pilaster past foundation due to expansion of a long wall to the left in the photo.

expansion and contraction, weathering reactions, and crystallization of soluble salts. Bricks are certainly known to weather; the causes of relatively rapid weathering are the focus of continuing investigation.

PREVIOUS WORK

Early research at the Illinois State Geological Survey resulted in two significant publications. A report by Hosking, White, and Parham (1966) gave an excellent review of the literature to that date, outlined the main purposes for continuing studies, and showed the magnitude of the moisture problem in Australia as well as in the United States (Illinois). They showed the variation in the amounts of expansion resulting from changes in composition and suggested several methods of reducing or adjusting for expansion, such as firing well into the steel-hard range (<8% porosity), aging bricks before use, using lime-rich mortars, using sufficient expansion joints,

**Figure 4.** Expansion joints cut into existing walls to allow for future expansion.

and designing the structure to allow for expansion. White's research (1964) resolved some theoretical and practical problems created in the first investigation as well as initiated new experiments.

Schurecht and Pole (1929) found that magnesite inhibited expansion and subsequent crazing in ceramic tile. Later work by Goldfinch (1980) showed that additions of MnO, basalt, and brown coal can reduce total expansion. Hosking, White, and Parham (1966) also discussed the increased expansion associated with illite-rich raw materials and the compensating effect of reduced expansion due to additional fluxes often associated with illitic clays. Cole (1975) further emphasized the importance of the fluxes CaO and MgO in reducing expansion by showing reduced total expansion associated with increased $CaO + MgO/Na_2O + K_2O$ ratios. Although apparent chemical control of expansion suggests variations caused by formation of different high-temperature phases, the fundamental causes of moisture expansion are still not clear.

Holland and Stevens (1968) proved that fired ware stored in vacuum while being cooled from 400°C to ambient did not expand. Their work further proved that normal expansion began as soon as the bricks were exposed to air; they also showed that significant expansion began at 400°C during the cooling cycle. Segnit (1970) showed that expansion was not associated with formation of a glass phase, while Stevens and Holland (1972) continued their studies by reporting that exposure to absolute methanol led to expansion similar to that associated with moisture. Expansion in alcohol suggested to them that the $OH^-$ ion was of central importance in moisture expansion.

White (1964) shows the importance of exposure to high-moisture conditions, for instance, bricks kept indoors are slower to expand than those stored outside. McDowall and Birtwistle (1971) have developed a 4-hour steam treatment of Australian bricks to predict expansion up to 4 years with an excellent confidence level. When bricks were exposed to natural conditions after steam treatment, McDowall and Birtwistle (1971) confirmed the possibility of steam treatment as a pre-expansion method. Bricks that had been steamed for 4 hours were retarded in their expansion for a few months. After about 12 months, however, treated and untreated bricks had expanded equally, which suggests the danger of coating bricks with a sealer. Breakdown of the moisture barrier may result in full expansion of the bricks after the mortar is completely set and cause problems where design of the structure does not allow for normal expansion. At least one brick producer coats its bricks with a silicone agent to seal them against moisture, but the effectiveness of this treatment is unknown.

Although the expansion of brick has been thoroughly studied, research on the deterioration of brick due to mechanical and chemical reactions associated with weathering is very limited. Robinson, Holman, and Edwards (1977) compared results from ASTM methods of assessing brick durability with results of freeze-thaw testing on a large sample of commercial bricks. They found that several test methods to determine water absorption could cull the nondurable brick to adequate levels (<5%), but any method usually rejected many that were found to be durable by freeze-thaw or salt-tolerance testing. Failure of brick in freeze-thaw conditions can be due to excessive permeability and/or to remnant lamination and cracking. Since water absorption and friability are both decreased by thorough firing, it seems again that complete firing to steel hardness will increase durability.

No studies of long-term weathering effects on brick are known to the authors. Rossi-Manaresi (1976), Gauri, Gwinn, and Popli (1976), Arnold (1976), and Gauri (1980) reviewed many of the causes of building-stone deterioration; however, similar studies on causes of brick weathering have not been made. The availability of calcium in limestone and sulfate in the atmosphere leads to extensive weathering of limestone and marble by gypsum crystallization. When mortar, concrete, and calcareous stone are neighbors to brick, gypsum is likely to become an agent of brick deterioration. Hydrated salts are also a concern. Some bricks are treated with salts to inhibit efflorescences, and these treatments may at least reduce salt movements into brick. The treatments often reduce the temperature of steel hardness, fix vanadium in an insoluble form, and reduce permeability. Reduced porosity and permeability inhibit movement of salts.

