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2002

The Evaluation of Protective Coatings and Their Effect on Salt Formation on Brick Substrate

Sherry Nichole DeFreece *University of Pennsylvania*

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The Evaluation of Protective Coatings and Their Effect on Salt Formation on Brick Substrate

Disciplines

Historic Preservation and Conservation

Comments

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THE EVALUATION OF PROTECTIVE COATINGS AND THEIR EFFECT ON SALT FORMATION ON BRICK SUBSTRATE

Sherry Nichole DeFreece

A THESIS

In

Historic Preservation

Presented to the Faculties of the University of Pennsylvania in Partial Fulfillment of the Requirements for the Degree of

MASTER OF SCIENCE

2002

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Chapter 1: A History of Paint on Brick and Stone Exteriors in Europe and Colonial to Modern America

1.1 Introduction

It is well known that architectural masonry exteriors have been painted since ancient Greece, and though coatings were often brightly colored, the true reason for the application is not known. Was the paint applied solely for decorative purposes, or was this decoration borne of a perceived need to protect the masonry? Ultimately, paint is essential for both reasons, and paint was applied to different elements to perform different functions. The purpose of this chapter is to give a brief history of the European and colonial to modem American tradition of paint on architectural masonry exteriors.

Some recent publications discourage the use of paint on brick and stone, and even state that its application is detrimental to the continued stability of the substrate. In Guy E. Weismantel's Paint Handbook, a section on brick begins, "According to most experts, a brick masonry wall should never be painted. Brick in itself is a finished material, and any painting of brick is often due to a problem."' However, a literature survey tends to favor the belief that paint has been seen as a protective and decorative coating for mgsonry up until the development of more modem paint films, and their application has given forth the notion that painting masonry is"bad". The paints used until this point not only provided decoration, but helped to create a "sacrificial layer" on the masonry to extend its life and "renewed" surfaces in the absence of cleaning strategies.

¹ Guy E. Weismantel, *Paint Handbook*, (Boston: McGraw Hill, 1981), 11-20.

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1.2 Paint and Porous Masonry Materials—Science behind the Theories

Surface coatings applied to brick and porous stone will be successful depending on a variety of factors. The porosity of the stone is one of the most important factors to consider. As substrate porosity increases, paint may become more readily absorbed, thereby changing the degree to which the paint can serve as a film. Surface smoothness also is determinant of a successful film. Much of the adhesion of paint to the substrate is due to mechanical keying as opposed to a chemical bond. Therefore, if a substrate is too smooth, i.e., with highly fired or glazed bricks, a film-forming paint will not adhere properly. However, if it is too rough, a continuous film cannot be achieved. $²$ </sup>

Of course, the addition of paint can alter the water vapor permeability of the stone or brick as well, and this is an important factor to consider. Every paint type and even brand will affect permeability in a different way, and this is extremely significant when studying why views have changed over time concerning the appropriateness of painting masonry.

The general alkalinity of brick and stone (primarily due to the mortar) is another property that can affect paint performance. In older oil based paints, used often until relatively recently, the oil reacts with the alkalies producing a soap. The paint layer then becomes soft and eventually flakes off the substrate. Therefore, either oil based paint that cannot saponify should be used, or a non-oil based primer such as "latex" should be used first. However, oil paint has been shown to have poor water vapor permeability and does not allow masonry to "breathe" leading most texts and industry documentation to recommend using a complete synthetic emulsion water-based system for masonry. Before

 2 H.E. Ashton, "Coatings for Masonry Surfaces," Canadian Building Digest 131, (1970): 1.

"latex" systems were developed, surfaces were often treated with a solution of zinc sulfate. This solution would allow "the precipitation of free lime as calcium sulfate (gypsum) thus rendering the surface neutral."

Efflorescence is ^a common problem with masonry, with or without a paint layer. In addition to the damage that soluble salts do to brick and stone, it also affects paint performance. Salt crystallization can cause flaking and detachment leading to coating failure as it destroys the cohesive strength of the film as well as its bond to the substrate. Current theory regarding the relationship of salts and coatings states that the paint layer, reducing the water vapor permeability in the masonry, exacerbates damage. One can argue, regardless of the accuracy of this statement, that efflorescence and spalling continue past the time that any salts inherent in the masonry would be discharged, and are not a direct result of the application of a paint, but are a symptom of a larger problem that should be solved and not masked by a superficial coating. Often cases of increased moisture are a result of the removal or neglect of fimctional details such as gutters, overhangs and cornices. It is this removal of a building's line of defense against water infiltration that results in damage.

In addition to the natural weathering mechanisms of stone and brick, the effect caused by human action is also important. The deliberate destruction of works, or good intentions with disastrous consequences, like overpainting and stripping to return a work to its "original" state, contribute to the loss of historic appearance.

 3 Ibid, 2.

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1.3 Ancient Practices

Relatively little is known about ancient painting practices, but in the recent past, this has been acknowledged, spurring the pursuit of more research. Only fragmented evidence, at best, remains of painted architectural elements of Greece though we have exhausted the subject of its form. As interest expanded in the subject of Greek architecture in the 1830s and 1840s, a closer examination was made of the seemingly stark white marble. It was found that the pristine columns and entablatures of temples and older archaic architecture had been brightly painted. The painted decoration was a cohesive scheme, uniting architecture, sculpture and color. Vitruvius discusses the techniques of this decoration in his Ten Books on Architecture. Many of the decorated surfaces were intended to imitate more noble materials or were used to unify two disparate materials.

For protection, stones such as tuff were coated with pitch, and brick was commonly plastered. The latter was sometimes finished and polished to look like stone. Although just beginning to come into common use when Vitruvius wrote his treatise, marble was already highly admired for its strength, and most of all for its appearance. Some scholars believe it is unlikely that marble was protected with non-transparent coatings, since its beauty was so admired and imitated. Scientific evaluation confirms this, as there is evidence of weathering underneath surface coatings.

When Pompeii was discovered by Johann Joachim Winckelmann, he believed that the painted decoration on marble sculptures and arches were later additions to originally unpainted stone. Tragically, these were "cleaned" in the nineteenth century, and the paint

⁴ R. Rossi Manaresi, "Stone Protection from Antiquity to the Beginning of the Industrial Revolution," In Science and Technology for Cultural Heritage 2. (1993): 151-152.

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was removed.⁵ Brick largely dominated Roman architecture, and for many years, it was assumed that the expertly laid brick walls were left exposed. However, it has been discovered that they were usually covered in marble, tiles or mosaics, the brick acting as a structural element covered with decorative cladding. Lime washes were also applied as an initial covering. Evidence of this exists on several major monuments including the arches of Septimus Severus and Constantine and the column of Marcus Aurelius and Trajan's Column. There is also evidence of painting for the purposes of unifying and protecting structures that were repaired.⁶

1.4 European Traditions

Little has been written regarding the coating of brick and stone during the middle ages, though the Romanesque and Gothic periods yield some information. Many examples of European architecture show evidence of painted exteriors from the time of their construction. While the practice indicates that aesthetic and ideological reasons formed its basis, paint also served as a form of protection. Examples of this are common in Northern Europe where polychromy was prevalent. In other areas, white marble was used for its aesthetic qualities, as is shown in Pisa and Lucca Cathedrals.⁷ At Siena and Orvieto Cathedrals, a transparent coating called "cera colla" was applied. This treatment

['] Jukka Jokilehto, "Painted Surfaces in European Architecture," In Seminar on Building Surface Treatments, (Rome: ICCROM, 1991), 7.

[^] Ibid, 7-8.

R. Rossi Manaresi, "Stone Protection from Antiquity to the Beginning of the Industrial Revolution," In Science and Technology for Cultural Heritage 2. (1993): 152-154.

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was a mixture of wax and resin, and was certainly a protective measure, however, it is not known if this was applied originally or after deterioration had already occurred.⁸

In the Renaissance and Baroque periods, it was common knowledge that stones decayed, and that this was primarily the result of water infiltration. This is examined in detail by Leon Battista Alberti in *de re Aedifectoria*, in which he calls for the seasoning of stones to ensure durability. Plaster and stucco coatings were encouraged for protection of brick and softer stones, but their primary use was aesthetic, to imitate marble or other stone. This was even done on what were considered durable stones like travertine, thereby reinforcing the evidence that the coatings were aesthetic.^ At this time, paint was also applied either directly on masonry, or was part of an intonaco (lime plaster) layer that could imitate other materials or draw attention to specific elements or special values.

While texts of the fifteenth and sixteenth centuries do not mention the use of clear protective coatings, scientific investigation has indicated their presence. Treatments such as wax mixed with colophony, honey and mutton tallow have been found, and varnish made from sandarac, nut oil, incense and potash alum is recommended for stone protection in the sixteenth century Marciana Manuscript. Other documents refer to the use of varnishes and oils, but it is unknown if the substances were for protection or aesthetics.¹⁰ "The first specific indication of stone treatment with the declared purpose of protection is dated ¹ 567, and is an exception for such an early date. It refers to the Public Palace of Louvain, which was 'built in porous stone that was easily alterable due to frost.

 $⁸$ Ibid.</sup>

 $⁹$ Ibid, 154.</sup>

 10 Ibid.

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so that the habit of painting it with oil was adopted'...and was continued until 1829 ^{"11}" These practices continued until the second half of the nineteenth century, when advances in coatings and materials technology provided for the formulation of more elaborate mixtures with the intention of forming a thick coat on stone (i.e. white lead-based coatings). After this, the development of chemical treatments like silicates and fluosilicates allowed for greater diversity in treatment options.¹²

In medieval as well as classical architecture, elaborate schemes of polychrome painting were also introduced. Weimar, Germany was filled with polychromed buildings dating from the fifteenth and sixteenth centuries that, until recently, had been overpainted in yellow and white.¹³ While the use of color and artistic theory during the medieval period was abundant, especially in Italy, much of it took place within the interior of buildings and involved the skill of fine artists. In the Baroque and Rococo periods paint color and its resulting dramatic effects were ultimately realized. However, much of the experimentation during this time also took place within interiors.

As early as the nineteenth century, knowledge regarding the painting of medieval interiors was disseminated and interior as well as exterior paint were truly examined. Ruskin was especially concerned with the exterior of the architecture of this period, desiring to emphasize the skill of the artist and the inherent age of the material. The Romantic movement created new interest in the architecture of the past, and sought to give meaning to the surrounding landscape. Scholars like Viollet-le-Duc believed that the period preceding them was excessive, and sought to return architecture to their

 $¹¹$ Ibid, 155.</sup>

 12 Ibid, 155-156.

¹³ Jokilehto, "Painted Surfaces in European Architecture", 9.

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perceived ideal. This resulted in the "stripping" of many elements and the addition of others, causing the realization of a period that never was. John Ruskin, on the other hand, despised the idea of painting for paint's sake, and preferred bare materials. Nevertheless, it created a new interest in the architecture of the past, but with the fashion of stripping of masonry to the bare brick or stone without concern for the reason that paints and coatings were applied, an assumption is made, creating a structure that never was.

7.5 Early Developments

A painter's guild was first formed in London in ¹⁴⁸⁷ and was united with the stainer's guild in 1502. They were allowed to use oil paints, while members of the plasterer's guild used "whiting, blacking, red lead, red and yellow ochre, and russet... in size water."¹⁴ The English guild tradition was carried over into America when Thomas Child of Boston brought the first paint mill to the country ca. 1701 ^{15} From then on, the craft continued and flourished. However, in America, the guild system eventually collapsed through the overturn of British rule. It became possible to acquire paint materials including pigments, oils and other necessities from merchants or painters. People could paint for themselves or hire unskilled labor to perform the work.

Despite the early availability of painters and paint materials in America, buildings were rarely painted in the seventeenth century. Only later in the eighteenth century does documentation show an increase in house painting. At this time, painting was usually done with whitewash, and any other means of exterior coating was extremely rare until

¹⁴ Richard M. Candee, "Housepaints in Colonial America: Their Materials, Manufacture and Application," originally appearing in Color Engineering Magazine in four parts: September-October 1966; November-December 1966; January-February 1967 and March-April 1967 (New York: Chromatic Publishing Co.): I. 15 Ibid.

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well into the nineteenth century. ¹⁶ Paint other than whitewash was prohibitively expensive and painters were rare. The exception to this rule is with public buildings and churches, which were painted earlier.

Since the Colonial period, most houses in America were constructed in wood. Forests had a seemingly unending supply of trees, and early on, sawmills were operating while brick kilns took much more work and resources. Other obstacles lay in the way of early masonry. Obtaining suitable limestone in great quantities for burning was also impossible in many areas, requiring Rhode Island to be the chief supplier of the Colonies' limestone as the climate did not permit using clay mortar (a common practice in England at the time). Oyster shell lime was common until 1724 and along the Connecticut River, no lime was used before 1679 ¹⁷

Stone was also rare in some areas like coastal Virginia, and transportation of large quantities was, of course, not possible. Even where fieldstone was plentiful, as in Massachusetts, the lack of lime made building difficult. This does not mean that masonry buildings did not exist. Bricks were produced as early as 1611 in Jamestown, and one of the first settlers was trained as a bricklayer. Virginia produced bricks, and a kiln was first recorded in 1629 in the Massachusetts Bay Colony. In Philadelphia, a bricklayer was in residence before the city was laid out. Bricks were first used for chimneys and houses for the wealthy. Once bricks could be produced economically, they replaced stone as the primary masonry material in the Colonies.¹⁸ From then on, brick and stone masonry evolved; Colonists and people of early America used various styles, bond patterns and

 $¹⁶$ Ibid, 2.</sup>

¹⁷ Fiske Kimball, Domestic Architecture of the American Colonies and of the Early Republic, (New York: Dover Publications, Inc., 1966), 35.

 18 Ibid, 38-40.

building plans throughout the seventeenth century. In Pennsylvania and Rhode Island, both building stone and limestone for mortar could be found, and thus, these two areas developed an early and strong masonry tradition. The first brick buildings in the Colonies were built as early as 1707 and were a direct result of the desire for more permanent structures.¹⁹ Often these came in the form of government buildings and the houses of the wealthy. This desire drove the development of brick kilns that could produce quality bricks in an economical fashion.

One of the most distinctive masonry traditions to develop during this time was the Quaker patterned brick tradition. As it relates to the subject at hand, they show that quite obviously, many buildings of brick were to be seen without paint. In the Delaware Valley (consisting of West New Jersey, Delaware and Pennsylvania,) the tradition of patterned brick houses and meetinghouses flourished. The scheme, design and meaning of the buildings were reflective of Quaker society. A network of builders and consumers united the region with webs of readily identifiable buildings with slight stylistic variations. As a common thread, the gable ends of brick houses and meetinghouses of nearly identical form within a community were decorated with glazed headers set in a distinctive pattern. These were often "diaper" or diamond shaped.²⁰

The coming of the Georgian period to America marked the time when buildings for common use were regularly painted. This period was begun in England around 1700 by Sir Christopher Wren, but reached architects and builders in America somewhat later. In 1715, when architect Andrea Palladio's Works was first translated into English, and as

¹⁹ Ibid, 36. " Michael J. Chiarrapa, "The Social Context of Eighteenth-Century West New Jersey Brick Artisanry," in Perspectives in Vernacular Architecture IV, edited by Thomas Carter and Bernard L. Herman (Columbia, MO: University of Missouri Press, 1991).

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other handbooks like Colen Campbell's Vitruvius Britannicus (1715-25), James Gibbs's Book of Architecture (1728), William Salmon's Palladio Londinensis (1734) and Robert Morris's Select Architecture (1757) were published, architects began to use "Georgian" elements, which were often painted. 21 As Kimball describes, the Academic styles that came into being during the eighteenth century and spread through texts such as these called for a more

abstracted composition of space, mass and surface... As received from Jones, its greatest English protagonist... architecture should be 'solid, proportionable according to rule, masculine and unaffected.... In the hands of Wren the style became less austere and more intimate, something of a baroque surprise and movement appeared... Under Dutch influence brick became the favored material. 22

The use of paints increased as the popularity of these designs, eventually being adapted for both public buildings and private (if usually elite) dwellings, spread. As the century continued, masonry also became more common, especially among the wealthy.

In the Middle Colonies and the south, houses were commonly made of brick. In England, masonry buildings became the norm as the decimation of forests made wood prohibitively expensive. While these are the norms, there are certainly exceptions in all of these cases, as taste and preference played a significant part in the choice of construction materials, as it does today. When considering the use of masonry, local conditions perhaps played the largest part, above stylistic concerns. As stated above, grand houses of stone were really only common in Pennsylvania, despite the dictate of tastemakers and writers of freatises.

²¹ John C. Poppeliers, S. Allen Chambers, Jr., and Nancy B. Schwartz, What Style is It?: A Guide to American Architecture, (New York, John Wiley & Sons, Inc., 1983), 18.

