

PERFORMANCE-BASED EVALUATION OF SALT CRYSTALLIZATION INHIBITORS AS A
MEANS TO MITIGATE SALT DAMAGE IN TERRACOTTA

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To my father:

*for being the solid foundation for me to build on, the net to catch me when I fall, and
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Table of Contents

Acknowledgments	iii
List of Figures	viii
List of Tables	viii
Chapter 1: Introduction	1
1.1 Abstract	1
1.2 Literature Review	2
Chapter 2: Physical and Chemical Composition of High-Fired Terracotta	13
2.1 General	13
2.2 Physical Composition	14
Chapter 3: Deterioration of Terra-Cotta	16
3.1 General	16
3.2 Deterioration of Terra-Cotta by means of Salt Weathering	16
3.2.1 General.....	16
3.2.2 Efflorescence.....	18
3.2.3 Subflorescence	19
3.4 Source and Description of Common Types of Salt in Building Materials	20
3.4.1 Sources of Salt Contamination.....	20
3.4.2 Most Damaging Salts.....	21
3.4.3 Chlorides (Cl ⁻)	22
3.4.4 Sulfates (SO ₄ ⁻)	23
3.4.5 Nitrites and Nitrates (NO ₂ ⁻ & NO ₃ ⁻).....	24
3.5 Mechanisms of Salt Decay	24
3.5.1 Physical decay	24
3.5.2 Crystallization.....	25
3.5.3 Hydration damage	26
3.6 Physico-Mechanical Effects Salt Crystallization has on Terracotta	26
3.6.1 Blister/Material Spall/Pitting	26
3.6.2 Loss of Cohesion/Sugaring	27
3.6.3 Exfoliation	27
Chapter 4: Traditional Conservation Approaches to Desalination	28

4.1	Physical Intervention.....	28
4.2	Water-Immersion Treatments	28
4.3	Poulticing	29
Chapter 5: Recent Research of Crystallization Inhibitors		31
5.1	General	31
5.2	Ferrocyanides	31
5.2.1	General.....	31
5.2.2	Sodium Ferrocyanide $\text{Na}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$	34
5.2.3	Potassium Ferrocyanide $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$	34
5.3	Phosphates	35
5.3.1	Sodium Hexametaphosphate $(\text{NaPO}_3)_6$	35
5.4	Previous Laboratory Testing	36
Chapter 6: Case Study: Western Clay Manufacturing.....		38
6.1	General	38
6.2	History of WCMC	40
6.3	History of Kiln #8	44
6.4	Premise for Thesis Research	48
Chapter 7: Part 1 of Testing Program: Identifying Salts in WCMC Samples.....		51
7.1	Analysis of Contemporary Research.....	51
7.2	Preliminary Testing	51
7.2.1	General.....	51
7.2.2	Salt Strip Testing.....	52
7.2.3	XRD Testing	54
7.2.4	Conclusions	55
Chapter 8: Part 2 of Testing Program: Physical Tests of Terracotta Samples		58
8.1	General	58
8.2	Petrofabric Analysis.....	59
8.2.1	Introduction	59
8.2.2	Petrographic Summary	60
8.2.2.1	<i>Original Fabric, Terra-cotta from WCMC (Tile C)</i>	60
8.2.2.2	<i>Sample Fabric, Terra-cotta from Sandkuhl Clay Works (Tile A)</i>	61

8.2.3	Fabric Comparison	61
8.3	Cold Water Absorption by Total Immersion	63
8.4	Capillarity.....	64
8.4.1	Results.....	65
Chapter 9: Part 3 of Testing Program: Salt Contamination and Testing of Salt Crystallization		
Inhibitors		67
9.1	General	67
9.2	Cold Water Absorption by Total Immersion with Inhibitors	67
9.2.1	Results & Discussion	69
9.3	Evaporation Test	72
9.3.1	Results & Discussion	74
9.4	Crystallization Test	75
9.4.1	Durability Test 1	75
9.4.2	Durability Test 2	77
9.4.3	Results & Observations	78
9.4.3.1	<i>Sodium Chloride Contaminated Samples</i>	<i>81</i>
9.4.3.1.1	NaCl Control	82
9.4.3.1.2	NaCl + SFC	83
9.4.3.1.3	NaCl + PFC	84
9.4.3.1.4	NaCl + PFC + SHMP	86
9.4.3.1.4	NaCl + SFC + SHMP	87
9.4.3.2	<i>Sodium Sulfate Contaminated Samples</i>	<i>87</i>
9.4.3.3	<i>Sodium Chloride/Sodium Sulfate Contaminated Samples</i>	<i>89</i>
9.4.3.3.1	NaCl/Na ₂ SO ₄ Control	90
9.4.3.3.2	NaCl/Na ₂ SO ₄ + SFC	90
9.4.3.3.3	NaCl/Na ₂ SO ₄ + PFC	91
9.4.3.3.4	NaCl/Na ₂ SO ₄ + PFC + SHMP	91
9.4.3.3.5	NaCl/Na ₂ SO ₄ + SFC + SHMP	92
9.4.3.4	<i>Discussion</i>	<i>92</i>
Chapter 10: Conclusion & Recommendations.....		95
10.1	Conclusions	95

10.2 Recommendations	97
10.2.1 <i>Recommendations for Test Replication</i>	97
10.2.2 <i>Cold Water Immersion (Absorption) & Evaporation Test Recommendations</i>	98
10.2.3 <i>Durability Test Recommendations</i>	99
10.2.4 <i>Recommendations for Analysis Out of Scope</i>	100
10.2.5 <i>Final Considerations</i>	101
Bibliography	102
Appendix A: WCMC Samples	110
Appendix B: Petrographic Images	114
Appendix C: Raw Data	121
Appendix D: Durability Test Images	134
Appendix E: SEM Images	177
Appendix F: ASTM & SDS Sheets	189
Index	234

List of Figures

Figure 1-Schematic of capillary rise and evaporation.....	17
Figure 2-Efflorescence on the top of two terracotta tile	19
Figure 3-Material spall on terracotta.....	20
Figure 4- Example of incipient spall in terracotta.....	27
Figure 5-Images of calcareous stone slabs.	33
Figure 6- Panorama of the kiln complex of Western Clay Manufacturing Co.	39
Figure 7-A Sanborn map last updated in 1930 Helena, MT.....	43
Figure 8-Interior view of the perforated floor of kiln #8.	45
Figure 9-Photograph of Archie Bray, Sr. shoveling salts into Kiln No. 7.	47
Figure 10-Interior of Kiln #8.....	48
Figure 11-Efflorescence and deterioration in Kiln #8.	49
Figure 12-EM Quant Salt Strip test results.....	54
Figure 13- Performing Gravimetric Analysis.	69
Figure 14-Large desiccator designed for evaporation test.	73
Figure 15-Capillary Suction program setup.	77
Figure 16-All samples were inspected with a Leica MZ16a Microscope	83
Figure 17-Example of Dendritic Efflorescence Growth of NaCl+SFC	84
Figure 18-Example of individual tufts of dendritic growth on NaCl+PFC	85
Figure 19- Crystallographic change: Day 4 of NaCl + PFC + SHMP.....	86
Figure 20-Sodium Sulfate control cohort after four weeks of Durability Test 2.	88
Figure 21-the only observed anomalous crystallization.	89

List of Tables

Table 1- List of Samples from Western Clay Manufacturing	52
Table 2- EM Quant Salt Strip Key	53
Table 3- EM Quant Salt Strip Results for Salt Families Present.	56
Table 4- XRD Results for Salt Families Present	56
Table 5- Sandkuhl Clay Works 6" terracotta drain pipe MSDS.	58
Table 6- Capillarity of New Samples..	66
Table 7- Capillarity of New Samples: $\sqrt{t}$ Time	66
Table 8- Cold Water Absorption by Total Immersion Results: Percent Difference from Controls.....	71
Table 9- Porosity After Water Immersion.....	72
Table 10- Average Time to Reach RH Equilibrium	74
Table 11- Evaporation Rate of Sodium Sulfate Samples.....	75
Table 12- Durability Test 2: Results.	80
Table 13- Durability Test 2: Breakdown of % Total Weight Loss	81

Chapter 1: Introduction

1.1 Abstract

The impetus for this research was the need for a conservation treatment of salt-laden terracotta inside kiln #8 at Western Clay Manufacturing Co.- a historic brickyard in Helena, Montana. Western Clay stands as an example of how traditional methods of mitigating salt damage, like water-immersion and poulticing, are not possible or effective in certain circumstances. Therefore, the focus of this study was to investigate salt crystallization inhibitors as a method to mitigate and potentially prevent salt damage in terracotta, as an alternative to traditional desalination methods. Salt damage is one of the most common mechanisms of deterioration in porous building materials, which makes the results of this research widely applicable. A performance based evaluation of select salt crystallization inhibitors was conducted, using sodium and potassium ferrocyanide, each with and without the addition of sodium hexametaphosphate. These chemical reagents were applied to terracotta samples contaminated with sodium chloride, sodium sulfate, and an equal mixture of the two. It was found that there was no measurable change in the sodium sulfate contaminated samples. However, it was found that all inhibitors had the ability to increase supersaturation, delay nucleation, and effectively changed the morphology of salt crystallization of sodium chloride, which was evident through the dramatic increase in efflorescence and a reduction of material loss that was observed in the sodium chloride and sodium chloride/sodium sulfate contaminated samples. It was found that potassium ferrocyanide and potassium ferrocyanide with sodium hexametaphosphate had the greatest effect. The positive results of this research

warrants further testing and analysis, as salt crystallization inhibitors show promise of being a conservation treatment of the future.

1.2 Literature Review

Salt crystallization is one of the most destructive and ubiquitous deterioration mechanisms in porous building materials and contributes greatly to the loss of cultural heritage (Winkler 1973; Amoroso & Fassina 1983; Charola & Weber 1992; Theoulakis & Moropoulou 1999; Doehne and Rodriguez-Navarro 1999; Franceschini et al. 2015). Salt crystallization of soluble and hydrate-forming salts can occur on the surface of a material as efflorescence or below the surface within a material's pore structure as subflorescence or cryptoflorescence caused by the cooling or evaporation of salt solutions. (Rodriguez et al. 2002; Doehne 2002; Lombardo et al. 2004; McGraw & Lewis 2009; Doehne & Price 2010; Franceschini et al. 2015). Although efflorescence of salts is visually obtrusive, damage due to salt weathering results largely from subflorescence. When a crystal grows within a pore, the crystal exerts pressure on the pore walls, which increased over time, can cause cracking of the material. A variety of deterioration symptoms caused by salt crystallization has been documented, including granular disintegration, scaling, flaking, and spalling (Doehne 2002). It is proposed that this deterioration will increase as a result of changing climate trends, specifically in what are now temperate climates (McCabe et al. 2013). Therefore, salt decay and subsequently salt remediation in building materials have become a greater subject of study over the last thirty years in the field of architectural conservation.

There are several ways in which building materials become contaminated with salts. Beginning from the ground up, salt can migrate via rising damp from the soil or groundwater

beneath a structure. Air pollution often carries sulfates and nitrates, and wind-blown salt from the ocean or desert, as well as driving rain can force salts into the pores of a building material. Salt can also be introduced by human interaction; inappropriate cleaning products, incompatible building materials, deicing salt, salt or gunpowder storage, garden fertilizers, even animal manure and urine are all sources (Torraca 1981; Doehne & Price 2010; Charola 2010). Lastly, salts can be inherent in a building material through the elemental materials or water they were made with, or from nearby materials like gypsum mortar.

Salt enters a material dissolved in water or vapor. The depth to which a material draws moisture in depends on the material's surface area, total porosity and pore-size distribution as well as the ambient conditions of temperature and relative humidity (Feldman & Sereda 1970). In the liquid water state, capillarity and infiltration are the two mechanisms that draw water in. Water is adsorbed to the capillary pore walls as a result of the attraction between water molecules and the pore wall material as well as the surface tension of the liquid. Depending on the permeability or interconnectedness of the pore structure of a material, infiltration occurs with the force of hydrostatic pressure (Torraca 1981; Feldman & Sereda 1970; Charola 2010).

As a vapor, moisture can enter a porous material by means of hygroscopicity and condensation. Hygroscopicity is a general term that describes the act of attracting moisture from the air. A porous material can physically adsorb or absorb moisture on its own. If material has a large surface area, then moisture will be continuously adsorbed, absorbed or evaporated in order to reach equilibrium with the relative humidity (RH) of the surrounding environment. Salts also are considered hygroscopic in that they absorb moisture if the relative humidity of the surrounding environment is above their designated equilibrium RH. Usually soluble salts will deliquesce, or absorb so much water that they will dissolve into a saturated solution. Once

deliquescence takes place “classical osmosis” can occur. A salt solution having lower vapor pressure than uncontaminated water increases the ability to condense environmental water vapor in order to reach equilibrium. The second means of moisture uptake is through condensation, when a substrate’s surface is cooler than the dew-point temperature of the exterior air, water vapor molecules join to form a liquid film on the surface of the porous building material. Water can then be adsorbed as liquid water (Torraca 1981; Massari 1993; Charola 2000).

Salt migrates through a material only when dissolved in water or vapor, which means the way water moves through a pore-structure is integral to how the material will degrade. So not only is the material’s porosity, permeability and porosimetry a factor, but also the wetting, drying and storage of moisture within the capillary pores. After moisture is carried in it can move as a liquid by means of capillarity or pressure flow, and as a vapor by means of diffusion and convection (Straube 2002). The narrower the capillary pore, the greater the capillary suction or wicking will be. Moisture always moves from an area of high temperature and moisture content to an area of low temperature and moisture content. If soluble salt ions are present, the solution moves toward the opposite electrical charge (electro-osmosis) (Torraca 1981; Lewin 1982; Massari 1993). This explains why moisture continues to move deeper into the porous material even if the water source has been cut off.

There have been major advances in the understanding of salt damage within the past 15 years, though there is still a lack of understanding as to how to predict damage potential of salt mixtures within porous building materials, as well as some confusion as to the deterioration mechanism at play when damage occurs (Zehnder & Arnold 1989; Doehne 1994; Rodriguez-Navarro et al. 2002, Doehne & Price 2010). It has generally been understood for over a century

that soluble salts act as a deterioration mechanism within inorganic porous building materials. Two thorough reviews of these early published works were produced in the in the late 1960s by J. Ifiiguez Herrero (1967) and I. Evans (1969-70). Beginning in the early 1980's Ichiro Sunagawa demonstrated through testing that salt morphology and crystal growth are dependent on the degree of supersaturation reached when crystallization first occurs, which is ultimately dependent on the solution concentration and physical/environmental factors at play such as RH, temperature, and substrate surface area and texture (Doehne & Selwitz 2002). Thus this led to the understanding that crystallographic characteristics of a particular salt controls the pattern and degree of damage created when crystallization and growth take place within a pore. The morphology and growth rate of the newly formed salt crystals appear to be important keys to understanding this particular decay phenomenon (Zehnder & Arnold 1989; Doehne & Rodriguez-Navarro 1999). For example, often when a substrate is dry with a slow evaporation rate, an acicular crystal will form as opposed to when there is more moisture present, an exterior crust is more likely to form (Doehne & Selwitz 2002).

Decay occurs within a pore structure under several circumstances. As initially suggested by Thomson in 1862, the primary source of damage is a result of when moisture evaporates and soluble salts crystallizes, which subsequently increase volumetrically within a material's pores which generates and exerts pressure outward, so much as to overcome the material's tensile strength, causing fracture (Doehne & Rodriguez-Navarro 2000; Rijniers et al. 2005; Doehne & Price 2010, Shiro 2012). Much research has also been focused on the type and amount of pressure that builds within a pore. It has been concluded that crystallization pressure is largely a function of salt solution supersaturation and crystallization location in the body which are inherently related to salt type and rate of evaporation (Doehne and Rodriguez-Navarro 1999).

Hydrostatic pressure develops specifically when the volume of the precipitating crystals and residual solution is larger than the volume of initial solution (Lewin 1982; Charola 2000).

Ultimately a crystal can only grow if solution can squeeze between the crystal and pore wall. If the pressure becomes excessive, growth stops-leading to a push and pull dynamic between several opposing forces of the material/solution/crystal interface surface energies. This repulsive force is created by the mismatched surface energies when the pore wall and salt crystal surface come within approximately 10 nm of one another, with solution in between. This disjoining pressure similar to the tension between two magnets is what actually causes material spall. This disjoining pressure has been proven by direct evidence produced by ESEM, TMA, NMR, and AFM (Rijniers et al. 2005; Doehne & Price 2010).

Another source of deterioration is the special circumstance of hydration damage. First discovered by the geomorphologist, H. Mortensen this decay mechanism was inaccurately considered a more common occurrence until recently (Rijniers et al. 2005; Charola 2000). Hydration damage is an increase in volume that occurs when anhydrous salt hydrates. Sodium sulfate exemplifies this as it can exist in multiple hydration states; as the anhydrous salt thenardite (Na_2SO_4) or the decahydrate mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$). When thenardite converts to mirabilite, it triples in volume after dissolving and recrystallizing (Doehne 2002; Espinosa, Marzal and Scherer 2008; Shiro 2012).

Salts can increase the rate and severity of physico-mechanical weathering. Because of salt's hygroscopic nature, salt contamination will promote water retention and delayed evaporation, effectively promoting crack propagation, by weakening the stone's ability to resist stress (Charola 2000; Freedland 1999; Rodriguez-Navarro et al. 2002). Secondly, the narrowing of capillary pores inside a porous body due to salt encrustation can actually increase capillary

rise, promoting absorption. Alternatively, if a relatively insoluble salt is absorbed, it has the ability to clog pores, which in turn can obstruct proper water vapor transmission, causing accelerated damage. The stress from differential thermal expansion, as well as freeze-thaw cycles, which are increased by the presence of NaCl, will over time overcome a material's tensile strength and cause powdering, cracking and spalling of that porous material's surface (Torraca 1981; Lewin 1982; Freedland 1999; Doehne & Price 2010).

One of the greatest driving factors for salt weathering remediation research is the consequences of climate change. Since the 'initiator' of change in porous building materials is the immediate climate, particularly changes in temperature and RH; climate change has become a growing concern in regard to the intensification of salt weathering (McCabe et al. 2013:1226). This is an example of what has been coined 'heritage climatology' which is defined as:

the study of the climate parameters that affect monuments, materials and sites. The parameters used in heritage climatology differ from those typical in meteorology (e.g. temperature or relative humidity) and focus on cycles and combinations of meteorological parameters that relate to material damage. (Grossi et al. 2013: 2577).

Incremental change in climatological conditions has an exponential effect on salt phase fluctuations. A non-hydrated salt like NaCl has the capacity to crystallize at a fixed humidity regardless of temperature, however the crystallization of a hydrated salt like Na_2SO_4 is directly linked to both temperature and RH changes (Grossi et al. 2011). McCabe et al. estimate that in lieu of climate change, porous materials will hold salts in solution for longer periods of time ('deep wetting') due to prolonged wetting in winter months (2013). Because of this, ion diffusion could become a more prominent way for molecular constituents to mix, resulting in an increase of chemical damage of a building stones' matrix, particularly in sandstone. Salts will also be able to move deeper into a porous body, the longer it remains wet. The change in

climate has its biggest implications in typically dry, desert areas that are now experiencing greater rainfall. According to Grossi et al., “temperate fully humid climates seem to offer the highest potential for salt damage and possible higher number of transitions in summer” (2011). This has great implications for climates becoming more humid over time. Salts that rarely deliquesce, will more often, which will likely be very damaging to heritage sites in these locations.

Desalination methods for the treatment of cultural heritage were published as early as 1905 in Friedrich Rathgen’s *Preservation of Antiquities*. The first method of desalination specified “steeping” objects in a water bath in order to dissolve and wash out soluble salts over the course of several baths of clean water. Titration was the initial method to analyze what percentage of salt remained in each bath’s solution (Rathgen 1905: 92-4).

Desalinization through prolonged immersion and successive water bathing, and poulticing, have generally become the accepted methods of salt remediation in the conservation field. However, in some cases these now “traditional” methods are not appropriate or effective in long-term conservation (Cassar et al. 2008; Pel et al. 2010; Doehne & Price 2010; Franceschini et al. 2015). Successive water immersion is a simple and effective method for a mobile object that has the ability to be immersed in water but not an option for a building assembly.

Poulticing requires a wet slurry to be applied to the contaminated substrate to be treated, where it dwells for a period of time, slowly drying and drawing out salt from the interior of the porous body. Paper, sand or clay poulticing has been successful at desalinating walls locally, especially in recent years in which the paper and clay poultice components have been better customized to match individual building substrate characteristics. An EC project, Assessment of Desalination Mortars and Poultices for Historic Masonry (DESALINATION) 2006–9

has focused on creating and disseminating guidelines on increasing the efficiency of desalination poultices (Doehne & Price 2010; Lubelli & van Hees 2013). These guidelines promote using less water, finer layers of poultice, and using a poultice material that has a finer particle size than the building material substrate. The issues with poulticing of any kind are that it often takes several applications to effectively desalinate, increasing labor and conservation costs. Negative consequences of poulticing can result in low rate of extraction of salts due to poor adherence, shrinkage and early detachment, unexpected mobilization of salts by using excessive water, and rapid re-appearance of salts after treatment, especially if the source of salt was not properly interrupted (Lubelli & van Hees 2007; Doehne & Price 2010; Lubelli & van Hees 2013). Moreover, more often historic masonries and certain archeological sites are contaminated beyond the point in which the total removal of salt is impossible or the source of salt cannot be stopped (Cassar et al 2008; Franceschini et al. 2015).

A more recent tactic to mitigate salt weathering is that of thermodynamic modeling and preventive conservation, due to the fact that the severity and frequency of fluctuations in the environment are important in influencing the extent of salt damage (Doehne 2002, Doehne & Price 2010, Camuffo 2014). Thermodynamic modeling has been used to predict the weathering caused by a mixture of salts under specific environmental conditions. Calculations proved that hygroscopic salts were present in undamaged areas and soluble salts that frequently crystallize were in areas that were damaged. Predictions can now be made by computer programs as to what the “safe” ranges of RH and temperature are in which crystallization damage may be minimized or halted. (Doehne & Simon 2006; Price 2007, Camuffo 2014). However, predictions can only be made on conditions at equilibrium, not on the rate at which damage will occur (Doehne & Price 2010). Regardless, these calculations are used to support preventative

conservation in which the microclimate is controlled. This usually involves interventions to the environment that focus on preventing water ingress, and balancing the relative humidity and temperature around the contaminated porous building material so as to avoid crystallization. Such systems are successful in indoor environments, but are extremely difficult and costly in outdoor environments (Doehne & Price, 2010, Camuffo, 2014).

Salt crystallization inhibitors are now gaining much attention as an alternative preventative and remedial technique for porous materials as a means to arrest and prevent future salt crystal growth as opposed to removing it entirely (Rodriguez-Navarro et al. 2002; Selwitz & Doehne 2002; Lubelli & van Hees 2007; Ruiz-Agudo et al. 2008). Salt crystallization inhibitors have the potential to delay nucleation, increase solubility and change the morphology of salt crystallization in order to reduce their damaging effects on porous building materials (Lubelli & van Hees 2007, Doehne & Price 2010). Inhibitors tested and acknowledged for their effectiveness in industrial uses have been largely studied as a potential treatment for ornamental building stone in the last 15 years. These include families of ferrocyanides, surfactants, carboxylates, polyacrylate acid derivatives, benzotriazoles, and phosphates (Rodriguez-Navarro et al. 2002; Moon 2002; Doehne & Selwitz 2002; Ruiz-Agudo et al. 2008; Lubelli & Van Hees 2007). To date, SCI have been tested primarily on limestone, sandstone, and brick, but never terracotta.

It has become clear that inhibitors affect salt weathering differently depending on the salt present, and the characteristics of the substrate such as the pore distribution. The salt families most commonly present in building materials are chlorides (Cl^-), nitrates and nitrites (NO_3^- & NO_2^-) and sulfates (SO_4^{2-}). As expected, these are the predominant salts used in recent analytical testing. Sulfates being the most destructive salt species have responded poorly to

most salt crystallization inhibitors, though a study completed this year concluded that phosphates enhanced transport to the surface, delayed nucleation, and altered the crystal morphology, while potassium ferrocyanide showed slightly positive results in the past (Lubelli & van Hees 2007; Ruiz-Agudo 2008; Franceschini et al. 2015). Phosphates have been used as inhibitors (of sulfates and carbonates mainly) in industrial and technological settings for years, commonly used in oil-extraction pipelines, industrial boilers, heat-exchangers, house-appliances, water pipes, mining and mineral processing, as well as in desalination plants (Rodriguez et al. 2002). Sodium Chloride has responded more readily to inhibitor treatment. However, the efficacy of the inhibitor is also greatly dependent on the microstructure of the building material. Sodium ferrocyanide has shown to promote solubility and drying at the surface of salts in limestone and brick, but had no effect on salt in sandstone (Lubelli & van Hees 2007). Also ionic and non-ionic surfactants such as Triton XL 80, Orvus and sodium-dodecyl sulfate were tested for their inhibiting abilities yet proved to be mildly effective on their own; Rodriguez-Navarro suggests exploring the possibility of using surfactants as a secondary inhibitor (Rodriguez-Navarro et al. 2000; Moon 2002).