Of special concern is the type and degree of deterioration of brick due to acid rain. Likens (1974), Glass, Glass, and Rennie (1980), and Nicholas and Boyd (1981) have provided excellent perspectives on this problem. Nicholas and Boyd (1981) showed the range of acid compositions and pH levels encountered in different parts of the United States; sulfuric- and nitric-acid ratios vary from predominantly one acid through all intermediate ratios to predominantly the other acid. Nicholas and Boyd (1981) also point out the importance of residence time required to convert sulfates and nitrates to acid molecules. Complete acidity may take 4 days to develop from particulate sources, and possible transport of particulates and acids may involve great distances and obscure relationships to source materials.

## THE BRICK PROJECT

The Illinois State Geological Survey project set up by J. S. Hosking, W. E. Parham, and W. A. White in 1959 was a comparison of Australian and Illinois ceramic materials, especially with respect to moisture expansion. Their project led to a publication in 1966. W. A. White continued the earlier project and added new experiments to resolve some questions about the effect of additives and composition on expansion. Individual test bricks were measured for 10 years; however, the entire project, including measurements, extended over a total of about 20 years. The project continues in a modified form with investigation of the long-term weathering of brick and the contribution of acid rain to brick deterioration.

Computer files of the many thousands of measurements are being processed and analyzed at the Illinois State Geological Survey. More than 60 ceramic plants were operating in Illinois at the start of the investigations by Hosking, White, and Parham. Although only representative products were sampled, the wide range of industrial compositions and artifical mixtures used in test bricks gives these files special value.

### Raw Materials

An important variable in studies of expansion and deterioration of ceramic products is the composition of raw materials. Illinois has many different sources of raw materials for red-fired ware. Loess, till, and lacustrine materials of Pleistocene age have been used for these products. Also, many shales, clays, and siltstones of Pennsylvanian age have been used alone or in combination with Pleistocene units to give a wide range of colors, textures, and physical properties. The optimum raw material contains minerals with a wide range of melting temperatures and can be fired steel-hard at reasonable temperatures without bloating. Raw materials must contain enough clay particles to give adequate plasticity; however, excessive clay content generally results in cracking and warping during drying, increased shrinkage during drying and firing, reduced penetration of oxygen during firing (longer firing is required to produce red), black cores and bloating, and the probability of increased moisture expansion in the final product. Blends of rock units can be used to change color and physical properties of the bricks without altering the firing schedule or producing bricks of inferior quality because of underfiring. Additives may be used to change color or shades of color. In general, various chemical additions produce the following: alkalies give red colors; calcium causes yellowing; magnesium lightens existing colors; aluminum gives whiteness; and iron in the absence of alkalies produces a brown color. If raw materials are rich in calcite, dolomite, pyrite, and/or siderite pebbles, bricks may develop excessive cracking and spalling due to "lime pops."

We find no records of rocks older than Pennsylvanian being used for brick in Illinois, but older clays and shales are used in other states and could be used in Illinois. Table 1 presents an estimate of the approximate mineralogical composition of the raw materials used for red-fired ware in Illinois.

Table 1. Estimated clay mineral composition of Illinois brick materials.

| | **Pleistocene** | **Pennsylvanian** |
|---|---|---|
| Illite | 15-50 | 30-75 |
| Quartz | 20-70 | 15-30 |
| Kaolinite | 0- 5 | 5-25 |
| Chlorite | 0-10 | 0-25 |
| Expandables | 0-40* | 0-40* |
| Feldspars | 5-25 | 0-10 |
| Calcite | 0-20 | 0- 5 |
| Dolomite | 0-20 | 0- 5 |
| Siderite | — | 0-10 |
| Pyrite | — | 0- 5 |

*Usually <5%

### Factors Related to Expansion

Kiln design is a major factor. At the time these investigations began in 1959, beehive kilns were extensively used in Illinois for firing bricks and similar wares. The tunnel kiln is more commonly used today because it allows continuous movement of bricks and uniform temperature control. Usually, little variation is observed in the products from a tunnel kiln. The design and structure of a beehive kiln result in cooler areas, often producing underfired bricks that expand more than well-fired materials. Figure 5 illustrates the expansion of brick taken from different areas of beehive and tunnel kilns. Note the high rate and total magnitude of expansion from Areas E and F in a beehive kiln. Scove kilns used in the past were constructed in such a way that the unfired bricks formed the kiln. The design often resulted in less than uniform temperature distribution, although some variation in heat distribution might result from the firing schedule and possibly from the type of fuel used.