 22 Kimball, Domestic Architecture of the American Colonies and of the Early Republic, 53.

Kimball suggests that to gain ^a better understanding of the development of masonry architecture (and hence, its decoration and protection), one should look not to texts that were prescriptive tools, but to the buildings themselves. The type and method of masonry construction and the detailing of the exterior reveal ^a great deal. Typically, brick of this period was laid in Flemish bond, but this was not the rule. Occasionally, there were deviations from this; dark or glazed headers were used in a pattern as described above. Moulded bricks were used for the water table, and other differences indicate a progression in masonry construction and aesthetics. All the while, artists and masons improved their skills.

Figure 1.1 Mount Pleasant. From Roger W. Moss, *Historic Houses of Philadelphia*, 1998, p. 95.

From an early date, stucco was employed as a covering for brick and rubble masonry, especially in Charleston and the Philadelphia area. According to Kimball, "increased warmth and weatherprootlng seem to have been the principal reasons for its employment rather than a desire to imitate stone."²³ He illustrates this argument by discussing Mount Pleasant in Philadelphia (1763-65). where the facades are finished in

 23 Ibid, 68.

 ϵ \mathcal{A} stucco struck like ashlar while the brick quoins are left unfinished, (Figure 1.1) and states that only after the Revolutionary War did the appearance of exposed brick become aesthetically objectionable.

Along with architectural texts previously discussed, newspaper advertisements and early city directories show that the availability of paint materials and the number of professional painters increased. The businessmen featured in these publications include importers, merchants selling pigments, and painters themselves. While some painters were rooted in a specific area, usually a city, it was more common in the late eighteenth and early nineteenth century for a painter to take his business "on the road", painting in rural areas.^{24} The practice gained momentum, when in 1736, the first ready mixed paints became available; although, they were not widely used until the 1860s when re-sealing paint cans were developed. Until then, paint was mixed much as it had been for millennia: by mixing dry pigments and binder (often oil) with a muller on a marble or other smooth stone slab.

Different techniques were used for interior and exterior painting. Due to the lack of physical evidence for many of the instances of exterior coatings, one must look to the surviving documentation for clues. English estimator's books, reprinted in America in the early eighteenth century, list the prices for each element that was to be painted and the most popular colors: "stone, fimber, and blue for painting 'windows, doors, rails and banisters, for stair-cases, shop-windows, and mundilions...'"; while the 1700 edition of a similar book describes painting "outside works; as doors, shop-windows. Window Cases, Pediments, Architraves, Friezes and Cornices, and all other Timber-works which are

²⁴ Candee, "Housepaints in Colonial America: Their Materials, Manufacture and Application," 2-3.

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exposed to the weather..."²⁵ As these books do not list the cost or materials for painting exteriors, even clapboards, this supports the case that trim was pamted, while often, the rest of the facade was not. While this could mean that the painting of trim was the first step in exterior painting in America, it may also indicate that those who could afford to paint their trim could also afford to have a stone or brick house that was not painted. Thus, many Georgian buildings of the eighteenth century only had painted trim. This is evidenced at Thomas Turner's Cliveden in Germantown, Pennsylvania, (Figure 1.2) where in 1766 only the bargeboards, cornices, eaves, windows, shutters, doors and door cases are painted on an otherwise brick house.²⁶ It should also be noted that the trim was the first element to be painted (usually with a paint having insecticidal or biocidal qualities), sometimes before construction was complete, giving support to the thought that it would have been painted regardless of stylistic concerns.²⁷

Figure 1.2 Cliveden, From Roger W. Moss, Historic Houses of Philadelphia, 1998, p. 117.

The earliest large-scale exterior coating in America was done on wood clapboards with tar, obviously for protective reasons. This practice was done throughout the

 25 Ibid, 4.

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 27 Frank G. Matero, personal communication, December 7, 2001.

 $\bar{\omega}$ ϵ \sim \sim eighteenth century and carried over to the protection of the lower portion of brick buildings. It was certainly not as desirable as painting in oil, which was done on finer framed houses early in the century; this became more popular by ¹ 760, when exterior painting was listed in an estimator's book. Over time, however, exteriors made their way out of these handbooks as interior painting became more complex and the focus of many $vainters.²⁸$

Little has been written describing the exteriors of buildings before the Revolutionary War, but Candee indicates that the practice of painting buildings in oil was more common in urban areas and larger towns where a person dedicated to the craft was likely to do a steady business. He bases this argument on the fact that rural areas show little evidence of painted buildings until the turn of the century. It is only after the Revolutionary War that documentary evidence indicates that exteriors were painted. Candee accounts the writings of a French traveler in Philadelphia in 1796: "'An attempt is made to enliven the facades by painting them brick colour, then painting symmetrical white lines in squares, thus seemingly outlining the divisions between the bricks. The window trim is painted white in imitation of cut stone.' Another brick treatment is described in a journal of 1782. 'Ye Painter at work this week painting ye roof of our House and Back Buildings with Brickdust."²⁹

Brick dust was often used as a pigment for painting brick or roofs. This gave fireproofing protection to wood and gave a more pleasing color to poor quality brick. The desire to imitate a more noble material was also attempted by using sand applied onto a

²⁸ Candee, "Housepaints in Colonial America: Their Materials, Manufacture and Application," 5. 29 Ibid.

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coat of white lead in oil to simulate cut stone. This was done in Boston at the Brattle Street Church in a 1744 renovation and at Mount Vernon in 1799.³⁰

Documents detailing the application of paint prior to the nineteenth century are very rare. However, the few documents that remain and the physical evidence indicate that for exterior painting three coats of oil based paint (with turpentine added) were applied, with wood intended to be repainted every few years when the white lead became chalky. Often the secondary façades were painted in Spanish brown. Other common shades were used, as well as compound colors consisting of ochres, lampblack, indigo, $etc.³¹$ One must consider, however, regional differences in painting styles. This is less evident in the existing literature, and can be examined only through the buildings themselves. Texts were often intended for use by architects and painters and do not necessarily reflect how or in what style vernacular buildings were painted.

After the Revolutionary War the materials used in construction in the United States remained the same, though the forms changed. Brick houses began to be seen in greater numbers in New England, as did the numbers of cut stone houses (but to a lesser degree.) One example of a stone house begun during this time was the famed house of Robert Morris in Philadelphia (began ¹ 793, never completed) which was to be faced with marble. As time went on, innovations in the treatment of materials were seen. Chiefly, stucco was increasingly struck to look like ashlar, as seen at Solitude, also in Philadelphia (1784) ; this technique began to be used more frequently after the turn of the century with the buildings of Benjamin Henry Latrobe and Robert Mills.³² Thus, the application of

 30 Ibid.

 31 Ibid, 6.

 $\frac{32}{32}$ Kimball, Domestic Architecture of the American Colonies and of the Early Republic, 152.

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exterior finishes, in this case stucco, was becoming increasingly an aesthetic rather than protective treatment. The stylistic effect, however, can be applied to paint. While it certainly served the purpose of protection, the impetus was the appearance of a more noble material.

1.6 Traditions of the Early to Mid-Nineteenth Century

By the beginning of the nineteenth century, exterior paint was much more common than had been in previous years. Travelers' accounts note many examples of white houses with green shutters (much to the dismay of A.J. Downing, who thought this practice deplorable); and in 1818 brick houses of Boston were "painted white or stone color... the frame houses are painted more variously, according to the fancy of the owners or occupiers."³³

It is certainly easier to study paint on exterior buildings within the United States in the nineteenth century, as most existing historic structures were built during this time. 34 Paint was often applied for what painters called the "economic" part of the building, meaning that it was for protection of the exterior materials, but the century saw many changes: not only in building technology, but in paint technology as well. By the 1830s, red brick was rarely seen. In New England, where the stucco technique was not as prevalent as in other areas, brick was often painted gray. Some buildings where this technique can be seen are Boston's Franklin Crescent, and the Gore House in Waltham, Massachusetts. In areas where wood buildings were still common, the most prestigious

 33 Candee, "Housepaints in Colonial America: Their Materials, Manufacture and Application," 5-6.

³⁴ Pamela W Hawkes, "Economical Painting: The Tools and Techniques Used in Exterior Painting in the 19th Century," The Technology of Historic American Buildings, (Fredricksburg: APT, 1983), 189.

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used smooth boarding in lieu of clapboards set with close joints with the wood painted and sanded to resemble cut stone; this technique became a favorite of Bullfinch.³⁵

As the century progressed, taste began to play an increasing role in the lives of Americans. A. J. Downing's Cottage Residences (1873) was released in the United States and detailed not only proper design for all situations from townhouses to houses for the clergy, but also mandated taste. Downing felt that a building's materials should reflect its style and use, if not the class of the occupant, and vice versa. Mansions should be made of stone, and wood should not imitate more noble materials, contrary to common practice (though brick could be painted to resemble stone). The "Pointed" or "Tudor" style was appropriate only when built of stone or brick covered in stucco. "To erect a dwelling in this style of so light and frail a material as wood, under any circumstances, would be a complete violation of good taste, as there would be an entire discordance or incongruity between the style adopted and the material employed. 36

When compared to previous handbooks, one can also see the progression of architectural types and their details through time. For instance. Downing states that while stone is the most desirable and durable building material "both in expression and reality" brick "is being used in increasing numbers," and goes on to explain that brick's solidity and permanence is appropriate for houses in a rural setting. This statement shows that brick was accepted in locations other than the city, where we find the majority of masonry buildings. While this treatise is mostly about proper taste, it also gives clues that

 35 Kimball, Domestic Architecture of the American Colonies and of the Early Republic, 153.

³⁶ Andrew Jackson Downing, Victorian Cottage Residences (New York: Dover Publications, Inc., 1981), 57.

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masonry was cost-efficient at the time. However, Downing indicates that the use ot brick

in the country was for structural stability instead of visual effect.

The offensive hue of red brick walls in the country is easily removed by coloring them any agreeable tint, which will also render them drier and more permanent. Brick and stucco (that is, a wall built of rough brick, and coated exteriorly with a [stucco]) is, when well executed, one of the best materials for cottages or villas. It is much warmer and drier than wood, or even stone, and is equal to the latter in external effect, when marked off and colored to resemble it.³⁷

DESIGN VIII A VILLA IN THE ITALIAN STYLE

Figure 1.3 Downing's Houses. From Victorian Cottage Residences, 1873.

From this statement, it can be seen that paint and stucco were seen as measures that resulted in both an aesthetic and visual effect. Downing details the methods in which

 37 Ibid, 8.

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stucco should be applied, detailed and tinted to resemble "agreeable" light colored stones. This technique was favored for "English" or "Rural Gothic" style cottages and villas in the "Italian" style. (Figure 3) Other styles deemed suitable by Downing also utilize masonry construction. For his "suburban cottage for a small family," brick finished with stucco was appropriate "as the projecting roof would afford perfect security for the dryness and preservation of the walls," and advocates using rough (i.e., hand-molded) brick as it would accept the stucco better, and "in many districts where bricks are easily obtained...will be found as cheap as wood."³⁸ Stucco was a common finish for brick from the Colonial period onward, and was often scored and painted to resemble stone. Stone dwellings were appropriate for mansions and Tudor cottages, as stated above, but it was also considered suitable for "ornamental" farmhouses. However, in farmhouses, the stones should be laid irregularly of rough or slightly dressed stone, with the trim except for sashes and doors painted the same color as the stone.

Downing also supports applying paint directly to brick. In the "bracketed", "irregular old English" and "Italian" styles, he states that to "destroy" the "raw and disagreeable color of new brick" it should be painted in three coats of oil of a "soft, pleasing shade" with (in the case of the "Italian" style) wood trim painted and sanded to resemble stone. 39

Downing was not alone in his beliefs, as evidence shows. Samuel Sloan in The Model Architect supported painting brick to disguise its color but conceded, "The public have acted very differently and urged by motives of economy, have built the principal part of our cities and towns of this cheap and durable material." Lewis Allen in Rural

^{&#}x27; Ibid, 30.

³⁹ Ibid, 89, 133, 144.

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Architecture (1852) credits brick as being able to take on any color given to them by the "taste of the builder."⁴⁰ Much of the exterior brick of the nineteenth century and earlier was painted. Although, on many occasions itwas painted red with white joints painted in. This gave the appearance of using a higher quality of brick and joinery than may have been feasible, either due to resources or location. High-fired brick was often unavailable or cost ten times the amount of common brick.⁴¹ Often builders used high fired brick on the front facades of buildings and painted side walls, constructed of common brick to match. Paint was also used to blend patches with old brick when new work was installed.

When brick was to be painted, a mason would lay the units tightly. The wall was then rubbed down with a broom and covered with linseed oil. This oil served as a protective water repellent for high-fired brick or was an absorption retarder when finished with paint. Brick primer could also be used. This was a diluted wood primer or a commercially available mix such as D.S. McDannell's Waterproof Priming for Brick, containing shellac, sodium bicarbonate, water and rosin. Following these treatments were the finish coats. These were either commercial mixes or homemade versions. One mix consisted of Venetian red, orange chrome ground in turpentine, boiled oil and japan (wax produced from the lacquer of the sumach tree). Then the work was often finished with striking artificial joints in white. 42

The newer styles of brick, including mottled brick were also imitated with paint. The emergence of these techniques tends to support the argument that during this time an increasingly complicated combination of aesthetics and economy were at work. Poor

⁴⁰ Hawkes, "Economical Painting: The Tools and Techniques Used in Exterior Painting in the 19th Century," 206.

 41 Ibid, 205.

 42 Ibid, 207.

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quality bricks were used due to cost, but instead of being painted to resemble stone or simply for color, they were disguised as other bricks. Obviously, it was not brick itself that was considered unattractive. The brick technique was attractive but the materials did not allow for their exposure.

Another consideration, which should be made concerning the impetus for painting brick, was the use of decorative treatments like marbleizing, sanding and graining. These techniques were obviously intended to hide the brick substrate and have been in use since the twelfth century. Materials that are more common were sanded or painted to imitate expensive marbles and other stones. This was done in the United States as well as Europe; it is seen at Washington's Mount Vernon (1799). Sanding was also considered a protective measure, though there has been no evidence to support this commonly held belief in the available literature.

/. ⁷ New Developments—the Industrial Revolution to ¹⁹⁵⁰

As stated above, the nineteenth century was witness to many changes in both building and paint technology. In addition to advances in the science behind paint, painters also revised their approach. Unions like the Decorating Contractors of America (1884) and the International Brotherhood of Painters (1887) were established and public education took the place of apprenticeship.⁴³ Individual businesses also grew by the end of the century while the absence of guilds in the United States allowed people to paint their own buildings and houses. Handbooks published for architects, builders and homeowners were distributed from the beginning of the nineteenth century had short

⁴³ Ibid, 190-192.

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recipes for whitewash or sections dedicated to paint. Even before these texts were published, people regularly whitewashed their own buildings. After the Civil War the publication of handbooks dealing specifically with painting such as F.B. Gardner's Everybody's Paint Book (1888) and Anson Gilman's Every Man His Own Painter (1871), as well as household magazines and technology and architectural journals only made the practice simpler and more popular. These sources, along with actual specifications have become the primary sources for information on historic painting practices.

Through the early twentieth century, the materials of exterior paints did not radically change. In addition to common whitewash, most were white lead and pigments ground in linseed oil (in some areas, fish oil was used). In the 1850s, the addition of zinc white to the available repertoire served as an alternative to harmful white lead. Furthermore, driers like metallic salts of lead, manganese or cobalt were added, and mineral spirits and turpentine were used as thinners. Mineral paints, which form a chemical bond with the substrate while allowing for water vapor transfer, were developed during this time as well.

In order to attract the common consumer, paint catalogues featuring colored swatches or color lithographs showed variations of paint schemes for the architect or average home owner; and whether appropriate or not, paint manufacturers were touting the advantages of paint. "Paint is a necessity: do not spare it either inside or out, whether your buildings be brick, stone, plaster or wood."⁴⁴ In fact, this claim serves to illustrate the question at hand: why were stone and brick painted? It would seem that while

⁴⁴ Ibid. 195.

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necessity and aesthetics served to be the underlying reasons for the practice in previous centuries, with the development of large-scale marketing, the practice was due to an entirely different reason. People were told to use the material on everything, with no precedent to justify it except the fervent claims of the manufacturer; and use it people did: Americans alone consumed over $174,000,000$ pounds of mixed paint in 1868.⁴⁵

As paint materials developed and with the addition of synthetic binders and other previously unknown ingredients, the claims did not change. Painting masonry and brick was continuously encouraged, though these materials were the same that had been in use before the developments in paint technology. Only painting manuals intended for professionals discouraged painting too often. In fact, the inappropriate use of the modem paints may have led to the question of the use of paint on masonry, as old paints like whitewash and oils did not threaten the fabric of old structures.

By the early twentieth century, changes in mechanization and scientific research as well as the ability to transport materials on the railroad, brought advances that resulted in better tools and better, less expensive paint. Many of these developments have been rejected as a product of the momentum of progress, but many more, such as titanium dioxide (available 1916) have been retained and have formed the basis of the modem paint industry.