Ferrocyanides (FC) also known as the yellow prussiates, have been used for their crystallization inhibition and habit modifying properties as anti-caking agent in deicing salts and in the food industry (Rodriguez-Navarro et al. 2002; Lubelli & van Hees 2007). Experimental analysis has been conducted on the effects of FC in reference to NaCl morphology since the early 1960s, and has been rigorously explored more recently. According to Rodriguez-Navarro, FC proved to significantly change the induction time, evaporation rate, habit morphology, and critical supersaturation of NaCl from 1.3% to 8%, effectively delaying nucleation and moderately inhibiting growth. Subflorescence was greatly reduced and the majority of salt solution

effloresced on the stone surface. His research also showed that a great concentration of FC was still present and available to act as a nucleation inhibitor for a long time after the experiment. However, it was also found that the positive increase in supersaturation also resulted in the negative consequence of higher internal pressures when the salts finally did crystallize, resulting in harsher damage (Rodriguez-Navarro et al. 2002; Lubelli & van Hees 2007; Ruiz-Agudo et al. 2008, Doehne & Price 2010).

More and more about their positive abilities to inhibit crystallization and promote desalination in building materials is being discovered, yet a great deal of research is still necessary to consider crystallization inhibitors as a viable conservation treatment. Testing results of the last 20 years show that application of a salt crystallization inhibitor is a major determining factor of the efficacy of the treatment. In most laboratory testing thus far the inhibitor is added to the bulk salt solution prior to contamination of the sample and both are absorbed into the sample at the same time through capillary action (Rodriguez-Navarro et al. 2002; Selwitz & Doehne 2002; Lubelli & van Hees 2007). Barbara Lubelli later identified that the positive increase in nucleation and crystal growth inhibition was greatly limited when applied to a salt-laden substrate as opposed to being absorbed in the salt solution. A move toward adding inhibitors to previously contaminated samples is the next step. Early applications of inhibitors via spraying proved to increase damage to the sample substrate due to rapid deliquescence and evaporation. More recent methods of using cellulose poultices in-situ to apply inhibitors have been studied (Lubelli & van Hees 2007; Franceschini et al. 2015). In the case of the Roman Mosaic of Orpheus and the Beasts in Perugia, Italy this application was successful (Franceschini et al. 2015). It is evident that even with the developments in research over the last decade a

greater amount of testing is still necessary due to all of the variables involved in mitigating salt damage.

Chapter 2: Physical and Chemical Composition of High-Fired Terracotta

2.1 General

Terracotta, or ‘cooked earth’ in Italian, is not surprisingly a red earthenware clay, that is fired at a range of temperatures depending on the product. It is referred to as ‘faience’ if glazed, but is often slip-glazed or left unglazed depending on the ware (Ingham 2010: 163). Terracotta is a clay that has been used since antiquity, because it is an extremely abundant clay in many parts of the world. It is predominantly fired at low temperatures, proving to be a good clay for sculptures, tile, drain pipes, pottery and flower pots (Hansen 2008).

The Romans, Greeks and Etruscans were the first to use terracotta as architectural embellishment. After the Roman period terracotta fell out of use until it regained popularity in Italy in the late 15th and early 16th centuries. After this revival, terracotta’s popularity spread slowly to England. By the late-18th century terracotta had become an extremely popular alternative to stone and was used as its imitation (Henry et al. 2015: 660-70). Roughly the time between 1840-1910 AD is considered the official “Terracotta Revival” period which ushered in a time when high-fired terracotta was used widely in architectural assemblies structurally and decoratively. During this period terracotta created for architectural purposes was molded or extruded into four different iterations; brownstone, fireproof construction, ceramic veneer, and glazed architectural (Ingham 2010; 163, Tiller 1979; 1). Terracotta fell out of favor throughout the mid-20th century, due to its lengthy production time, and the increased use of modern

synthetic materials. Terracotta is still used a great deal industrially and has been having a modern-day revival due to its modern configuration as cladding and rain-screen.

2.2 Physical Composition

Like pottery, brick and other ceramics, terracotta composition and firing have generally remained the same throughout history (Henry et al. 2015: 654). Terracotta that is used for architectural or industrial purposes is a mass-produced clay product consisting of fine, high-grade pure clays, predominantly montmorillonite and illite, that are mixed with an additive called 'grog': a quartz sand or previously fired, pulverized ceramic material that considerably reduces shrinkage to 5-15% during the drying and firing process (Henry et al. 2015: 638).

Although there is variation, the Department of Scientific and Industrial Research determined the primary constituents of terracotta in general post-firing are silicon oxide, ferric oxide, calcium oxide, a small percentage of chemical water, organic material and traces of magnesium oxide (Henry et al. 2015: 654).

This clay is molded, often packed by hand into plaster molds, slip-cast, machine stamped, turned, or extruded into columns and cut into units by metal wire (Henry et al. 2015: 645). After the ware is 'bone-dry' or has lost the majority of its free physical water through evaporation, it is fired to anywhere between 1,000°C and 1,250°C in a kiln (Ingham 2010: 163-70). If the ware is fired above 1000°C, the silica content melts, thus the clay crystals are destroyed and a crystalline aluminum-silicate, or mullite is formed with additional quartz. Once cooled, the ware no longer consists of a crystalline microstructure, but of a hard amorphous, vitrified body. The glassy interior serves as cement for the mullite and quartz crystals (Torraca 1981: 104-05).

The ware is either left unglazed, or coated with an oxide wash, clay slip, or glaze in order to reduce porosity and increase weather resistance (Tiller 1979: 1). All terracotta forms what is called a “fire-skin” through the sintering process, since the exterior surface has the highest exposure to the heat source. The fire-skin is a thin vitrified layer in which the finest clay particles rise to the surface and solidify into a dense semi-protective layer that has a porosity as low as 3-4.5% (McColm 1994: 183, Searle 1924). The fire-skin in large part accounts for terracotta’s resistance to weathering, and is impossible to replace. Once removed often rapid deterioration ensues due to exposure of the porous underbody.

Terracotta is similar to brick in that it generally is made of the same raw material and shares a similar compressive strength (40-55.2 MPa).¹ However, several aspects differentiate the two. Most often terracotta is made of finer “milled” clay particles, that have had most impurities removed from the dry clay mix, allowing for greater compaction (Henry et al. 2015: 637). Greater compaction effectively reduces the material’s porosity and increases the density of its fire-skin.

Terracotta generally has a porosity between 5-10%, making it a low-porous product but not impervious to moisture. The day the ware is removed from the kiln, is the driest and smallest it will ever be. When removed each piece immediately begins to gain atmospheric moisture and recombine chemically, causing the ware to expand and gain mass. The amount of rehydroxylation that occurs is dependent on the clay minerology and firing temperature. Firing temperature also influences terracotta’s thermal expansion coefficient and percent porosity.

¹ Terracotta is comparable to Class B Engineering brick (50-70MPa) according to Historic England.

Chapter 3: Deterioration of Terra-Cotta

3.1 General

Terracotta was once advertised as self-cleaning and water-proof in its heyday, yet a century later it is evident that without proper maintenance, this robust material deteriorates when exposed to the elements over time, like all other common building materials. Terracotta's durability relates directly to its degree of vitrification and how intact its fire-skin and surface finish is. Its durability is also dependent upon its installation, and as to whether it was installed with incompatible materials; over time many terracotta units have failed due to the failure of rusted ferrous fasteners. According to Historic England, causes of deterioration of terracotta can ultimately be categorized into four groups; inherent, environmental, inappropriate surface treatments, and accidental damage (Henry et al. 2015: 687-88). Salt weathering, the mechanism of decay that is of focus of this study falls under the environmental category, yet works in tandem with almost all other mechanisms of deterioration.

3.2 Deterioration of Terra-Cotta by means of Salt Weathering

3.2.1 General

The effects of soluble salts have long been understood as damaging but the process by which they are, has long been misunderstood. Soluble salts can cause deterioration in several ways, the most notable being through salt crystallization in pores beneath the surface, known as subflorescence. Damage is incurred when an aqueous salt solution fills the capillary pores of terracotta and salts crystallize upon evaporation or cooling. Ultimately, damage is caused when

the stresses overcome the material's tensile strength, and the material ruptures (Doehne & Price 2010: 15).

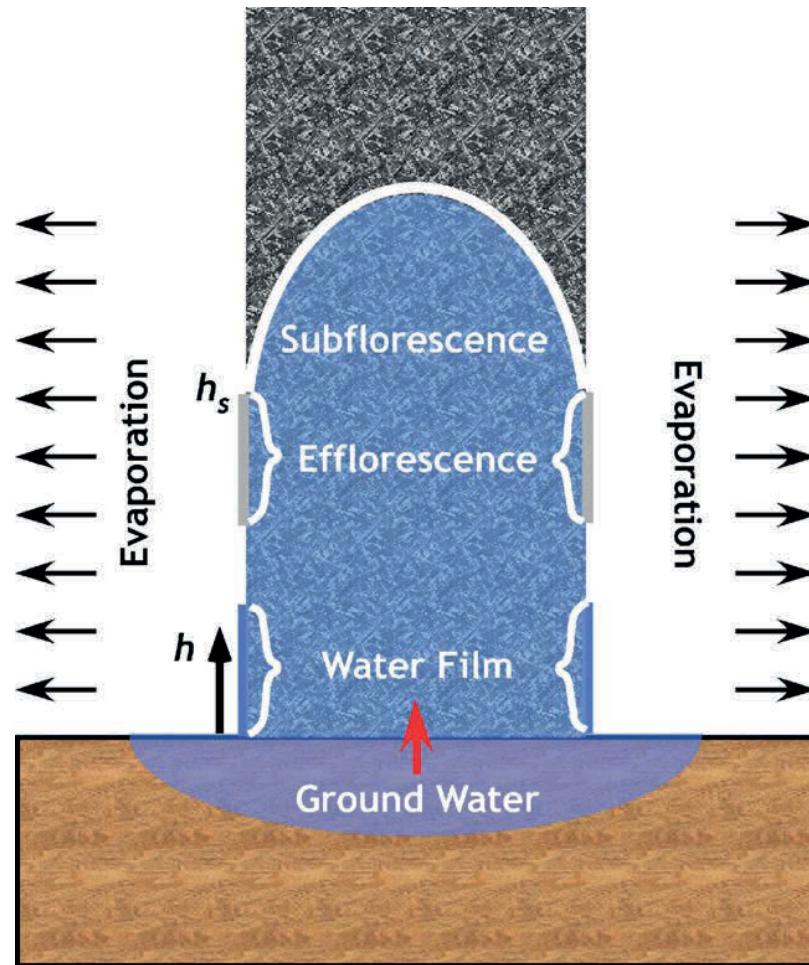


Figure 1- "Schematic of capillary rise and evaporation from a wall in contact with damp soil. Groundwater rises into the wall at a rate that decreases with height, while evaporation from the surface occurs at a nearly uniform rate. Near the ground, where the rate of rise is fast compared with the rate of evaporation, there is a liquid film on the surface of the wall." (Scherer 2004: 1614).

This leads to material spalling, powdering, and even fracture. Alternatively, efflorescence is when salts crystallize on the surface of the material. This is usually only a cosmetic problem, as efflorescence alone isn't damaging. However, it is an indication of salt contamination, and can be an indication that subflorescence is or will eventually occur (Freedland 1999: 8). Soluble salts

can come in contact with terracotta through surrounding mortars, air pollution, and saline water ingress. Sulfates, nitrates, chlorides, carbonates, and oxalates are the most common families of salts found in porous building materials, and often several are present at one time. Together they can increase the effects of damage exponentially, and this reality has made salt weathering very difficult to predict.

3.2.2 Efflorescence

Efflorescence is when an aqueous soluble salt crystallizes on the surface of a material. This occurs when the rate of evaporation is slower than the rate of aqueous salt solution migration, which allows for the salts to migrate out of the porous body. It appears as a 'white bloom' ranging from a sheer powdery crust to great boils of euhedral salt crystals depending on the crystallography of the precipitate. Efflorescence can significantly alter the appearance of a building, leading to the degradation of its aesthetic integrity (Freedland 1999: 8). For a long time, efflorescence was considered physically harmless, though recent studies have linked its presence to increased hygroscopicity, and delayed evaporation. It can also stand as an indicator that some salts have not migrated to the surface and have begun crystallizing beneath the surface (Grimmer 1984: 11).



Figure 2-Efflorescence on the top of two terracotta tile

3.2.3 Subflorescence

Subflorescence or cryptoflorescence is the phenomena when salts precipitate out of solution (crystallizes) in the open pores, channels, and crevices just below the surface of the substrate, when the rate of evaporation is faster than aqueous salt solution migration (Amoroso 1983: 33). In this scenario, a 'dynamic balance' is struck; the rate of water vapor diffusion through a layer of dry porous material at the surface (Fick's Law) equals the rate of capillary migration of aqueous salt solution to the interface between the wet and dry portion (Poiseuille's Law). This produces subsurface crystallization (Hewat 1996: 28). This crystallization is what causes material deterioration, as the crystallization eventually creates a 'heave mechanism' parallel to frost heave (Torraca 1981; 31).

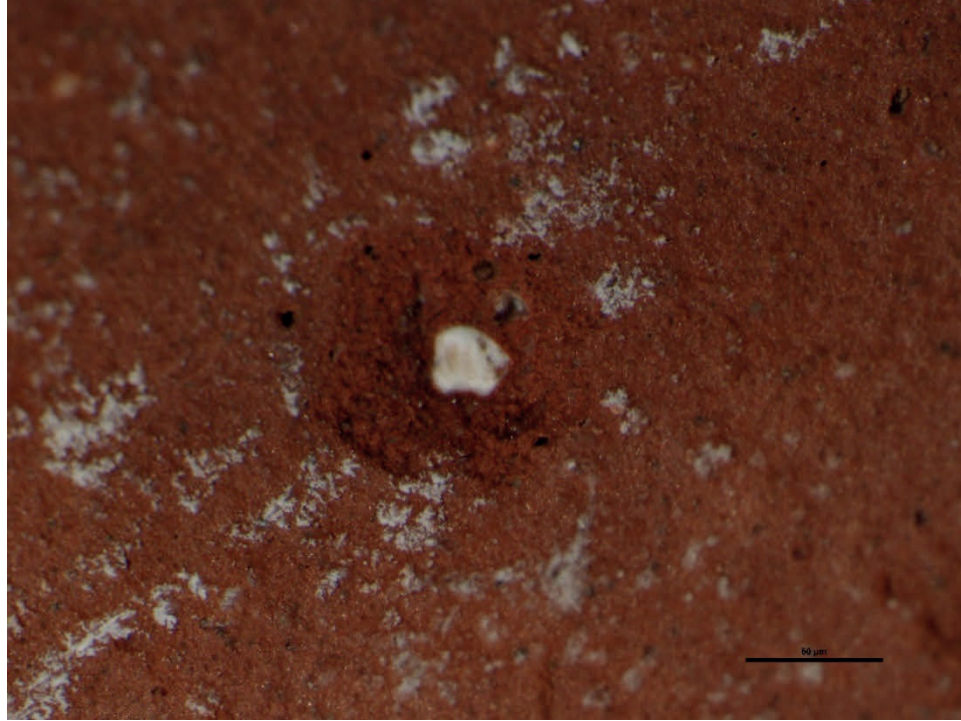


Figure 3-Material spall on terracotta, subsurface crystallization visible as a large yellowish white mass.

3.4 Source and Description of Common Types of Salt in Building Materials

3.4.1 Sources of Salt Contamination

Terracotta can become contaminated intrinsically or extrinsically. Soluble and hydrate-forming salts that are intrinsic are introduced during the manufacturing process. For example, alkali and alkaline earth sulfates commonly result from the oxidation of sulfides present in the clay during firing. Extrinsic soluble salts are introduced environmentally, post-manufacturing soluble salt can migrate into a porous building material through capillary suction, also known as rising damp from the soil or groundwater beneath a structure. Gypsum is commonly absorbed from surrounding mortar, concrete, and pargetting (Hewat 1996: 29). Air pollution often carries

sulfates and nitrates to a building surface. Wind-blown salt from the ocean or desert, as well as driving rain can force salts into the pores of a building in close proximity. Salt can also be introduced by human interaction; the use of inappropriate cleaning products, exposure to de-icing salt, salt or gunpowder storage, garden fertilizers, animal manure and urine, as well as decomposing human remains in the instance of burial are all examples (Charola 2010: 329).

3.4.2 Most Damaging Salts

There is a direct correlation between a salt's solubility and its deleterious impact on a porous material. The salts that do not induce damage are those that are practically insoluble. This is because they do not produce crystals because the concentrations of salt in solution is minimal when fully saturated. Those salts that are slightly soluble tend to be the most aggressive because of their tendency to crystallize right below the surface, causing significant spalling and degradation of the surface. Highly soluble salts are dangerous because of their ability to accumulate in one location. High concentration leads to increased hygroscopicity, which draws more moisture into the material increasing a material's risk of physical deterioration. Highly soluble salts actually stay in solution in humid climates, and therefore can change hydration states, increasing in size due to temperature change. It is not uncommon that highly soluble salts will migrate out of a porous body through evaporation in a drier climate crystallizing as efflorescence. However, if the source of salt solution is continuous and that dynamic balance is struck (see: subflorescence), soluble salts can crystallize both on top of and beneath a material's surface depending on the evaporation front.

Beyond solubility, the way salts hydrate is an important aspect of their damage potential. For instance, sodium sulfate has two common hydration states, the less damaging

thenardite and more damaging mirabilite. When thenardite hydrates, mirabilite is created, which increases in size by over 300%. This dramatic increase in volume causes considerable pressure within a pore-structure (Borrelli 1999: 5).

The 'soluble salts' generally refer to chloride, nitrate, sulfate, carbonate and bicarbonate of sodium, potassium, magnesium, and calcium. The solubility and precipitation of each salt varies, and changes dramatically and unpredictably when combined into a mixture of salts (Siegesmund et al. 2003; 269).² It is generally accepted that in a pore system, if two salts are present that do not have like ions, then solubility will increase, particularly for the less-soluble salt due to the solution having higher ionic strength. An example of this is the combination of sodium chloride and calcium sulfate. If the solution has several salts that have like ions, such as sodium chloride and sodium sulfate, then solubility of both will decrease (Charola 2010: 330). A significant variety of different crystalline salts, as well as a significant variety of double salts consisting of two different ions have the ability to precipitate out of solution. The most damaging being salts that can exist in an anhydrous and different hydrated states (Siegesmund et al. 2003: 269-70).

3.4.3 Chlorides (Cl⁻)

Chlorides are probably the most commonly encountered salt in coastal areas, from sea spray, and in northern regions where de-icing salts are so frequently used. Chlorides are also sourced from sand used in mortar mixes, and from hydrochloric acid produced from industrial pollution (Borelli 1999: 7). The most prevalent chlorides are halite (NaCl), sylvite (KCl), and antarcticite (CaCl₂·6H₂O). Chlorides tend to crystallize slowly in the smaller capillaries at the air-

²It is almost always the case that a mixture of salts is present in a porous building material that is deteriorating.

solution interface, resulting in euhedral cubic crystals at low supersaturation ratios, which is not necessarily damaging. Though it has been observed that at low RH, NaCl grows prismatic and hopper crystals which are damaging. Chlorides at times will plug small capillaries, reducing the porosity of a material (Doehne & Rodrigues-Navarro 2000: 199). Chlorides are particularly damaging because they are highly soluble and have the capacity to migrate quickly and deeply into a porous substrate (Hewat 1996: 30). In addition, the high level of hygroscopicity of chlorides induces a higher moisture content at equilibrium, creating potential for greater physical deterioration during freeze-thaw cycling (Borelli 1999: 7).

3.4.4 Sulfates (SO_4^{--})

Sulfates are a hydrated salt, and generally come from atmospheric pollution. Notably, they are also borne from agricultural land as ammonium sulfate, as calcium sulfate in inorganic binders like portland cement in mortar or grout, as magnesium sulfate in sea spray, and deposited from micro-organism metabolization. Sulfates prove to be the most damaging of salt families. Being slightly soluble and less mobile, they tend to crystallize just below a substrate's surface. Sulfates tend to precipitate rapidly, though if a slow hydration process occurs sulfates have the ability to precipitate very large, aggressive crystals as hydrate salts on pore walls, that can then become anhydrous (Hewat 1996: 31). Anhydrous salts do not dissolve if humidity remains low, and can change hydration states due to temperature change, increasing in volume over 300%. This hydration pressure can cause significant material deterioration from within the pore-structure. Rodriguez-Navarro and Doehne suspect that the high damage potential of sulfates is due to its tendency to rapidly grow well defined needle-like prismatic crystals (1999; Doehne & Price 2010; 15).

3.4.5 Nitrites and Nitrates (NO_2^- & NO_3^-)

Nitrites and nitrates predominantly come from the decomposition of nitrogen-containing organic matter. The two most common sources are human or animal excrement such as in fertilizers, and burial sites. Nitrates, being the oxidative product of nitrites are more commonly found in building materials. Nitrates also are products of airborne photochemical smog. As in the case with sulfates, micro-organisms such as nitrous and nitrobacteria can metabolize nitrogen compounds into nitrite and nitrate. Similar to chlorides, nitrates are highly soluble, and cause deterioration mainly by increasing physical decay phenomena through increased hygroscopicity and subsequent increased moisture content (Borelli 1999; 7).

3.5 Mechanisms of Salt Decay

3.5.1 Physical decay

Salts can increase the rate and severity of physico-mechanical weathering. Because of salt's hygroscopicity, salt contamination will maintain a higher moisture content, producing osmosis and effectively weakening the material's mechanical strength, and increasing the impact of freeze-thaw cycles (Charola, 2000; Borelli 1999: 7). This was exhibited through an experiment performed by Dunning and Huf (1983) in which the presence of moisture in the pores of a porous stone increased the rate of crack propagation when the stone was subjected to stress (Doehne & Rodrigues-Navarro 2000: 193). The accumulation of salt crystals within a pore-structure can lead to the narrowing of a materials capillary diameter. This can increase capillary rise, promoting absorption. On the other hand, if a practically insoluble salt enters the capillaries, it has the ability to clog pores. This congestion can obstruct water vapor transmission, and accelerate damage.

3.5.2 Crystallization

The most important salt decay mechanism is a result of when moisture evaporates or cools and the concentration of salt increases causing crystallization inside a porous body, also known as subflorescence. It has been proven that the type of salt, relative humidity and rate of evaporation determine the severity of salt crystallization. If salts precipitate and accumulate, the increase in volume within a material's pores generates and exerts pressure outward, so much as to overcome the material's tensile strength, causing fracture (Doehne & Price 2010; 15). The crystallization pressure is largely a function of where the salt is crystallizing and a salt solution's supersaturation ratio (Doehne & Rodriguez-Navarro, 1999). This pressure begins to develop at the point when the volume of the precipitating crystals and residual solution is larger than the volume of initial solution (Lewin 1982; Charola 2000).

Very recent research has further studied the nature of this pressure. At first, it was seen as a pressure exerted directly from the contact of the crystal against the pore wall. Most recently it has been confirmed that ultimately a crystal can only grow if solution can squeeze between the crystal and pore wall. When the pressure exerted physically from the crystal builds to excess and squeezes the solution out of the space between the wall and crystal, growth of the crystal stops. This results in a push and pull dynamic, where the crystal vacillates between growing and stopping, creating a differential between the surface energies of the porous material, the salt solution and crystal interface, similar to the repulsive force between two magnets. This force is created by the mismatched surface energies when the pore wall and salt

crystal surface come within approximately 10 nm of one another, with solution in between. This disjoining pressure is what actually causes material spall (Doehne & Price, 2010: 17).³

3.5.3 Hydration damage

Hydration damage has been inaccurately considered a more common decay mechanism until recently (Charola 2000: 327-28). Hydration damage is an increase in volume that occurs when a salt hydrates. As stated previously, sodium sulfate is an example of a salt that can exist in multiple hydration states as the anhydrous salt thenardite (Na_2SO_4) or the decahydrate mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$). When thenardite converts to mirabilite, it triples in volume after dissolving and recrystallizing (Shiro et al 2012: 1).

3.6 Physico-Mechanical Effects Salt Crystallization has on Terracotta

3.6.1 Blister/Material Spall/Pitting

Blistering leads to material spall induced by the heave action of subflorescence. Blistering is characterized as, “Swelling accompanied by rupturing of a thin uniform skin across and parallel to [the surface]” (Grimmer 1984: 3). Material spall is when the larger outer-surface layer breaks off unevenly. Often spalling caused by salt cycling occurs in the shape of circular pits and is officially referred to as ‘Pitting’ by Historic England (Grimmer 1984: 20; Henry et al. 2015: 724).

³ This disjoining pressure has been proven by direct evidence produced by ESEM, TMA, NMR, and AFM (Doehne & Price, 2010: 17).