Bricks can be underfired for other reasons. Light fired colors such as buff and light red were often produced at low firing temperatures, which led to extreme cases

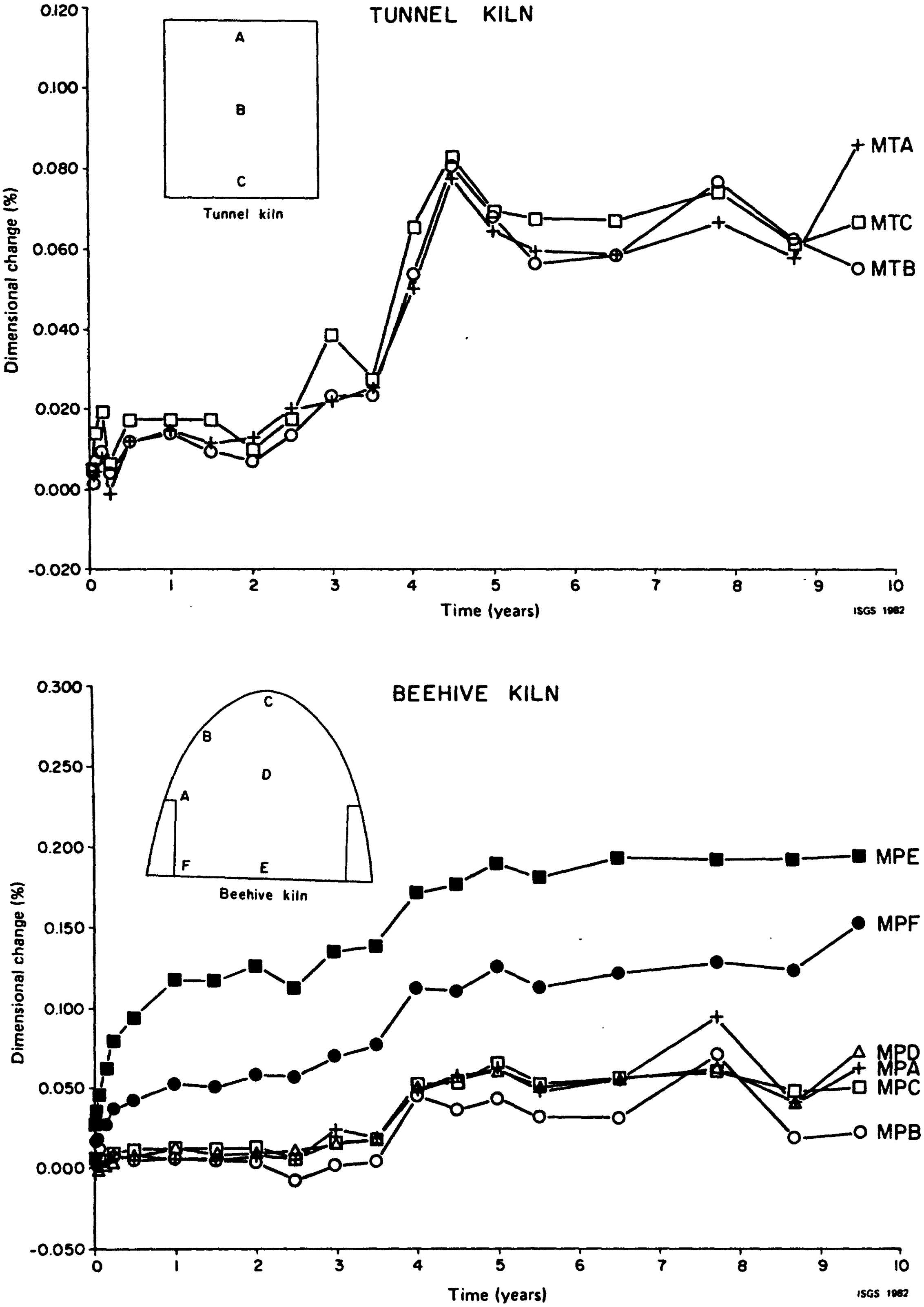

**Figure 5.** Expansion of bricks fired in different locations of a beehive or tunnel kiln.

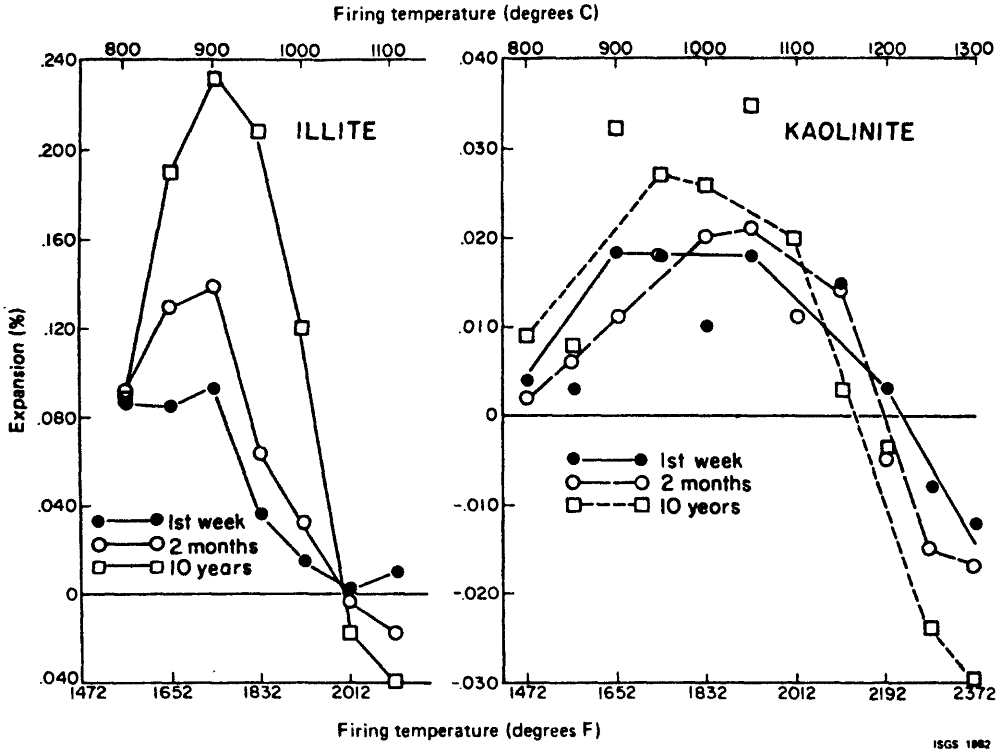

**Figure 6.** Expansion of illite and kaolinite test bricks fired to different temperatures.

expansion (fig. 6). Figure 6 also illustrates the variation in total expansion for some test bars made from illite and kaolinite and fired at different temperatures. After firing at very low temperatures, bricks containing these materials lack durability; but at higher temperatures they develop adequate hardness although moisture expansion will be excessive. Greater quantities of nonclay minerals will often reduce the potential for expansion, but the requirements of adequate plasticity and suitable firing range restrict the additions of sand and silt. Since the high cost of energy is a significant part of making any ceramic product, a strong economic incentive to conserve fuel may result in some underfiring. At the least, normal variations of raw materials will lead to different temperatures for similar batches.

Figures 6 and 7 suggest reduced expansion when kaolinite, rather than illite, is the dominant phase. Reduced expansion of bricks rich in kaolinite may result from higher firing temperatures associated with the more refractory kaolinite and/or from formation of different high-temperature phases. Hosking, White, and Parham (1966) concluded that kaolinite is associated with reduced expansion, and that nonclay fluxes may reduce expansion even when illite becomes the dominant clay mineral in many raw materials. Cole (1975) showed that CaO and MgO are dominant fluxes that reduce expansion. A future study will examine the unfired and fired mineralogy of raw materials and their associated bricks.

White (1964) found that bricks exposed to outside conditions expanded more rapidly than bricks kept in a controlled laboratory atmosphere.