Between World War ^I and World War II, the paint industry experienced rapid changes. Processes and formulas developed for the war efforts were put into common use, including latex paints and other materials, mainly due to the expanding petrochemical industry. Although synthetic materials such as celluloid and plastic were

⁴⁵ Ibid, 211.

produced in 1870, they were not used in paints until after World War I. They are now widely used.⁴⁶

The common use of paint changed during this period as well. Marketing increased and harnessed the forward-looking vision of the emerging society. Paint companies like Benjamin Moore sought to capitalize on this hopeful and idealistic consumer driven society, as their publications illustrate (Figures 1.4, 1.5). Once again, consumers were encouraged to paint everything: wood, brick, stone, even cars, and they responded by doing so. This was an age of unapologetic consumption. (Figure 1.6).

Figure 1.4 Benjamin Moore Brochures 1924 (L) and 1934 R), from: www.benjaminmoore.com /archives

⁴⁶ Caleb Hornbostel, Construction Materials: Types, Uses and Applications, (New York: John Wiley and Sons, Inc., 1991), 574.

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Figure 1.5 Benjamin Moore Cement Paint Brochure, 1916 and 1935, from: www.benjaminmoore.com /archives

Figure 1.6 Benjamin Moore's & One-Coat House Paint mid-1950s, from: www.benjaminmoore.com/ archives

1.8 Modern Approaches—¹⁹⁵⁰ to the Present

Paint manufacturing processes have become much more complex since 1950. Paints are now developed in the laboratory after many testing procedures and standards are applied to the proposed coating. Computers generate exact color and chemical proportions to streamline the development process. Synthetics have reached an all time high for production and use, along with chemical bonding systems such as epoxy paints. These new materials have met with varied success. Epoxy and alkyd paints may cause damage to masonry substrates due to their poor water vapor permeability. These and other paints contain environmentally harmful chemicals that have been restricted from use, eliminating the choices that painters and architects had in the past.

When faced with painting masonry, current choices are usually alkyd, mineral, latex or simulated whitewashes. Often the painter or purchaser of the coating either lacks the knowledge to make a proper decision, or the cost in combination with the desires of the client overshadow the necessity for proper materials and application. With the development of higher firing techniques masonry materials that usually do not need to be protected, their coating has become largely aesthetic.

1.9 Current Thought

As has been shown, the tradition of paint on masonry has progressed through time from a protective to an aesthetic treatment, with periods in which the line between the two is blurred. The subject of whether brick should or should not be painted is debated in current texts and information directed toward the building professions. Not only do texts

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differ in recommendations, but they often acknowledge the dispute.^{47} Failures have been reported; these include older coatings flaking off buildings, impermeable coatings causing water to be trapped within the brick, leading to freeze-thaw cycling and thus causing subsequent spalling, and the failure of coatings that are applied to bricks treated with water repellents. Ashton states, however, that this last problem may be prevented by using "latex" paints, which have a higher rate of vapor permeability, allowing moisture to escape from the substrate. In his 1970 article "Coatings for Masonry Surfaces", he also recommended the use of two other types of coatings: "rubber base" paints with binders of vinyltoluene-acrylic, styrene-butadiene and chlorinated rubber which did not economically compete with "latex", and a "breathable" asbestos-sand coating for masonry, including brick. Obviously, the asbestos paint is now restricted. Also mentioned were cement paints used before the formulation of "latex" paints, which chalked and were difficult to renew.⁴⁸

According to Ashton in 1970, "masonry surfaces can be successfully painted if the correct type of coating is used for the substrate in question and if good design and construction have prevented leaks and openings in the structure.¹⁴⁹ His article states that paint serves as a protective coating "by preventing rain penetration" as well as performing an aesthetic function.

Recent and even current fashion has resulted in the removal of paint from historically painted buildings. It has resulted from owners' desire to avoid repainting. As can be determined from evidence given above, these coatings were often applied as a

Ashton, "Coatings for Masonry Surfaces," 3. ' Ibid, 3-4.

^{&#}x27; Ibid, 4.

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Chapter 2: Salt Weathering Processes

2. 1 The Salt Weathering Process

Salts are naturally present both in earth and in water. They also result from air pollution, inappropriate chemical treatments (including conservation treatments like acidic and alkaline cleaning solutions, Portland cement, waterglass products, etc.⁵¹), deicing salts, by-products of organisms, and alterations to the water table due to irrigation, over-pasturing and flooding.⁵² While devastating to the environment for many reasons, the focus of this chapter will be on damage salts cause to the built environment.

The characteristics of the material used for building plays a large role in its deterioration by salts. Primarily, these characteristics influence how water is transported within the material. The porosity and water vapor permeability of masonry are the most important factors to consider. Salts enter a building transported in solution with water, and according to Arnold and Zehnder (1990), the water that is contained within a building is largely a diluted salt solution.⁵³ The pore structure of masonry allows for the capillary transport of water from the ground or driving rain. Water in the vapor state enters through condensation at the surface and within pores and through the hygroscopicity of the material and the salts (the ability of a material to attract moisture from the air). 54

⁵¹ Andreas Arnold and Konrad Zehnder, "Salt Weathering on Monuments", in *The Conservation of* Monuments in the Mediterranean Basin: Proceedings of the Ist International Symposium, Bari, 7-10 June 1989, Fulvio Zezza, ed. Brescia, Italy: Grafo, 1990, 33.

 52 Andrew Goudie and Heather Viles, Salt Weathering Hazards, New York, John Wiley & Sons, Inc., 1997, 49-50.

 $⁵³$ Arnold and Zehnder, "Salt Weathering on Monuments," 32.</sup>

⁴ A.E. Charola, "Salts in the Deterioration of Porous Materials: An Overview," *Journal of the American* Institute for Conservation 39 (2000), 328.

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2.2 Influence of Porosity and Material Composition

The porosity of ^a material is the controlling factor in determining how it will weather. The pore size, radii distribution, total porosity and surface properties all affect the weathering phenomena by allowing (or not allowing) the formation of secondary materials (including salts) within the pore structure. These factors also determine how damaging a weathering agent will be.⁵⁵ Porosity originates in three ways: primary porosity is created when the rock forms, secondary porosity occurs when the primary pores are modified during the final deposition and crystallization of the rock, and weathering porosity is created by the process of weathering. Additionally, the type of porosity defines the permeability of a material. Open porosity occurs when the system of pores is interconnected and is accessible from the stone's surface. This means liquid water and its vapor can enter at the surface and is distributed throughout the material via flow pore channels. Pores can also be inaccessible to moisture and have non-through flow pore channels.⁵⁶ These do not contribute to weathering unless the pore walls are destroyed and water is allowed to enter.

The location of pores is also important in determining the weatherability of a material. Interparticle porosity is the space between the particles of a stone and is the primary type. Intraparticle porosity is the space within these particles. Finally, the pore space within the crystal lattice of a material is called intracrystalline porosity.⁵⁷ Each of these types plays a role in the weathering of stone. However, some types and locations of

⁵⁵ Bernd Fitzner, "Porosity Properties and Weathering Behaviour of Natural Stones: Methodology and Examples," In Second Course on Stone Material in Monuments: Diagnosis and Conservation, Heraklion, Crete, C.U.M. University School of Monument Conservation, Bari: 1993, 44. ⁵⁶ Ibid. 44.

 57 Ibid.

pores are more prone to weathering than others. Fitzner (1993) has defined four porosity groups based on their weathering behavior during freeze-thaw cycling and/or salt crystallization, identifying those most susceptible to deterioration. Group ¹ consists of stones with a high total porosity consisting of large pores with large entry points. He found these stones to be very sensitive to freeze-thaw but resistant to salt crystallization. Group II is comprised of stones consisting of a high total porosity and large pores with small entry points. These stones were resistant to freeze-thaw cycling as well as salt crystallization. Group III stones exhibit the most damage, being sensitive to both freezethaw cycling and salt crystallization. These stones have a high total porosity comprised of large amounts of both small and large pores with large or small entries. Finally, Group IV, with low to medium total porosity stones with a high volume of small pores exhibit resistance to both freeze-thaw and salt crystallization.⁵⁸

From his observations, Fitzner concludes, "The destruction of the granular skeleton by salt crystallization is caused by the proportion of large to small pores assuming a sufficient total porosity. Stones with a sufficient volume of larger pores and a higher volume of smaller pores which are interconnected can be considered as significantly sensitive to physical weathering." This study forms the basis of current beliefs regarding salt crystallization processes. Fitzner goes on to say:

Due to thermodynamical reasons the salt crystallization starts in large pores. Small dimensioned pore space serves as supply reservoir for salt solutions allowing the growth of salt crystals. After filling the large pores the crystallization process continues in direction of the small pores. The filling degree of pores controls also the area of pore space and the intensity of mechanical stone destruction caused by salt hydration procedures due to volume increase of the salt body. As the formation and the growth of ice crystals in the pore space follow the same laws, the stone

 58 Ibid, 45.

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of the porosity group III can be considered also to be sensitive to freeze thaw stress⁵⁹

As stated above, the deterioration caused by salt crystallization and freeze thaw cycling causes mechanical failure by breaking the intergranular bonds between particles. While salt crystallization is the focus of this study, it is also important to examine other degradation processes like freeze-thaw cycling and expansion and contraction of clays, which, along with salts, act to destroy masonry.

In general, porous materials swell to a major or minor degree upon exposure to moisture; this effect is called hygric dilatation if moisture is absorbed in relative humidity ranges of 0-95% and hydric dilatation if the swelling is due to immersion in liquid water.^{60} When in a salt-free environment, the material shrinks again upon drying; this cycle can be repeated with some material fatigue, but the material will remain essentially the same volimie. If temperatures allow for freeze-thaw in combination with dilatation and contraction, the material fatigue is more pronounced and the expansion of the grain structure is irreversible "due to the volume of ice against liquid water" when the material has been saturated; but "in the case of partial saturation, however, the freezing causes a contraction of the pore structure."^{61} This is related to the phenomenon (discussed by Fitzner and presented above) wherein larger pores are filled first drawing liquid from finer pores which are then emptied, creating a "capillary underpressure" and causing the grain structure to contract to a point where irreversible material fatigue is inevitable.⁶²

⁵⁹ Ibid, 51.
⁶⁰ R. Snethlage and E. Wendler, "Moisture Cycles and Sandstone Degradation," in Saving Our Architectural Heritage: Conservation of Historic Stone Structures, N.S. Baer and R. Snethlage, Editors, New York: J. Wiley & Sons, (1997): ⁹

⁶¹ Snethlage and Wendler, "Moisture Cycles and Sandstone Degradation," 9.

 62 lbid, 9, 11.

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The effect of swelling and shrinking is often increased or, alternatively, reversed in the presence of salts; stones will contract while wet and then expand as they dry. Further complicating the matter is the fact that the swelling does not reduce, and is compounded with each additional cycle. 63 These cycles of swelling and shrinking can result in material fatigue. This effect is not yet well understood, and Snethlage and Wendler (1997) conducted experiments to attempt to elucidate the phenomenon.

Snethlage and Wendler immersed blocks of Sander Schilf sandstone in NaCl solution, then dried the samples at 35% relative humidity and observed any shrinking and swelling. (See Figure 2.1) They found that contraction took place in the presence of salt solutions (instead of expansion) due to the "formation of dense hydration shells between the grains, which become denser as electrolytes become stronger."^{64} Then during drying, expansion occurred.

Figure 2.1 The Effect of Introducing Salts and Water to a Colloid System of Clays. From Snethlage and Wendler (1997) Figure 2.7 p. 14, after Snethlage (1990).

While the reason that expansion takes place when the samples dry is not clear,

Snethlage and Wendler propose that this may be due to salt crystallization within larger

 63 Ibid, 12-13.

 $⁶⁴$ lbid, 13.</sup>

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pores or by "the formation of salt films which adhere tightly to the grains and push them apart while they are growing."⁶⁵

While the relationship between salts and freeze-thaw cycling is debated, Goudie and Viles present nine reasons they may affect one another. One of these mechanisms is surface sealing, where salts that have crystallized near the surface create water entrapment below the sealed layer of substrate. The second is the combination of salt and ice crystal growth, which may cause pore space reduction and greater crystal growth from both solutions. The third mechanism isosmotic pressure; in this case, pressure causes breakage in micropores as solutes released during ice crystal growth reach unfrozen portions of the substrate. The fourth is the expansion of the large amount of ordered water that has collected after a delay in freezing due to the presence of salts. The fifth mechanism is a greater saturation of some substrates due to increased hygroscopicity when salts are present. The sixth is increased water mobility as low concenfrations of salts may increase the rate of flow through the substrate, causing increased crystallization pressure and crystal growth. The seventh possible mechanism is"leapfrogging" of the freezing front where crystallization takes place; this is due to salt crystallization being forced further away from ice crystallization fronts as it is rejected by those crystals. "In the zone where salts become concentrated freezing may be temporarily prevented so that the freezing front may jump this zone, reforming on the other side. An unfrozen layer might be expected to experience pressure as the adjacent frozen layers expand."⁶⁶ The eighth is the lower freezing rate of a salt solution compared to that of water, leading to more time for salt crystals to form becoming larger and more destructive. The last

 65 lbid.

^{&#}x27; Goudie and Viles, Salt Weathering Hazards, 159.

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mechanism is corrosion by salts, which act with ice to disintegrate stones. 67 These mechanisms should be studied further, as other sources do not necessarily support these conclusions.

The pH level of a salt can also contribute to its weathering ability. Sodium carbonate is alkaline with pH levels above 11 in saturated solutions. Those salts with pH levels above 9 have greater mobility. This, coupled with the chemical deterioration properties of the salt, aids in increasing the mobility of material components of the substrate that have been attacked. For instance, "when limestones are submerged in concentrated solutions [of sodiimi carbonate] appreciable quantities of iron go into solution."⁶⁸

2.3 Transportation of Salts and Crystallization Zones

Salts are typically transported through walls via masonry units and the permeable mortar joints between them through groundwater, rainfall, dew or fog.⁶⁹ Water evaporates from these solutions and the salts concentrate. "Where and when supersaturation is reached, different phases precipitate, and fractionate from multicomponent systems, forming mostly spatial sequences of different salts. They become locally concentrated as efflorescences on surface areas and as invisible subflorescences behind the surface of the porous materials."⁷⁰ They are fractionated and are concentrated in areas identified by Arnold and Zehnder (Figure 2.2) according to ion activity with the less soluble and less hygroscopic salts (like sulfates and carbonates) being deposited near the lower portions of

⁶⁷ Goudie and Viles, Salt Weathering Hazards, 159-60.

⁶⁸ Ibid, 153.

 69 Ibid, 79.

 $\frac{70}{10}$ Arnold and Zehnder, "Salt Weathering on Monuments," 36.

 a wall, while the more soluble and hygroscopic chlorides and nitrates gather in the upper portions. Finally, in zone D, no damage is observed as this area is beyond the reach of capillary rise.⁷¹ In zone A, there is less deterioration than in B, where most salt efflorescences, mostly consisting of sodium carbonate, sodium sulfate, magnesium sulfate, calcium sulfate and potassium nitrate, appear and cause disintegration, crumbling and scaling. In zone C, which can be several centimeters to several meters high, is where chlorides and nitrates usually accumulate and result in "dark and humid" patches.⁷² humidity may be taken up and spread over larger areas of the walls.⁷³

Figure 2.2 The Different Zones Observed in the Area of Rising Damp on ^a Wail. From Arnold and Zehnder(1990, Figure 1, p. 39.)

^{&#}x27;Ibid, 37-8.

 \blacksquare Ibid, 36-7. 1 Ibid, $37.$

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Once inside the stone, salts can then exacerbate previous damage by crystallizing within fractures and act with other deterioration mechanisms (i.e. freeze-thaw cycling), further decaying the stone.

Snethlage and Wendler (1997) further explain moisture (and consequently, salt) distribution within masonry walls. In each masonry unit and, on a larger scale, a wall, moisture is distributed according to the properties of the material and the environmental conditions (relative humidity, temperature). The moisture distribution can be calculated and the maximum moisture content zone found. Usually the maximum moisture zone is nearer the interior of the masonry unit and not at the surface, but this can vary depending on the permeability of the stone. When a stone is highly permeable, the moisture is distributed more evenly. 74

The importance of the maximum moisture content and its relationship to possible damage is related to the critical moisture content (Ψ) . The critical moisture content is defined as: "a material constant that is defined by the transition from capillary to water vapor transport. It depends mainly on the porosity and the pore-size distribution."⁷⁵ Above the critical moisture content, solutions are transported through capillaries in liquid form. Below this level, water is transported in the vapor state. "Therefore," Snethlage and Wendler state, "during drying, salts will be enriched in that part of the stone where liquid pore water is retained for the longest time, i.e., within the zone of maximum moisture content. Later, when the moisture content in this zone drops below the critical value, the velocity of electrolyte transport is strongly reduced. The salts are trapped and finally

¹⁴ Snethlage and Wendler, "Moisture Cycles and Sandstone Degradation," 15. " Islam 15. " Islam 15. " Islam 15. " I

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precipitate as a result of supersaturation of the solution"^{76} and the salts crystallize. The results of supersaturation and crystallization are discussed further in section 2.4.