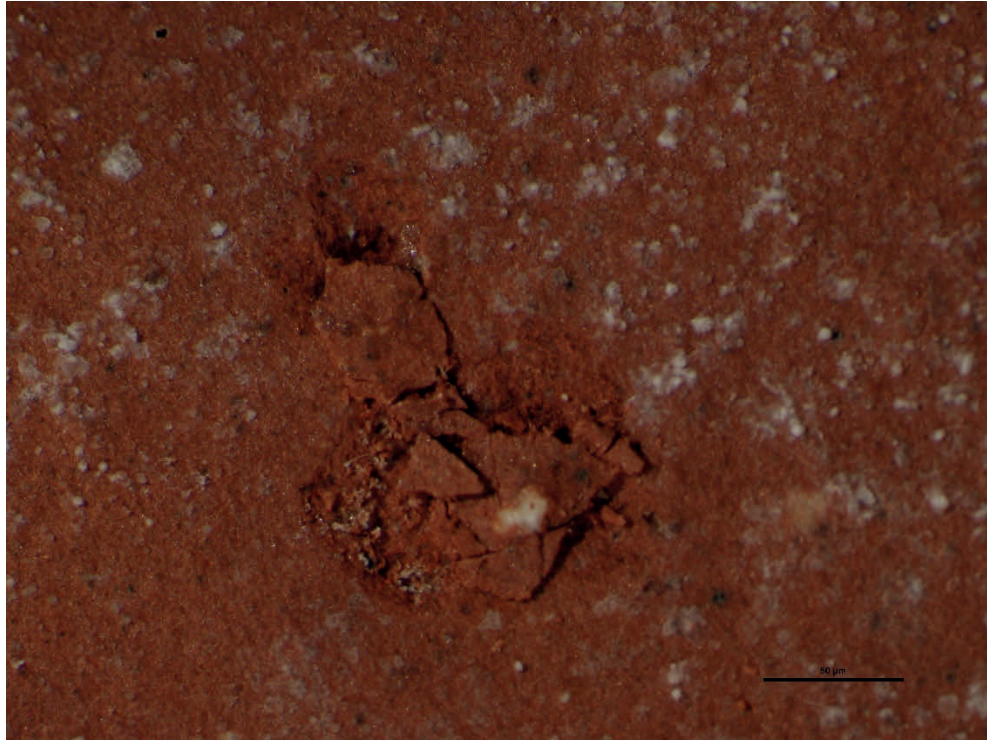


Figure 4- Example of incipient spall in terracotta.

3.6.2 Loss of Cohesion/Sugaring

This is gradual surface disintegration in which small constituent grains are loosened and eventually fall away. This can be caused by subflorescence or a dissolution of clay/stone matrix (Grimmer 1984: 23).

3.6.3 Exfoliation

Exfoliation lies between sugaring and spalling. It is typically a term used to describe the flaking, peeling, or scaling off of thin surface layers of a material. This is caused by the expansion and contraction of trapped moisture (Grimmer 1984: 13).

Chapter 4: Traditional Conservation Approaches to Desalination

4.1 Physical Intervention

The first step in remedying salt damage is by cutting off or slowing down the source of soluble salts. An old technique that is still incredibly viable is installing a hydrophobic damp-proof course (DPC) at the base of a building. Today material and chemical DPC's are used. This has yielded good results prior to contamination and mixed results after (Doehne & Price 2010: 34-5). Installing a physical damp-proof course as opposed to injecting a wall with a chemical one can be costly and damaging if not done correctly. This is so because it requires cutting-in a layer of damp-proof material such as slate at the base of an existing wall. The other greatest danger of post-installation of a DPC is that it can actually trap interstitial moisture, by preventing evaporation (Hutton 2012).

4.2 Water-Immersion Treatments

Water-immersion, water-bathing, or "steeping" has been a recorded desalination treatment as far back as 1905, when Friedrich Rathgen prescribed it in his book, *The Preservation of Antiquities; a Handbook for Curators*. For portable objects it is a very effective desalination method. The method's general steps consist of constructing a large water-proof container that will host the object, filling the container with deionized water, immersing the object, and changing the water in cycles based on the percentage of salt still present (Heritage et al. 2013: 75).⁴ Though the size and frailty of an object makes this method complicated,

⁴ A conductivity meter is often used to measure the percentage of salt still present in solution.

whatever needs to be desalinated must be able to be immersed in a container, and must not have any water-soluble or friable components (Heritage et al. 2013: 21).

4.3 Poulticing

The concept of a poultice draws from a medical origin, where a cleansing pack is applied to the body to draw out toxins. On objects and buildings, poultices are used primarily for cleaning and desalinating. The “pack” usually is made of kaolin, attapulgite or sepiolite clays, or cellulose-based material such as paper pulp and wallpaper paste (carboxymethylcellulose or CMC) (Henry 2015: 153). Other materials have been used including diatomaceous earth, chalk, talc and even flour. In the simplest terms the base material is mixed with water into a slurry and applied to a substrate. First the moisture from the poultice travels into the material and dissolves the salts. The salts are extracted as the poultice dries and the salt solution is pulled out into the poultice material on the surface (Woolfitt & Abrey 2000). Poultices extract by one of two processes, diffusion or by capillary water flow (Pel et al. 2009: 59-60). “Plain” or unadulterated poultices are most often used for desalination, but in some cases chemical additives are mixed into the poultice to enhance extraction (Woolfitt & Abrey 2000).

A great deal of research was performed between 2006-9 for the Assessment of Desalination Mortars and Poultices for Historic Masonry, organized by the European Commission. A diverse group of professionals spent that time perfecting the guidelines for more efficient poulticing practice. The main principles clarified were: that it is important to match poultice characteristics to the substrate’s pore characteristics, and that a poultice should always have a smaller pore size than the substrate. Also it was found that thinner and drier poultices, were more effective (Heritage et al. 2013: 4-5).

Although the science of extraction through poulticing has been perfected in the last ten years, this method is not worthwhile if the source of salt contamination cannot be stopped, as it can cause a deeper level of contamination by drawing in more salt. Other negative consequences of poulticing can result in low rate of extraction of salts due to poor adherence, shrinkage and early detachment, unexpected mobilization of salts by using excessive water, and rapid re-appearance of salts after treatment, especially if the source of salt was not properly interrupted (Doehne & Price 2010).

Chapter 5: Recent Research of Crystallization Inhibitors

5.1 General

Crystallization inhibitors (CI) are chemical reagents that have shown the ability to alter soluble salt crystallization processes. Many of these additives have well-known inhibiting and habit-modifying capabilities and have been used previously in technological and industrial settings. Recently research has focused on applying these classes of chemicals to building stone as a means to mitigate or prevent salt crystallization damage caused by subflorescence. How CI's mitigate salt damage is by preventing or delaying nucleation and/or by reducing the crystallization rate of specific crystal faces, effectively modifying the habit of the salt crystals, as well as increasing salt solution transport to the surface of the substrate (Lubelli & Van Hees 2007: 1). A wide variety of chemicals have been tested, the most successful being surfactants, phosphates, carboxylates, polyacrylic acid derivatives, and benzotriazoles. The application of alkali ferrocyanides has been researched along with these other classes of chemicals, and have shown positive results in increasing supersaturation for nucleation, specifically in regard to NaCl (Doehne & Selwitz 2002: 208). As cited by Selwitz and Doehne in their 2002 study of the effect of ferrocyanide ions on crystal morphology, ferrocyanides provide the highest supersaturation for nucleation in NaCl, being 3.9%, 5.1%, 11.6%, 22.0% and 31.0% for 1, 10, 200, 1600, and 6300 ppm, respectively.

5.2 Ferrocyanides

5.2.1 General

Experimental analysis has been conducted on the effects of ferrocyanide ions (FC) on NaCl morphology since the early 1960s. In 1962, Boistelle et al. found that ferri- and

ferrocyanides ions significantly modified NaCl crystal habit, which was followed by research published in 1965 by Van Damme-Van Weele. This research confirmed that ferrocyanides much more so than ferricyanides had the ability to induce high supersaturations, which often promoted the less damaging dendritic crystal growth as opposed to cubic or columnar growth (Rodriguez-Navarro et al. 2002: 512). The extensive research performed by Rodriguez-Navarro clarified the process by which FC work and many of the positive and negative effects of FC when applied to ornamental building stone. This research revealed that FC increased the critical supersaturation from 1.3% to 8%, having a dramatically positive effect in enhancing efflorescence and reducing subflorescence. This occurs because salt tends to crystallize where the highest supersaturation occurs i.e. at the evaporation front, which with the addition of FC occurs on the substrate's surface. The increase in efflorescence exponentially increases the evaporation rate of absorbed moisture due to the increase in surface area of the evaporation front which in turn actually increases the supersaturation rate even further (Rodriguez-Navarro et al 2002: 506-7). FC has a great propensity to dissolve in an aqueous solution, which reduces the concentration of available solvent, in this case water which also increases supersaturation. In addition, FC acts as Na⁺ scavengers; the dissolved FC readily adsorbs Na⁺ ions which interferes with ion transport toward developed NaCl masses. This cycle exhibits that the primary action by which FC is effective is that it strongly suppresses and/or delays nucleation, with minor growth inhibiting abilities (Rodriguez-Navarro et al. 2002: 513). His research also showed that a great concentration of FC was still present and available to act as a nucleation inhibitor for a long time after the experiment.

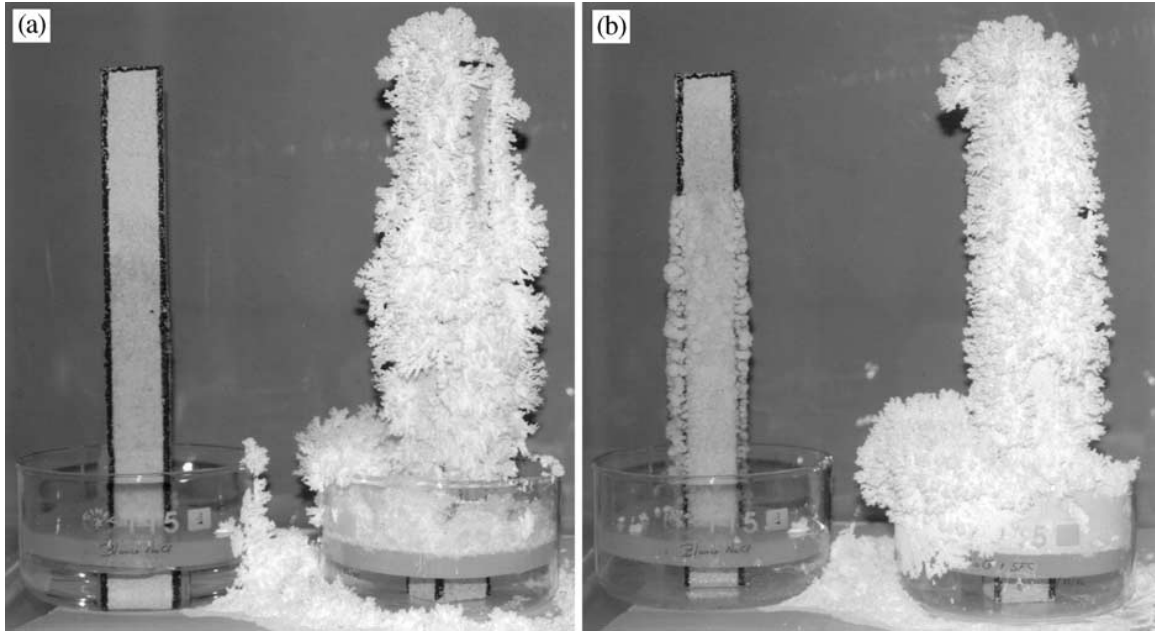


Figure 5-Images of calcareous stone slabs following 48 h (a) and 7 days (b) NaCl saturated solution flow-through and pure solution (left slab) and a solution with $[Fe(CN)_6]^{4-}$ (right slab)

(Rodriguez-Navarro et al. 2002: 509).

There are serious considerations that have not yet been entirely addressed in crystallization inhibitor research. Following Correns's equation that determines crystallization pressure exerted by salt in a confined pore, it is proven that the higher the supersaturation, the higher the crystallization pressure exerted in the pore will be.

$$P = \frac{RT}{V_m} \ln \frac{C}{C_0}$$

Where R is the gas constant, T is temperature, V_m is the molar volume of the solid phase and $C=C_0$ is the supersaturation (Rodriguez-Navarro et al. 2002: 508). This equation theoretically exhibits a greater degree of damage when nucleation, i.e. crystallization actually occurs,

because of built up pressure. This is a critical aspect that will have to be remedied before inhibitors are applied in situ (Lubelli & Van Hees 2007: 2).

5.2.2 Sodium Ferrocyanide $\text{Na}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$

Sodium Ferrocyanide (SFC), also called “*yellow prussiate of soda*,” is a yellow crystalline salt similar to potassium ferrocyanide, used in making iron blue pigments, blueprint paper, and dyes,” (Merriam Webster Dictionary 2016). SFC is considered to have a low-order toxicity, since the cyanide bonds to the iron, illustrated by the fact that it is also used as an anti-caking agent in food-grade salts (“NCBI-PubChem” 2016).⁵ Lubelli and Van Hees observed in a study they conducted that a solution with 0.001M concentration of SFC enhanced drying when applied to both limestone and brick substrates contaminated with NaCl. Also observed in the same study was the powerful effect sodium ferrocyanide had on NaCl crystal morphology. Efflorescence changed from cubic to dendritic crystals and subflorescence changed from a crust to an agglomeration of crystals (Lubelli & Van Hees 2007: 6-7)

5.2.3 Potassium Ferrocyanide $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$

Potassium Ferrocyanide (PFC) is a “yellow soluble crystalline compound, also called potassium hexacyanoferrate (II), and yellow prussiate of potash,” and is the precursor compound to the pigment, Prussian Blue (Collins English Dictionary 2012). It is fairly nontoxic, only having the potential to cause irritation of the skin or respiratory tract when in contact with large amounts, and causing gastrointestinal upset if ingested in large doses. Prior to its testing

⁵ At a level not to exceed 13 ppm, according to the FDA. National Center for Biotechnology Information. PubChem Compound Database; CID=26129, <https://pubchem.ncbi.nlm.nih.gov/compound/26129> (accessed Mar. 27, 2016).

on building stone, potassium ferrocyanide (in the parts per million range), was used to prevent clogging in brine-sodium chloride rock formations in petroleum production. As stated, potassium ferrocyanide increases supersaturation of a salt solution, effectively delaying nucleation- specifically in NaCl.

Apparently the crystal habit of NaCl changes from cubic, to dendritic, to whiskers when the concentration of potassium ferrocyanide it increased by 1.0%.⁶ Selwitz and Doehne discovered that adding 0.10%-1.00% of potassium ferrocyanide to 5% and 20% solutions of NaCl, changed salt deposition from primarily subflorescence to almost entirely efflorescence, that left the stone substrate undamaged. In the same study it was found that a 15% sodium sulfate solution with the addition of potassium ferrocyanide, experienced increased salt solution transport and in a high humidity/draft-free environment, crystallized mainly as efflorescence (Doehne & Selwitz 2002: 215).⁷

5.3 Phosphates

5.3.1 Sodium Hexametaphosphate (NaPO_3)₆

Sodium hexametaphosphate has historically had many diverse uses, because it is the only phosphate that readily dissolves in water. HMP is a white translucent solid used as a corrosion inhibitor, water softener, deflocculent in the ceramics industry, used to make industrial cleaners, and used in the food and beverage industry (“SHMP from China” 2008: 16-18).

Polyphosphates, including sodium hexametaphosphate (HMP) have had the greatest research performed on the capacity of inhibiting calcium sulfate (gypsum) and calcium

⁶ From 10 to 10,000 ppm.

⁷ 5-20% salt solutions with the addition of potassium ferrocyanide did show considerable subflorescence damage in an unmoderated environment.

phosphate crystallization.⁸ Hamdona and Hamza discovered that at low concentrations, HMP was able to reduce the rate of gypsum precipitation from a supersaturated NaCl solution by 57.05% (49).⁹ Selwitz and Doehne cited in their research that at 110, 920 and 5700 ppm, HMP increased salt solubility of NaCl by 3%, 4%, and 6%, respectively (Doehne & Selwitz 2002:207). The process by which phosphate molecules inhibit crystal growth is by adsorbing on the salt crystal surface, which blocks surface crystal growth sites (Lin & Singer 2005: 8).

5.4 Previous Laboratory Testing

Although previous lab testing has shown positive results in regard to the inhibiting abilities of the stated chemical additives, very little testing has been done in a laboratory that would mimic in-situ conditions, and only a few research campaigns have actually applied the inhibitors in-situ. Until the last few years, most laboratory experiments performed dissolved the inhibitor in the same solution as the salt, that was then simultaneously introduced to the unadulterated substrate. This produced results that reflect how inhibitors can be used as a preventative method for crystallization, but does not reflect how these chemicals will react to a previously contaminated substrate. Lubelli and van Hees in their 2007 study actively pursued replicating in-situ conditions, and applied ferrocyanides to a previously contaminated substrate, as well as in-situ in a poultice application. Their results were primarily inconclusive, and found that a far greater amount of research should be conducted on the method of application of

⁸ In 1960, Fleisch and Neuman observed that a number of phosphates, including ADP, trimetaphosphate, pyrophosphate, hexametaphosphate, and long chain polyphosphates, inhibited nucleation of calcium carbonate concentrations of 1.0×10^{-5} . Bernhardt, Asenath M., Stan C. Kunigelis, and Karl M. Wilbur. 1985. "Effects of Phosphates on Shell Growth and Calcium Carbonate Crystal Formation." *Aquatic Toxicology* 7 (1–2): 1–13. doi:10.1016/0166-445X (85) P 1.

⁹ A concentration as 30×10^{-6} mol. L⁻¹ of inhibitor.

inhibitors. A 2015 study did find poulticing with inhibitors in combination with a controlled environment produced positive desalination and crystal inhibition results. (Lubelli & van Hees 2007; Franceschini et al. 2015). A move toward adding inhibitors to previously contaminated samples is the next step. Early applications of inhibitors via spraying proved to increase damage to the sample substrate due to rapid deliquescence and evaporation. More recent methods of using cellulose poultices in-situ to apply inhibitors have been studied (Lubelli & van Hees 2007). In the case of the Roman Mosaic of Orpheus and the Beasts in Perugia, Italy this application was successful (Franceschini et al. 2015). It is evident that even with the developments in research over the last decade a greater amount of testing is necessary due to all of the variables involved in mitigating salt damage.

Chapter 6: Case Study: Western Clay Manufacturing

6.1 General

Located three miles from the downtown of Helena, in Montana's Prickly Pear Valley, is the historic industrial site of Western Clay Manufacturing Company (WCMC) and the adjacent Archie Bray Foundation for the Ceramic Arts, nestled on 26 acres, against the wooded foothills of the Rocky Mountains (archiebray.org, 2016). Brickmaking commenced on the site in the early 1880s, and hollow clay tile manufacturing began a few years later continuing until the plant's failure in 1960. Today the majority of the brick plant's original fabric remains intact, including several of the downdraft beehive kilns, now a rare typology in the United States. Many of the extant buildings and machinery have decayed due to disuse and inconsistent maintenance, however the entire site exhibits a high degree of integrity. A Montana Historical Inventory and Survey was conducted in 1985/1986 and the site was ultimately listed on the National Register of Historic Places at that time. However, the site has remained predominantly left to ruin until a few years ago.

Beginning in 2011, Chere Justo, Executive Director of the Montana Preservation Alliance (MPA) approached Frank Matero, Director of the Architectural Conservation Laboratory (ACL) of



Figure 6- Panorama of the kiln complex of Western Clay Manufacturing Co. in 2013. Photo taken by Joseph E.B. Elliott.

the University of Pennsylvania in order to obtain an opinion on the deterioration of the beehive kilns. With the support of the J.M. Kaplan Fund and the blessing of the Archie Bray Foundation (ABF) members of the ACL performed documentation, and subsequent stabilization of the kiln complex. To date, the ACL has produced a full set of architectural drawings of kiln #7 and a plan of the kiln complex, The MPA has hosted two summer University of Pennsylvania Historic Preservation (HSPV) Praxis classes, several HSPV architectural conservation interns, including myself, and has had staff and volunteers out to perform stabilization of the kiln complex shed structure and roofs. In 2015 the full stabilization of Kiln #7 was brought to completion. Theses on the preservation of WCMC were produced by Sharon Reid (2012) and Brett Sturm (2013), two students in the Historic Preservation Program at the University of Pennsylvania and lastly, a Kiln Complex Rehabilitation Preservation Report was written by Christopher M. Taleff through

the MPA.¹⁰ Now that Kiln #7 has been preserved, the MPA is interested in moving on to documenting and stabilizing the other kilns in the complex.

6.2 History of WCMC

The brickmaking industry was well established along the eastern seaboard by the time it began to advance westward during the second half of the 19th century (Reid 2012: 23).

Brickmaking in the United States had begun nearly two hundred years earlier, but industry followed settlement and operating brickyards were not recorded in the central and western states until the last quarter of the 19th century. Those brickyards probably began as temporary camps, using the clay from the land and local timber for fuel in order to build the first homesteads in the newly settled territories of the American West. Over time, some of these evolved into larger permanent manufactories and produced brick that built entire towns.

Brickmaking was often passed from generation to generation, and if yards went out of business it was usually due to being in close-proximity to a larger yard, which would either buy or drive it out of business. The pinnacle of the brickmaking industry was the turn of the twentieth century, and despite predictions made by the federal government in the 1940s that brickmaking would remain in demand indefinitely, by 1970 the Brick Industry Association (BIA) reported that in the U.S. only 400 brick plants were still in operation (Reid 2012: 10-12). Western Clay Manufacturing Co. had humble beginnings similar to many other brickyards of the west. Brickmaking commenced on the site in 1883 under the dominion of Charles C. Thurston. Thurston, the son of a brick maker was previously trained in his home state of New Hampshire. Thurston worked in

¹⁰ All of the associated documents can be found here:
http://www.conlab.org/acl/western_clay/wecl_history_Overview.html

the building trade and practiced brickmaking in the nearby city of Butte before buying a 300-acre ranch on the outskirts of Helena to erect a permanent brickyard (Reid 2012: 13). Nicholas Kessler, Thurston's neighbor, who also managed a small brickmaking operation and brewery across the creek bought Thurston's yard in 1885, when Thurston took off to work at Marcus Daly's copper-smelting operation in the boomtown of Anaconda (Sturm 2013b: 6). Kessler had exhausted his supply of clay on the adjacent tract of land, leading him to seek out new clay deposits. Charles H. Bray a brick maker from Tavistock, Devonshire, England, had come to the yard two years' prior, working a short stint for Thurston. Kessler, aware of Bray's clay working knowledge, decided to make him the superintendent of the Brick Works, which proved wise. At the time only common brick was being produced via oxen and horsepower and fired in clamp or scove kilns (Quivek 1985: 2).

Under Bray's management the simple manufactory expanded into a multi-faceted industrialized enterprise which made pressed, ornamental, fire, and vitrified brick as well as terracotta sewer pipe, fire-proof ware, flower pots, lawn vases and more. Bray was incredibly forward-thinking and proved extremely progressive in his choice to keep the works outfitted with the most cutting-edge brick and tile making technologies. In addition to Bray's skilled and focused efforts- high demand for fire-proof building materials was stimulated by the rebuilding and expansion of Helena after it experienced successive fires. Toward the end of the 19th-century WCMC doubled its production and swiftly became the largest industry and commercial asset in Helena (Reid 2012: 21-22). Due to rapid production, the Kessler Works quickly exhausted their clay deposit once again. Kessler merged his business with his only remaining competitor- Alsatian Jacob Switzer, owner of Switzer Brick and Terra-Cotta Company as well as the 280-acre clay deposit in nearby Blossburg. This clay, generally used for terracotta, was

located up in the Rocky Mountains across the continental divide and was touted for its superior quality.

It makes sense that in 1908 when Mr. Kessler passed away, Bray chose to become a stockholder in the corporation that was organized thereafter. That is when the Kessler Brick and Sewer Pipe Works officially became the Western Clay Manufacturing Company (WCMC). Bray was then appointed official secretary and general manager at this time, and only became more deeply entrenched as time went on. In 1920, Bray bought Jacob Switzer's shares, and eight years later bought the Kessler family's shares, making him the sole owner and President of the Company. Archie (Sr.) and Ray, Charles' two sons subsequently helped run the Company from then on out. At the time, WCMC was the top producing heavy clay industry, allegedly producing twice as much product as competitors in Billings, Butte and Great Falls (Sturm 2013b: 6). Bray continuously developed the manufactory, outfitting it with the most advanced brick and tile making technologies, until his death in 1931. The presidency then was transferred to Archie Bray, Sr. who by that time had worked as the Company's superintendent after graduating from Ohio State University's ceramics engineering program. Archie Sr. had no trouble managing the Company as he proved to be an adept businessman and clay worker, and took great interest, like his father, in the latest clay working technologies. He upgraded the fuel source of the manufactory from coal to natural gas, and installed the first de-airing machine for brick production west of the Mississippi River (Quivek 1985: 13; Sturm 2013b: 36).