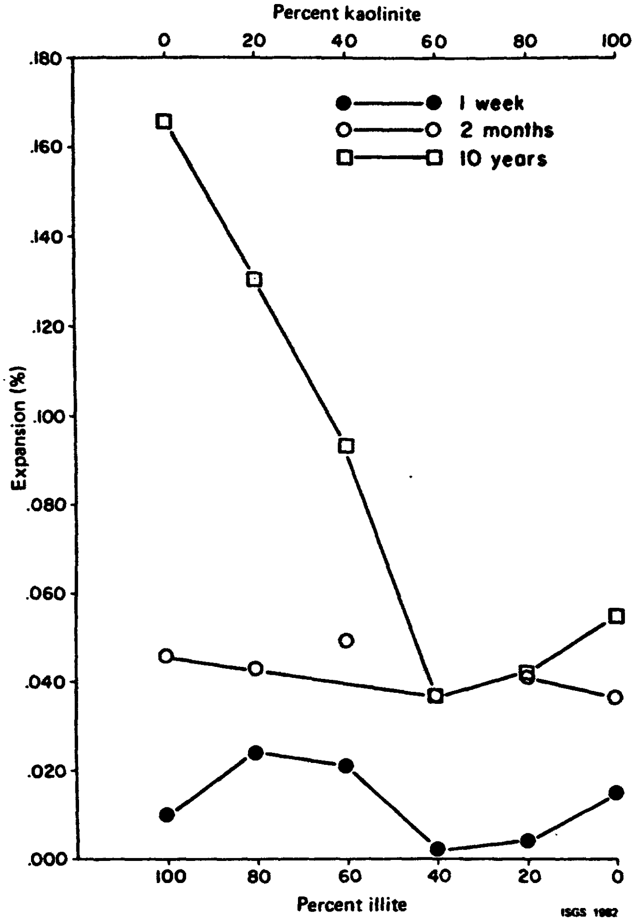

**Figure 7.** Expansion in test bricks with different ratios of illite:kaolinite.

Although this difference in rate of expansion (fig. 8) suggested a permanent difference in magnitude of expansion due to conditions of exposure, the study of McDowall and Birtwistle (1971) indicated an absolute magnitude of expansion for each brick with only the rate of expansion changed by exposure. Bricks in place in a wall probably will expand at a lower than predicted rate due to protection from weather on five faces; and also, the restraint of the wall as a unit will reduce the predicted amount of expansion (Wyatt, 1976). If freeze-thaw cycles, wet-dry cycles, growth of biota, pH of rain, and acid composition in rain are established as the main elements of exposure, a detailed study of brick weathering and its relationship to expansion will obviously require a sizable effort.

Some additives inhibit or increase expansion: figures 9, 10, and 11 show the effect of additions of MgO, $CaF_2$ (fluorite), and $K_2O$ to brick mixes. Although the first two chemical modifications are beneficial, $K_2O$ seems to increase