Salts appear in buildings as efflorescence (crystallized salts on the surface of a material) and subflorescence (crystallization below the surface or within a material). Often efflorescence can be brushed off a masonry surface, leaving little visual damage. Both can pose a threat to porous building materials, but subflorescence is generally accepted as the most damaging, since more material is lost when cracking, spalling and other damage takes place.

Where crystallization takes place, resulting in either efflorescence or subflorescence. depends on the rate of evaporation of the water borne solution versus the rate the solution is supplied. The rate of evaporation is determined by the temperature, humidity and air currents of the environment; the supply of the solution is a factor of "surface tension, pore radii, viscosity of the solution, and the path length from the source of the solution to the site of the evaporation."⁷⁷ Efflorescence results when the supply of salt solution to the crystallization site is at or greater than the rate of evaporation, causing the solution to deposit on the surface. Subflorescence occurs when evaporation is quicker than supply, causing a dry area to form beneath the surface of the substrate.

The damage caused by salt crystallization has been described in much of the literature in qualitative terms rather than in quantitative ones, since this process is as yet not fully understood. Lewin (1990) summarizes the lack of strong evidence for the proposed theories regarding salt decay through crystallization. One theory is that of

 76 Ibid, 16-17.

⁷⁷ Seymour Z. Lewin, "The Mechanism of Masonry Decay Through Salt Crystallization," In Conservation of Historic Stone Buildings and Monuments: Report to the Committee on Conservation of Historic Stone Buildings and Monuments, Washington, D.C., National Academy Press (1982), 120.

 $\label{eq:2.1} \frac{1}{2} \int_{\mathbb{R}^3} \frac{1}{\sqrt{2\pi}} \, \frac{1}{\sqrt{2\$ \bar{z} "crystallization pressure," existing when "a growing crystal that has become confined within a pore in stone (due to its growth) continues to grow even after there is no longer any void space, and in so doing exerts a pressure against the confining walls which can ultimately lead to the disruption of the host by the guest." But, he goes on to say that this does not explain the damage, that "the term is rather anthropomorphic, suggesting that the crystal feels a 'need' to grow... the origin, nature and parameters of that putative pressure must be expressible in terms of the laws of physics and chemistry." 78 Lewin (1981) also states that after evaporation has taken place, leaving a saturated solution, that at ordinary temperatures about 26 percent solid material would be left behind in the pore or fissure. Therefore, after several hydration-dehydration cycles, the void would fill up. Since Lewin conducted this research, more has been discovered about the salt crystallization process.

Salt crystallization occurs when the water portion of the solution evaporates or when the environment changes, with the reduction of the surrounding relative humidity.⁷⁹ Crystallization takes place within the stone at the wet-dry interface, with salts crystallizing on the edge of the solution film. This results in a "fine grained microporous salt body" that "enhances the capillary flow toward the edge of the film, advancing the crystallizing front."⁸⁰ The type of salt that results (that is, the particular crystal habit) is determined by the environmental conditions to which the solution or already formed crystal is exposed. The formation of these crystals results in crystallization and hydration pressures that place force on the surrounding pores and cavities. This can result in

⁷⁸ As quoted by Andrew Goudie and Heather Viles, Salt Weathering Hazards, New York, John Wiley & Sons, Inc., 1997, 125-6.

^{&#}x27;' Arnold and Zehnder, "Salt Weathering on Monuments," 3 ¹

^{*°} Charola, "Salts in the Deterioration of Porous Materials: An Overview," 330.

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spalling, flaking and blistering.^{81, 82} The determination of the location of crystallization is crucial, as has been determined by Lewin (1982), with decay only occurring within the pores of the masonry, at least a fraction to a few millimeters from the surface. He states, "the necessary condition for surface decay is the establishment of a steady state in which the rate of difftision of water through a thin layer of the porous solid at the surface is balanced by the rate of replenishment of water to that site from the source (reservoir) of the solution." 83 He determined that the few millimeters between the surface and the crystallization front is the thickness of the blister or spall that will be lost. Then, once that layer is lost, providing that all factors remain steady, the same thickness will be lost after the next decay cycle.⁸⁴ This finding corresponds to the statements of Snethlage and Wendler (1997) in that the maximum moisture area and the location of salt crystallization are necessarily the same and parallel to the stone surface, with this depth being the place of detachment. "In this zone salts are enriched, while the surface scale and the interior volume of the stone are leaching areas that deliver the dissolved matter." 85

Snethlage and Wendler (1997) elaborate on the types of damage that will be seen as a result of the location of maximum moisture content. If the zone is located on the surface, damage consists of sanding off (in the case of sandstones). Scaling will result if the zone is within one to two millimeters of the surface; the deeper within the material the maximum moisture content, the deeper the scaling. "The actual location depends on the moisture fransport coefficient of the stone and on the transition coefficient of the surface,

⁸¹ Arnold and Zehnder, "Salt Weathering on Monuments," 31.

⁸² Lewin, "The Mechanism of Masonry Decay through Salt Crystallization," 120.

⁸³ Ibid, 122.

⁸⁴ Ibid, 140-2.

⁸⁵ Snethlage and Wendler, "Moisture Cycles and Sandstone Degradation," 17.

the control of the c i.e., on the conditions of the building."⁸⁶ They conclude that when wet-dry cycles are quick, scales are likely to form, but where cycles are longer and material stays wet, sanding off is the more favorable result with flakes and exfoliations to be interpreted as intermediate conditions. They stress that the zone of maximum moisture content moves through the stone in a "moisture wave" transporting "trapped" salts that cannot migrate out into lower moisture content areas.⁸⁷

Snethlage and Wendler use this concept of the "moisture wave" and moisture fluctuations resulting in the above damage to elaborate on the rising damp model. They question the role that capillary transport plays in the transport of moisture, considering that broken mortar joints or other voids within a system are prevalent and would inhibit capillary transport. Therefore, they introduce other mechanisms in addition to the capillary transport explanation, stating that the fluctuations are a necessary mechanism for the transport of solutions through a wall to the surface and result from "changing moisture in the earth or... a periodic water supply from the surface, due to occasional rain or moisture condensation."⁸⁸ They argue "the capillary transport of liquid water is much faster than the ionic diffusion, so that salts would not have time to withdraw backwards from the area of evaporation into the diluted solutions... [and] therefore, it seems justified to consider additional moisture sources that are periodically effective, e.g., rain and condensation, for the transport of the salts to the surface..."⁸⁹ They summarize that "in

⁸⁶ Ibid.

 87 Ibid, 18.

⁸⁸ Ibid, 20.

 89 Ibid, 20-1.

addition to a steady vertical moisture flow from the ground, periodically active moisture sources are needed to produce salt efflorescences and damage." 90

2.4 Damage by Crystallization

Two mechanisms result in salt crystallization. The first is the precipitation of crystals out of a solution. Precipitation takes place when evaporation causes a solution to become supersaturated. Supersaturation occurs when the "ion activity product is greater than the equilibrium constant. . .Thus the ion activity product determines whether or not a salt can precipitate."⁹¹ This condition is obtained when the rate of capillary migration and the rate of evaporation reach equilibrium. 92

The other mechanism that results in crystallization is the hydration or dehydration of crystals as an effect of the hygroscopicity of a salt. Salt initially crystallizes as a hydrate through high relative humidity or low temperatures; it can dehydrate and rehydrate with environmental fluctuations.⁹³ The point at which hydration or dehydration takes place for a particular salt is defmed by its equilibrium relative humidity. This can be calculated from the following equation:

$$
RH^* = (P_{\text{salt}}/P_{\text{s}}) \cdot 100
$$

"where P_{salt} is the vapour pressure of the saturated solution of the salt and P_{s} is the atmospheric water vapour pressure at that known temperature.^{"94} The point at which a salt will absorb moisture from humid air and precipitate on ^a surface takes place when the

 90 Ibid, 22.

 91 Arnold and Zehnder, "Salt Weathering on Monuments," 38.

⁹² Charola, "Salts in the Deterioration of Porous Materials: An Overview," 335.

³³ Arnold and Zehnder, "Salt Weathering on Monuments," 31.
⁹⁴ Goudie and Viles, *Salt Weathering Hazards*, 154.

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environmental relative humidity is above its equilibrium relative humidity (a constant value). It is at this point that a salt will deliquesce if it is highly soluble.⁹⁵ If the relative humidity of the air remains above this equilibrium constant, the salt will stay in solution and will not cause damage.⁹⁶

"For example, for thenardite (Na_2SO_4) to hydrate to mirabilite $(Na_2SO_4:10H_2O)$ at 20°C, the relative humidity must exceed 71%... Both sodium carbonate and sodium sulfate show particularly high volume expansions on hydration and they [are effective deterioration agents]."⁹⁷ Other salts are also deleterious, though sodium sulfate and sodium carbonate are perhaps the most damaging. These both have characteristics that lend themselves to damage in the context of the built environment, and will be discussed further in Chapter 3.

Once conditions are favorable for crystallization, the salts can crystallize with different habits. Efflorescences usually appear as prisms and whisker shaped crystals with the less soluble salts like sodium carbonate and sodium sulfate forming compact crusts of "acicular, columnar or isometric crystals."⁹⁸ The shape and growth of crystals are determined by the environment and conditions within a specific part of a wall, degree of supersaturation of the solution and any impurities it may contain, as well as the crystal lattice and habit of the solution.⁹⁹ As environmental conditions change, the salts will take on different crystal habits. Crystals begin as bulkier isometric shapes when they are first formed from solution and remain as long as they are saturated with the solution. As the

^{&#}x27; Charola, "Salts in the Deterioration of Porous Materials: An Overview," 329.

⁹⁶ Arnold and Zehnder, "Salt Weathering on Monuments," 47.

⁹⁷Goudie and Viles, Salt Weathering Hazards, 106.

⁹⁸ Arnold and Zehnder, "Salt Weathering on Monuments," 47.

^{&#}x27; Ibid, 48.

solution dries out, they transform into "whiskery", needle shaped crystals that grow from the thinning solution film. "In between all transitions from isometric equilibrium shapes to prisms, needles and hairlike crystals are formed according to the decreasing thickness of the solution film while the substrate is drying out." 100

As previously stated, Lewin (1982) established that the location of crystallization was crucial when determining the level of salt damage that a material could sustain. Arnold and Zehnder elaborate on this, stating that salt crystals can only grow within pores and other voids. This can be in the form of subflorescence, but some efflorescence can also take place underneath the surface, depending on the solution supply and the evaporation rate.¹⁰¹ When a material is inhomogeneous, a zone of preferential crystallization develops where pore structure varies. This inhomogeneity can result from a paint layer, fireskin or other difference between materials. To illustrate this phenomenon, Arnold and Zehnder (1990) describe salt crystallization within highly porous ceramics and mortars painted with the fresco technique. This example is particularly useful for the current study, as it supports the belief of Franke and Reimann-Oenel, that instead of forming within the subsfrate, salts will form between layers at the film-subsfrate interface.

Arnold and Zehnder (1990) exposed frescoed ceramics and lime mortars with 30% porosity to sodium nitrate and other salts and then dried them at 32% and 69% relative humidity. They found that less efflorescence formed on materials dried at 32% relative humidity and these showed more crystallization within the material. This showed that the location of crystallization is effected by the relative humidity of the environment;

¹⁰⁰ Ibid, 48.

 101 Ibid, 48.

it also showed that the deeper the crystallization front, the more decay is present. 102 In their study, Arnold and Zehnder describe the process by which this deterioration occurs (Figure 2.3).

Figure 2.3 Model of Disruption Process by Crystallizing Salts (nitronatrite). From Arnold and Zehnder (1990, Figure 11 p. 42.)

First (Figure 2.3 a) salts crystallize in pores of about ¹ to 10 microns; smaller pores remain empty with these smaller pores and connecting channels supplying the solution for crystallization to occur. "Thus we assume that the pores in this phase and on this particular place are largely filled with a saturated or supersaturated solution."¹⁰³ In the next phase (Figure 2.3 b) the crystals have outgrown their original pores, grow into others, and begin to coat larger voids. Since the crystals are larger than the pores, "we presume that important pressures are built up on the pore walls resulting in a [tensile] stress perpendicular to the siuface. In consequence, this force will disrupt the structures preferentially by fissures parallel to the surface along a zone where the pores being filled

¹⁰² Ibid, 48-9.

¹⁰³ Ibid, 49.

by salt crystals are arranged close together, and preferentially where the material cohesion is reduced, e.g. at discontinuities such as paint layers..."^{104} In phase three (Figure 2.3 c) the space between the two materials is wider, allowing greater evaporation and thus, crystallization in this area. The crystals continue to grow if solution is still present, but if the expansion continues and evaporation exceeds supply (as stated by Lewin), the crystals will become columnar since the solution does not surround the crystal. These columnar forms can exert pressures on the walls of the material that will further widen the fissure.¹⁰⁵ Finally, in the last phase (Figure 2.3 d) the amount of solution is diminished. The crystals are reduced in size as the substrate dries. If there is enough solution present and the columns are in contact with them, whiskers will form which are powerful enough to separate the inhomogeneous layer. ^{106} At this point, spalls consisting of ceramic layers, loose layers of substrate or paint layers detach. It is this process which results in the visible damage that is so apparent when coatings are applied and subsequently lost.

This model is supported by the research of Snethlage and Wendler. In their study of dilatation and contraction of clays (explained above), they rejected the theory of hydration pressures and proposed a new model to elucidate stone deterioration. They propose "dilatation and contraction, i.e., the displacements of grains relative to each other, under the influence of moisture and dissolved ionic species is the only process needed to explain the deterioration of stones"; they also suggest that, "This process provides the open spaces in the grain structures where the salts can precipitate.

Ibid.

Ibid.

 106 Ibid.

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¹⁰⁴ Ibid.

 105 Ibid.

¹⁰⁶ Ibid.

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Displacements within the sak deposits due to changing moisture may enhance the formation of gaps in the grain structure... It is most probable that salt crystallization pressure occurs only in strongly salt-enriched stones where the coarse pores can be filled up with salt crystals."¹⁰⁷

¹⁰⁷ Snethlage and Wendler, "Moisture Cycles and Sandstone Degradation," 15.

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Chapter 3: Sodium Sulfate and Sodium Carbonate: Experimental Part II

3. 1 Introduction

Sodium sulfate originates, in part, due to air pollution, which provides sulphur to the system; the sodium being provided by ground water, the building material, de-icing salts or cleaning fluids that contain sodium. The reaction of these substances causes sodium sulfate to form. Sulfates can also result from "sea spray, volatile biogenic sulphur, desert dust, marine gypsum and anhydrite as well as pollution sources."^{108} They can also be inherent within a material; bricks, if not fired at a sufficiently high temperature, will contain sodium sulfate.

Sodium carbonate can also originate from salt spray in marine environments. Highly alkaline solutions will absorb $CO₂$ from the atmosphere, leading to the formation of alkali carbonates, as in the case of Portland cement. It can also result from the use of alkali silicates (a.k.a. waterglass) for stone and plaster consolidation and as a binding medium for silicate paints. Waterglass produces sodium carbonate and potassium carbonate as part of its reaction

Alkali carbonate salts can, furthermore, react with atmospheric pollution to form the more harmful sodium and potassium sulfate. 109 Certain carbonate stones are prone to sulfate attack, while some granite types contain minerals that wear preferentially to

¹⁰⁸ McCardle and Liss, 1995 as quoted by Andrew Goudie and Heather Viles, Salt Weathering Hazards, New York, John Wiley & Sons, Inc., 1997, 87.

¹⁰⁹ Arnold and Zehnder, "Salt Weathering on Monuments," 34.

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others, increasing its porosity and thereby leaving behind larger pores vulnerable to further attack. 110

Even concrete can be prone to salt decay. The calcium aluminum sulfate mineral ettringite is formed by sulfates reacting with alumina containing phases of hydrated cement, producing a high sulfate form of calcium aluminate $(3CaO·A₁O₃·3CaSO₄·$ $32H₂O$). While ettringite formation at the beginning of setting is desirable, it has been found in cracks and voids in older concrete structures. This is known as delayed ettringite formation (DEF).¹¹¹ As explained by Livingston (2001), ettringite formation occurs when water from the atmosphere enters the equation:

MONOSULERATE +
$$
2Ca^{2+}
$$
 + $2SO_4^{2-}$ + $20H_2O \longrightarrow$ EITRINGITE

The critical element in the formation of ettringite, however, is the hygroscopicity of the potassium content of the cement; the potassium sulfate contamed in Portland cement

undergoes an exchange reaction with calcium and hydroxide ions to produce a dilute potassium hydroxide solution and calcium sulfate:

$$
K_2SO_4 + Ca^{2+} + 2OH \longrightarrow 2K^+ + 2OH + CaSO_4^+
$$

 \dots However, over time the solution reacts with atmosphere $CO₂$ to produce potassium carbonate:

$$
2K^+ + CO_3 = \longrightarrow K_2CO_3
$$

which has a very low critical relative humidity for deliquescence (RH $=$ 43%). Consequently, under prevailing temperature climate conditions, the compound would typically be in a saturated solution rather than in solid form... high exposure to moisture would tend to drive the equilibrium of [the] equation to the right, favoring the formation of ettringite... In

 110 Goudie and Viles, Salt Weathering Hazards, 93.

¹¹¹ R.A. Livingston, "The Role of Potassium Hygric Cycling in Delayed Ettringite Formation," Presented at the Conference of the Geochemical Society, Goldschmidt, 2001, unpublished, I.