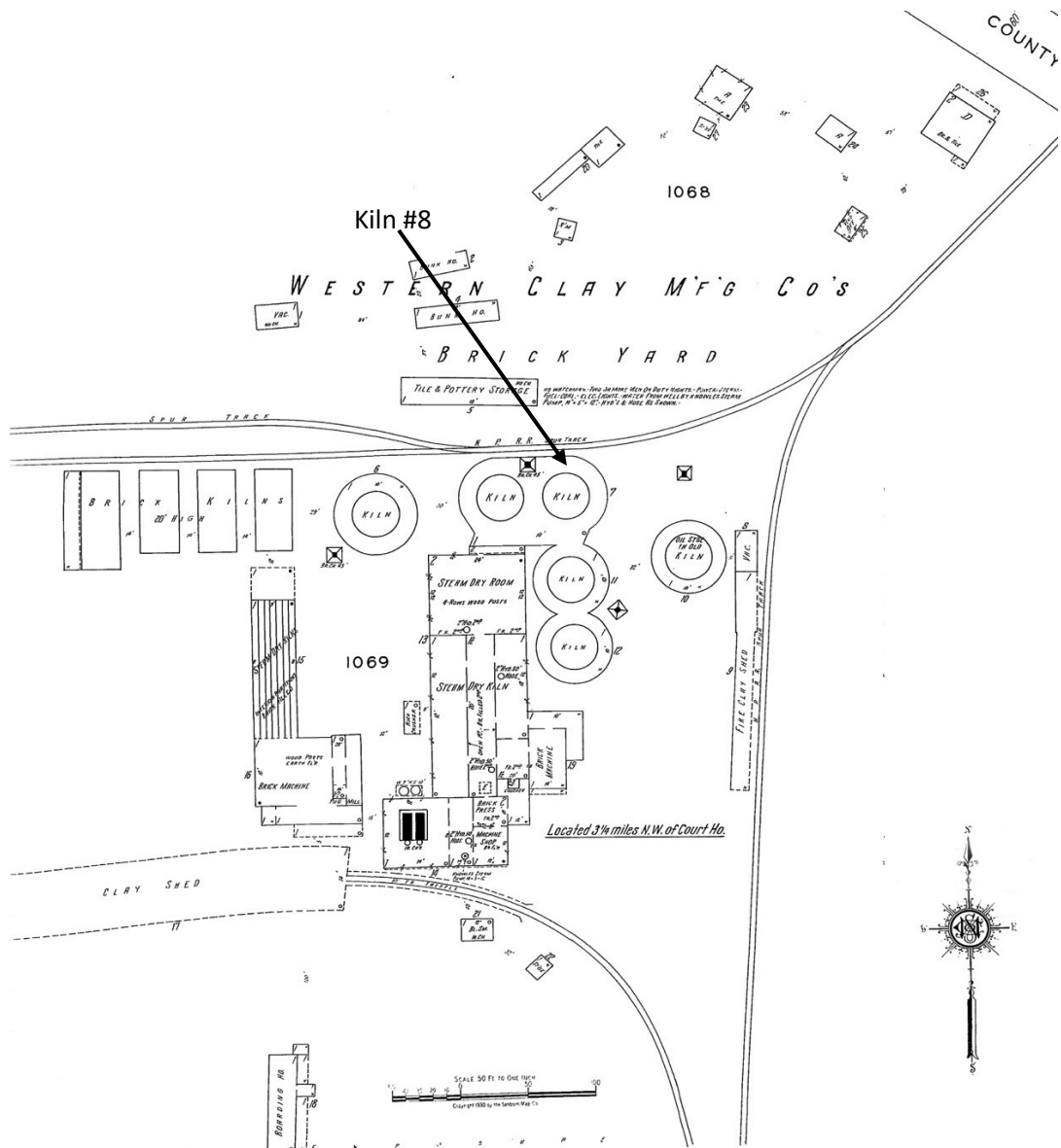


Figure 7-A Sanborn map last updated in 1930 Source: Reid, (In)Forming and Pressing Matters.

155. "Western Clay." Sanborn Company Fire Insurance Map, 1892 updated to 1922, Montana, Plate 148. Courtesy of the Montana Historical Society. Helena, MT.

Production slowed due to a decline in demand after World War II. Archie Sr. invested more of his time and energy at that point into the arts; his passion for artistic clay production

led him to establish a small pottery next to the brickyard with friend Peter Meloy and Branson Stevenson in 1951. The pottery was built by Western Clay employees and was funded by brick revenue. It was a small seed, that would germinate over several years, expanding greatly under the direction of Peter Voulkos and Rudy Autio, later becoming officially known as the Archie Bray Foundation. In these early years while the pottery operation grew, the brick plant was slowly becoming obsolete. Two years after the pottery was erected Archie Sr. passed away, leaving the WCMC to Archie Jr. Archie Jr., a pilot by trade struggled to manage the declining brick manufactory. Attempting to continue his family's legacy, Archie Jr. installed a tunnel kiln in 1957 as a means to further modernize the plant and reduce production time and costs. Unfortunately, Archie Jr.'s investment was shortsighted, and the combination of technical problems, and a waning market left him unable to repay a loan to the Small Business Administration. WCMC closed in 1960 and was subsequently sold to the Medicine Hat Brick and Tile Company out of Canada (later I-XL Industries) who mothballed the entire plant. It was not until 1984 that the brick plant was bought back by the Archie Bray Foundation, which had flourished over that time (Reid 2012: 65, Sturm 2013a: 132).

6.3 History of Kiln #8

Speculated to have been built between 1908 and 1922, the intermittent downdraft beehive kiln (#8) at WCMC was the last built in the kiln complex (Sturm 2013: 31). It is a load-bearing brick masonry structure roughly 36 feet in diameter, supported by large iron bands secured by massive turnbuckles. It is situated east of kiln #7, west of kiln #6, and northeast of #4 and #5. The downdraft kilns replaced previously used updraft clamp or scove kilns, transforming the primitive brickyard into a permanent state-of-the art brick plant. Adding to the

plant's permanent nature, the wood and corrugated metal kiln sheds erected around the kilns changed production from a seasonal endeavor to an all year operation.

An updraft kiln is generally an impermanent, rectilinear box with a flat or arched roof and one or more chimneys out of the roof built of green bricks. Heat enters through flue holes on the sides and escapes out of the chimney. A downdraft kiln is square or a "beehive" dome shape with contained fireboxes built into the sides of the interior, so that when heat enters the flues it does not have direct contact with the ware. The heat rises up the walls and then is deflected downward, sucked down through a grated floor and into an underground network of flues that direct the air out of an adjacent freestanding chimney stack (Searle 1911: 244).

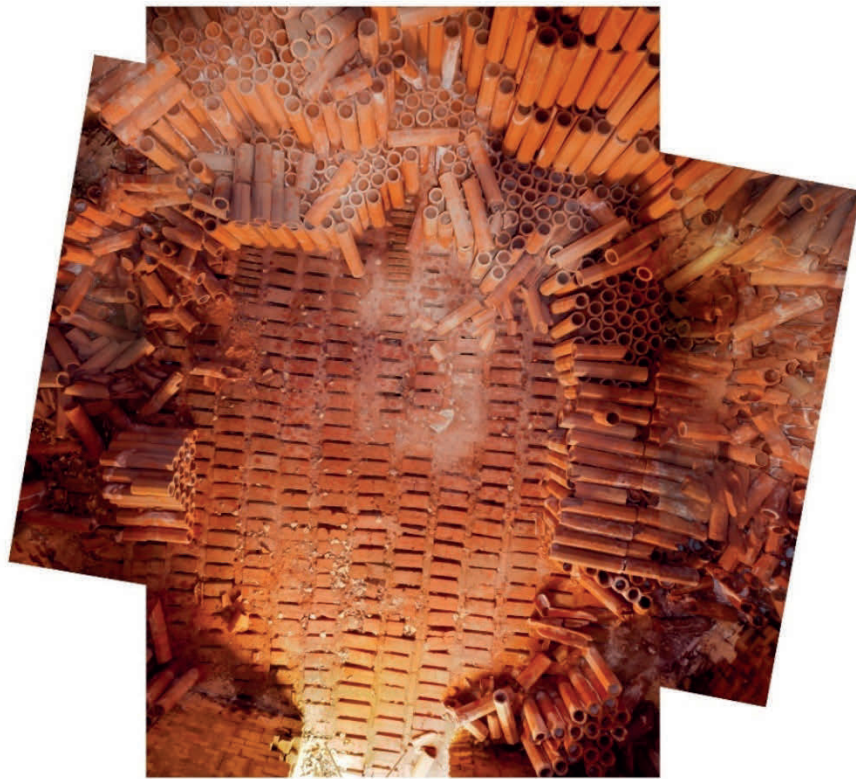


Figure 8-Interior view of the perforated floor of kiln #8. This is where the draft is sucked down into and out through an exterior chimney. Photo by Joseph E.B. Elliott.

The switch from updraft to downdraft technology afforded a more even and efficient firing of the ware within the kiln with a more consistent and clean burn of fuel (Searle 1911: 248-49). Because heat transfer was indirect in downdraft technology, less fuel was used and even less ware was discarded post-firing due to over or under firing, yielding much higher production rates than before. Kiln 7 and 8 had the capacity to churn out up to 50,000 bricks in each firing (Sturm 2013: 37). Higher production of specialty ware was also cited, due to the fact that the downdraft kiln design allowed for a greater ability to control the firing process, and heat exchange (Lovejoy 1913: 55). As opposed to the rectilinear shape of the clamp kiln, the dome shape, and open-plan chamber allowed for the firing of more complexly shaped products, which gave Charles and Archie Bray the opportunity to make a wider variety of inventory such as salt-glazed sewer pipe, ornamental face brick and earthenware flower pots (Quivek 1985: 9-10).



Figure 9-Photograph of Archie Bray, Sr. shoveling salts into Kiln No. 7. Source: ACL Files.

Kiln #8, along with adjacent Kiln #7, were specifically used to glaze-fire Western Clay's famous, salt- and zinc-glazed face brick. Zinc glazed the brick face dark green, while salt-glazing gave a vitrified luster to the surface. Thick buildup of a glaze crust coating on the interior walls of the two kilns bears the history of years and years of this type of firing. To perform this type of firing, rock salt (sodium chloride) and zinc would be shoveled into the kiln when it was red hot, in which the salts would volatilize and be carried along with the draft toward the top of the kiln and then down through the kiln bottom. The volatilized salt and zinc would interact at the

surface of the ware with the silica and alumina in the clay body to create a flux that would solidify into a vitrified glaze as the kiln and ware cooled (Sturm 2013a: 34).

6.4 Premise for Thesis Research



Figure 10-Interior of Kiln #8, exhibiting the extant stack of terracotta drain pipe. Photo by Joseph E.B. Elliott.

Kiln #8 is one of the last five remaining extant kilns of WCMC. It is especially significant because it is the only kiln in the complex that was left, “as is” on the final day of its firing. Inside the kiln stands a half set stack of terracotta sewer pipe, bisque-fired and ready to be unloaded. Except it was never unloaded and the terracotta ware has remained primarily untouched since the plant closed in 1960. It is unclear as to why the pipe was fired in Kiln #8, as kilns 4 and 5 were traditionally used to bisque-fire “more open things” like hollow

structural clay tile, flue lining, and flower pots, according to Archie Bray Jr. in an interview with Brett Sturm. It is conjectured that at the time of the last firing, employees had resorted to firing the small orders of ware all in one kiln, most likely that which was in the best condition.

Today the stack of terracotta is collapsing, due to extensive damage caused by salt weathering. Soluble salts, have heavily contaminated the interior walls of the kiln and fireboxes as well as the stack of sewer pipe, and fire brick that constitutes the kiln bottom. The salt source is assumed to be the residual salt that did not vitrify; accumulated over forty years of salt-glazing. When the kiln was in near continuous use, it is likely that it stayed hot and dry enough that these salts did not deliquesce often. Even if deliquescence occurred, ware generally was not



Figure 11-Efflorescence and deterioration indicates salt weathering is the main culprit in Kiln #8.

left inside the kiln, unglazed and vulnerable to salt weathering for more than a few days while the kiln was being loaded. It is ultimately the microclimatological conditions of abandonment that created the right conditions for soluble salts to become a deterioration mechanism in these porous materials. The kiln now is a victim to rain, snow and ice. The summer conditions prove the most troubling as extremely short rain showers are followed by high heat and sun exposure, causing rapid wetting and drying in the kiln.

Extensive damage has been observed over the last several years and the MPA feels that stabilizing and conserving this kiln and the ware inside is imperative.

Currently it is believed that soluble salts are deep within all of the porous materials inside kiln #8 and to attempt to desalinate this structure and the ware inside would be unbelievably labor-intensive, extremely expensive and potentially ineffective. This has led to the investigation of salt crystallization inhibitors. Certain chemicals that act as crystallization inhibitors if found effective could potentially be used in-situ at WCMC in order to halt crystal growth within kiln #8, subsequently halting further damage caused by salt weathering. SCI also have the potential to promote efflorescence as opposed to subflorescence and could potentially aid in minor desalinization of the porous materials within the kiln. SCI have been tested on building stone and brick, but have never been tested on terracotta.

Chapter 7: Part 1 of Testing Program: Identifying Salts in WCMC Samples

7.1 Analysis of Contemporary Research

In order to craft the most effective testing program, research was conducted on what the scientific community has already accomplished in terms of understanding what salt crystallization inhibitors can do when applied to heritage materials. Scholarly articles, conservation journals, and case studies were collected to enhance this study. Due to the fact that testing on crystallization inhibitors is still in its early stages, the testing procedures thus far have lacked diversity. The lack of diversity is what informed my experimental testing approach. As my methodology illustrates, I spent much of the fall semester, performing a literature review, in an attempt to fully understand salt weathering, desalination methods, and what laboratory research had been performed on inhibitors to this point. It was decided that in addition to studying the effects of inhibitors in terracotta that my research would also focus on how inhibitors performed when they are used alone and as an admixture. Lastly I am studying the difference of the performance of inhibitors on single-salt solutions and a mixed salt solution.

7.2 Preliminary Testing

7.2.1 General

Salt species were identified using EM Quant salt strips and powdered x-ray diffraction. The commercial scientific EM Quant salt strips were used to test for three salt families in order to investigate whether the suspected salts were present within the samples. These results were then cross-referenced with the results of powdered x-ray diffraction, once XRD was performed on the same samples. These combined results then informed future testing using salt crystallization inhibitors.

7.2.2 Salt Strip Testing

Four terracotta samples were used from Western Clay Manufacturing. In order to get an accurate sample of the test population, each sample was taken from a different location of the kiln in which they are located:

List of Samples from Western Clay Manufacturing							
Sample Tag	Material State	Material	Sent as	Location in Kiln	Date taken	Taken by:	Photo of location
A5	Granular / Powder	Terracotta	Loose	interior perimeter, mid stack	9/8/20 15	Matt Morgan	ABF_00561
A6	Granular / Powder	Terracotta	Loose	interior perimeter, floor stack	9/8/20 15	Matt Morgan	ABF_00562
A7	Granular	Terracotta	Loose	interior center, mid stack	9/8/20 15	Matt Morgan	ABF_00564
A8	Solid, Piece	Terracotta	Loose	interior center, floor stack	9/8/20 15	Matt Morgan	ABF_00558

See Appendix B for photographs.

Samples were prepared by pulverizing the material to pass through a no. 3 mesh. Then, 20 g of each ground sample was placed in 500 ml of deionized water and agitated on a mechanical hot plate using a magnetic stir bar for 30 minutes. This was done in an effort to encourage the salts

in the dry terracotta samples to deliquesce. Four solutions positive for nitrates, nitrites, sulfates, and chlorides were prepared as controls, using:

- 10 g of Sodium Nitrate (Fisher Science Education Lab Grade S2558A)
- 10g of Sodium Chloride (Fisher Scientific certified A.C.S)
- 10g of Potassium Sulfate (Fisher Science Education lab grade S25505)
- 10g of Sodium Nitrite (Fisher Scientific certified A.C.S)

Three different EM Quant Strips were used: Chloride, Sulfate, and Nitrate/Nitrite. Each change in color indicated a different concentration in order to provide semi-quantitative information.

EM Quant Salt Strip Key			
Salt Strip	Low	Medium High	High
Chloride	0-500 Mg/L	500-1000 Mg/L	1000-2000 Mg/L
Color	Yellow	Yellow-Brown	Dark Brown
Sulfate	<200->400 Mg/L	>400->800 Mg/L	>800->1600 Mg/L
Color	Pink	Pink/Yellow	Yellow
Nitrate	-	+	++
Color	White	Light Purple	Dark Purple
Nitrite	0-50 ppm	50-200 ppm	200-500 ppm
Color	Lightest Purple	Purple	Dark Purple

These controls were tested with test strips to determine the positive results for comparison with the unknown. These positive results were also tested against the correct colors provided by the containers to make sure they were still accurate.

After thirty minutes of agitation each solution was tested with the three different EM Quant strips. Strips were inserted directly into the 500mL beaker and immersed for 5-10 seconds. Strips were then removed and allowed to dry on a paper towel.



Figure 12-EM Quant Salt Strip test results.

7.2.3 XRD Testing

X-Ray Diffraction took place at the University of Pennsylvania's School of Engineering and Applied Science's Laboratory for Research on the Structure of Matter (LRSM). Samples were prepared by grinding them to pass through a 100 mesh, and then mounting them to a glass

slide, using deionized water. Samples were scanned in the XRD machine for 15-45 minutes and data was collected and translated using X'Pert High Score Software.

7.2.4 Conclusions

Results of the Salt Strip tests and the XRD analysis were not entirely congruent. Salt Strip testing showed that all four samples had medium to high amounts of chlorides and none had nitrites. Samples A5, A6, and A8 had high amounts of sulfates but A7 showed none. Samples A5 and A8 had low-medium amounts of nitrate. In Contrast, XRD analysis showed all samples had high amounts of sodium chloride and sodium sulfate, while none had nitrates or nitrites (see tables below).

EM Quant Salt Strip Results for Salt Families Present			
Sample	Chlorides	Sulfates	Nitrates
A5	>2000 mg/l	> 1600 mg/l	25 mg/l
A6	>2000 mg/l	> 1600 mg/l	0 mg/l
A7	2000 mg/l	N/A	0 mg/l
A8	1000 mg/l	>1600	50 mg/l

XRD Results for Salt Families Present							
Sample	NaCl	Type	Score	Na ₂ SO ₄	Type	Score	NaNO ₃
A5 (Z45276)	Yes	Halite	71	Yes	mirabilite, thenardite	3, 4	No
A6 (Z45279)	Yes	Halite	68	Yes	mirabilite, thenardite	2, 30	No
A7 (Z45280)	Yes	Halite	70	Yes	mirabilite, thenardite	Strong, Unmatched	No
A8	Yes	Halite	Strong	Yes	mirabilite, thenardite		No

Most likely was a testing error with A7 and a repeated test could be beneficial. Also, in comparing the results it is possible that the presence of nitrates by the salt strips, but not from

the XRD could mean that the samples taken from the larger sample amount for XRD may not have been representative, or that the concentration is so low that they were only detectible in solution. It is also possible that a longer XRD analysis could reveal low concentrations of nitrates.

Beyond the possible discrepancies in testing, it is clear that high amounts of sodium sulfate and sodium chloride are present in the majority of samples. It would be helpful to run all four samples through the XRD again at longer testing times to see if a more nuanced report would reveal a presence of nitrates or nitrites. It would also be beneficial to salt strip test alternative samples from the larger samples to evaluate homogeneity across the population.

Chapter 8: Part 2 of Testing Program: Physical Tests of Terracotta Samples

8.1 General

Given the fragile state and potential variability of the original Western Clay Manufacturing Company terracotta drain pipe new clay pipe samples were used instead for testing. The samples- 6" terracotta drain pipe (tile), were acquired from Sandkuhl Clay Works, a family owned and operated manufactory in Spencerville, Ohio. All their drainage products meet ASTM C 4 – 00 (Grade-Extra Quality). According to the MSDS Sheet the tile are predominantly aluminum silicates and quartz, (see table):

Sandkuhl Clay Works 6" terracotta drain pipe MSDS				
PRODUCT COMPONENT(S)		% BY	ACQIH	OSHA
COMPONENTS	CAS NO.	WEIGHT	TLV	PEL
ALUMINUM SILICATES	VARIOUS	75-85	10 MG/M ³	15 MG/M ³
IRON COMPOUNDS	VARIOUS	0-5	5 MG/M ³	10 MG/M ³
CALCIUM COMPOUNDS	VARIOUS	0-12	15 MG/M ³	15 MG/M ³
QUARTZ	14808-60-7	VARIES	0.025 MG/M ³	10 MG/M ³
			(RESPIRABLE)	%SI02+2
BARIUM COMPOUNDS	VARIOUS	0-3	NE	NE
MANGANESE COMPOUNDS	VARIOUS	0-3	NE	NE

Taken from the Sandkuhl Runner-Tube MSDS Sheet, that can be seen in the appendix.

Though all of their products are have a porosity between 11-13%, the facsimile samples were also analyzed in the Architectural Conservation Laboratory at the University of Pennsylvania.

The pipes were 12" tall by 1" thick, by 6" in interior diameter. They were cut with a diamond blade wet-saw to approximately 3.14"x 4" squares. After the samples were cut they were washed with water and well mixed into one large group, as to avoid bias.

Cohorts were divided into groups of three and impregnated with a 16% salt solution in an effort to reduce variability in testing. Three solutions were used:

- Sodium chloride, $NaCl$ (16% by wt.)
- Sodium sulfate, Na_2SO_4 (16% by wt.)
- $NaCl + Na_2SO_4$ (8% by wt. & 8% by wt.)
 - (Fisher Science Education-sodium chloride, lab grade-S25542A) CAS: 7647-14-5
 - (Fisher Science Education-sodium sulfate, anhydrous, lab grade-S25568A) CAS: 7757-82-6

8.2 Petrofabric Analysis

8.2.1 Introduction

The objective of my petrographic research was to compare the petrofabric of the original terracotta drain pipe from inside Kiln #8 at Western Clay Manufacturing Co. to the petrofabric of the newly manufactured terracotta drain pipe that was purchased to use for laboratory testing. Fabrics were being studied in an effort to ascertain if the newly produced drain tile could be representative of the drain tile manufactured 70 years ago. Though they are the same industrial product, it was suspected that there would be some slight variation.

Petrography is the description of minerals, rocks, and ceramic material in thin section that are observed using a polarizing light microscope (MacKenzie & Adams 1994: 9). A polarizing

or petrographic microscope is that which has a rotating stage and two types of light, plane polarized light (PPL) that is emitted from the polarizer below the stage, and crossed polarized light (XPL) that is emitted from the upper polarizer or analyzer (Nesse 1994: 16-18). PPL is similar to transmitted light and it reflects through a mineral to reveal optics of isotropic material. XPL is light that crosses PPL and reveals optics of anisotropic material (Nesse 1994: 11). Optical mineralogy and thin section petrography are used to characterize composition and can reveal aspects of production in an effort to discover provenance, trade habits and routes, and other details about life of ancient sociocultural groups (Quinn 2013: 71). This type of analysis can also be performed for more recent cultural material. For this petrographic analysis, standard thin sections were ground in oil and embedded in blue epoxy to display porosity.

8.2.2 Petrographic Summary

8.2.2.1 *Original Fabric, Terra-cotta from WCMC (Tile C)*

Dense, iron-rich, coarse-grained matrix-supported fabric with rock fragments, grog, shale, quartz, feldspars (plagioclase, orthoclase), chert, and muscovite mica. Fabric has low porosity with pores being predominantly channels. Inclusions are medium to coarse sand-size, and are poorly sorted with a slight orientation, parallel to the substrate. Evidence of firing temperatures of at least 1160° C, because calcite has melted completely and felsic inclusions exhibit the beginning stages of melting with diffuse boundaries (Rice, 1987). Common inclusions, such as quartz are heavily altered signifying the inclusions were stressed. Temper consists of crushed rock fragments and two types of ceramic grog, one being most likely consisting of the same body. Iron-rich concentration features and large inclusions of shale show

what could potentially be temper, but due to the variability in size of particles is most likely naturally occurring.

8.2.2.2 Sample Fabric, Terra-cotta from Sandkuhl Clay Works (Tile A)

Iron-rich, coarse-grained matrix-supported fabric with rock fragments, shale, quartz, calcite, feldspars, pyroxenes and muscovite mica. Fabric has very low porosity, with pores being channels that have an orientation parallel to the substrate. Inclusions are medium to coarse sand-size, and are moderately sorted. Evidence of firing temperatures between 870-1160°C, as the calcite has melted partially, some being partially present as rims around open pores, as well as fully present with discernable melt rims around grain boundaries. Felsic inclusions also exhibit the beginning stages of melting with diffuse boundaries, which means that this fabric most likely reached the higher temperature but only soaked at 1160°C for a very short time (Rice, 1987). Common inclusions, such as quartz and feldspars are heavily altered signifying the inclusions were stressed. Temper consists of crushed rock fragments and two types of ceramic grog, one being most likely consisting of the same body. Iron-rich concentration features and large inclusions of shale show what could potentially be temper, but due to the variability in size of particles is most likely naturally occurring. Clay pellets, identical to the matrix signifies that even though this clay was industrially produced, the clay constituents were not fully crushed and weathered before clay mixing.