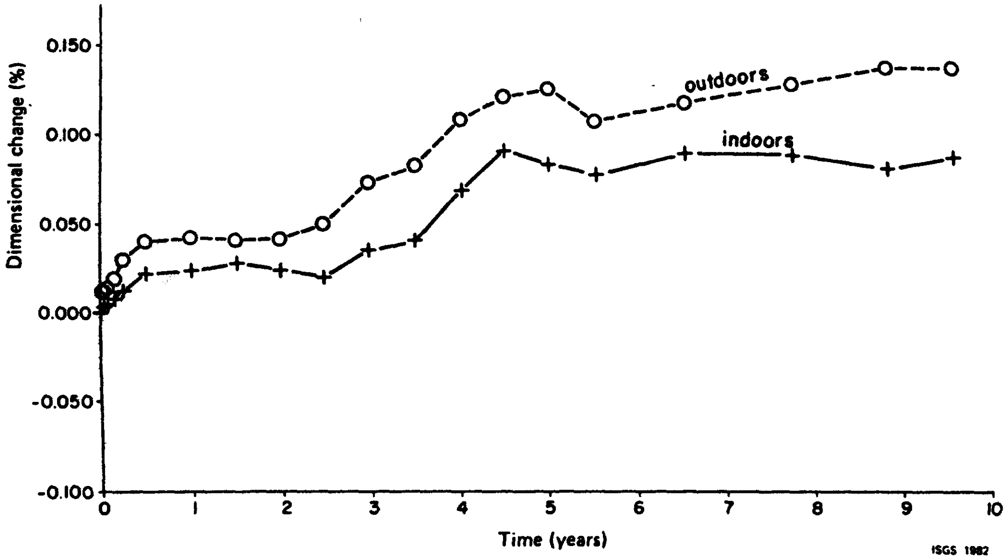

**Figure 8.** Comparison of rate and magnitude of expansion for bricks stored indoors or outdoors.

expansion. The addition of MgO has been shown by Schurecht and Pole (1929) to inhibit expansion, but the exact cause is not understood. Manganese dioxide, brown coal, and basalt fines (Goldfinch, 1980) also inhibit expansion of Australian bricks. Formation of minerals rich in Ca, Fe$^{+2}$, Mg, and Mn would explain much of the inhibiting effect of these additives. It seems likely that the quantity of fluxes, the minerals present, the size range of the minerals, their melting- or firing-temperature range, and firing conditions are all important factors. Phases formed at high temperatures have widely different tendencies to rehydrate. Ratios of $Na_2O$:$K_2O$ or $Na_2O$, $K_2O$:CaO, MgO may be important, and iron minerals and/or carbon-rich materials may influence oxidation-reduction reactions during firing as well as mineralization on firing.

Possibly, a better approach to the problem of composition versus moisture expansion would be two-fold: (1) to determine the optimum composition (that which produces the least expansion) and (2) to distinguish the high-temperature phases associated with low and high levels of expansion. If certain high-temperature phases are found to be associated with low-moisture expansion, additives can be designed to increase favorable fired compositions. Each starting composition has a firing temperature associated with a specific maximum of moisture expansion. This temperature seems to correspond to maximum porosity and permeability. The temperature associated with maximum expansion is about the temperature of the greatest number of nucleation sites of newly forming

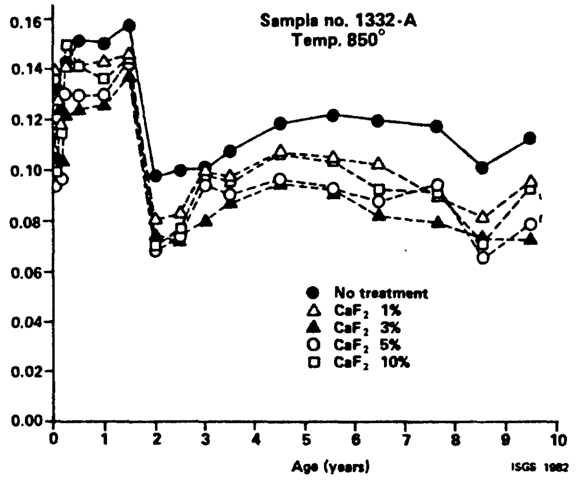

Figure 10. Expansion in test bricks with different levels of fluorite additions.

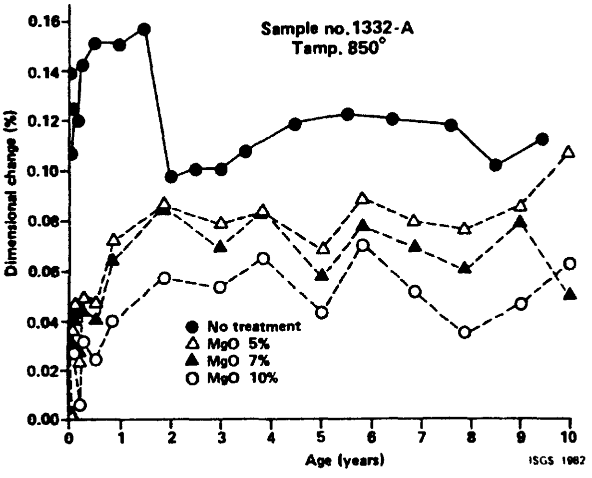

Figure 9. Expansion in test bricks with different levels of MgO additions.