à. \sim \sim addition to promoting the DEF, the potassium content may be the cause of the damage itself. 112

This damage "involves an increase in the volume of the reacting solids $[K_2CO_3]$, a pressure build up, expansion, [subsequent accumulation of more moisture] and in the most severe cases, cracking and deterioration.... The volume change on the formation of ettringite is very large, and is even greater than that produced by the hydration of sodium sulphate."¹¹³ "Moreover, the osmotic pressure difference between the saturated potassium carbonate solution at the crack surface and the unsaturated potassium hydroxide porewater inside the cement paste gel would be on the order of ¹ 200 Mpa. This stress would drive crack propagation."¹¹⁴

Additionally, thaumasite $(CaSiO₃CaCO₃CaSO₄+15H₂O)$ is formed through a sulfate reaction with concrete. Like ettringite, it causes expansion, but it also causes softening of the cement and disintegration in bricks that have been plastered with Portland cement.¹¹⁵

As stated above, sodium carbonate efflorescence can form as a result of salt spray in marine environments as well as from the presence of soluble alkali ions in Portland cement, which leach out and form carbonate salts, including trona (NaHCO₃· Na_2CO_3 : $2H_2O$ ¹¹⁶ (see Figures 3.1 and 3.2). Large amounts of these salts can be can be produced. Arnold and Zehnder (1990) state:

The amounts of Portland cement used in walls being very large the quantities of soluble salts may become very important too. As an example, 100 kg of Portland cement with a content of 0.1% of soluble Na₂O may

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¹¹³ Goudie and Viles, Salt Weathering Hazards, 142.

¹¹⁴ Livingston, "The Role of Potassium Hygric Cycling in Delayed Ettringite Formation," 1.

^{&#}x27; Goudie and Viles, Salt Weathering Hazards, 142-3.

^{&#}x27; Ibid, 76.

 ~ 10 \bar{z} $\mathcal{L}^{\text{max}}_{\text{max}}$, where $\mathcal{L}^{\text{max}}_{\text{max}}$ produce 460 g of natrite (Na₂CO₃·10H₂O) or when reacting with sulfuric acid from the polluted air 520 g of mirabilite $(Na_2SO_4:10H_2O)$.¹¹⁷

The leaching of trona by the filtering of water through cement can cause the destruction of masonry, including granite, as was demonstrated by Charola and Lewin (1979) .¹¹⁸

Figure 3.1 Space Model of the NaHCO₃· Na₂CO₃·H₂O System. From Hill and Bacon (1927, 2494.)

Figure 3.2 Trona Crystal. From http://www.gc.maricopa.edu/earthsci/imagearchive/picture50.htm.

¹¹⁷ Arnold and Zehnder, "Salt Weathering on Monuments," 33.

 118 A.E. Charola, and S.Z. Lewin, "Examples of Stone Decay Due to Salt Efflorescence," In 3^{rd} International Congress on the Deterioration and Preservation of Stones, Venezia 24-27 October 1979. Padova: Universita degli Studi di Padova, 1979, 161-2.

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After masonry is damaged by salt, failure can present itself not only visually, but mechanically as well. The loss of compressive strength (exemplified by uniaxial compressive strength tests and wet-to-dry strength tests), weatherability and durability, the increase in porosity and water absorption, and a change in the pore structure are all consequences of salt infiltration of masonry. 119

3.2 Comparison of Sodium Sulfate and Sodium Carbonate

Some salts, including sodium carbonate (Na_2CO_3) and sodium sulfate (Na_2SO_4) , have certain characteristics that make them strong weathering agents. Goudie $(1977)^{120}$ has identified a set of five characteristics that make sodium sulfate particularly effective. The first of these is the high degree of volume change from the dehydrated thenardite state (density 2.68) to the hydrated mirabilite state (density ¹ .46) and the speed with which this takes place, repeating up to several times a day (with dehydration of mirabilite to thenardite taking twenty minutes at 39°C. The second characteristic is the rapid solubility decrease of sodium sulfate as the temperature drops below 32.3°C. Thirdly, "because sodium sulphate is so highly soluble substantial quantities of sulphate are available for the process of crystal growth when solutions are evaporated by high diurnal temperatures. Evaporation would also help to create a saturated solution from which crystals could grow on cooling." The fourth characteristic is solubility of sodium sulfate. Its solubility does not increase linearly with an increase in temperature, but decreases as

¹¹⁹ E.N. Caner-Saltik, I. Schumann and L. Franke, "Stages of Damage in the Structure of Brick Due to Salt Crystallization," In Conservation of Historic Brick Structures, Edited by N.S. Baer, Dorset, England: Donhead Publishing, Ltd., 1998, 52-55.

¹²⁰ Presented in Andrew Goudie and Heather Viles, Salt Weathering Hazards, New York, John Wiley & Sons, Inc.. 1997, 107-8.

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temperatures rise above 32°C. The final attribute of sodium sulfate is the shape of its mirabilite crystals, which form long, needle-like prisms that may be particulariy destructive. It is important to note that these characteristics are also applicable to sodium carbonate.

In addition to the above, both of these salts have the ability to crystallize, deliquesce (dissolve in their crystallization water) and recrystallize as a lower hydrate either within a porous material or independently due to changes in the relative humidity and temperature of the environment. Often these changes cause the salt to take on another crystal habit. (It should be stressed that the phase changes from solution to solid or from one crystalline state to another are sufficient for sodium sulfate deterioration to take place.¹²¹) The occurrence of the above characteristics is dependent upon the nature of the salt and its hygroscopicity (the ability to absorb water from the air and form a saturated solution). 122 The equilibrium relative humidity and solubility curves for sodium sulfate and sodium carbonate are presented in Figures 3.4 and 3.5. Other relevant data are presented in Table 3.1.

²¹ David J. McMahon et. al, "Deterioration Mechanisms of Sodium Sulfate," in *Proceedings of the* $7th$ International Congress on Deterioration and Conservation of Stone Lisbon, Portugal 15-18 June 1992, Ed. by J. Delgado Rodrigues, Fernando Henriques and F. Telmo Jeremias, Lisbon: Laboratorio Nacional de Engenharia Civil, 1992, 706.

 122 Goudie and Viles, Salt Weathering Hazards, 131.

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Figure 3.3 Equilibrium Curves for Sodium Sulfate and Sodium Carbonate.

Figure 3.4 Solubility of Different Salts in Relation to Solution Temperature. From Goudie (1977: figure 6). Adapted from Goudie and Viles (1997, 109.)

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	$Na_2CO_3 \cdot H_2O$ Thermonatrite	Na ₂ SO ₄ Thenardite	$Na_2CO_3 \cdot 10H_2O$ Natron	$Na2SO4 \cdot 10H2O$ Mirabilite
Crystal Structure	Orthorhombic dipyramidal		Monoclinic prismatic	
Molecular Weight (g/mol)	124	142	286	322
Density $(g/cm3)$	2.25	2.68	1.46	1.44
Molecular Volume (cm3/mol)	55.0	53.0	198.7	220.0
Volume Increase Hydration %			261%	315%
Solubility $(g/100)$ ml)	39.0 (32°C)	49.7 (33°C)	21.5(0°C)	$11.4(0^{\circ})$
Solubility (mol/100 ml)	0.31	0.35	0.075	0.035
Heat of Solution (Kcal/mol)	-2.3 (exothermic)	-0.3 (exothermic)	$+16$ (endothermic)	+18.9 (endothermic)
Heat of Hydration (Kcal/mol)	$+3.3$		$+18$	$+19$
Decomposition Temperature (°C)	105° C		33° C	32.4°C
Crystallization Pressure (C/Cs=2)	333 (50°C)	345 (50°C)	92 (50°C)	83 (50°C)
Hydration Pressure (atm)			400 (30°C)	$280(31^{\circ}C)$
Equilibrium RH	53.7% RH $(0^{\circ}C)$	60% RH $(0^{\circ}C)$	92% RH (18.5°C) 87% RH (24.5°C)	93% RH (20°C) 87% RH (25°C)

Table 3.1. Data on Sodium Sulfate and Sodium Carbonate Salts. From Charola (2002, Proceedings in Preparation)

Figure 3.5 Hydration rate of Na₂SO₄ and Na₂CO₃ at 20°C and at a Relative Humidity of 90%. From Kwaad (1970: figure 3). Adapted from Goudie and Viles (1997, 137.)

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Figure 3.6 Left: Hydration rates of Na₂SO₄ and Na₂CO₃ pre-dried for 24 hours at 105°C and set into 90% at 25°C. Right: Hydration rates for blocks of York stone immersed in saturated solutions of these salts, dried and set into 90% RH at 25°C. From Goudie and Viles (1997, 138-9.)

The pressures developed during crystallization or hydration are stated in many texts as the most important causes of salt weathering. It should be noted that the calculated crystallization pressures are similar for both salts under any of their forms. However, hydration pressures are higher for sodium carbonate; therefore, the damage induced by this salt should, in principle, be larger.

Goudie and Viles point out that the speed at which hydration takes place is also very important, with sodium carbonate having a much higher hydration rate than sodium sulfate. (Figures 3.5 and 3.6.) It should be noted, however, that Goudie and Viles used the anhydrous salts for these experiments (drying them at 105°C), though the anhydrous form of sodium carbonate does not readily occur in nature. This may explain the higher

 \mathcal{L}_{max} and

hydration rates they observed for sodium carbonate. The complex interaction of the support in the hydration rate of sodium sulfate is shown in Figure 3.7. It has been shown that both the substrate and the previous history of the salt plays an important role in the moisture absorbing capability of sodium sulfate.¹²³

Figure 3.7 Moisture Absorption Rates for Sodium Sulfate Powders and Sodium Sulfate/Stone Powders. Based on data from Charola and Weber (1992).

3.3 Deterioration Due to Sodium Sulfate

The studies of McMahon et al. (1992) advanced the knowledge of why sodium

sulfate is one of the worst deteriorating agents. They conducted laboratory experiments in

¹²³ From data prepared for A. Elena Charola, and Johannes Weber. "The Hydration-Dehydration Mechanism of Sodium Sulfate." In Proceedings of the 7th International Congress on Deterioration and Conservation of Stone. Lisbon, Portugal 15-18 June 1992. Ed. by J. Delgado Rodrigues, Fernando Henriques and F. Telmo Jeremias. Lisbon: Laboratorio Nacional de Engenharia Civil, 1992.

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which sodium sulfate was crystallized under varying conditions of temperature and relative humidity into its anhydrous (thenardite) state and its decahydrous (mirabilite) state. The deterioration was then observed. All states were found to cause some deterioration, but the decahydrous (mirabilite) state was particularly damaging.

McMahon et al. found that simple calculations did not adequately explain any difference between deterioration mechanisms and sought to elucidate the deterioration by sodium sulfate by isolating the possible mechanisms, such as volume increase as a result of hydration or crystallization from a supersaturated solution, comparing the deterioration caused by each. The different conditions produced: rapid crystallization of mirabilite by immersion in sodium sulfate solution then rapid cooling; crystallization of mirabilite through evaporation; crystallization of mirabilite through evaporation and low temperature fluctuations; crystallization of thenardite through evaporation and hydration cycles; and crystallization of thenardite through evaporation.¹²⁴

Figure 3.8 Volume Increases During the Precipitation of Mirabilite from ^a Supersaturated Solution. From McMahon et al. (1992) Figure 4, ⁷¹ 1.

¹²⁴ McMahon et. al, "Deterioration Mechanisms of Sodium Sulfate," 709-710.

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McMahon's results show that there is a volume increase of the solution as mirabilite forms, with the greatest increases seen in the larger supersaturation ratios (Figure 3.8).

From the different tests, crystallization of mirabilite from immersion and rapid cooling produced "complete loss of integrity"; crystallization of mirabilite through evaporation produced "negligible" surface deterioration; crystallization of mirabilite through evaporation and temperature fluctuations led to significant deterioration; crystallization of thenardite through evaporation and hydration produced significant surface flaking and crystallization of thenardite through evaporation led to "negligible" deterioration.¹²⁵ From these tests, they concluded that thenardite was not the most significant deterioration mechanism in the sodium sulfate system. Most importantly, McMahon et al. found that "solid-state hydration of thenardite did not occur. Instead, through-solution hydration occurred." 126 They found that deterioration was significant only when thenardite was converted to mirabilite in a process where thenardite (instead of hydrating) dissolves and creates a supersaturated solution from which mirabilite crystallizes. This, in turn, "results in volume increases of the sodium sulfate-water system. This mechanism is best termed through-solution hydration rather than hydration." 127 It was also observed that the faster this took place (with instantaneous crystallization in a rapid cooling environment), the more damage occurred, as the pore

 125 Ibid, 711-12.

 126 Ibid, 710.

 127 Ibid, 712.

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volume increase was around 3% for ^a supersaturated solution. This volume is achieved quicker than ice formation.¹²⁸

McMahon et al. conclude that the pressure developed during the crystallization of mirabilite is

transferred directly between the mirabilite crystals and the walls of the porous media, and [therefore] could be called 'crystal growth pressures.' However, in saturated systems where crystal growth causes the pore solution volume to increase, the crystal growth displaces nearby pore fluid, which is induced to flow under a pressure gradient toward areas of lower pressure... When the pore fluid is not forced out of the porous material quickly enough to prevent the buildup of significant tensile stresses, this causes failure within the porous material by cracking.¹²⁹

These observations are supported by Charola and Weber (1992) who conducted further experiments with sodium sulfate. They also sought to elucidate why sodium sulfate was such a strong deterioration agent. They observed the dehydration of mirabilite and the subsequent reprecipitation of thenardite and mirabilite under various conditions. They found that when mirabilite was heated it first released its hydration water, appearing to "melt" (Figure 3.10 a-f). Both mirabilite and thenardite crystals are precipitated from this crystalline water as it evaporates with the mirabilite continuing to dehydrate (Figure 3.10 g-i) until only thenardite remains (Figure 3.10 j).¹³⁰

Thenardite hydrated very slowly in a humid environment compared to the quick dehydration of mirabilite (the dehydration of mirabilite conducted for this study took approximately 20 minutes.) Charola and Weber found that small cracks between particles

¹²⁸ Ibid, 713.

 129 Ibid.

¹³⁰ A. Elena Charola and Johannes Weber, "The Hydration-Dehydration Mechanism of Sodium Sulfate," In Proceedings of the 7th International Congress on Deterioration and Conservation of Stone Lisbon, Portugal 15-18 June 1992, Ed. by J.Delgado Rodrigues, Fernando Henriques and F. Telmo Jeremias, Lisbon: Laboratorio Nacional de Engenharia Civil, 1992, 582-3.

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began to close at two hours, and at five hours a skin formed on the thenardite consisting of "small transparent crystals."¹³¹ This skin inhibited rehydration, and caused water to condense on the surface until enough water was present to dissolve it. Only after the skin dissolves does thenardite recrystallize.¹³² In translating this to its application to building stones, Charola and Weber observe that, "The recrystallization from the solution will tend to occur in larger pores, and depending on the thermohygrometric conditions, mirabilite or thenardite will crystallize. Thus, the presence of the salt in the stone will effectively increase capillary condensation by drawing the liquid away from them."^{133} They found that the thenardite crystals are very hygroscopic once the skin is dissolved and "enhance capillary condensation"; they are also highly porous and do not contribute to swelling and therefore, do not cause the buildup of hydration pressure.^{134} Charola and Weber conclude that, "The increased deterioration can only be attributed to the multiple crystallizations taking place during the dehydration of the hydrated salt." 135

The "skin" observed by Charola and Weber (1992) forming on thenardite crystals was sudied by Eric Doehne under the environmental scanning electron microscope. In his experiments, he observed sodium sulfate through-solution hydration and dehydration in stone pores. Doehne (1994) took into account the previously described mechanisms of deterioration, including Arnold and Zehnder's fractionation model (1990) (Figure 2.2), and the crystallization discoveries of McMahon et al. (1992). He continued the

¹³¹ Ibid, 583.

¹³² Ibid, 583-4, 587.

¹³³ Ibid, 588.

 134 Ibid.

 135 Ibid, 589.

the control of \bar{z} $\bar{\epsilon}$ investigation into the mechanisms of sodium sulfate hydration, dehydration and crystallization by using time-lapse video.