8.2.3 Fabric Comparison

Ultimately the original and sample fabric are similar, but definitely not identical. The fabrics have essentially the same types of inclusions, and the overall material composition is

very much the same. The differences between the two fabrics has to do with the difference in clay preparation, and firing. The WCMC fabric, though “industrially” manufactured, shows that the clay and temper constituents were not ground to a consistent mesh size. Instead the fabric is very densely populated with poorly sorted, roughly crushed, coarse aggregate. A variety of materials were used as temper, and it was clear that there was far less standardization in terms of clay recipe and mixing. Additionally, it also exhibits a higher porosity than the sample fabric, having many interconnecting micro-channels, which most likely has to do with the way it was manufactured. Both samples were extruded, but the original, appears less compacted, a product of being extruded through a machine that had less compressive power. As for the sample material, which is ASTM grade- the fabric is far more homogeneous and less dense and porous, most likely extruded through a high-pressure, state-of-the art extruder, exhibited in the stronger parallel preferred orientation of inclusions and pores. The sample fabric has a greater amount of open matrix, and therefore phyllosilicates in addition to the inclusions that are moderately sorted and ground to smoother more homogeneous shape.

Both fabrics were clearly fired in an oxygen-rich environment, being bright red, and appear to be fired generally to the same temperature. What differentiates them is that the original fabric was likely brought up to 1160°C and soaked at that temperature for several days, as all calcite has melted. The sample fabric either was fired to a lower temperature, or more likely was brought up to at 1160°C but only briefly soaked at this temperature, perhaps less than a day. It is hypothesized that the latter took place because of its diminished visible porosity, darkness in color, and melting felsic materials.

It is likely that these materials would perform similarly, but not exactly the same. The original fabric could potentially be stronger in terms of material strength, due to it being slightly more vitrified than the sample fabric, but being more permeable and porous, exhibiting dominant micropores, and frequent meso and macropores, means it would be more susceptible to moisture ingress and a higher level of subflorescence. Recent research has confirmed that crystallization takes place in micropores, where larger pores act as reservoirs which collect and supply solution to the capillaries. This means the variation in size of the pores in the original fabric, makes it even more susceptible. The sample fabric, having far less pores total, generally has mesopores, which are less susceptible to being the site of crystallization with high supersaturation (Doehne & Rodriguez-Navarro 1999: 206). Therefore, it can be assumed that the sample material would be slightly more durable when subjected to salt weathering, and that observed deterioration would be slightly less severe than what would occur in the original fabric. The sample fabric, being highly standardized can be considered representative of all mid-range industrial terracotta.

8.3 Cold Water Absorption by Total Immersion

In an effort to obtain the water absorption rate of the facsimile samples, the “*Water Absorption by Total Immersion*” laboratory test, based on ASTM C97-96 and C67 – 12, was conducted. It was a conscious choice to perform this test as opposed to the ASTM C20 – 00 in order to observe how these tiles, an example of industrial terracotta ware, would absorb moisture similarly to field conditions. This test was also performed because the absorption rate of the uncontaminated samples was later compared to the absorption rate of salt-contaminated tiles, which would provide skewed results if heated, as specified by ASTM C20-00.

The porosity and rate of absorption of one cohort of facsimile samples was calculated as a function of water absorption using gravimetric analysis. Samples were dried in an oven to a constant weight at 75°C. At constant weight they were removed and allowed to cool to room temperature in a desiccator for 40 minutes. Samples were then weighed and immersed into a non-reactive container filled with room-temperature deionized water. Samples were placed with the largest upward curved surface pointing up, and were replaced in the same position after each measurement. Each cohort was stored in its own plastic immersion bin and was covered with a plastic lid between measurements to avoid excess evaporation or contamination. When measuring, excess bulk moisture on the surface of the samples was blotted with a paper towel before being weighed. Measurements of absorption were taken at 5, 20, 40, 60, 120, 180, and 480 minutes, followed by every 24 hours from the initial immersion time until the samples reached full saturation. Full saturation was characterized by being within 0.01 grams of the same weight over two days. After saturation, samples were weighed hydrostatically, in deionized water and in air, hung by a wire. Samples were also immersed in a beaker with a known amount of water, and their apparent volume was recorded using Archimedes Principle. The indirect measurement of porosity, apparent and real volume, and apparent and real density were calculated from measurements (see table).

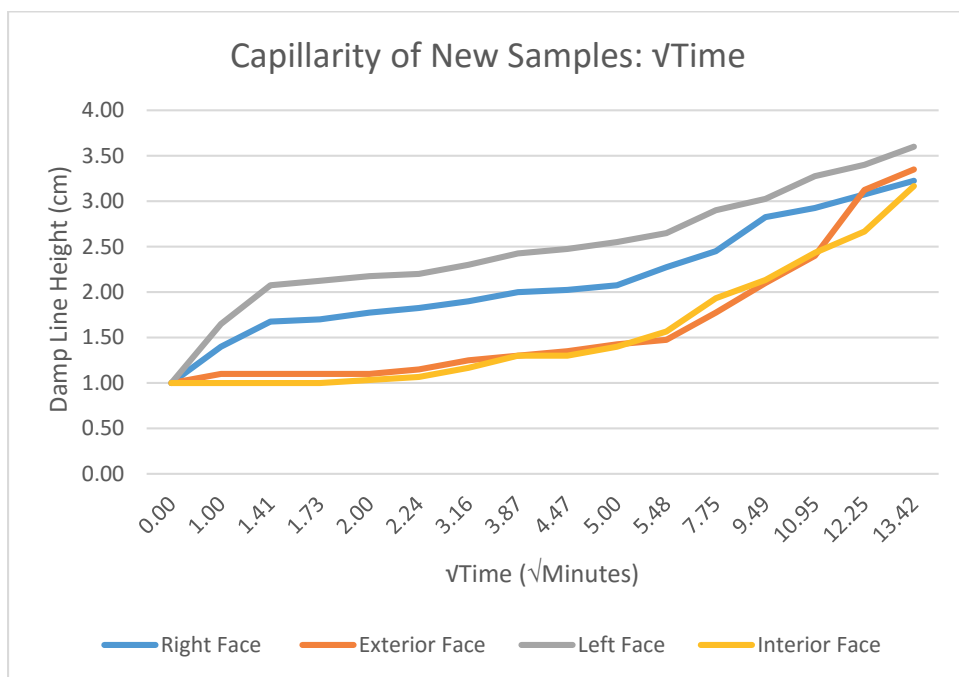
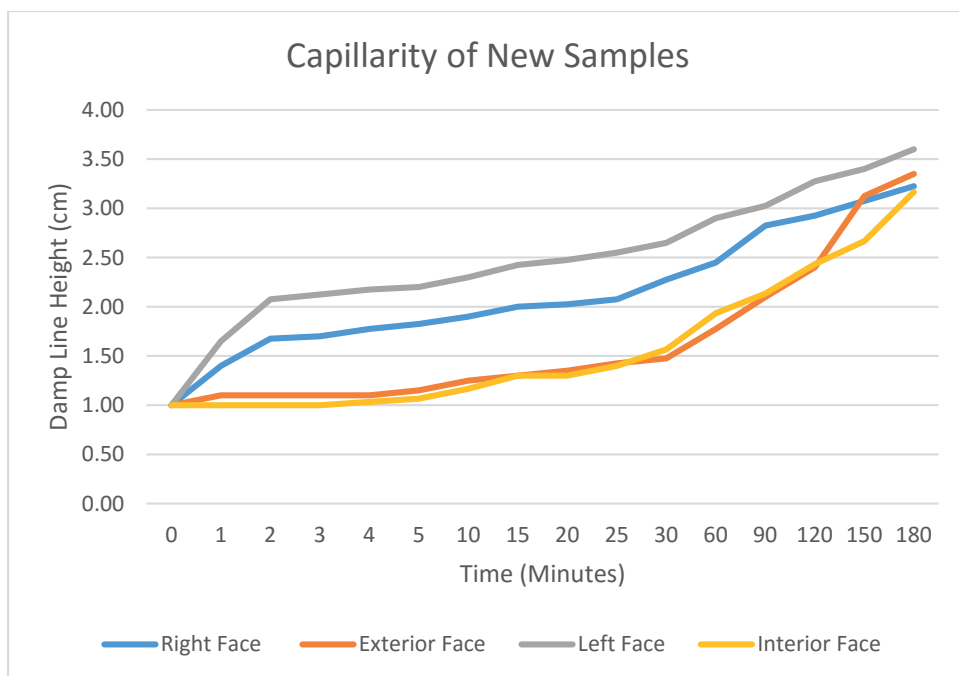
8.4 Capillarity

The capillary suction of the facsimile samples was tested using the, *“Initial Rate of Absorption (Suction) (Laboratory Test)”* specified in ASTM C67 – 12. Samples were dried in an oven to constant weight at 75°C. At constant weight they were removed and allowed to cool to room temperature in a desiccator for 30-40 minutes. Samples were then set upright, on top of a

layer of glass rods, laid inside of a square non-conductive container. Room-temperature deionized water was added until 1 cm of the base of the samples was immersed in water. Water was added periodically to maintain the 1 cm depth. The height of the advancing damp line was measured on each face of each sample every minute for five minutes, then every five minutes until 30 minutes. After, measurements were taken at 60, 90, 120, 150, and 180 minutes (See appendix).

8.4.1 Results

The results reveal that the interior and exterior faces are less porous and permeable, as the capillary suction was extremely slow until about 30 minutes into the test, when the base was potentially saturated from the cut sides in contact with the water. The interior and exterior are however porous as the continuous curve upward illustrates. This is not a surprise as these are the faces that have the “fireskin” which is an accumulation of clay fines that were vitrified into a dense, nearly non-porous layer on the exterior surfaces of the ware. The other two faces were the narrower sides (1” thick) that had been cut with a diamond saw, exposing the clay underbody that is much more porous and permeable. It is likely that the two surfaces with the fireskin began to gain moisture when the interior reached saturation from capillary uptake taking place through the two cut faces. This test provides insight into how terracotta takes up water when it’s fireskin is intact (i.e. the interior and exterior faces), and when a surface has experienced surface erosion, or spalling (i.e. the cut faces).



Chapter 9: Part 3 of Testing Program: Salt Contamination and Testing of Salt Crystallization Inhibitors

9.1 General

The tests were designed in an effort to reproduce in-situ conditions that were moderately controlled as to obtain viable results. Hence, the tests were designed differently than the majority of previous lab experiments on the effectiveness of inhibitors published up to this point. That is why the inhibitors were not mixed into the initial salt solution but applied on previously salt-contaminated samples.

Application of four different solutions of inhibitors were applied separately to contaminated cohorts while leaving the controls untreated. The four different inhibitor solutions were:

- potassium ferrocyanide (0.1 % w/w) (PFC)
 - potassium ferrocyanide trihydrate Reagent Grade S25489A (Fisher Science Education)
- sodium ferrocyanide (0.1 % w/w) (SFC)
 - sodium hexacyanoferrate (II) decahydrate 99% W29B008 (Alfa Asar)
- potassium ferrocyanide (0.1 % w/w) + hexametaphosphate (0.1 % w/w) (PFC+SHMP)
 - sodium hexametaphosphate SX0583-3 (EMD)
- sodium ferrocyanide (0.1 % w/w) + hexametaphosphate (0.1 % w/w)¹¹ (SFC+SHMP)

9.2 Cold Water Absorption by Total Immersion with Inhibitors

The porosity and rate of absorption of uncontaminated, contaminated, and treated samples were calculated as a function of water absorption using gravimetric analysis. Each test

¹¹ After samples were treated with the inhibitor solutions was it found that the deionized water that the solutions were made with was highly acidic. It was then found that the deionizing filters had expired, and all deionized water being produced at that time had a pH of approximately 4.6. The pH of the inhibitor solutions fell between a pH of 4.6 and 5. The effects of this on the performance of the inhibitors is unknown, and if this test be replicated, it should be replicated with pH neutral deionized water.

was carried out threefold, being three samples to a cohort. Samples were dried in an oven to a constant weight at 75°C. At constant weight they were removed and allowed to cool to room temperature in a desiccator for 40 minutes. Samples were then weighed and immersed into one of three non-reactive containers filled with one of three 16% w/w aqueous salt solutions. After 24 hours, samples were removed from salt solution and dried to a constant weight. After, one cohort was established as the contaminated salt control and were fully immersed in clean deionized water. The rest were immersed in one of four different 0.1% (SFC & PFC) or 0.2% (SFC+SHMP & PFC+SHMP) w/w inhibitor solutions. After 24 hours all tiles were removed, patted dry with a cotton cloth and weighed. They were put in an oven at 75°C and dried to a constant weight.¹² At constant weight they were removed and allowed to cool to room temperature in a desiccator for 40 minutes.

Samples were then placed in a bin filled with room-temperature deionized water with the largest upward curved surface pointing up. Each cohort was stored in its own plastic immersion bin and was covered with a plastic lid between measurements to avoid excess evaporation or contamination. When measuring, excess bulk moisture on the surface of the samples was blotted with a paper towel before being weighed. Samples were replaced in the same position after each measurement. Weight was measured at 5, 20, 40, 60, 120, 180, and 480 minutes, followed by every 24 hours from the initial immersion time until the samples reached full saturation. Full saturation was characterized by being within 0.01 grams of last measurement. After saturation, samples were weighed hydrostatically, in deionized water and in air, hung by a wire. Samples were also immersed in a beaker with a known amount of water,

¹² About 7 days.

and their apparent volume was recorded using Archimedes Principle. The indirect measurement of porosity, apparent and real volume, and apparent and real density were calculated from measurements (see table).



Figure 13- Performing Gravimetric Analysis.

9.2.1 Results & Discussion

Ultimately SFC with the addition of SHMP was the only inhibitor that produced results that were statistically significant in increasing porosity and increasing the percent of water absorption over time¹³, specifically only in the cohort contaminated with sodium chloride.¹⁴ However, the reduction of porosity that occurs when sodium chloride crystallizes inside a pore

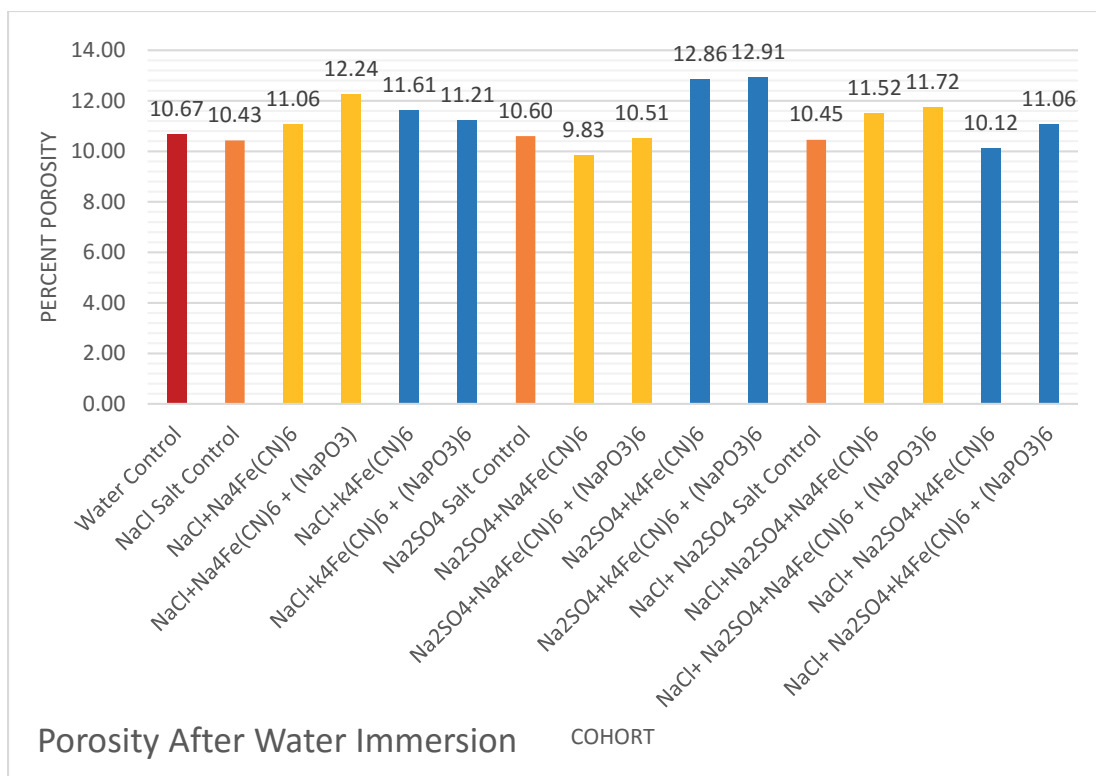
¹³ 96 hours

¹⁴ Percent of porosity of the treated cohorts were compared to the percent porosity of the untreated cohort using a paired T-Test for means, with a 95% confidence level.

system is not particularly damaging; sodium chloride has a tendency to crystallize at the air-salt solution interface in small capillaries; in effect cementing the pores closed, which actually reduces further damage (Doehne & Rodriguez-Navarro 1999: 201). So in this circumstance, the increase in porosity and water absorption of a sample contaminated with NaCl is not beneficial. Increased porosity and water absorption would be beneficial in the case of sodium sulfate crystallization, as it is the slow capillary flow and low surface tension of the solution that contributes to the causation of subflorescence. Faster replenishment of liquid water could contribute to salt solution transport to the surface, increasing the chance that evaporation would occur at the surface as opposed to beneath the surface, in effect reducing subflorescence (Doehne & Rodriguez-Navarro 1999: 204-05). This test however, did not produce any reduction in porosity that was statistically significant or increase porosity and water absorption in the sodium sulfate cohort.

Results regarding the percentage of water absorption after 24 hours from the absorption test were cross-referenced with the data produced from the evaporation test, as the samples for the evaporation test also soaked in deionized water for 24 hours before beginning the monitored evaporation. Results were conclusive that the treated cohorts did not produce statically significant results regarding water absorption increase or decrease.

Cold Water Absorption by Total Immersion Results: Percent Difference from Controls			
Cohort	Percent Porosity (%)	Difference From H ₂ O Control (%)	Difference from Salt Control (%)
Water Control	10.84		
NaCl Salt Control	9.61	-0.23	
NaCl+Na ₄ Fe(CN) ₆	10.84	0.39	0.63
NaCl+Na ₄ Fe(CN) ₆ + (NaPO ₃) ₆	13.06	1.57	1.81
NaCl+k ₄ Fe(CN) ₆	12.86	0.94	1.18
NaCl+k ₄ Fe(CN) ₆ + (NaPO ₃) ₆	7.26	0.54	0.77
Na ₂ SO ₄ Salt Control	12.85	-0.06	
Na ₂ SO ₄ +Na ₄ Fe(CN) ₆	11.16	-0.83	0.77
Na ₂ SO ₄ +Na ₄ Fe(CN) ₆ + (NaPO ₃) ₆	10.81	-0.16	0.09
Na ₂ SO ₄ +k ₄ Fe(CN) ₆	12.78	2.20	2.26
Na ₂ SO ₄ +k ₄ Fe(CN) ₆ + (NaPO ₃) ₆	11.46	2.25	2.31
NaCl+ Na ₂ SO ₄ Salt Control	9.38	-0.21	
NaCl+Na ₂ SO ₄ +Na ₄ Fe(CN) ₆	12.83	0.85	1.06
NaCl+ Na ₂ SO ₄ +Na ₄ Fe(CN) ₆ + (NaPO ₃) ₆	11.81	1.06	1.27
NaCl+ Na ₂ SO ₄ +k ₄ Fe(CN) ₆	12.07	-0.66%	0.33
NaCl+ Na ₂ SO ₄ +k ₄ Fe(CN) ₆ + (NaPO ₃) ₆	12.74	+0.27%	0.61



9.3 Evaporation Test

The rate of evaporation of uncontaminated, contaminated, and treated samples was calculated using gravimetric analysis. Each test was carried out threefold, being three samples to a cohort. Samples were dried in an oven to a constant weight at 75°C. At constant weight they were removed and allowed to cool to room temperature in a desiccator for 40 minutes. Samples were then immersed into one of three non-reactive containers filled with one of three 16% w/w aqueous salt solutions. The control cohort was immersed in deionized water. After 24 hours, samples were removed, weighed and stored at 20.5°C ± 5° 25% RH ± 15 in a large desiccator, to promote constant evaporation and to avoid re-precipitation or hydration of salts.¹⁵ Samples

¹⁵ Variability in controlled conditions was due to the discovery that the desiccant in the desiccator had expired and was no longer effective. After new desiccant was acquired, the variability was reduced. If test be replicated, conditions should be controlled to a greater degree, using fresh desiccant.

were then weighed every 24 hours thereafter until weight stabilized within 0.01 g of last measurement.

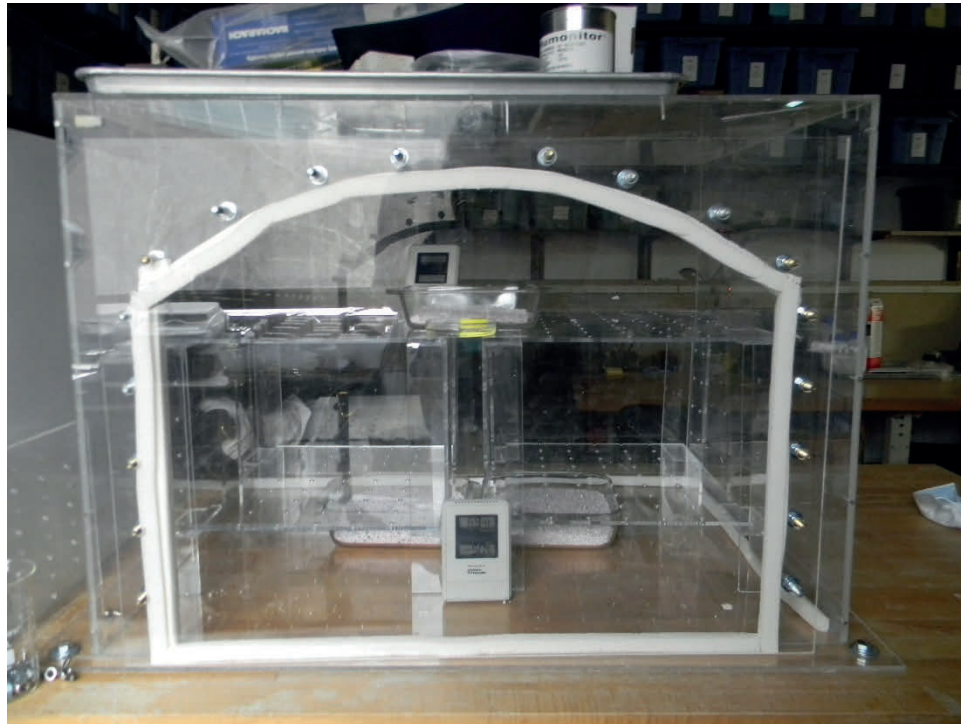
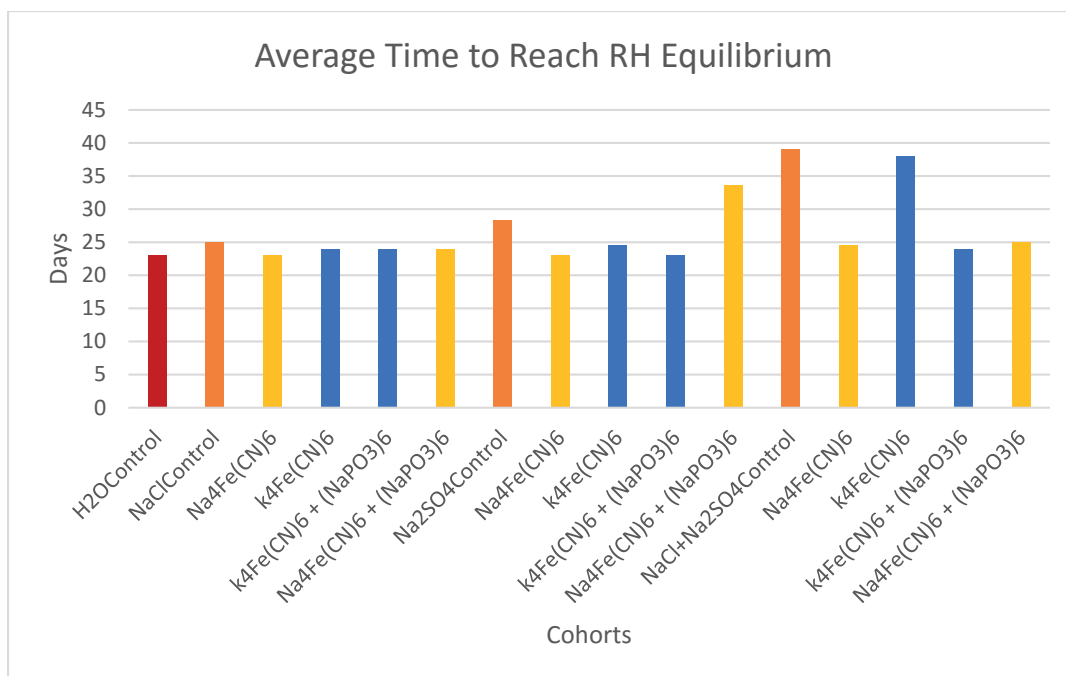


Figure 14-Large desiccator designed for evaporation test.