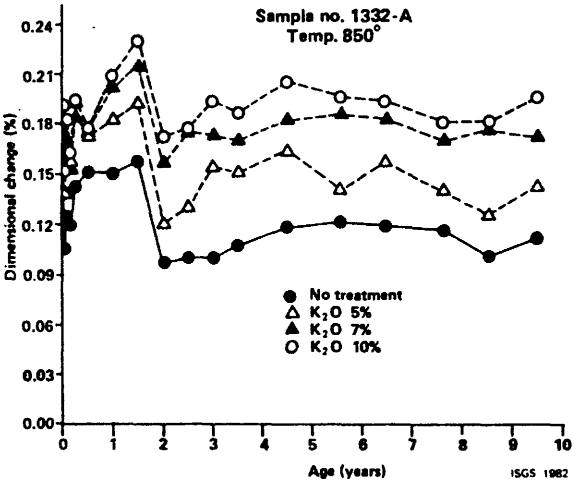

Figure 11. Expansion in test bricks with different levels of $K_2O$ additions.

phases. As the temperature increases beyond the maximum expansion point, phase nuclei grow in size and decrease in number. The process of phase crystallization corresponds to reduced porosity and permeability and to reduced moisture expansion.

Since water is the prime agent of brick expansion, treating bricks with water is one of the best ways to reduce later expansion. Figure 12 shows the results of adding water during the cooling cycle of test bricks. This pre-expansion clearly reduces later expansion and may be crucial for the durability of some bricks. Certain products made from calcite- or dolomite-rich raw materials in Illinois will deteriorate in a few weeks unless they are steam-treated during cooling; this behavior suggests the value of saturating any active adsorption sites within the brick with $OH^-$ ions, which seem to anneal the brick against later reactions with $CO_3^=$ and $SO_4^=$. The latter ions are larger than hydroxyl ions and could be expected to cause greater expansion. It is not yet known whether only bricks made from originally calcite- and dolomite-rich raw materials will show selective responses among different anions, but at least part of the reduced expansion illustrated in figure 12 could be due to sealing the brick by steam treatment and avoiding adsorption of larger anions. The differential expansion of bricks exposed to indoor and outdoor conditions illustrated in figure 8 could also result, in part, from differences in anion composition in the two environments.

Different clay materials, fired to the same temperature, often show different responses to moisture expansion. A hotel, circa 1885-1890, in Hillshore, Illinois, seems to have been built with brick fired at about 900°C. The hotel shows no sign of cracking or expansion. In the 1960s, one of the Illinois Power Company buildings had major cracking due to expansion in less than one year. Bricks used for the Power Company building were fired near the temperature of maximum expansion, and cement mortar was used. The hotel in Hillsboro certainly benefited from the use of lime mortar, which allowed for expansion.