Like Charola and Weber (1992), Doehne found that anhydrous sodium sulfate crystals initially formed a skin upon hydration. This restricted hydration until there was enough liquid water to dissolve it. This water can be observed as ^a swelling of the surface, then "liquid water surround[s] the crystal and subsequent dissolution of the anhydrous sodium sulfate and... form[s]... sodium sulfate solution."¹³⁶ From this solution, the decahydrate (mirabilite) crystallizes. During dehydration, Doehne found that mirabilite forms "submicron aggregates" of sodium sulfate, resulting in a "highly porous, high surface area salt structure consisting of sub-micron particles" after which hydration and dehydration rates become approximately equal.¹³⁷ Then, sodium sulfate decahydrate crystals form with the dissolution of these fine particles. This phenomenon occurred regardless of the speed at which the process was conducted.

Doehne concludes that the breakdown of sodium sulfate into fine particles may explain why it is highly damaging, as they would allow "the penetration of water vapor and liquid water films deeper into the sodium sulfate, substantially increasing the salt's rate of water adsorption after several cycles. The physical breakdown into small particles may also play a role in the penetration of sodium sulfate into micropores. Transport may occur by 'floating' solid crystals into micropores on solution films or by direct precipitation from solution.... Rapid expansion during subsequent hydration of sodium

¹⁵⁶ Eric Doehne, "In Situ Dynamics of Sodium Sulfate Hydration and Dehydration in Stone Pores: Observations at High Magnification Using the Environmental Scanning Electron Microscope," in /// International Symposium on the Conservation of Monuments in the Mediterranean Basin, Venice, 22-25 June 1994, Ed. by Vasco, Fassina et al., Venice: Soprintendenza ai Beni Artistici e Storici di Venezia, 1994, 145.

 137 Ibid, 146.

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sulfate in micropores would result in fracturing of the stone.... The salt pressures generated by such crystallization are generally an order of magnitude greater than the strength of the stone." 138

Doehne further explains that this crust occupies ^a similar volume in both states and the small increase observed in the crystals is held within the intercrystalline spaces. He also suggests that it is not the humidity cycling of these states that creates significant damage, but it is the rapid formation of large, well-ordered mirabilite crystals from solution and the resulting pressure on pore walls.¹³⁹ This statement supports the observations of McMahon et al and Charola and Weber.

3.4 Experimental I: The Dehydration of Mirabilite to Thenardite and Natron to **Thermonatrite**

The dehydration processes of sodium carbonate and sodium sulfate was captured through photomicrography for this study and is illustrated here. Following the experiments of Charola and Weber (1992), crystals of the hydrated salts were grown in the laboratory. Crystals growing in solution form as their higher hydrates as long as the temperature is below the transition temperature of 32.4°C. If these are exposed to temperatures above the transition temperature or a lower relative humidity they will dehydrate. They will eventually dehydrate into their lower hydrates with no volume increase. Even in the event of rehydration, crystals will not generate any more force than was originally experienced due to initial crystallization.

¹³⁸ Ibid, 147.

 139 Ibid. 147-8.

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Figure 3.9 a) Mirabilite Crystal Structure, from Dana and Dana, 1966, p. 440: b) Natron Crystal Structure, from Dana and Dana, 1966, p. 483; c) Thenardite and Thermonatrite Crystal Structure, from Dana and Dana (1966), 405.

The habits of the salt crystals studied are illustrated in Figure 3.9^{140} In order to compare the dehydration of mirabilite and natron, crystals of these salts were placed on a hot plate under gentle heat and their changes observed under ^a microscope. When mirabilite is heated, it first begins the formation of a white film on the exterior of the crystal (Figure 3.10 a-c). It then begins to release its hydration water, and surrounding the large crystal, small white thenardite crystals begin to form (Figure 3.10 d-e). It then appears to "melt", forming a puddle on the edge of the crystal (Figure 3.10 f), with this process continuing while thenardite crystals form at the edge and translucent mirabilite crystals form in the center. As observed by Charola and Weber, both mirabilite and thenardite crystals precipitate from this crystalline water as it evaporates. At this stage, some large crystals and many small ones form dendritic growth. The mirabilite continues

 $\frac{140}{11}$ it is important to note that natron crystallizes in the same way as gypsum, whose crystal structure is featured in Figure 3.9 b. Similarly, thermonatrite crystallizes like thenardite. illustrated in Figure 3.9 c.

 \sim \mathcal{L}^{\pm} \mathcal{A}^{\pm} to dehydrate (Figure 3.10 g-i) until only thenardite remains (Figure 3.10 j) leaving a crusty film on the surface.

The dehydration of natron was also observed. The behavior of one large transparent crystal was followed (Figure 3.1 ¹ a). Upon exposure to heat, the crystal formed an opaque film of thermonatrite on the surface (Figure 3.1 ¹ b). It quickly dissolved, however and became a puddle of saturated solution (Figure 3.1 ¹ c). During this phase, smaller opaque crystals began forming at the edges of this solution and the puddle appeared to cave in on itself (Figure 3.1 ¹ d). From the outer edges of the central portion of the puddle more transparent crystals of thermonatrite began to form working their way inward toward the center (Figure 3.1 ¹ d-e). The smaller crystals on the outer ring of the puddle continued to grow in opacity, as did the central core as it dehydrated (Figure 3.11 f-g). At this point small crystals dehydrate until the entire formation was opaque (Figure 3. ¹¹ h-j). The thermonatrite crystals in the center grew larger, as did those at the edge. The main difference between the dehydration of these salts is that while sodium sulfate produces many extremely small crystals of thenardite, sodium carbonate forms lesser and bigger crystals of thermonatrite.

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Figure 3.10 Dehydration of Mirabilite Crystals to Thenardite Under Gentle Heat; Nikon SMZ-U Zoom I-Stereoscope with Quartz Halogen Lamp. Magnification 1.25 x.

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Figure 3.11 Dehydration of Natron to Thermonatrite Under Gentle Heat; Nikon SMZ-U Zoom 1-10 Stereoscope with Quartz Halogen Lamp. Magnification 1.25 x.

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3.5 Salt Weathering Test

The effect of hydration and dehydration of these salts within ^a porous substrate was also studied. This test aimed to evaluate the weathering capacities of two salts, sodium carbonate and sodium sulfate. As stated above, the two salts are comparable in their solubility and relative humidity equilibrium curves. However, the damage they cause is different, with sodium sulfate being seen as a more "destructive" salt. To test this the following testing procedure was conducted.

Table 3.2 Experimental Matrix for Salt Weathering Tests

Samples (see Table 3.2) were immersed in deionized water, sodium carbonate and sodium sulfate solutions for twenty-four hours. They were then dried to a constant weight in an oven at 60 \degree C to avoid dehydrating the sodium carbonate (which crystallizes as the monohydrate). This took approximately 16 days for the samples immersed in salt solutions, and shows how the drying rate is significantly slowed when salts are present.

After a constant weight was achieved, the samples were cycled between a 100% relative humidity environment for three days, then in a desiccator at low (10% to 20%) relative humidity for three days. The samples were weighed each day. This cycle was repeated twelve times. (See Appendix A.)

Samples treated with sodium sulfate and sodium carbonate monohydrate gained about the same amount of weight when cycling initially began. Then as the cycling progressed, samples treated with sodium carbonate monohydrate began to show increased

weight gain and ^a greater difference in weights between low RH and high RH as compared to sodium sulfate decahydrate treated samples.

Figure 3.12 Results of Cycling Sodium Carbonate and Sodium Sulfate Impregnated Bricks Between 20% RH and 100% RH; Cycling period: ³ days each condition, repeated for ¹² cycles.

Sodium carbonate showed a greater range in weight change throughout the cycles and continued this trend throughout the duration of the experiment (Figure 3.12). From the data presented above, itcan be seen that sodium carbonate monohydrate is more hygroscopic than sodium sulfate and that with continuing cycles the samples picked up increasing amounts of moisture. The absorption properties of the porous substrate also would have contributed to a small portion of this weight gain. The degree to which the substrate alone absorbed water and dehydrated is observed in the control samples.

Since no visible damage was observed after twelve cycles, the samples were then subjected to immersion in the respective salt solutions for approximately twenty-four hours and then left to dry in a wind tunnel environment for approximately twenty-four

hours. This cycle was repeated six times, but by the fifth cycle, no visible damage occurred except for some minor losses in the form of a powdery residue at the bottom of the solution containers. This was evident in both the sodium carbonate and sodium sulfate treated samples. While damage was not readily apparent, their resulting efflorescences took on totally different appearances; those of sodium sulfate had greater amounts of "fluffy" or "whiskery" efflorescence, while those of sodium carbonate saturated solution exhibited a haze resembling efflorescence. This could be due, in part, to the more hygroscopic nature of sodium carbonate.

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Chapter 4: Coatings in the Presence of Salts

4. Introduction

The question of whether paints and other protective coatings cause harm to masonry has been discussed in various papers (Grissom et al, 2000, Charola, 2001, Franke and Reimann-Oenel, 2001). As previously stated, it is still currently believed that once salts enter into a porous material, a coating can be harmful in that it will enhance deterioration. However, L. Franke and R. Reimann-Oenel (2000, 2001) have called this belief into question based on the results of their laboratory experiments on Cottaer, Obemkirchener and Sander Schilff sandstones where sodium sulfate was introduced to both coated and uncoated stone specimens in a wind tunnel environment.

4.2 The Effect of Coatings

The experimental results of L. Franke and R. Reimann-Oenel (2000, 2001) showed that the presence of a coating may lessen damage by causing the salt front to form nearer the surface than in an untreated control specimen.

Experiments involving four sandstone types and two coating systems were conducted. The coated samples and control samples were exposed to sodium sulfate decahydrate and calcium sulfate dihydrate in a wind tunnel (details follow in Chapter 5). They sought, through their experiments, to document the apparent damage in untreated and treated samples and also determine the point in time where damage emerged and observe the damage through the complete destruction of the surface. They defined the

beginning of damage as the point where surface irregularities (raising, cracking) formed.¹⁴¹

Franke and Reimann-Oenel assert that damage mechanisms and causes may not be the result of paints or clear coatings like silicone and methacrylate resins, but a series of other factors. These include: damage already done to masonry prior to application of the treatment, the stone and its inherent flaws, and salts. Then, if there are salts present, the result is the loss of the coating making damage visible. They go on to say that this visible damage in the form of a flaking coating has been used as the argument against coating masonry, but this reveals that a coating should not only be chosen for its aesthetics, but its performance on salt loaded stone.^{142} They acknowledge that most sources maintain that coatings on stone endanger the buildings, but this is mostly observed in cases of improper planning and execution of the treatment. They state that a coating must reduce water absorption while maintaining water vapor permeability.¹⁴³

The experiments showed that there were clear differences between treated and untreated samples. They found that samples treated with a silicone resin glaze (Lasur) subsequently exposed to sodium sulfate decahydrate and calcium sulfate dihydrate only deteriorated at the coating and substrate interface, while untreated samples of the same stone type had surface damage consisting of two to three millimeters of detachment. Salt crystallization on the treated samples was limited to areas above the coating (due to the coating's high water vapor permeability), leaving the stone itself unharmed. Remarkable

¹⁴¹ L. Franke and R. Reimann-Oenel "Untersuchung des Einflusses von Lasuren auf die Lebensdauer von Natursteinfassaden," Internationale Zeitschrift für Bauinstandsetzen und Baudenkmalpflege 7, Jahrgang, Heft 1.(2001): 33-5.

 142 Ibid, 31-3.

 143 Ibid. 30.

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above all, Franke and Reimann-Oenel state, is that not only was the extent of damage reduced with the application of a coating, but also the life span of the stone was extended. The time span varied upon the sandstone variety, but most samples were improved by the application of the coating.¹⁴⁴

In their paper, Franke and Reimann-Oenel present case studies in which treatments have been successful. These include the U.S. Capitol, where a repair made in the 1980s revealed up to 40 layers of oil, latex, alkyd and emulsion paints. A Lasur was applied, and was observed to give good adhesion and cover as well as good chemical and aesthetic characteristics. Another successful treatment involving Lasuren was applied to the Federal Building in Harmover and the Osnabriick City Hall, both sandstone buildings in Germany. After fifteen years, an investigation in 1995 revealed that the treated facades were conserved by the coating and the stone had not experienced damage.¹⁴⁵

However, Charola (2001) raises the question of adhesion strength or bonding of the coating to the substrate. These results need to be confirmed with reports of water vapor permeability and adhesion, for if the adhesion strength between the substrate and coating is higher than the cohesive strength of the substrate, a portion of the surface of the substrate will be lost when failure takes place.¹⁴⁶ This question is addressed in a first approximation in the experimental procedure and results, presented in the following chapters. But first, the coatings used for this experimental procedure are described.

¹⁴⁴ Ibid, 35-6.

 145 Ibid, 30-1.

¹⁴⁶ A.E. Charola, "Water Repellents and Other 'Protective' Treatments: A Critical Review" In: *Hydrophobe* III, 3rd International Conference on Surface Technology with Water Repellent Agents, Ed. by K. Littmann and A.E. Charola, Aedification Publishers, Freiburg: 2001.

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4.3 Experimental Coating Properties

For the purposes of the present study, a series of coatings were used. They were chosen to give a variety of characteristics including different adhesion strengths, water vapor transmission rates, water repellent properties, etc. These coatings include: a Benjamin Moore Acrylic system, the Keim Granital Mineral coating system, PROSOCO, Inc. Siloxane WB water repellent system and Atofina Kynar RC-10, ¹⁵² PWD PVDF used as a water repellent system.

The Benjamin Moore Acrylic system consisted of Moore's® High-Build Acrylic Masonry Primer and SuperspecTM 100% Acrylic Exterior Masonry Coating. These products were designed to seal masonry and provide a waterproof surface while maintaining good adhesion.¹⁴⁷ Both of these are 100% acrylic, lending durability, flexibility, stability (non-yellowing, temperature resistant), and resistance to abrasion and solubility.¹⁴⁸

The Keim Granital Mineral Paint system is a silicate based paint system specifically designed for mineral substrates. This product line was recommended for the experiment presented here by the Cohalan Company, distributors of the Keim system in the U.S. Although this paint system is unique in that it is not a film former, per se, it is important to consider this type of coating in the presence of salts. Product literature for this system claims that it is "the best imaginable protection for a building... [being] highly water repellent without sealing the pores... the humidity of the substrate can still diffuse out. There is no chance for mould, and the hard silicate surface makes [it] highly

¹⁴⁷ Benjamin Moore & Co., "Benjamin Moore Focuses on Masonry Solutions," [online] 2001 [cited 6 April 2002]; available from http://www.benjaminmoore.eom/c/cl l.html.

¹⁴⁸ Guy E. Weismantle, ed. Paint Handbook, Boston: McGraw-Hill, 1981, 3-19-20.

and the contract of resistant to weather, industrial pollution and fire."¹⁴⁹ Mineral paints form a chemical bond with the substrate, essentially becoming a part of the material. Since the paint is alkaline in nature, it does not react with the alkaline substrate on which it is applied. One problem that can be encountered, however, is the difficulty in removing the paint, since it does form such a good bond.

PROSOCO, Inc.'s Weather Seal Siloxane WB is ^a water-based water repellent system consisting of a "blend of monomeric silanes and oligomeric siloxanes... designed for dilution with fresh water... [producing] a penetrating water repellent that is ideal for dense or porous surfaces."^{150} This product is also designed to "repel surface water without trapping water vapor."¹⁵¹ All water repellents should add hydrophobic properties to the pores of a material without hindering water vapor transmission or forming a fihn on the surface. The intention of these coatings is to "extend [masonry's] usefiil life by increasing weather resistance and reducing spalling, cracking, and efflorescence." "

Another water repellent coating used was Atofina Kynar RC-10, ¹⁵² PWD PVDF (hexafluoro-propylene-vinylidine-fluoride copolymer). This is an engineering thermoplastic fluoropolymer designed to be fabricated into "pipes, fitting and valves, pump assemblies, sheet and stock shapes, films and tubing."¹⁵³ While not yet marketed as such, it has been tested for use as a water repellent coating when the powder form is

¹⁴⁹ Research and Applied Technologies Pty Ltd., "Keim Mineral Paints: Keim Granital," [online] 2001 [cited 25 October 2001]; available from http://www.spec-net.com.au/keim/granital.htm.
¹⁵⁰ "PROSOCO, Inc.: Water Repellents 07190," *Spec-Data, Architect's First Choice*, Construction

Marketing Data Group: 2001.

¹⁵¹ PROSOCO, Inc., "Section 07190: Water Repellents," [online] 1999 [cited 25 October 2001]; available from http://www.prosoco.com.

¹⁵² Weismantle, Paint Handbook, 16-12.

¹⁵³ Atofina Chemicals, Inc., "Kynar® and Kynar® Flex PVDF: Overview," [online] 2000 [cited 7 January 2002]; available from http://www.atofinachemicals.com/kynarglobal/overview.cfm.

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combined with acetone to form a 5% weight by weight solution.¹⁵⁴ Atofina Kynar's properties include "mechanical strength and toughness, high abrasion resistance, high thermal stability,... [resistance] to most chemicals and solvents, [resistance] to ultraviolet... radiation, [resistance] to weathering and fungi, [and] low permeability to most gases and liquids."¹⁵⁵ The last characteristic mentioned is of concern, as one requirement for water repellents is water vapor permeability. However, this may not be applicable since the above properties are not specifically for Kynar's use as a water repellent for masonry, but for engineering component manufacture.