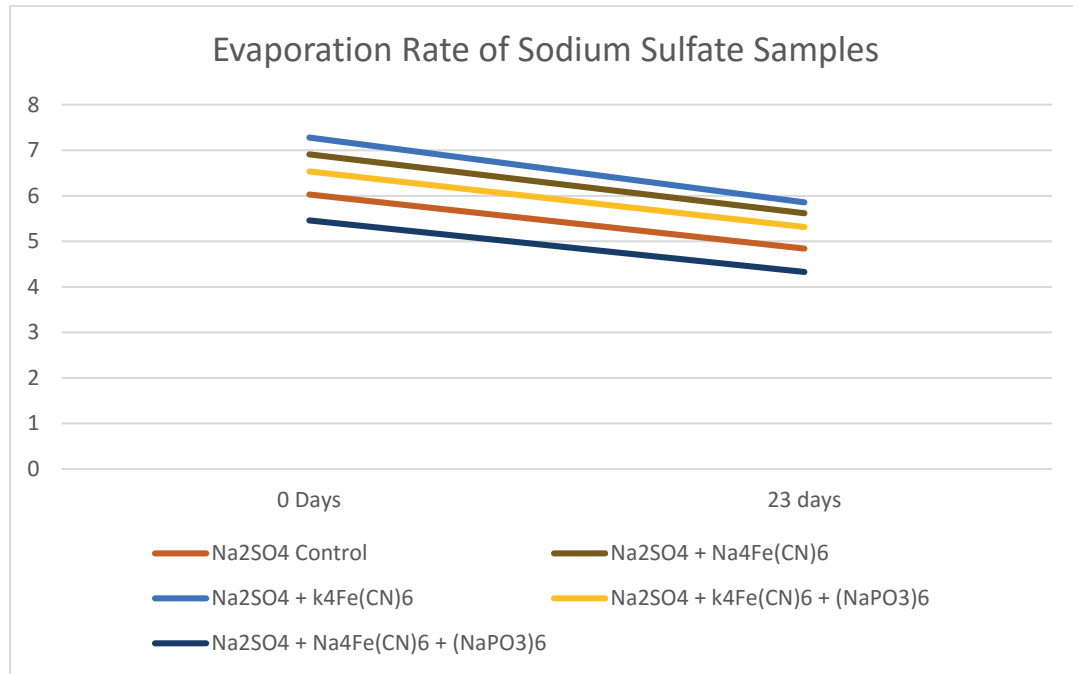


9.3.1 Results & Discussion

Subjecting the samples to low RH conditions promoted a more rapid rate of evaporation overall. It was observed that only SFC with the addition of SHMP had an effect on slowing the evaporation rate specifically of sodium sulfate, however that result was not statistically significant. SFC did significantly increase the rate of evaporation¹⁶ over a 23-day period, of the sample cohort contaminated with sodium sulfate, however this result should be further investigated, as SFC did not have this effect in any other case. Ultimately, it was found that all inhibitors, except for SFC when applied to sodium sulfate, did not significantly change the

¹⁶ Rate define as percentage of weight (grams) loss over time (23 days).

evaporation rate at all, which can be considered positive as increasing the evaporation rate would increase damage potential (Doehne & Rodriguez-Navarro 1999: 205)¹⁷.



9.4 Crystallization Test

9.4.1 Durability Test 1

Each test was carried out fourfold, being four samples to a cohort. Samples were dried in an oven to a constant weight at 75°C. At constant weight they were removed and allowed to cool to room temperature in a desiccator for approximately 60 minutes. Samples were then weighed and immersed into one of three non-reactive containers filled with one of three 16% w/w aqueous salt solutions, or deionized water (controls) for 48 hours. Samples were then

¹⁷ It was found by Rodriguez-Navarro & Doehne that increasing the evaporation rate of a salt solution actually increased the supersaturation ratio of the solution and promoted crystallization beneath as opposed to above the surface of a material.

removed from their respective solutions and placed into an oven at 75°C for 25 hours. This cycle was repeated once more and then traded for a capillary suction program. Samples were stood upright on a layer of glass rods in a non-reactive plastic bin, that was then filled with a ¼" of each group's respective salt solutions. Samples were stored like this, partially immersed, in open-air, in a room where the air changes are minimal and the ambient environment is generally 20.5°C ± 10 and 25% RH ± 18.

This capillary suction program was chosen, in an effort to induce rapid damage. Highest supersaturation ratios are achieved under constant capillary rise, at low RH (Doehne & Rodriguez-Navarro 1999: 201). Samples were also stored in front of a large window, exposed to daily light cycles. Salt solution was added to maintain contact with the base of the samples. Samples were left in this setup for four weeks, and were recorded visually through photography and photomicrography. When removed, the accumulated efflorescence was scraped off the samples' surface and they were put into an oven and dried until constant weight at 75°C. Samples were weighed to ascertain the amount of total loss, in terms of desalination and material loss. Spalled material was collected from each cohort bin, filtered, dried, and weighed in order to ascertain the amount of spall that occurred over the durability test. The first four samples of each salt solution (twelve total) were broken in half and studied by means of Scanning Electron Microscopy (SEM), using an FEI Quanta 600 model, equipped with an Energy Dispersive X-ray system of EDAX. Low magnification (100-500x) was used to identify salt location, distribution and clustering, and high magnification (2000-5000x) was used to study salt crystal morphology. A Back Scattered Electron (BSE) detector was used to distinguish salts from the terracotta substrate. The chamber pressure within the ESEM was set to 0.53 Torr, and the voltage was set to 5 KV.



Figure 15-Capillary Suction program setup.

9.4.2 Durability Test 2

The rest of the samples were then allowed to cool to room temperature in the open air. After samples were weighed, and then immersed in a plastic bin filled with one of four different inhibitor solutions, and the controls were immersed in deionized water. Samples were covered and stored for 24 hours, after which they were taken out and stored at 20.5 ± 6 25% RH $\pm 10\%$ in a desiccator for 7 days. The samples were then dried in an oven at 75°C until constant weight, and weighed. Samples were then set up in an identical capillary-suction program as before, except that the base was immersed in $\frac{1}{4}\%$ deionized water, as opposed to salt solution. Samples were left in this setup for four weeks, and were recorded visually through photography and photomicrography. When removed, the accumulated efflorescence was scraped off the samples' surface and they were put into an oven and dried until constant weight at 75°C . Samples were weighed to ascertain the amount of total loss, in terms of desalination and

material (spall) loss. Spalled material was collected from each cohort bin, filtered, dried, and weighed in order to ascertain the amount of spall that occurred over the durability test. After the second durability test, a sample from each cohort, including the control cohort (fifteen total) were broken in half and studied by means of Scanning Electron Microscopy (ESEM), using an FEI Quanta 600 model, equipped with an Energy Dispersive X-ray system of EDAX. Low magnification (100-500x) was used to identify salt location, distribution and clustering, and high magnification (2000-5000x) was used to study salt crystal morphology. A Back Scattered Electron (BSE) detector was used to distinguish salts from the terracotta substrate. The chamber pressure within the ESEM was set between 0.53-.75 Torr, and the voltage was set between 5-15 KV.

9.4.3 Results & Observations

It was observed that all tiles had a great deal of surficial powdering and spalls after durability test one, and was confirmed after filtering, drying and weighing each cohort's respective spalled material. It was observed that most tiles had some surficial powdering and spalls after durability test two, those primarily being the Na_2SO_4 and $\text{NaCl}/\text{Na}_2\text{SO}_4$ contaminated samples, and was confirmed after filtering, drying and weighing each cohort's respective spalled material.

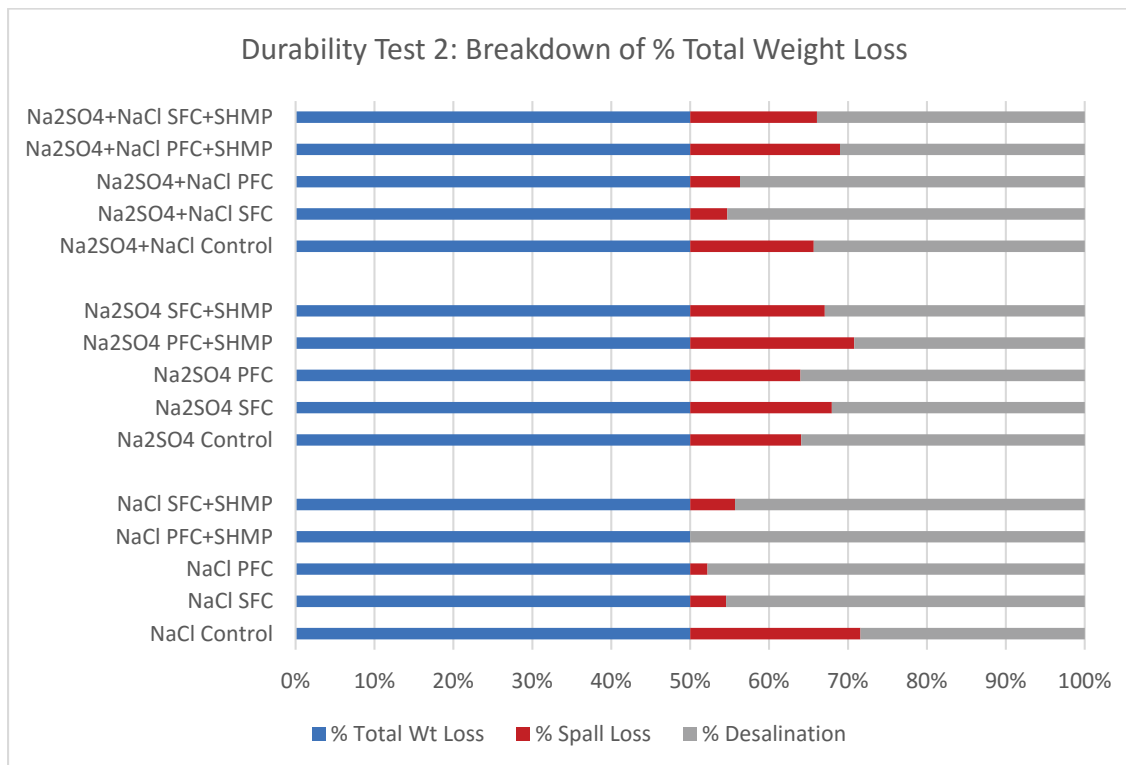
It was found that the amount of damage incurred during durability test 1 and 2 was different, being significantly less during test 2, even for the control cohorts.¹⁸ This could have been a product of one major variation; in durability test 1, the tiles were partially immersed in

¹⁸ Results were compared between test 1 and 2 using a paired T-Test for means, with a 95% confidence level.

their respective salt solution, whereas in durability test 2, samples, being contaminated already and treated, were partially immersed in just deionized water. Having samples set in salt solution most likely promoted a more accelerated weathering scenario, as opposed to the samples being set in water, where slightly more desalination could occur. It was decided that it would be inappropriate to compare the results from test 1 and 2, and instead, test 2 results from treated cohorts would be statistically compared to the untreated cohort.

Durability Test 2: Results			
Cohort	Total Wt. Loss (%)*	Spall Loss (%)*	Desalination (%)*
NaCl Control	0.95	0.41	0.54
NaCl+Na ₄ Fe(CN) ₆	0.88	0.08	0.80
NaCl+k ₄ Fe(CN) ₆	0.68	0.03	0.65
NaCl+k ₄ Fe(CN) ₆ + (NaPO ₃) ₆	0.91	0.00	0.91
NaCl+Na ₄ Fe(CN) ₆ + (NaPO ₃) ₆	0.88	0.10	0.78
Na₂SO₄ Control	1.03	0.29	0.74
Na ₂ SO ₄ +Na ₄ Fe(CN) ₆	0.78	0.28	0.50
Na ₂ SO ₄ +k ₄ Fe(CN) ₆	0.68	0.19	0.49
Na ₂ SO ₄ +k ₄ Fe(CN) ₆ + (NaPO ₃) ₆	0.77	0.32	0.45
Na ₂ SO ₄ +Na ₄ Fe(CN) ₆ + (NaPO ₃) ₆	0.85	0.29	0.56
NaCl/Na₂SO₄ Control	3.00	0.94	2.06
NaCl/Na ₂ SO ₄ +Na ₄ Fe(CN) ₆	1.38	0.13	1.25
NaCl/Na ₂ SO ₄ +k ₄ Fe(CN) ₆	0.87	0.11	0.76
NaCl/Na ₂ SO ₄ +k ₄ Fe(CN) ₆ + (NaPO ₃) ₆	1.08	0.41	0.67
NaCl/Na ₂ SO ₄ +Na ₄ Fe(CN) ₆ + (NaPO ₃) ₆	1.40	0.45	0.95

*All loss is expressed as a percentage of the weight of the tile. The weight of the spalled material from each cohort was subtracted from the average weight of total loss of each cohort to find the average percent of desalination.



9.4.3.1 Sodium Chloride Contaminated Samples

In comparing the percentage of total loss of the untreated cohort to each treated cohort, it is not immediately apparent that any inhibitors had a positive effect on the NaCl contaminated samples. However, when the percent total loss is broken down into the percent of spall and percent of desalination, it becomes apparent that each inhibitor significantly reduced the amount of spall in comparison to the control, being reduced as low as an imperceptible amount by the PFC+SHMP. PFC was the next most successful, reducing spall from 0.41% to 0.03% and SFC, as well as SFC+SHMP reduced spall to 0.08% and 0.10% respectively. In addition, the amount of desalination was also significantly increased by each inhibitor, being almost doubled by PFC+SHMP.

9.4.3.1.1 NaCl Control

The efflorescence observed over a four-week period developed from a thin uniform well-adhered crust that accumulated at the top of the tile, into a thick crust, that was adhered at the top surface but grew off the surface in tendrils. The crust appeared to be formed by microscopic halite crystals that enveloped the top of the tiles, along the capillary fringe. Surficial powdering and spall was observed as early as the first two days. SEM after four weeks, revealed fairly large, stacked rhombohedral crystals that were surrounded by skeletal non-equilibrium crystal growth inside the pores of the terracotta. The salt did not appear to fill the pores completely.

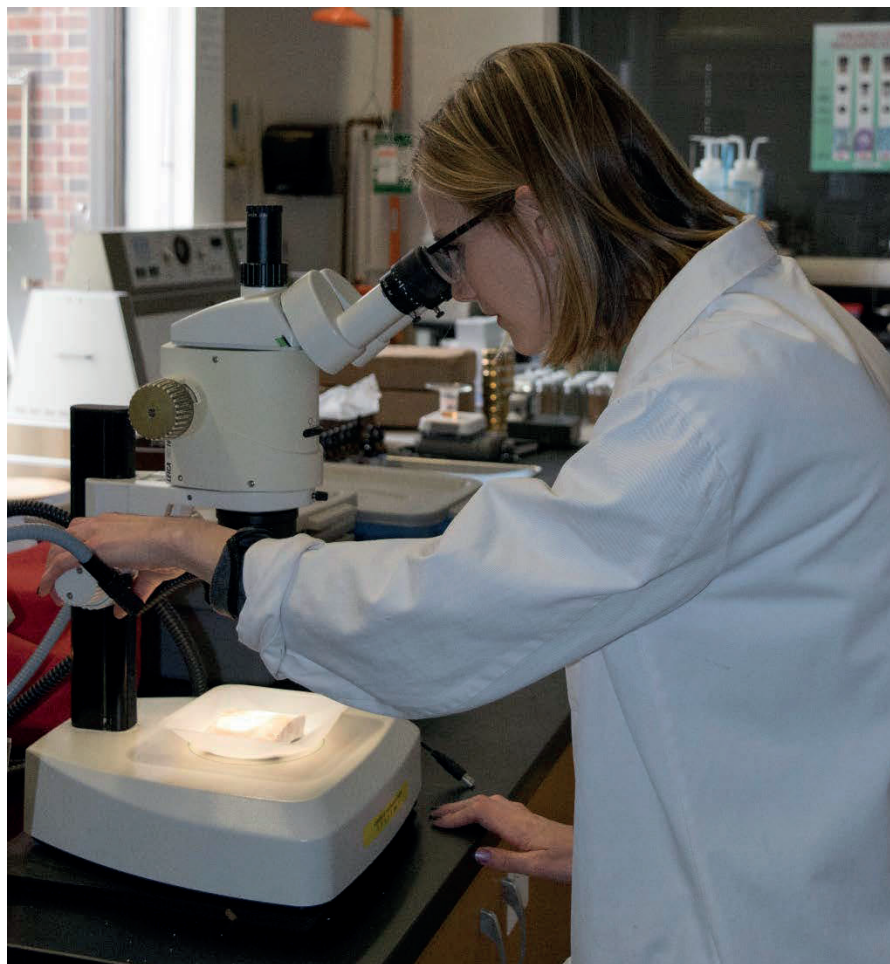


Figure 16-All samples were inspected with a Leica MZ16a Microscope periodically.

9.4.3.1.2 NaCl + SFC

The efflorescence observed began as individual plumes of white dendrite crystals. Very large crystals formed along the top edges initially along with sporadic smaller plumes that were low and closely adhered to the surface. They grew into large yellow dendrites that eventually merged to form large bulbous clumps that were extremely loosely adhered.¹⁹ The dendritic growth on two samples followed the distribution pattern of the untreated control. On these two

¹⁹ Dendrites would fall off with the slightest disturbance.

samples, dendrites remained shorter and more evenly distributed over the top of the tile at the capillary fringe. Two other tiles exhibited very little efflorescence growth after the initial growth fell off, having dendrites sprout mainly from the top corners of the tile and sporadically down about ¼" from the top. On these tiles crystals continuously fall off under their own weight. SEM showed that after four weeks a mixture of whisker, hopper, and prismatic crystal growth formed inside the pore. The crystals did not fill the interior of the pore, but amassed on one side of it.

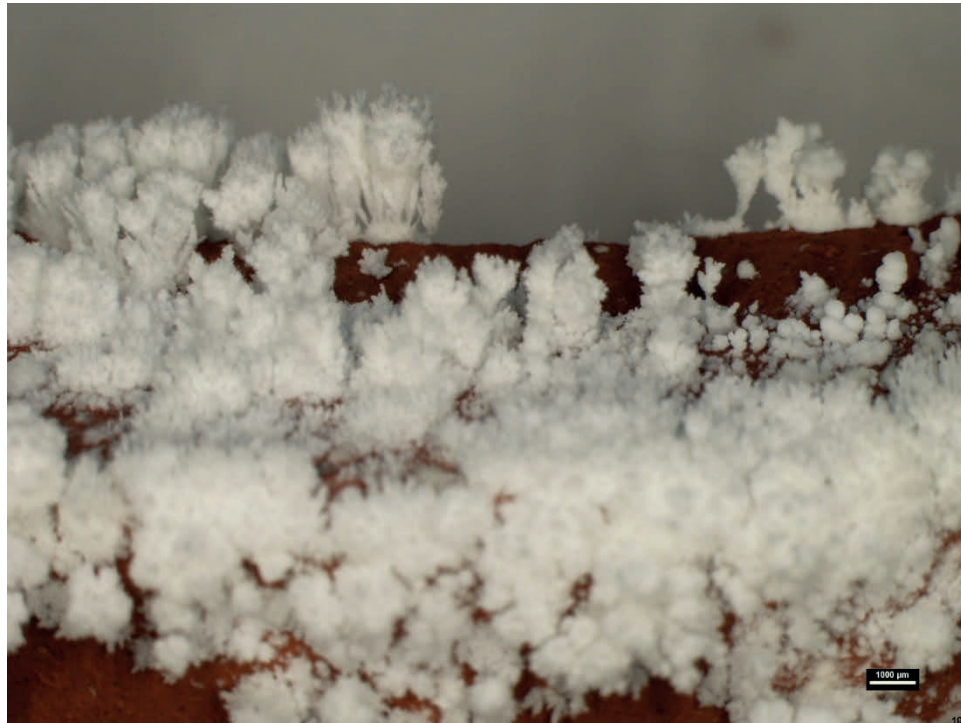


Figure 17-Example of Dendritic Efflorescence Growth of NaCl+SFC

9.4.3.1.3 NaCl + PFC

The efflorescence observed began as crawling spots of dendritic growth along with individual tufts of dendrite crystals that grew sporadically on the top half of the faces of the tile. Tall yellow dendrites sprouted straight out of the top edges and corners, forming large clumps in

areas. Over time the dendrites merged to form extended bulbous clumps that would periodically fall off under their own weight. However, when efflorescence was scraped off at the end of the durability test, some crystal growth on the front face of the tile, along the damp line were extremely tenacious, and were very difficult to scrape off. This occurred on two tiles that had crystal growth that largely followed the same distribution as the untreated control cohort, but with less density. The other tiles generally had growth along the top corners of the tile with sporadic crystals ranging within a ½" from the top of the tile, and those crystals were easily removed. SEM showed that after four weeks a fairly homogenous, non-equilibrium mass of crystal growth filled the interior of the pores. Crystals were skeletal and appeared to increase in density if the pore was smaller.

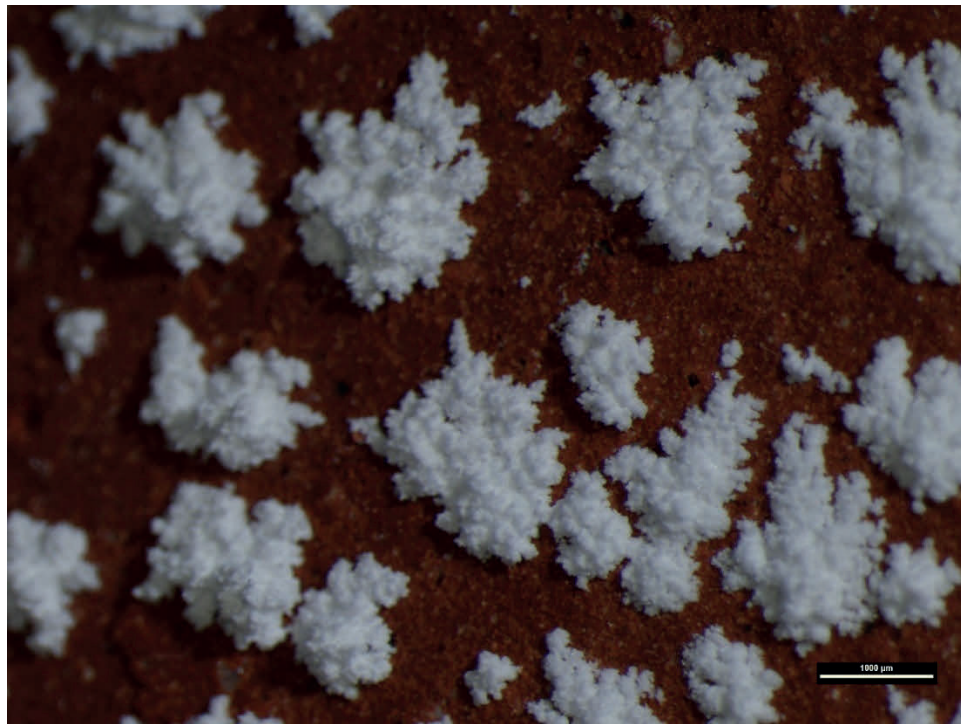


Figure 18-Example of individual tufts of dendritic growth on NaCl+PFC

9.4.3.1.4 NaCl + PFC + SHMP

Similar efflorescence was observed on three tiles where in that the crystals immediately appeared as loosely adhered, sporadic, individual, tall dendrites, that collected in bunches along the top edges and surface of the tiles. Dendritic tufts also sprouted sporadically on the faces of the tile within 1" from the top. The anomalous tile initially grew crawling spots of dendritic growth across the surface. Over time this tile grew a denser cover of yellow dendrites at the capillary fringe that then crept halfway down the tile surface. Density was still greatest at top edges where dendrites merged to form large yellowish clumps. SEM revealed that after four weeks, dense non-equilibrium/skeletal crystal growth filled the pores. Random prismatic crystals were also observed at 3000x.



Figure 19- Crystallographic change: Day 4 of NaCl + PFC + SHMP

9.4.3.1.4 NaCl + SFC + SHMP

On two samples, efflorescence began as a dense spattering of individual dendritic tufts that were closely adhered to the surface, and covered the top of the samples. That growth was replaced by tall yellow dendrites that stuck out perpendicularly to the substrate. Over time the dendrites merged to form large clumps that would periodically fall off under their own weight. By the end of the test, these tiles generally only had growth along the top surface and edges of the tile with sporadic crystals ranging within 1" from the top of the tile, and those crystals were easily removed. The other two tiles exhibited crystal distribution that was similar in location and density as the control cohort. There were taller dendrites along the damp line with sporadic crystals below the front (potentially "creep") as well. SEM showed that after four weeks, interior crystallization was similar to other treated samples, being generally non-equilibrium skeletal growth. Though, there was a high proportion of hopper crystals, and some random prismatic and tabular crystals. Growth observed filled the pores completely.