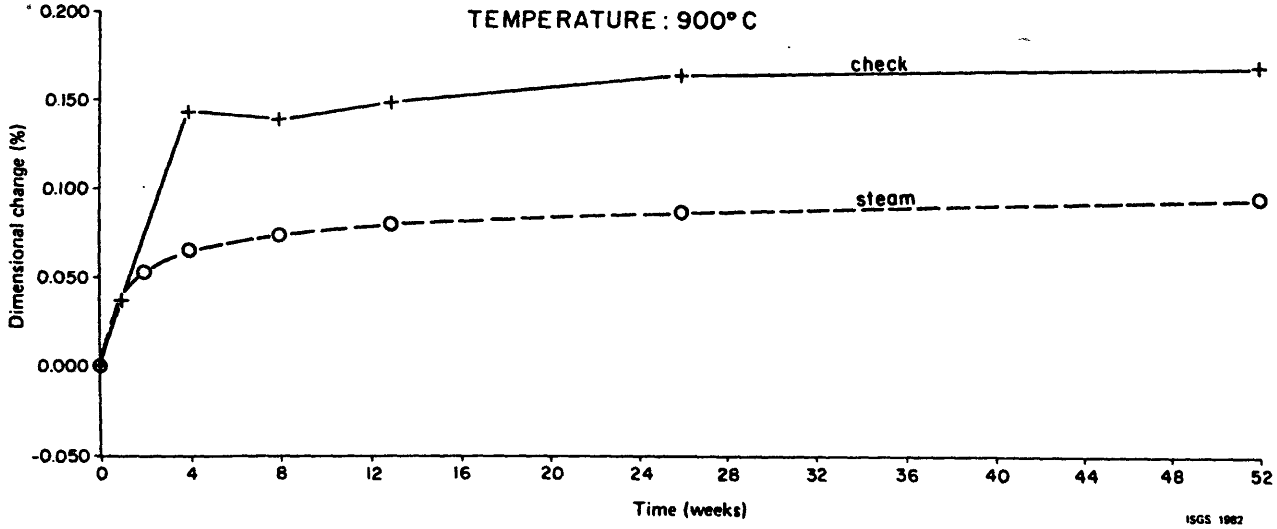

**Figure 12.** Pre-expansion of test bricks by steam treatment in kiln.

### Weathering of Brick

The reasons for the magnitude and degree of brick deterioration due to long-term weathering are not adequately understood at this time. The agents, reactions, and conditions that could cause weathering of bricks are extremely complex:

- chemical and mineralogical composition of raw material
- treatments and additives
- type of firing (kiln), position in kiln, and firing schedule
- exposure to humidity and precipitation (including wet-dry cycles)
- exposure to particulate, gaseous, and dissolved pollutants
- exposure to freeze-thaw cycles
- growth of biota
- type of neighboring materials, including mortar and wall backings

Most of these factors include several variables, which broadens as well as complicates the investigation.

Depending on original composition, the firing of normal raw materials for the production of brick results in several possible amorphous and crystalline phases. Most bricks contain phases that form on dehydroxylzation of clay minerals. Different clay minerals generate unique structures and lead to high-temperature phases with compositions traceable to parent minerals. Reactions between nonclay minerals (such as quartz, orthoclase, plagioclase, calcite, and dolomite), fluxes, and dehydroxylated clays give rise to new phases that have an important role in brick durability. The high-temperature suite of phases in a brick is obviously important in weathering reactions, but the subtle ways in which different compositions will weather has not yet been determined.

One way to generate an overall estimate of susceptibility to weathering by acid rain is to measure abrasion pH from slurries of brick powders. Phases with high-abrasion pH values will weather rapidly in acid waters. The principal factors that determine susceptibility of bricks to weathering are porosity and permeability, strength, lamination, and fired mineralogy (or chemistry as expressed by abrasion pH).

Gauri (1980) has shown the widespread occurrence of gypsum as a weathering product of limestone and acid rain. He found extreme development of gypsum in areas protected from direct wash of precipitation. Bricks have been found to be similarly discolored under sills and roof overhangs. In many cases a concrete or limestone sill may be the source of calcium ions for the staining, but it has been observed in protected environments with only the mortar as a source of calcium. The degree of deterioration associated with these stainings is unclear, although at least one building has been discovered with cement block replacements of the brick below every sill. At many sites it is virtually impossible to distinguish between the effects of underfiring and weathering as a cause for weak and friable bricks. At least some century-old face bricks in Chicago appear to be unaffected.

## SUMMARY

An experimental approach dealing with so many variables requires some simplifying assumptions and tests to measure the interaction of several factors. Retrospective studies can be used to isolate bricks showing deterioration, but usually little is known about the raw materials or firing history of the brick. Retrospective studies also suffer for lack of information about exact conditions of exposure. Determination of brick mineralogy, water absorption, and general physical properties of newly fired bricks can be used as a predictor of tendency to weather. Predictions based on general principles are only rough guides; a well-designed experiment is much to be preferred as the basis for predictions. Our experimental approach for future work involves the use of multiple-regression analysis to test freeze-thaw, wet-dry, acidity, acid composition ($H_2SO_4$:$H_2NO_3$), and possibly biological factors as agents in brick expansion and deterioration. Choices of raw material will determine differences due to composition, and firing levels will result naturally from the bricks tested.

The expansion observed during a relatively short time after firing can usually be allowed for in building design and construction. Proper design of buildings, use of sufficient expansion joints, use of optimum raw materials, use of aged bricks, use of certain additives and treatments, and complete firing will alleviate or eliminate most of the moisture expansion problems.

Determination of the high-temperature phases formed in the bricks fired for expansion studies will give direction to our future studies, and a comparison of unfired mineralogy with mineralogy at several temperatures will give indications of possible optimum conditions as well as increase our understanding of the method of production and weathering of old brick. A method of assessing short- and long-term durability of bricks is certainly needed as well as some practical methods for restoration.

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