The coatings described above were applied to low porosity brick samples and their characteristics compared using techniques similar to those of Franke and Reimann-Oenel. Water vapor transmission rates, of concern to Charola (2001) were also investigated. The experimental setup and results are presented in the following chapters.

¹⁵⁴ Kurt Wood, Atofina Chemicals, Inc., Telephone conversation with author, 8 January 2002.

¹⁵⁵ Atofina Chemicals, Inc., "Kynar® and Kynar® Flex PVDF: Overview."

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Chapter 5: Coatings and Sodium Carbonate: Experimental Part II

5.1 Introduction

In order to study the behavior of salts in coated brick, a number of laboratory tests were conducted. All tests used extruded high-fired brick from the same palette obtained from a local masonry supplier cut into appropriate sizes. Comparability was assured by identifying the source bricks for each sample. (This is illustrated by the experimental matrices for each test.) Tests included water vapor transmission of the coatings; capillary water absorption, total immersion and drying using deionized water and sodium carbonate with a brick substrate; salt weathering tests using both sodium sulfate and sodium carbonate; coating adhesion; and finally, a test that repeated as closely as possible the experimental setup used by L. Franke and R. Reimann-Oenel (2001) but using sodium carbonate as the testing salt.

Table 5.1 Experimental Matrix

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5.2 Characterization of Brick Samples

The brick samples were characterized using capillary absorption rates, imbibation capacity and drying rates. These tests were repeated using sodium carbonate solution. The following sample matrix was used:

Table 5.2 Experimental Matrix for Capillary Absorption Rates, Imbibation Capacity and Drying Rates

Capillary absorption rates were obtained for the sample brick following the NORMAL 11/85 procedure. Samples were cut into $5 \times 5 \times 5.5$ centimeter cubes from the center of the brick units for these tests. At least one side consisted of the "fireskin", through which absorption took place; the rest of the sides were cut using an electric wet masonry saw with a diamond blade. The capillary absorption curve obtained is presented below. (Figure 5.1)

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Figure 5.1 Capillary Water Absorption Rates of Sample Bricks

Porosity of the brick was found following total immersion procedures as recommended in NORMAL 7/81 and ASTM C 67-97. From this data, the percent apparent porosity was obtained. Results are shown below.

Table 5.3 Porosity of Brick Sample

Figure 5.2 Capillary Absorption Curves of Brick Samples: Comparison of Water and Sodium Carbonate Saturated Solution Absorption Rates

Table 5.4 Theoretical and Actual Salt Content Data

Table 5.5 Capillary Absorption Coefficient and Critical Moisture Content Data for Water and Saturated Sodium Carbonate Solution Treated Samples

Figure 5.3 Drying Curves of Brick Samples with Water and Sodium Carbonate

Figure 5.4 Drying Rate Curves of Brick Samples with Water and Sodium Carbonate

After capillary absorption (Figures 5.1 and 5.2) and total porosity (Table 5.3) were determined, both the drying curves and the drying rate of the samples were obtained following an adaptation of NORMAL 29/88. The results are presented above (Figure 5.3 and 5.4). (Also see Appendix B.) When comparing the results of the tests using sodium carbonate to those using deionized water, it is clear that the presence of salts slows down the drying process and increases the relative critical moisture content. Furthermore, while the critical moisture content for samples placed in deionized water is reached after approximately 10 to 15 hours, it is not reached until after 20 to 30 hours when placed in sodium carbonate solution. The increased moisture absorption of samples treated with sodium carbonate is due to the high hygroscopicity of this salt.

5.3 Water Vapor Transmission of Coatings

To test the water vapor transmission rates of the coatings, a modified version of ASTM E 96-80, Standard Test Methods for Water Vapor Transmission of Materials, was used.

Table 5.6 Experimental Matrix for Water Vapor Transmission Rates

The results of the water vapor transmission tests (see Table 5.7 and Figure 5.5) show that the Benjamin Moore Acrylic System reduced the water vapor permeability of the brick much more significantly than the other coatings used in the experiment. The Keim Granital Mineral Paint system, PROSOCO Siloxane WB, and Atofina Kynar water repellent did not significantly change water vapor transmission rates from that of the control. (Also see Appendix C.) It should be noted that the standard deviation of results obtained for the samples treated with Atofina Kynar was greater, indicating poor reproducibility of product application. Additionally, it is important to note the different results obtained for the cut and rough sides treated with epoxy. Sides that were cut were much more permeable and showed lower resistance to water vapor transmission than those left rough.

Table 5.7 Results of Water Vapor Transmission Tests

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Figure 5.5 Sampling of Water Vapor Transmission Rates

5.4 Coating Adhesion Test

As stated in Chapter Four, the adhesion of a coating to the substrate is significant to the greater question at hand in that if a coating's adhesive strength is stronger than the cohesive strength of the substrate, the integrity of the substrate may be compromised in the event of spalling. Therefore, the adhesion of the coatings used were tested using ASTM D 3359-97 Standard Test Methods for Measuring Adhesion by Tape Test. (See Appendix D for photographs and results matrix.) All of the coatings used throughout the course of the experiments were tested, including the epoxy coatings. The results of this test showed a variety of adhesion strengths among the coatings tested and that adhesion strength is greatly altered when the crystallization of sodium carbonate occurs (Table 5.8).

	Untreated	Benjamin Moore Acrylic	Keim Granital	Atofina Kynar	PROSOCO Siloxane WB	Epoxy Cut Side	Epoxy Rough Side
without exposure	N/A	$<$ 5% removed	$5\% - 15\%$ removed	entire coating	N/A	0% removed	not tested
to $Na2CO3$				removed			
with exposure to $Na2CO3$	N/A	35%-65% removed	5% removed	$15% - 35%$ removed	N/A	$>65\%$ removed	$< 5\%$ removed

Table 5.8 Average Adhesion Strengths of Coatings both Subjected to and Not Subjected to Treatment with Na_2CO_3

No change was observed between samples treated with sodium carbonate and those untreated in samples coated with Prosoco Siloxane WB water repellent. This is because this is not a film-forming treatment. Samples treated with Benjamin Moore Acrylic paint showed very good adhesion, with less than 5% of the coating removed during the test. When the samples were exposed to sodium carbonate, the amount removed increased to an average of 35% to 65%, with portions experiencing blistering due to salts completely removed leaving a salt film underneath.

Samples treated with Keim Granital Mineral paint showed an increase in adhesion strength after exposure to sodium carbonate, from an average of 5% to 15% removed to approximately 5% removed once samples were exposed. This phenomenon was also seen in samples coated with Atofina Kynar with adhesion strength increasing from the film being completely removed to only 15% to 35% removed after salt exposure.

Samples coated with Axson Wood & Stone Transparent Polyester Epoxy showed complete removal of the coating when the cut sides were exposed to sodium carbonate; however, sides that were rough and left uncut showed very little adhesion loss, with less than 5% removed. Those samples left unexposed to sodium carbonate lost no adhesion strength, and the test resulted in only a loss of surface gloss.

5.5 Salt Deterioration in the Presence of a Coating

In order to repeat the tests conducted by Franke and Reimann-Oenel (2001), bricks were cut to prisms that measured ⁵ x 5.5 x 9 cm. The "fireskin" was retained on at least two sides—the coated and the absorbing surfaces. All samples were coated with Axson Wood & Stone Transparent Polyester Epoxy on the vertical sides. The bottom surface was left as the absorbing (untreated) surface and the tops were coated (Table 5.9).

Table 5.9 Experimental Matrix for Repetition of Franke and Reimann-Oenel Tests

As seen in Tables 5.9 and 5.10, three samples were used as controls and were not coated on the top. The rest were coated with various coating systems to see if the coating type and its properties had an effect on salt crystallization distribution in the brick samples.

Product Name Manufacturer **Generic Description Application Procedure** Moore's High-Build 1 coat High-Build Acrylic Latex Acrylic Masonry Primer Primer Benjamin Superspec 100% Acrylic Moore & Co. l coat Superspec Acrylic **Exterior Masonry Coating** Potassium Silicate with Dilution: Granital Keim Granital 1 coat Primer 1:2 Keimfarben GmbH **Acrylic Emulsion** Potassium Silicate 1 coat Granital 1:20 Keim Dilution Hexafluoro-Atofina Kynar RC-10, 152 propylene 5% w/w Kynar in PWD PVDF Water Atofina Vinylidine Fluoride Acetone Repellent Copolymer PROSOCO Siloxane WB 1 part Siloxane WB to 7 **PROSOCO** Siloxane Water Repellent Water Repellent parts potable water

Table 5.10 Coating Systems Evaluated in Experimental Program

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After sample preparation, the coatings were allowed to cure for twelve days. The prisms were then set into individual plastic containers with the uncoated, "absorbing" surface resting on glass beads. The containers were filled with saturated sodium carbonate monohydrate solution to the level of the glass beads. The tops of the containers were pierced to allow the prisms to be exposed to the air, with the gap between the prisms and the cutout filled with paraffin. This mechanism restricted movement of the solution to capillary rise through the height of the sample. Each day, the prisms were exposed to a household fan for approximately four hours on high speed that provided a wind tunnel effect (see Appendix E.) Samples were rotated each day to expose every side to the wind. The experiment was conducted in a controlled environment that averaged 20°C and 20% to 25% relative humidity. Observations were made each day to assess damage.

The day after testing began, crystals began forming in the bottom of the sample apparatuses. To ensure proper liquid flow, these crystals had to be broken up periodically by massaging the containers. On the tenth day of testing, the first signs of damage were seen on samples coated with Atofina; efflorescence began to form under the coating films along the pattern of the brushstrokes of two of the three samples treated with this water repellent.

After this initial damage, efflorescence began to form in an unexpected area. This occurred by day 17, and consisted of efflorescence forming under the epoxy coated vertical surfaces (even when the tops showed no signs of efflorescence.) This phenomenon was first observed on untreated samples and those coated with Benjamin Moore paint. It later appeared on more samples in patterns and at levels that were indicative of the depth at which the salt fronts were forming within (this was later

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confirmed after the samples were broken open.) By day 22, the surface of one Benjamin Moore treated sample began to blister, and the paint film was soft to the touch. By day 29, a second Benjamin Moore treated prism exhibited blistering of the coating layer. Between day 29 the tenth week, an increase in the visible deterioration explained above was observed.

It appears that the samples coated with Keim and PROSOCO coatings most closely resemble untreated samples. All samples coated with Benjamin Moore and Atofina exhibited active deterioration: in the form of visible efflorescence in the case of Atofma (with the salts actually increasing adhesion strength), and blistering in the case of Benjamin Moore. Neither Keim nor PROSOCO treatments exhibited any surface deterioration. All of the samples exhibited efflorescence imder the vertical surfaces coated with epoxy, with the most appearing on untreated and Benjamin Moore treated samples.

After ten weeks of testing, the samples were broken open and photographed under magnification to determine the level at which the salt front developed. The following was observed (see Table 5.11 and Appendix E for photographs):

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Table 5.11 Salt Fronts Developed in Coated Samples Exposed to Sodium Carbonate Saturated Solution The results presented above support the conclusions drawn by Franke and Reimann-Oenel. In the case of paints, damage is readily observed when the water vapor permeability is significantly affected (i.e., Benjamin Moore Acrylic Paint) but no salt front is formed if water vapor permeability is not affected (i.e., Keim Granital Mineral paint). Damage will be delayed as compared to the control, where a distinct salt front is formed.

In the case of water repellents, the penetration depth of the product determines the site for the salt front formation. The higher penetration depth of PROSOCO Siloxane WB concentrated salts at about one centimeter from the surface. Damage in the form of spalling will eventually occur at this location. For the Atofina product, efflorescence formed on the surface and the salt was uniformly distributed, a desirable feature; however, the performance of this product as a water repellent was not evaluated. (It

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should be noted that the product formed ^a rubbery, hazy film on the surface of the substrate rather than penetrating deeply.) It is expected that damage would result in sanding of the surface rather than flaking.

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Chapter 6: Discussion and Conclusions

Several conclusions can be drawn from the experiments conducted during this study. Before presenting these, it is important to acknowledge that the material used for these tests had a large impact on the results. By using a high fired low porosity brick (average percent apparent porosity of $3.40 \pm 0.56\%$), the damage that could possibly occur was limited. While the use of new bricks assured that variables to consider would be minimal (i.e. they were from the same palette and had not been exposed to pollutants and weathering) this minimized visible damage. It can be assumed that, considering the relationship of high porosity with salt damage, by using a material with a higher porosity and lower mechanical resistance, damage due to salt weathering would be more dramatic.

It has been shown that both sodium carbonate and sodium sulfate are harmful when introduced into porous materials. However, significant differences are observed in the field depending on the nature of the masonry used. While the reasons for this difference are not yet fully understood, the experiments conducted here served to contribute to their elucidation. These, conducted on highly fired, low porosity brick showed that sodium carbonate monohydrate is more hygroscopic than sodium sulfate. Hence, it is likely that less crystallization will occur, explaining in part the lower deterioration effect sodium carbonate has as compared to sodium sulfate.¹⁵⁶

Furthermore, the laboratory dehydration of single crystals of the decahydrate salts showed distinct differences between them. While sodium sulfate formed many small crystals, sodium carbonate generated fewer and larger crystals. Differences in the

Goudie and Viles, Salt Weathering Hazards, Table 4.13.

and the contract of effectiveness in the deterioration exerted by these salts could, in a first approach, be attributed to these dehydration differences, which could be significantly affected by the porosity (pore size distribution and shape) of the material. The results obtained on the effect of sodium carbonate crystallization on various coatings is summarized in Table 6.1.

Table 6.1 Summary of Results

The water vapor permeability of a coating has a direct effect on where salt forms within a porous substrate. In the case of paints, the least permeable coating tested: an acrylic system developed by Benjamin Moore, exhibited the most damage at the substrate and coating interface, while the Keim Granital system, with similar water vapor permeability characteristics to the untreated samples, exhibited salt crystallization deeper within the substrate.

In the case of water repellents, the Atofina Kynar RC-10, 152 PWD PVDF Water Repellent exhibited water vapor permeability characteristics similar to untreated material but was the first to show surface efflorescence. On the other hand, treatment of samples

with PROSOCO Siloxane WB, where ^a deeper penetration was obtained, resulted in the formation of a salt front related to the depth of coating penetration at about 2 centimeters below the surface. The untreated material showed a similar salt front at twice this distance.

Conclusions

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This study has confirmed that painting masonry surfaces will reduce damage and, for the case of silicate paints (*Lasuren*) that do not change the water vapor permeability properties significantly, the damage would be retarded. For the case of water repellents, the deterioration will be determined by the penetration depth of the product, and the eventual damage will be evident as detachment or powdering; though, at a lower depth than untreated materials.