9.4.3.2 Sodium Sulfate Contaminated Samples

The test results for test 2 show that no inhibitor had a positive effect on the durability of the Na_2SO_4 contaminated samples. In fact, it appears that each inhibitor slightly reduced desalination, while the amount of spall remained unchanged, signifying the inhibitors had a slightly negative effect. Spall was visible from the first several days, appearing in the water of each bin and detached in the efflorescence; the mixture of salt and terracotta spall appearing as a pink crust.



Figure 20-Sodium Sulfate control cohort after four weeks of Durability Test 2

Over four weeks, the efflorescence of the treated samples for the most part did not crystallize any differently than the untreated control, what little variation that occurred proved insignificant over time.²⁰ However, when SEM was performed after four weeks it was clear that the crystallization within the pore systems of the treated cohorts had changed. The crystallization of untreated sodium sulfate appeared as bulky bubble-like non-equilibrium crystals that filled the pores. With the addition of SFC, subflorescence appeared as large whisker crystals surrounded by small clumps of whisker and hopper crystals that only partially filled the pore. With the addition of PFC, subflorescence appeared as tiny acicular crystals, with a few large prismatic crystals, filling the pores. PFC+SHMP changed the sodium sulfate crystals to very

²⁰ The cohort treated with SFC exhibited a crust consisting of crystal “zones”, that had the appearance of crop circles (see Figure 21).

tiny voluminous whisker crystals. SFC+SHMP changed the crystal habit to very tiny clusters of short acicular crystals.

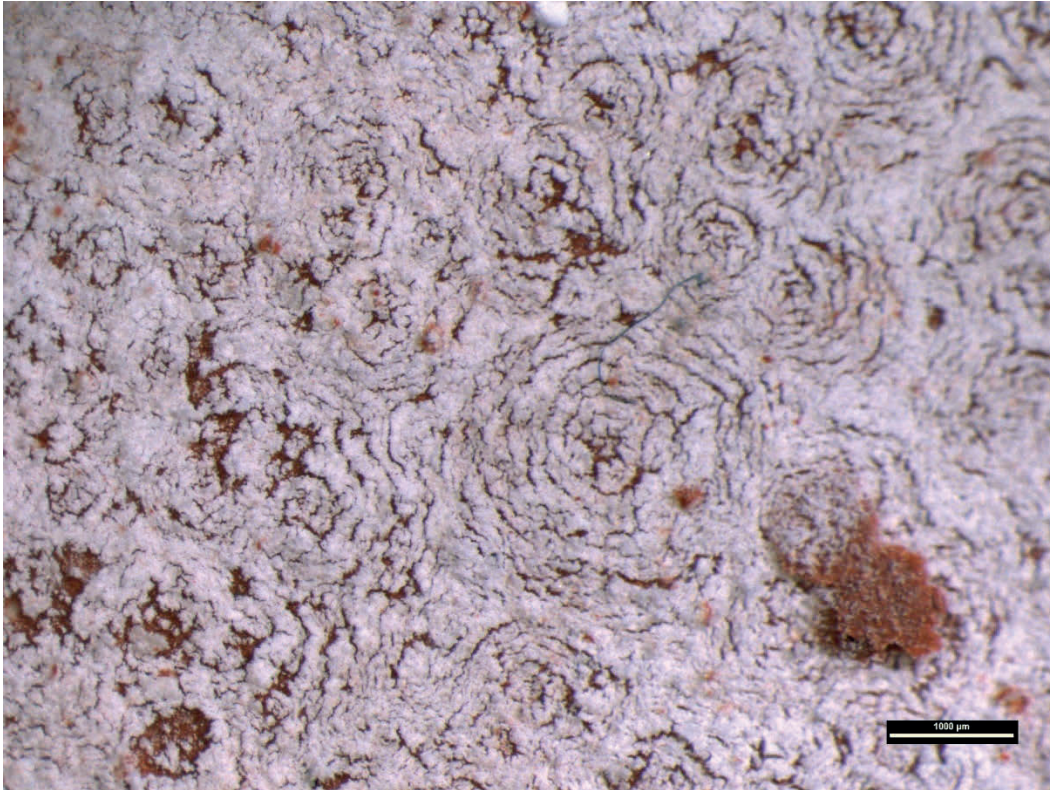


Figure 21-the only observed anomalous crystallization occurred initially on the sodium sulfate cohort treated with SFC. This did not prove to make a difference in durability.

9.4.3.3 Sodium Chloride/Sodium Sulfate Contaminated Samples

It is immediately apparent that the all inhibitors had a positive effect in reducing damage of the NaCl/Na₂SO₄ contaminated samples. When the percent total loss is broken down into its parts, it can be observed that SFC and PFC both reduced the amount of spall to about one-tenth of the amount of the control. Both also promoted a significant amount of desalination; SFC having the most at 1.25%. SFC+SHMP and PFC+SHMP cut the amount of spall in half, compared to the

control, and had a fair amount of desalination as well; SFC+SHMP having the greater amount at 0.95%.

9.4.3.3.1 NaCl/Na₂SO₄ Control

The efflorescence that developed over four weeks on the surface of the NaCl/Na₂SO₄ Control cohort began as a very thin uniform crust that turned into a thick, wet crust consisting of salt crystals and spalled material. It became the densest along the damp line, halfway to two-thirds down from the top of the samples. Two samples exhibited what appeared to be several evaporation fronts, crystallizing as several dense crusts. Distribution was fairly even across the top of the samples, being slightly higher or lower on the sample faces according to the capillary fringe. Below the evaporation front, the surface of the samples was littered with surficial powdering. The samples remained very wet the entire course of the test, appearing saturated in photomicrographs. SEM performed after four weeks revealed extremely small and dense hopper, whisker and acicular crystals coating the interior walls of the pores.

9.4.3.3.2 NaCl/Na₂SO₄ + SFC

Efflorescence began as a thin crust that began crystallizing heavily at the top of the samples. Over the course of four weeks the crystallization moved down the crystal face, crystallizing the densest at the damp line about halfway down from the top of the samples. Crystal habit was indecipherable, and accumulated as large round yellowish clusters. These samples also exhibited several damp lines. Above the densest collection of crystals were individual crystal clusters that were crystallizing in an even pattern across the top of the samples. SEM after four weeks showed that the crystal habit of the subflorescence appeared as stacks of tabular hexagonal crystals, in a formation that is assumed, if allowed to develop would

appear as the clusters of short acicular crystals seen in sodium sulfate samples treated with SFC+SHMP, as well as NaCl/Na₂SO₄ samples treated with PFC. Surrounding these stacks were voluminous non-equilibrium crystals.

9.4.3.3.3 NaCl/Na₂SO₄ + PFC

Efflorescence began as a smattering of individual dendritic tufts, as well as a crust that formed along the damp line, about halfway down the sample. These crystals were replaced by large dendrites that merged into larger clumps over the course of four weeks. The later crystallization had generally the same distribution as the control cohort, and moved down the crystal face from the top. These samples all exhibited two damp lines. The last succession of crystallization appeared to be dendritic at the top edges and corners, but crystals merged to form dense clusters that were indecipherable. Above the densest crystallization was sporadic crystal growth that form a very thin crust that covered the capillary fringe. SEM after four weeks revealed that the crystallization inside the pores was dense clusters of short acicular crystals, the same as those seen in the sodium sulfate samples treated with SFC+SHMP. Some voluminous non-equilibrium growth appeared around these clusters as well.

9.4.3.3.4 NaCl/Na₂SO₄ + PFC + SHMP

Samples initially showed efflorescence in the form of large sprawling dendritic spots, as well as very large dendritic plumes that grew straight out of the top edges and corners of the tiles. All was later replaced by yellowish dendritic growth that ultimately merged into large clumps. Over time crystallization moved halfway down the samples, but the densest crystallization remained at the top. The crystallization that occurred further down the samples tapered off into a loosely adhered crust. By the end of the test, two damp lines were visible on

all of these samples, the first being much denser. The overall crust had a similar distribution as the untreated control cohort, and was a mixture of salt crystals and spall material. Surficial powdering was visible in and around the edge of the crust. SEM after four weeks revealed that the subflorescence was a mixture of skeletal hopper growth with some prismatic growth.

9.4.3.3.5 NaCl/Na₂SO₄ + SFC + SHMP

Initially there appeared to be two distinct types of crystal growth, that which was tufts of dendritic growth that ranged in size with the sprawling dendritic spots, and a thin microcrystalline crust that was similar to crystallization on the sodium sulfate cohorts. These were shortly replaced by large plumes of yellowish dendrites. The dendrites quickly merged to form a bulbous crust along the edges and over the top surface. Crystallization tapered off into a thin crust from the top to about halfway down the sample. The distribution was relatively the same as the untreated control cohort, and surficial powdering was visible in and around the crust. Only one sample showed evidence of two separate evaporation fronts, while the others seemed to remain very thin and homogenous. SEM performed after four weeks revealed that the subflorescence was fairly inconsistent with any other instance in this testing. Visible was a mixture of larger hopper crystals, individual acicular crystals, clusters of acicular crystals, and some prismatic/tabular growth.

9.4.3.4 Discussion

Overall, it was found that the inhibitors tested had the most beneficial effects on sodium chloride crystallization, alone and in a multi-component mixture. Out of the four inhibitor solutions, PFC as well as PFC+SHMP had the greatest ability to reduce spalling, and increase desalination. This was confirmed gravimetrically and visually, as it was clear that both

dramatically changed the volume and crystal morphology of the efflorescence and subsurface crystallization in comparison to the untreated control. SFC and SFC+SHMP also were successful in reducing spall and promoting crystal habit modification, but to a slightly lesser degree.²¹

There was not an observable difference between the crystals produced by sodium and potassium ferrocyanide. The only observation that could differentiate between the two was that the efflorescence enhanced by PFC was slightly thicker initially. The addition of SHMP also did not change the crystal morphology, as the crystals appeared the same as those only treated with the ferrocyanides. In terms of comparing subsurface crystallization, NaCl crystals formed in the presence of SFC and PFC appeared the same, being generally skeletal with the tendency to fill the pores completely. Also the addition of SHMP to both ferrocyanides showed a higher percentage of prismatic crystals mixed in with the skeletal in both circumstances. The subsurface crystallization in the NaCl/Na₂SO₄ cohort was not as linear. Crystal morphology had similarities across the samples, but ultimately each sample had distinctly different subsurface crystallization. The sodium sulfate cohort generally showed acicular and whisker subfluorescence, most likely mirabilite and thenardite growth, respectively, except in the cohort treated with SFC+SHMP. In this cohort short acicular plumes filled the pores. These acicular plumes were found in several of the NaCl/Na₂SO₄ cohort as well.

The change in crystal morphology is actually a change in the growth rate of specific crystallographic faces. One face can grow rapidly while another can be stunted, causing

²¹ . It is now suspected that the measurement of spall of the NaCl/Na₂SO₄ samples treated with SFC+SHMP and PFC+SHMP, may be slightly inaccurate, because a noticeable amount of spall was visible as a part of the efflorescent crust that was subsequently scraped off before weighing (see recommendations).

elongated needle-like acicular crystals, or flat and wide tabular crystals, for example. This change in growth is caused by a variety of factors, including increased evaporation and/or cooling (i.e. an increase in supersaturation), the presence of impurities in the saline solution (i.e. inhibitors), and a change in solvent (Joshi 2012:414). Observations from previous research conducted by Rodriguez-Navarro and colleagues confirm what was found in this study; that the growth of the most common cubic crystal forms were stunted in the presence of ferrocyanides. They also found that efflorescence grown in the presence of these inhibitors promoted skeletal hopper and dendritic growth with poorly developed faces ((Rodriguez-Navarro et al. 2002: 511). Dendrites and hopper crystals are a products of extremely high supersaturations. The fact that dendritic growth on the exterior and hopper growth on the interior was found after treatment further proves that the inhibitors in this testing program had an overarching ability to delay nucleation and increase supersaturation of the salt solutions in the terracotta, effectively promoting efflorescence and reducing subflorescence (Rodriguez-Navarro et al. 2002: 512).

Chapter 10: Conclusion & Recommendations

10.1 Conclusions

The objective of this research was to build on previous laboratory research, using similar but modified methodologies as a means to evaluate the performance of crystallization inhibitors as a method to reduce salt deterioration in previously salt contaminated terracotta. The goal was to focus on how sodium and potassium ferrocyanide with and without the addition of sodium hexametaphosphate would change the influence of a single and double salt solution on terracotta's water absorption, porosity, evaporation, length of drying, and ultimate durability. It was found that out of the four different inhibitors studied, none had consistently positive effects.

In regard to the absorption and evaporation testing, in the presence of 0.2% of SFC+SHMP the porosity and percentage of water absorption of NaCl contaminated terracotta increased significantly over time. This may be linked to SFCs ability to enhance drying and therefore, capillary suction and salt solution transport. SFC was the only inhibitor to actually increase evaporation, specifically in the sodium sulfate cohort, an attribute also found in previous research. Though enhanced evaporation is not particularly positive as it can lead to the evaporation front retreating inside the porous material, causing damaging crystallization beneath the surface. Also it is not desirable as the increased efflorescence that is a common result of ferrocyanide treatment already increases evaporation, because it exists as a saturated porous sheath that greatly increases surface area, and therefore drying (Rodriguez-Navarro et al. 2002: 508). SFC and SFC+SHMP (0.1% and 0.2% respectively) did have a positive effect in reducing the damaging effects of sodium chloride in the second durability test. Both proved to reduce spall, increase efflorescence and desalination, and delayed nucleation, effectively

changing efflorescent crystals from cubic to dendritic in habit. However, it can be concluded that SFC did not perform as well as PFC, because of its variable effect in the other two tests.

PFC and PFC+SHMP (0.1% and 0.2% respectively) were highly successful in altering sodium chloride crystallization in the second durability test. Both PFC and PFC+SHMP were able to dramatically reduce spall and increase desalination in the sodium chloride and sodium chloride/sodium sulfate cohorts. They also effectively delayed nucleation, and increased supersaturation, proven by the significant increase in efflorescence and the visibly modified subflorescence and efflorescence crystal habits in both cohorts. NaCl subflorescence was changed from predominantly rhombohedral to skeletal hopper growth, and efflorescence changed from uniform crusts to loosely adhered dendritic growth. It should also be noted that the presence of PFC and PFC+SHMP were without effect in regard to changing evaporation or absorption and porosity. This could be seen as unremarkable, but ultimately PFCs inactivity is positive as it reduces damage without interfering with the natural wetting and drying processes of terracotta.

The primary mechanism at which the inhibitors reduced damage during the durability test was through increasing supersaturation, and subsequently influencing crystallization to occur at the surface as opposed to below it. It was assumed that the impressive increase in efflorescence production would be sustained throughout the test, but it was not. It was observed that over a four-week period, a large amount of efflorescence was produced immediately on the surfaces of the treated samples, and then quickly tapered off. Within the first three days, large crawling dendritic growth as well as large loose dendrites formed. By day ten, most of this initial dendritic growth fell off and new, denser dendrites were formed after. The crystals that formed by day 21 were like merged bulbous dendrites that remained until the

test concluded, and by day 30, the efflorescence on all samples was either equal to, or less than the control cohorts (see appendix D). This tapering off of efflorescence production proves the treatment mechanism's effectivity wore off, or that the majority of salt precipitated out, and the treatment had little left to transport. Salt was observed inside some pores after four weeks, which proved that the samples were not entirely desalinated. However, it is inferred that since the inhibitors had a marked effect on changing crystal habit, that the altered crystal morphology of the remaining crystals in the treated sodium chloride and sodium chloride/sodium sulfate cohorts were rendered less damaging than the equilibrium crystal morphology in the untreated control cohorts, also contributing to the decrease in deterioration.

This testing was unable to provide sound results as to whether a mixed inhibitor solution was more effective than a single inhibitor solution, as both were equally successful in different circumstances. More testing is advised to monitor the effects of using two reagents together.

Although the inhibitors were highly successful in reducing material deterioration, there are still many factors that affect their efficacy that are not entirely understood. Additionally, this test among others only exhibits what these chemical reagents are capable of in a controlled environment, meaning, far more testing must occur to observe how effective they are in-situ before they are ever used as a treatment for cultural heritage like the drain tile at Western Clay Manufacturing Co. In conclusion, the positive results of this testing warrant further laboratory and in-situ testing and it is only a matter of time before crystallization inhibitors become a viable means to mitigate salt deterioration.

10.2 Recommendations

10.2.1 *Recommendations for Test Replication*

The most noteworthy recommendation that can be made for future testing is that the pH of the inhibitor solutions used to treat samples be monitored throughout testing. The SDS sheet for potassium ferrocyanide (see appendix) states that a 100g/l aqueous solution at 25°C be an average pH of 9.5. At 25°C, the pH of the 1g/l aqueous solutions used to treat the cohorts in this testing was found to have a pH of 4.5-5 due to the accidental use of highly acidic deionized water. It is suspected this affected performance, and it is highly recommended that all testing be performed again using solutions with the appropriate alkalinity. Another general recommendation is that terracotta samples be more regularly cut, reducing the margin of variability in dimension and weight. Slight variability is unavoidable in ceramic materials, but it can be reduced.

10.2.2 Cold Water Immersion (Absorption) & Evaporation Test Recommendations

The lack of results yielded from these two tests are thought to be a partial product of the fact that the samples were not weathered for a considerable amount of time, and that desalination may have occurred during water immersion, in effect, rendering the crystallization inhibitors less effective. Subjecting samples to longer accelerated weathering cycles, so as to develop salt crystallization and induce deterioration, could produce more pronounced results when the inhibitors are applied and tested. It is also recommended that conductivity of the water in each immersion bath be measured over time as to ascertain how much desalination occurs and potentially how this may correlate with fluctuations in porosity, water absorption and evaporation.

In regard to the evaporation test specifically, a greater control over environmental fluctuations may yield more consistent results. The tests were designed in an effort to

reproduce in-situ conditions that were moderately controlled as to obtain viable results.

However, it was found that it was difficult to draw conclusions with unmonitored fluctuation (even though the fluctuation was limited). It would be best to perform testing with no variation in the environment or to have controlled variation, which could be monitored for its effects.

10.2.3 Durability Test Recommendations

Finding that the two durability tests produced significantly different results supports the recommendation that a better methodology be explored. It is highly recommended that accelerated weathering occur first on all samples, following the prescribed methods for “Crystallization Cycles” in the “ARC Laboratory Handbook: porosity, salts, binders.” by Ernesto Borrelli. Cycling as opposed to the capillary suction bath used in this program, would allow the researcher to monitor loss over time more closely, and assess whether more damage was incurred initially or later.

It is recommended that after the samples are treated, that they should be kept in a controlled moderate environment, to enable very slow evaporation. This will lessen the possibility of causing greater damage due to a rapid increase in supersaturation through the mechanism of the inhibitor and fast evaporation. With that, it would also be beneficial to acquire results from several durability tests conducted in several different controlled environments of high and low temperature and relative humidity to ascertain how microclimate directly effects the efficacy of the inhibitors.

The capillary suction bath methodology was successful for the durability test and is recommended over wet and dry cycling as many of the chemical reagents break down under high heat. However, it is recommended that if this methodology be used that the immersion

bath be covered so as to avoid it being contaminated by the salt that falls off the tile as efflorescence. It is suspected that durability would increase if the bath be kept relatively free of debris.

In reference to collecting and filtering the spall material that falls off the untreated and treated samples, it is highly recommended that all efflorescence also be collected, dissolved, filtered and dried, as to obtain more accurate figures for total amount of loss. It is supposed that some percentage of spall was lost in this testing through the disposal of efflorescence.

10.2.4 Recommendations for Analysis Out of Scope

It is imperative that the negative effects of this treatment must be further researched as it has been found that the higher the supersaturation of a salt is, the higher crystallization pressure exerted in the pore will be. Which means that many of these chemical that increase supersaturation and stave of crystal nucleation, can potentially be more damaging when crystallization actually does occur, if not properly applied and monitored.

As said more testing must be performed in-situ, as the positive results of laboratory based testing will never be fully understood until subjected to environmental conditions. But before this happens a much greater deal of research focus on methods of inhibitor application to an already contaminated substrate. In very recent research, adding these reagents to poultice systems seems to be the most practical and beneficial in-situ.

It must be noted that as much as ASTM testing can be helpful in designing an experimental testing program to evaluate salt crystallization inhibitors, there is no test that actually addresses this testing, and that all testing programs analyzing these reagents have been

at the discretion of the researcher. Therefore, this line of research would greatly benefit from testing standardization.

10.2.5 Final Considerations

As a proposed means to mitigate salt damage in cultural heritage, the effects of these treatments on the aesthetic integrity of said heritage must be considered and potentially remedied. Ferrocyanides, being the precursor to the pigment Prussian Blue, have caused bluing of light-colored substrates.²² This was not observed in this testing program, but should be monitored in the future. Also, the excessive efflorescence that occurs with these treatments is ultimately visually obtrusive. This should be considered by any steward agreeing to this treatment, and it is recommended that an intensive system of efflorescence removal be established, when salt crystallization inhibitors become a viable conservation treatment for salt weathering.

²² Mentioned in an e-mail from Dr. Barbara Lubelli about previous research of her own.

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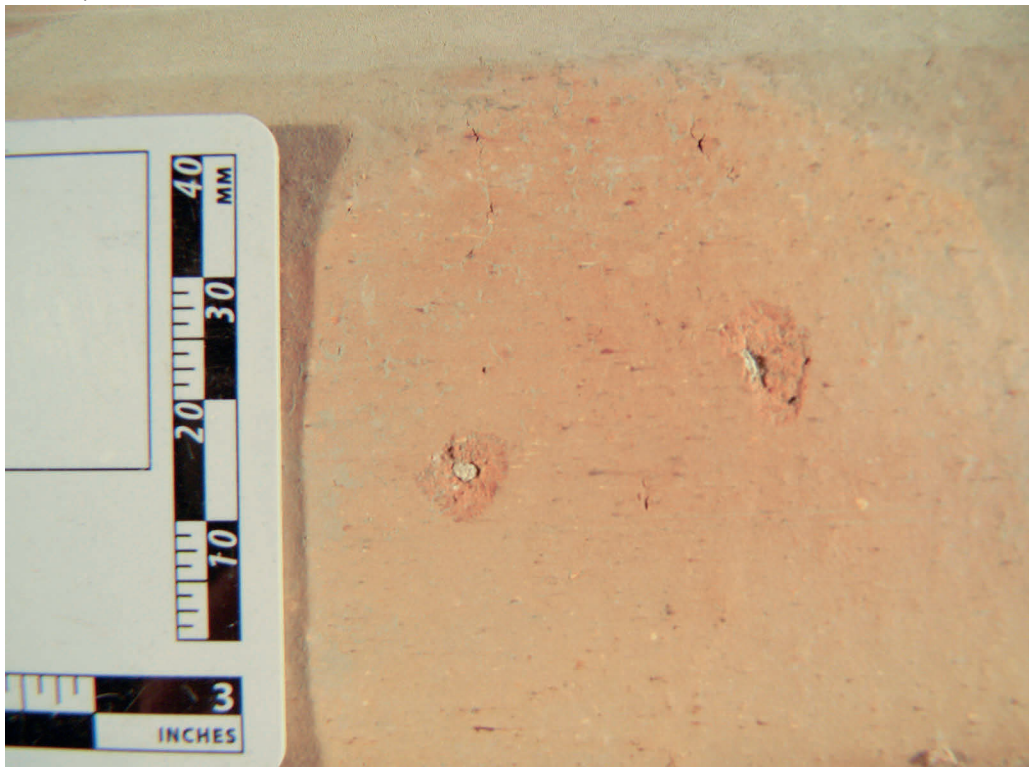
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Drain tile taken from WCMC