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APPENDIX A: SALT WEATHERING TESTS

SAMPLE PREPARATION FOR SALT WEATHERING

Porosity of Samples (determined from total immersion tests):

Potential Volume of saturated salt solution per 100g brick = 3.40 ml

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SALT WEATHERING CYCLES

Weight Change
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APPENDIX B: CAPILLARY ABSORPTION,

TOTAL IMMERSION AND DRYING

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CAPILLARY ABSORPTION OF SATURATED SODIUM CARBONATE SOLUTION: BRICK 1-2

CAPILLARY ABSORPTION OF SATURATED SODIUM CARBONATE SOLUTION: BRICK 1-2

end capillary action; begin total immersion
Sample size: 5 cm x 5.5 cm absorbing surface: 27.5 cm2

CAPILLARY ABSORPTION OF DEIONIZED WATER: BRICK 2-2

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Amount Absorbed	/ unit surface	(g/cm2)	0.00	0.03	0.04	0.04	0.05	0.05	0.06	0.06	0.06	0.06	0.07	0.07	0.07	$\frac{0.07}{0}$	0.08	0.08	0.08	0.08	0.08	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	010
	Amount	Absorbed (g)	0.00	$\overline{0.91}$	\Box	$\overline{22}$.36	1.46	1.56	1,66	1.75	1.74	1.87	1.95	1.97	2.03	2.10	2.10	2.24	2.25	2.30	2.35	2.42	2.46	2.57	2.57	2.52	2.54	2.55	764
	Weight of	Sample (g)	399.01	399.92	400.12	400.23	400.37	400.47	400.57	400.67	400.76	400.75	400.88	400.96	400.98	401.04	401.11	401.11	401.25	401.26	401.31	401.36	401.43	401.47	401.58	401.58	401.53	401.55	401.56	401.65
Square Root	Seconds	(cumulative)		17.32	24.49	30.00	34.64	38.73	42.43	45.83	48.99	51.96	54.77	57.45	60.00	62.45	64.81	67.08	69.28	71.41	73.48	75.50	77.46	79.37	81.24	83.07	84.85	86.60	88.32	90.00
	Time in Seconds	(cumulative)	0.00	300	600	900	1200	1500	1800	2100	2400	2700	3000	3300	3600	3900	4200	4500	4800	5100	5400	5700	6000	6300	6600	6900	7200	7500	7800	8100
	Time in Minutes	(cumulative)	\circ		$\overline{10}$	$\overline{5}$	\overline{c}	25	30 _l	$\overline{35}$	40 _i	45	50	55	$\overline{60}$	$\overline{59}$	$\overline{5}$	$\overline{5}$	$\overline{80}$	$\overline{\frac{85}{}}$	90	$\overline{56}$	00	105	$\overline{101}$		20	125	130	135
		Actual Time	$1:30 \text{ AM}$	1:35 AM	11:40 AM	$1:45$ AM	1:50 AM	11:55 AM	12:00 PM	12:05 PM	12:10 PM	12:15 P _M	12:20 PM	12:25 PM	12:30 PM	12:35 PM	12:40 PM	12:45 PM	12:50 PM	12:55 PM	1:00 PM	1:05 PM	1:10 PM	$1:15$ PM	1:20 PM	$1:25$ PM	1:30 P _M	1:35 PM	Nd 0t:1	M45H
		Date	2/9/2002	2/9/2002	2/9/2002	2/9/2002	2/9/2002	2/9/2002	2/9/2002	2/9/2002	2/9/2002	2/9/2002	2/9/2002	2/9/2002	2/9/2002	2/9/2002	2/9/2002	2/9/2002	2/9/2002	2/9/2002	2/9/2002	2/9/2002	2/9/2002	2/9/2002	2/9/2002	2/9/2002	2/9/2002	2/9/2002	2/9/2002	2/9/2002

CAPILLARY ABSORPTION OF SATURATED SODIUM CARBONATE SOLUTION: BRICK 2-2
1 OF 3

CAPILLARY ABSORPTION OF SATURATED SODIUM CARBONATE SOLUTION: BRICK 2-2

Sample size: 5 cm x 5.5 cm absorbing surface: 27.5 cm2

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CAPILLARY ABSORPTION OF SATURATED SODIUM CARBONATE SOLUTION: BRICK 3-2
2 OF 3

CAPILLARY ABSORPTION OF SATURATED SODIUM CARBONATE SOLUTION: BRICK 3-2

	0.31	$\overline{0.3}$	0.3	0.3	0.32	0.33 0.32	0.3	0.33	0.34	0.34	0.35	0.35	0.35	0.35	0.36	0.36	0.38	0.40	0.46	64.0	0.51	0.53	0.55	0.5	0.57
8.39	8.47	8.52	8.66	8.71	8.81	8.98	9.19	9.16	9.25	9.33	9.53	9.52	9.68	9.69	9.79	9.82	10.41	11.03	12.61	13.40	13.98	14.56	15.14	15.72	15.73
385.86	385.94	385.99	386.13	386.18	386.28	386.45	386.66	386.63	386.72	386.80	387.00	386.99	387.15	387.16	387.26	387.29	387.88	388.50	390.08	390.87	391.45	392.03	392.61	393.19	393.20
133.04	134.16	136.38	138.56	140.71	142.83	144.91	146.97	149.00	151.00	152.97	154.92	156.84	158.75	160.62	162.48	164.32	166.13	184.93	305.94	415.69	509.12	587.88	657.27	720.00	777.69
17700	8000	8600	19200	19800	20400	21000	21600	22200	22800	23400	24000	24600	25200	25800	26400	27000	27600	34200	93600	172800	259200	345600	432000	518400	604800
295	300	$\frac{310}{ }$	320	330	340	$\frac{350}{ }$	$\frac{360}{ }$	370	380	390	400	410	024	430	440	450	460	570	1560	2880	4320	5760	7200	8640	10080
4:25 PM	4:30 PN	4:40 PM	4:50 PM	Nd 00:S	5:10 PM	5:20 PM	5:30 PM	5:40 PM	5:50 PM	M ₃₀₀	6:10 PM	6:20 PN	$6:30$ PM	6:40 PM	MQ 0.30	7:00 PM	Md 00:6	11:00 PM	3:30 PM	1:30P _M	1:30 PM	1:30P _N	1:30 PM	1:30P _M	$1:30$ PM
2/9/2002	2/9/2002	2/9/2002	2/9/2002	2/9/2002	2/9/2002	2/9/2002	2/9/2002	2/9/2002	2/9/2002	2/9/2002	2/9/2002	2/9/2002	2/9/2002	2/9/2002	2/9/2002	2/9/2002	2/9/2002	2/9/2002	2/10/2002	2/11/2002	2/12/2002	2/13/2002	2/14/2002	2/15/2002	2/16/2002

Sample size: 5 cm x 5.5 cm absorbing surface: 27.5 cm2

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WATER ABSORPTION BY TOTAL IMMERSION: BRICK 1-2

*dry weight

Sample size: 5.7 cm x 5.1 cm x 5.5 cm volume: 159.89 cm3; surface area: 176.94 cm2 Weight after test (Waf) = 385.61 g
the versity [(Mmax - Maf)/Maf] x 100=3.88% hmbibation Capacity or % Apparent Porosity [(Mmax - Maf)/Maf] x 100=3.88% Weight imbibed sample at end of test (Wmax) = 400.58 g Dry weight before Capillary Action (Wdry): 385.59 g Total water content Uo (Wmax - Wdry) = $14.99 g$

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SATURATED SODIUM CARBONATE SOLUTION ABSORPTION BY TOTAL IMMERSION: BRICK 1-2

*dry weight

Sample size: 5.7 cm x 5.1 cm x 5.5 cm volume: 159.89 cm3; surface area: 176.94 cm2 Weight imbibed sample at end of test (Wmax) = $401.33 g$

Dry weight before Capillary Action (Wdry): 385.58 g

Total water content Uo (Wmax - Wdry) = $15.75 g$

Weight after test (Waf) = 387.06 g
mostly [(Mmax - Maf)/Maf] x 100=3.69%
mbibation Capacity or % Apparent Porosity [(Mmax - Maf)/Maf] x 100=3.69%

*dry weight

Sample size: 5.7 cm x 5.5 cm x 5.4 cm volume: 169.29 cm3; surface area: 183.66 cm2 Imbibation Capacity or % Apparent Porosity [(Mmax - Maf)/Maf] x 100=2.62% Weight imbibed sample at end of test (Wmax) = $409.81 g$ Dry weight before Capillary Action (Wdry): 399.05 g Total water content Uo (Wmax - Wdry) = $10.76 g$ Weight after test (Waf) = 399.36 g

SATURATED SODIUM CARBONATE SOLUTION ABSORPTION BY TOTAL IMMERSION: BRICK 2-2

*dry weight

Sample size: 5.7 cm x 5.5 cm x 5.4 cm volume: 169.29 cm3; surface area: 183.66 cm2 Weight imbibed sample at end of test (Wmax) = 410.43 g
Dry weight before Capillary Action (Wdry): 399.01 g Total water content Uo (Wmax - Wdry) = $11.42 g$

Weight after test (Waf) = 400.42 g
mosity [(Mmax - Maf)/Maf] x 100=2.50%
dmbibation Capacity or % Apparent Porosity [(Mmax - Maf)/Maf] x 100=2.50%

WATER ABSORPTION BY TOTAL IMMERSION: BRICK 3-2

*dry weight

Sample size: 5.5 cm x 5.2 cm x 5.5 cm volume: 157.30 cm3; surface area: 174.9cm2 Imbibation Capacity or % Apparent Porosity [(Mmax - Maf)/Maf] x 100=3.70% Weight imbibed sample at end of test (Wmax) = 391.47 Dry weight before Capillary Action (Wdry): 377.47 g Total water content Uo (Wmax - Wdry) = 14.00 g Weight after test (Waf) = 377.49 g

SATURATED SODIUM CARBONATE SOLUTION ABSORPTION BY TOTAL IMMERSION: BRICK 3-2

*dry weight

Sample size: 5.5 cm x 5.2 cm x 5.5 cm volume: 157.30 cm3; surface area: 174.90 cm2 Imbibation Capacity or % Apparent Porosity [(Mmax - Maf)/Maf] x 100=3.59% Weight imbibed sample at end of test (Wmax) = 392.42 g Dry weight before Capillary Action (Wdry): 377.47 g
Total water content Uo (Wmax - Wdry) = 14.95 g Weight after test $(Waf) = 378.82 g$

WATER AND SATURATED SODIUM CARBONATE SOLUTION ABSORPTION BY TOTAL IMMERSION

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DRYING CURVE WITH DEIONIZED WATER: BRICK 1-2 3 OF 3

*imbibed weight

**put in oven

Sample Size: 5.7 cm x 5.1 cm x 5.5 cm = 159.89 cm3 total surface area
Dry weight before Capillary Absorption: 385.59 g Dry weight at end of test (Wdry) = 385.61 g
Weight imbibed sample at end of test (Wmax) = 400.58 g
Recalculated Total Water Content Uo (Wmax - Wdry) = 14.97 g

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"put in oven
""end of test

Sample size 57 cm $\times 51$ cm $\times 5$ cm absorbing surface 159 89 cm3
Dry weight before Initial Capillary Absorption. 385 59 g Weight imb
bed sample at beginning of test (Wmax) = 401
 33 g
Recalculated Total Solution Content U
o (Wmax - Wdry) = 14
 27 g Dry weight at end of test $(W\text{dry}) = 387.06 \text{ g}$

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DRYING CURVE WITH DEIONIZED WATER: BRICK 2-2
2 OF 3

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DRYING CURVE WITH DEIONIZED WATER: BRICK 2-2 3 OF 3

*imbibed weight

**put in oven

*** end of test

Dry weight before Capillary Absorption: 399.05 g
Dry weight at end of test (Wdry) = 399.36 g
Weight imbibed sample at end of test (Wmax) = 409.81 g
Recalculated Total Water Content Uo (Wmax - Wdry) = 10.45 g

DRYING CURVE WITH SATURATED SODIUM CARBONATE SOLUTION: BRICK 2-2
2 OF 2

*unbibed weight

 $\ensuremath{^{\ast\ast}}\xspace\text{put}$ m oven

*** end of test

Sample size 57 cm x 5 s cm x 5 4 cm absorbing surface 16929 cm3
Dry weight before finitial Capillary Absorption 399 05 g Dry weight at end of test (Wdry) = 400 42 g
Weight mbbbed sample at beginning of test (Winax) = 410 43 g
Recalculated Total Solution Content Uo (Winax - Wdry) = 10.01 g

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DRYING CURVE WITH DEIONIZED WATER: BRICK 3-2

*imbibed weight

 139
 $+44$ end of test **put in oven

Sample size: 5.5 cm x 5.2 cm x 5.5 cm = 157.30 cm3 total surface area
Dry weight before Capillary Absorption: 377.47 g
Dry weight at end of test (Wdry) = 377.49 g
Weight imbibed sample at end of test (Wmax) = 391.47 g
Rec

the control of the control of the

DRYING CURVE WITH SATURATED SODIUM CARBONATE SOLUTION: BRICK 3-2

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*unbibed weight **put in oven ***end of test Sample size 55 cm x 52 cm x 55 cm absorbing surface 157 30 cm3 Dry weight before Initial Capillary Absorption 377-47 g
Dry weight at end of test (Wdry) = 378 83 g
Weight unbibed sample at beginning of test (Winns) = 392 42 g
Recalculated Total Solution Content Uo (Winns - Wdry) = 13

RELATIVE MOISTURE CONTENT % VERSUS TIME (HOURS)

RESIDUAL % MOISTURE CONTENT VERSUS TIME (HOURS) FOR WATER AND SODIUM CARBONATE SOLUTION

CHANGE IN MOISTURE CONTENT/CHANGE IN TIME VERSUS MOISTURE CONTENT

Capillary Absorption/ Total Immersion/ Drying with Saturated Sodium Carbonate Solution

Capillary Absorption

Total Immersion

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Drying 3 hrs

Drying 22 hrs

APPENDIX C:

WATER VAPOR TRANSMISSION OF COATINGS

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2/5/2002 7:30 PM 33875 360 40 - 1.36 362 40 - 1.36 362 40 - 1.36 362 40 - 1.36 46 - 1.36 46 - 1.36 46 - 1.36 46
- 2/5/2002 7:30 PM 33875 - 360 10 - 1.36 - 362 10 - 1.25 Note Test on Sample 2-1 Control an 3/16/2002 to 4/1/2

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WATER VAPOR TRANSMISSION RATES

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GRANTA CEL PER Capacity

Sample Preparation: Water Vapor Permeability

Coated Samples for Water Vapor Permeability Test

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Prepared Samples in Containers for Water Vapor Permeability Test

APPENDIX D: ADHESION STRENGTH TESTS

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ADHESION TEST RESULTS ¹ OF 2

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ADHESION TEST RESULTS 2 OF 2

 $\frac{\partial \mathcal{L}_{\text{max}}}{\partial \mathcal{L}_{\text{max}}}$

<u> 1990 - Jan Barbara (j. 1980)</u>

Before Adhesion Testing

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Control Samples (Not Exposed to Salts) Before Testing **Adhesion Test Results: Control Samples** Control Samples (Not Exposed to Salts) Before Testing Adhesion Test Results: Control Samples Adhesion Test Results: Salt Treate Adhesion Test Results: Salt Treated Samples **MARITA** Atofina Atofinal \sum_{13} $\ddot{}$ Atofina Atofina 6.2 5:r _ Prosoco
Si loxane WB Prosoco
Siloxane WB Prosoco
Sibane WB Prosoco 6.3 93 10.3 Siloxane WB Epoxy Epoxy $S.1A$ $6.1A$ Epoxy Epoxy Epoxy POXY $7.1B$ 61B

Atofina Kynar System

WB System ine⁻ to Silox

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Epoxy System: Cut Side

Lpoxy System: Rough (Uncut) Side

APPENDIX E: SALT DETERIORATION

IN THE PRESENCE OF A COATING

Sample Preparation: Atoflna Kynar System

Sample Preparation Using Kynar RC- 10.052 PWD PVDF and Acetone

Prepared Samples in Containers for Tests on the Influence of Coatings on Salt Formation

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Sample Preparation: Prosoco Siloxane WB Water Repellent ^S

Sample Preparation Using Prosoco Siloxane WB Water Repellent

Prepared Samples in Containers for Tests on the Influence of Coatings on Salt Formation

Sample Preparation: Benjamin Moore Acrylic System

Sample Preparation Using High-Build Acrylic Masonry Primer and Superspec 100% Acrylic Exterior Masonry Coating

Prepared Samples in Containers for Tests on the Influence of Coatings on Salt Formation

Sample Preparation: Keim Granital System

Sample Preparation Using Kiemfarben GmbH Granital with Keim Dilution Potassium Silicate System

Prepared Samples in Containers for Tests on the Influence of Coatings on Salt Formation

- key:
- $\begin{array}{ll} \bigcirc & \text{very light damage covering 1\% to 5\% of area} \\ \bigcirc & \text{finite damage covering 6\% to 25\% of area} \end{array}$
	- moderate damage covering 26% to 50% of area
	- severe damage covering 51% to 99% of area ō

 162 complete destruction of area

 $\label{eq:2.1} \left\langle \Phi_{\alpha} \right\rangle = \$

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Week Six

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Week Four

Week Six

 $\label{eq:2.1} \frac{1}{\sqrt{2}}\int_{\mathbb{R}^3}\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac{1}{\sqrt{2}}\right)^2\left(\frac$

 $\mathcal{L}^{\text{max}}_{\text{max}}$, where $\mathcal{L}^{\text{max}}_{\text{max}}$

Influence of Salt on Coatings: Keim Granital System

Salt Front Development: Control

Salt Front of Control Samples

Salt Front of Control Samples: Nikon SMZ-U Zoom 1:10 0.5x Magnification; 200 ASA
Salt Front Development: Atofina Kynar System

Salt Front of Atofina Kynar Treated Samples

Salt Front of Atofina Kynar Treated Samples: Nikon SMZ-U Zoom 1:10 0.5x Magnification; 200 ASA

 $\label{eq:2.1} \frac{1}{\sqrt{2}}\int_{0}^{2\pi} \frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^{2} \frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^{2} \frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^{2} \frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^{2} \frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^{2} \frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^{2} \frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\$

Salt Front Development: Prosoco Siloxane WB Water Repellent System

Salt Front of Prosoco Siloxane Treated Samples

Salt Front of Prosoco Siloxane Treated Samples: Nikon SMZ-U Zoom 1:10 0.94x Magnification; 200 ASA

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Salt Front Development: Benjamin Moore Acrylic System

Salt Front of Benjamin Moore Treated Samples

Salt Front of Benjamin Moore Treated Samples: Nikon SMZ-U Zoom 1:10 0.5x Magnification; 200 ASA

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Salt Front Development: Keim Granital System

Salt Crystallization in Keim Granital Treated Samples

Salt Crystallization in Keim Granital Treated Samples: Nikon SMZ-U Zoom 1:10 2.5x Magnification; 200 ASA

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