Detail: surface spall of WCMC drain tile



Appendix A

Photographs taken by Matt Mo gan



ABF_00565

Western Clay Manufacturing Co. Sample Location



ABF_00566

Appendix A

Photographs taken by Matt Mo gan



ABF_00558

Western Clay Manufacturing Co. Sample Location



ABF_00561

Appendix A

Photographs taken by Matt Mo gan



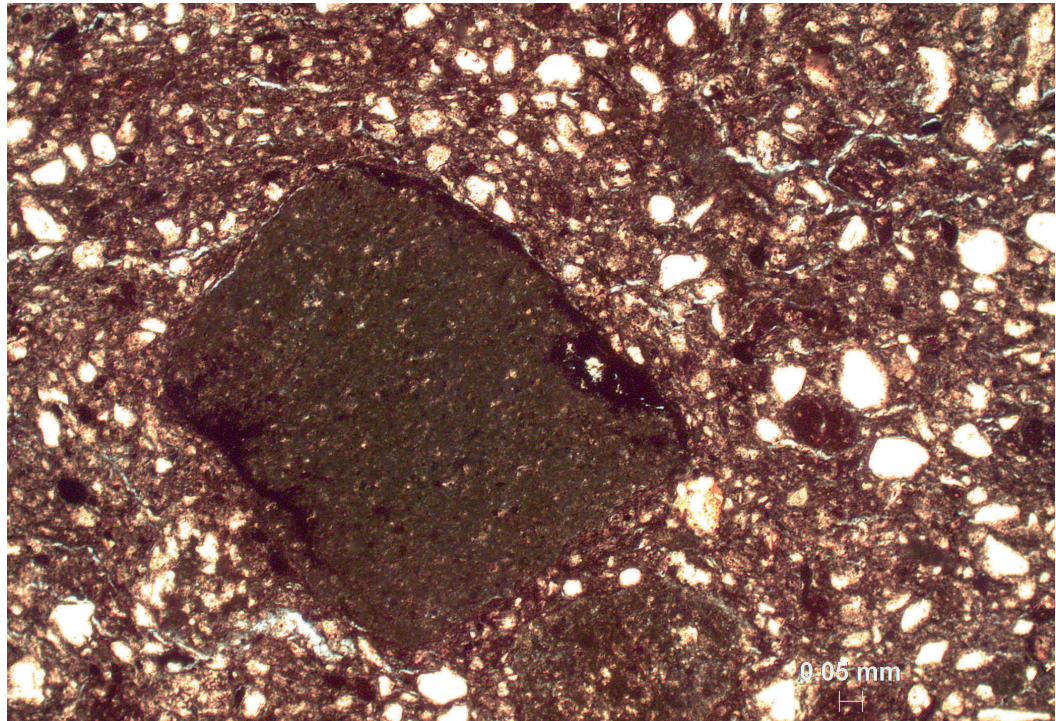
ABF_00562

Western Clay Manufacturing Co. Sample Location

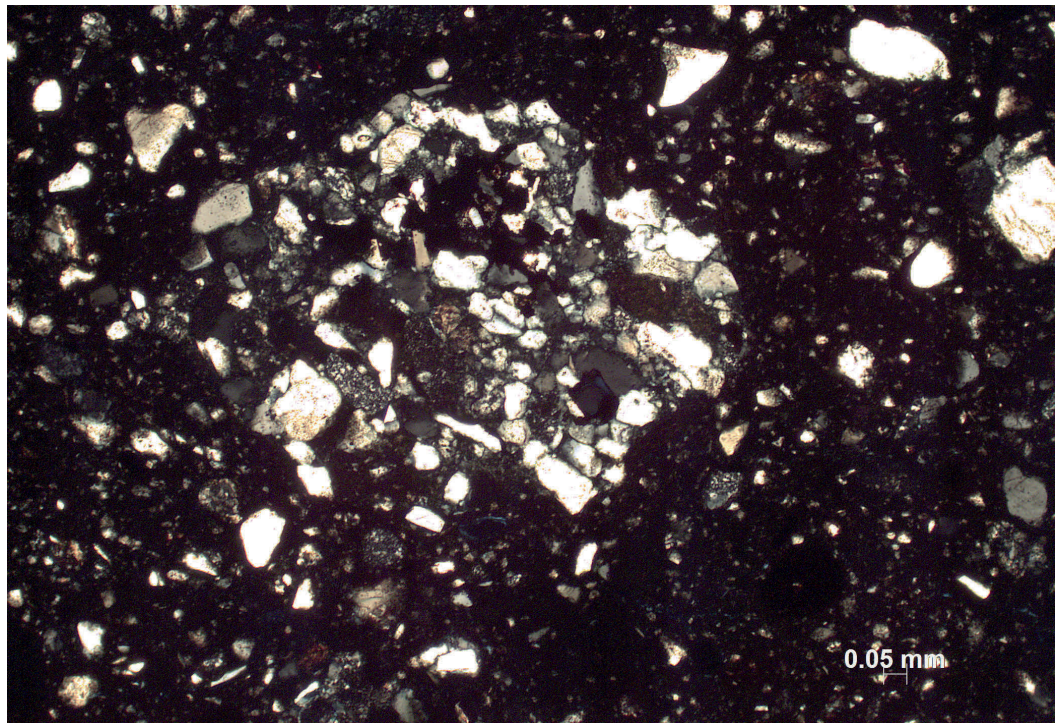


ABF_00564

Mag: 50x Light: PPL Notes: large shale inclusion used as temper



Mag: 50x Light: XPL Notes: large rock fragment used as temper

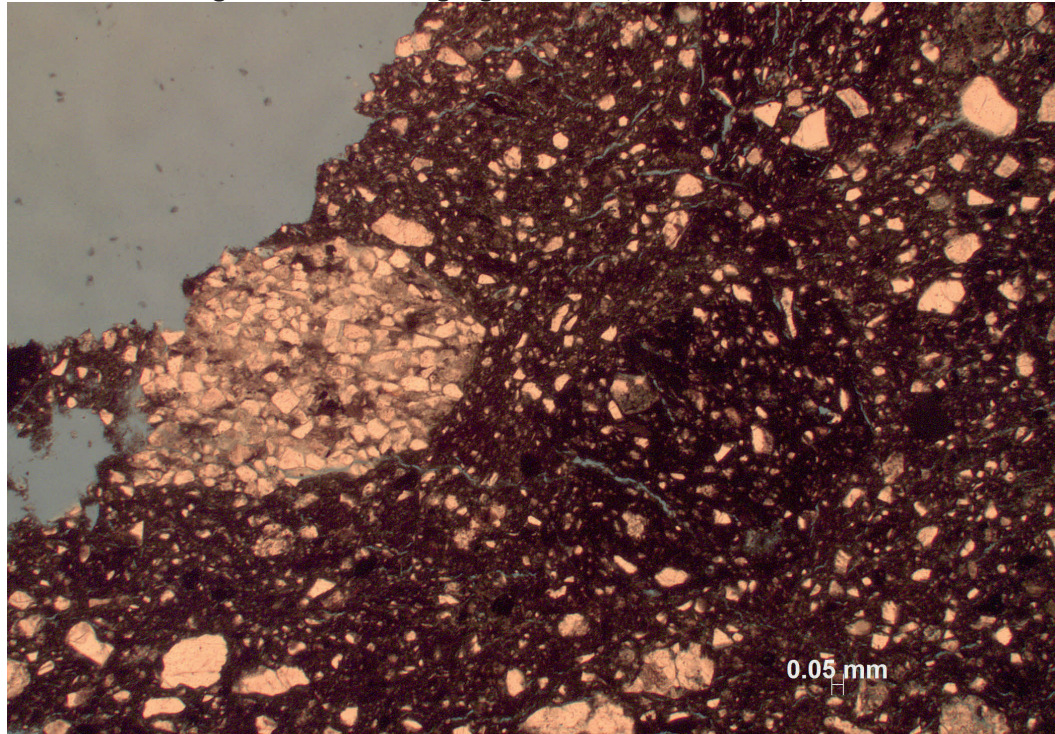


A Zeiss AxioScope A1 was used, and photomicrographs were taken using an AxioCam ICc3 with AxioVision SE64 software at the Ceramics Lab in the Center for the Analysis of Archaeological Materials.

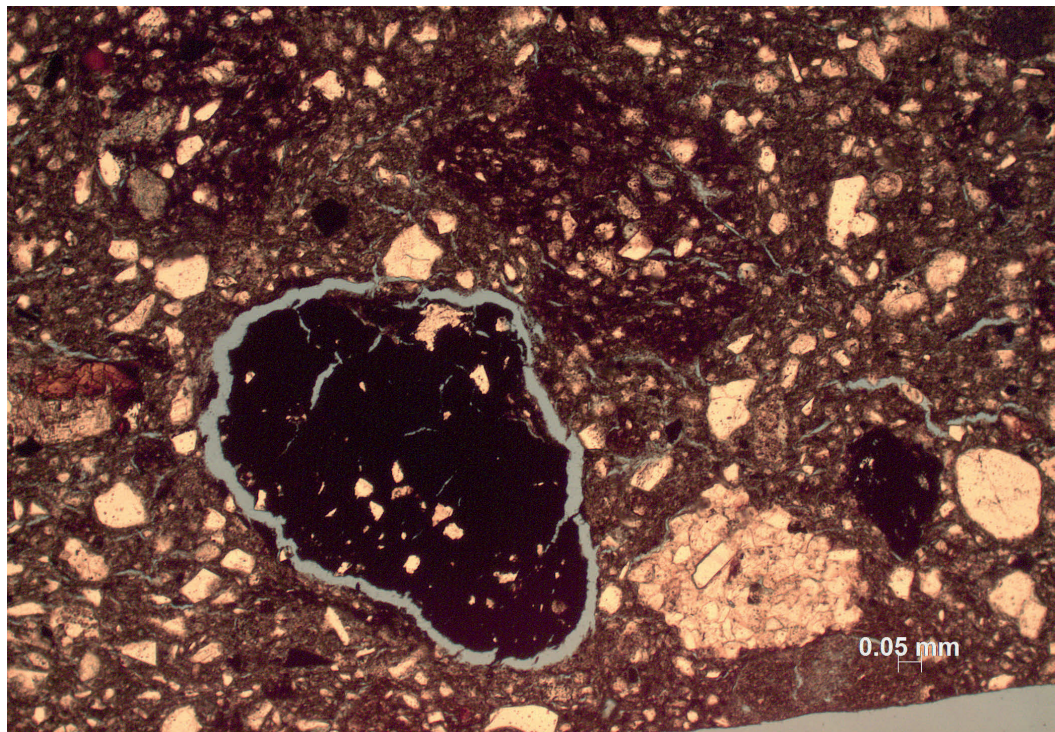
Appendix B

Western Clay Manufacturing Co. Tile Petrofarc Mag:

25x Light: PPL Notes: large white and red grog inclusions, used as temper

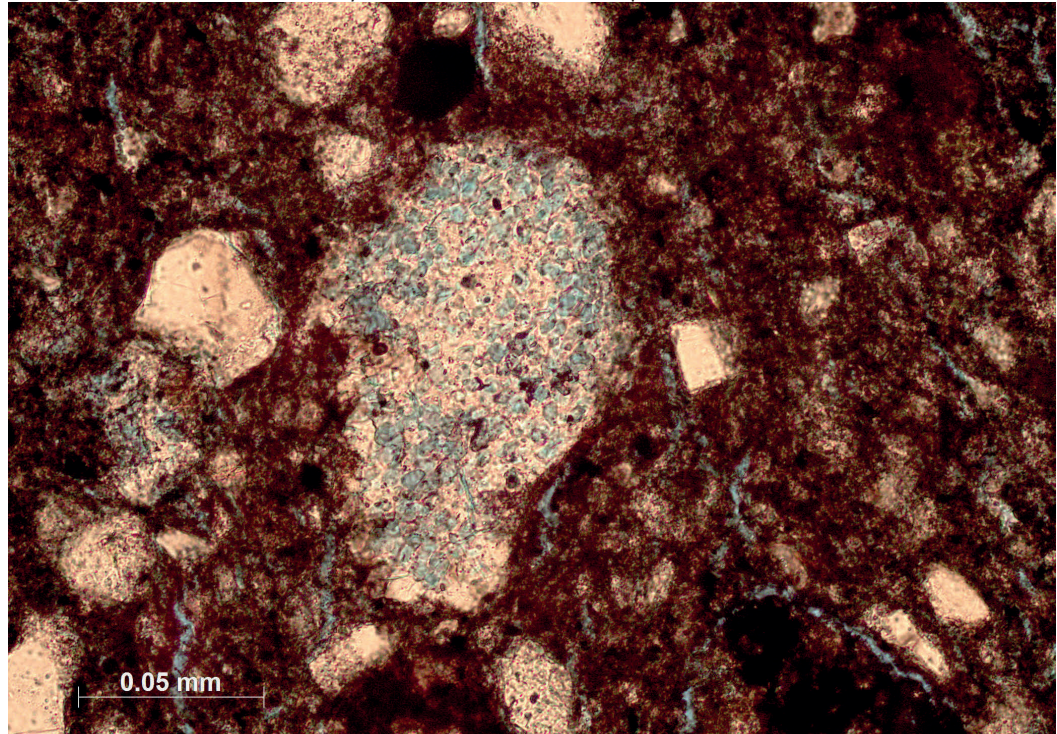


Mag: 50x Light: PPL Notes: concentration feature-large iron clay nodule

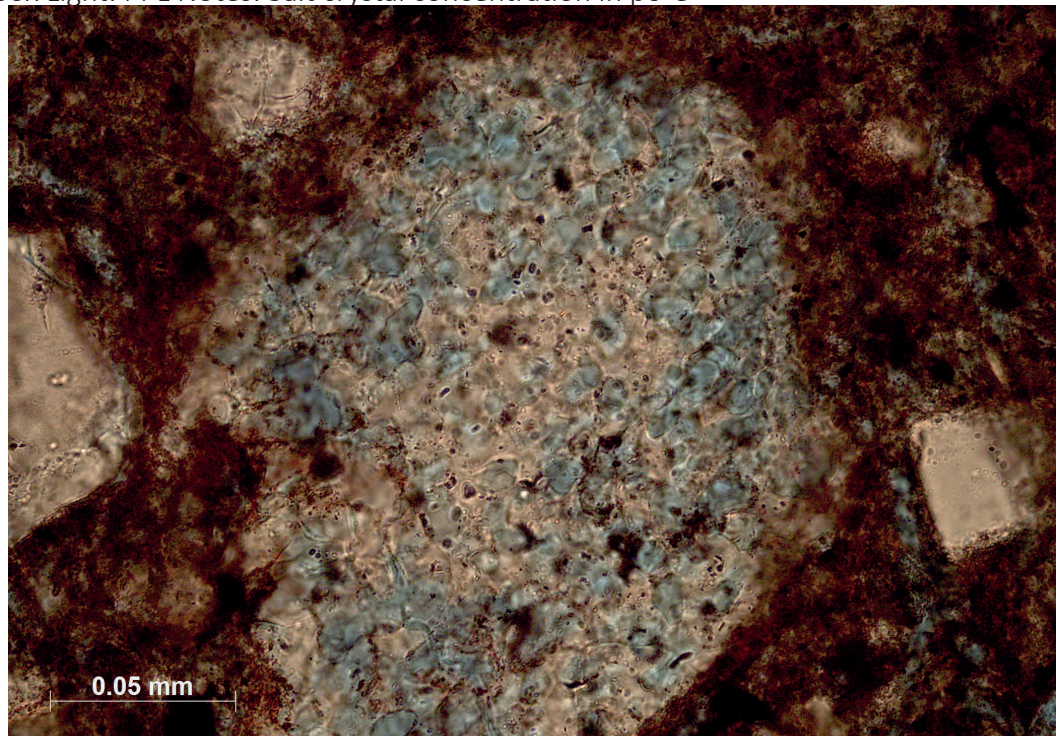


A Zeiss AxioScope A1 was used, and photomicrographs were taken using an AxioCam ICc3 with AxioVision SE64 software at the Ceramics Lab in the Center for the Analysis of Archaeological Materials.

Mag: 200x Light: PPL Notes: Salt crystal concentration in po e

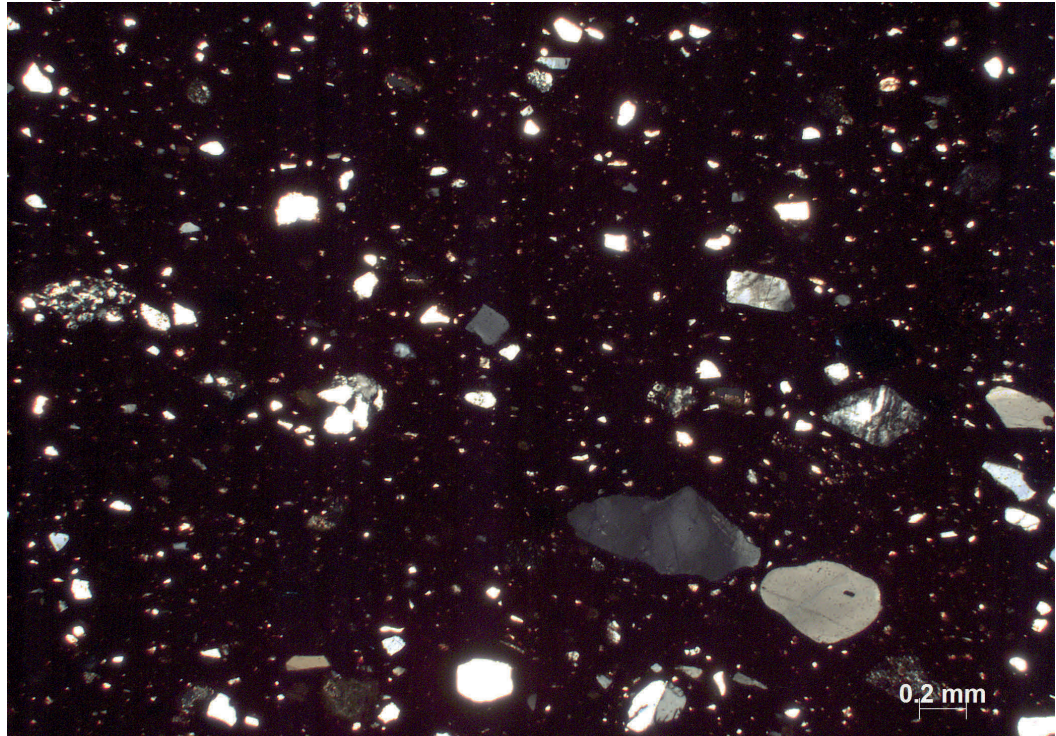


Mag: 400x Light: PPL Notes: Salt crystal concentration in po e

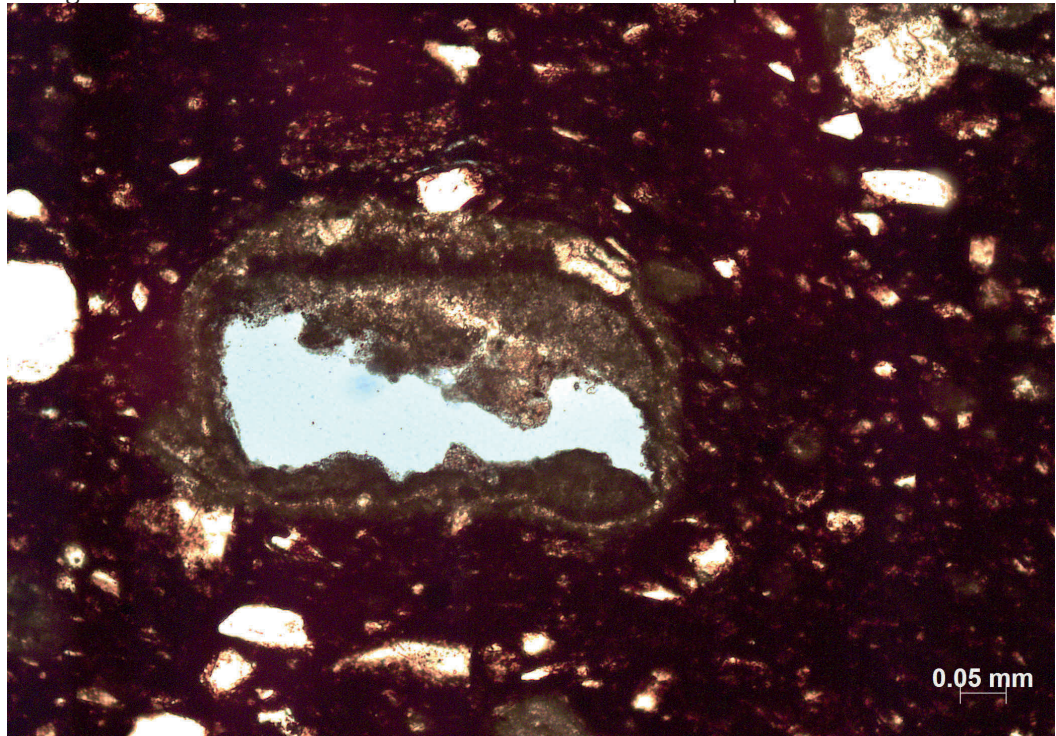


A Zeiss AxioScope A1 was used, and photomicrographs were taken using an AxioCam ICc3 with AxioVision SE64 software at the Ceramics Lab in the Center for the Analysis of Archaeological Materials.

Mag: 25x Light: XPL Notes: Groundmass

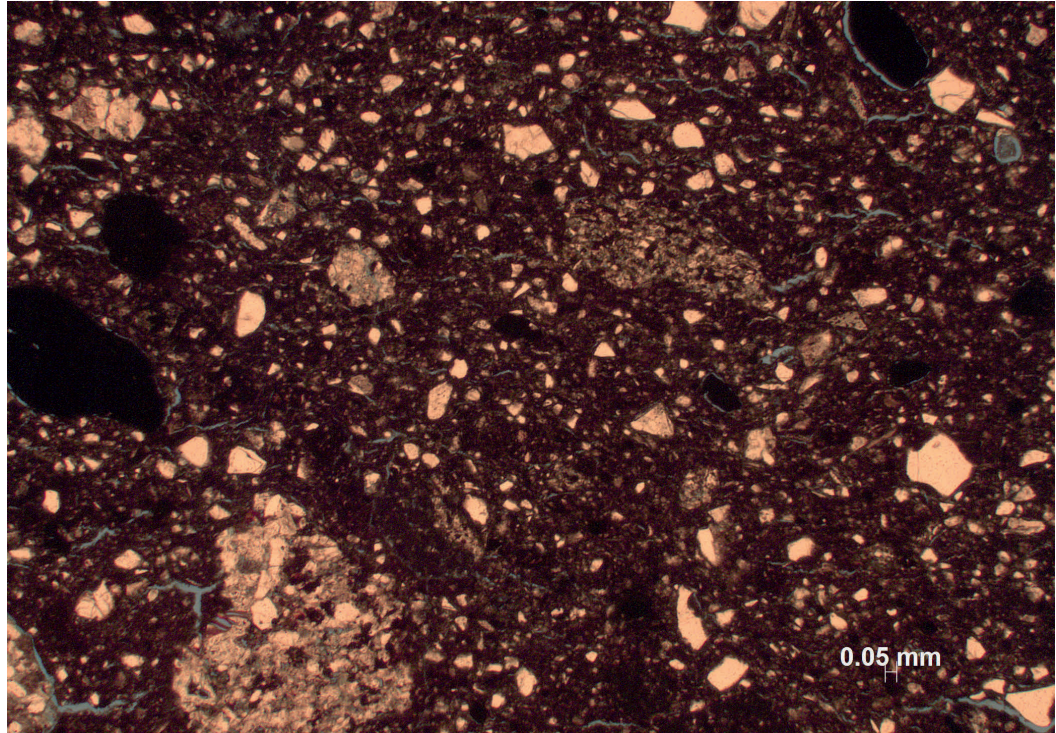


Mag: 100x Light: PPL Notes: calcium carbonate melt rim inside a pore

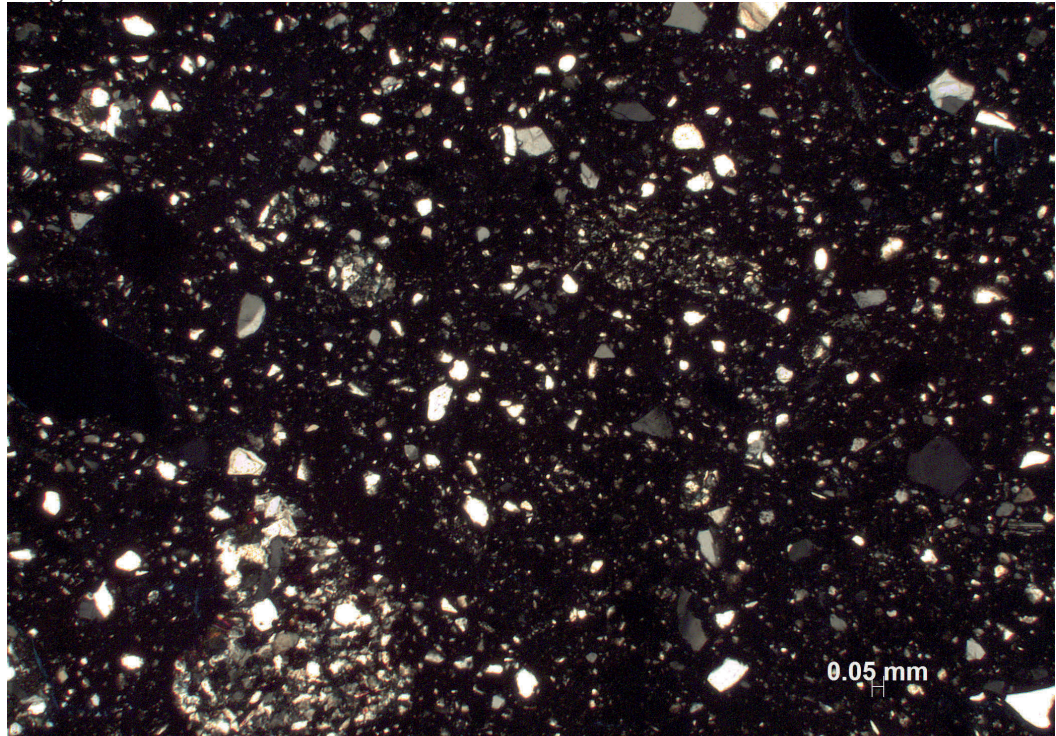


A Zeiss AxioScope A1 was used, and photomicrographs were taken using an AxioCam ICc3 with AxioVision SE64 software at the Ceramics Lab in the Center for the Analysis of Archaeological Materials.

Mag: 25x Light: PPL Notes: Groundmass

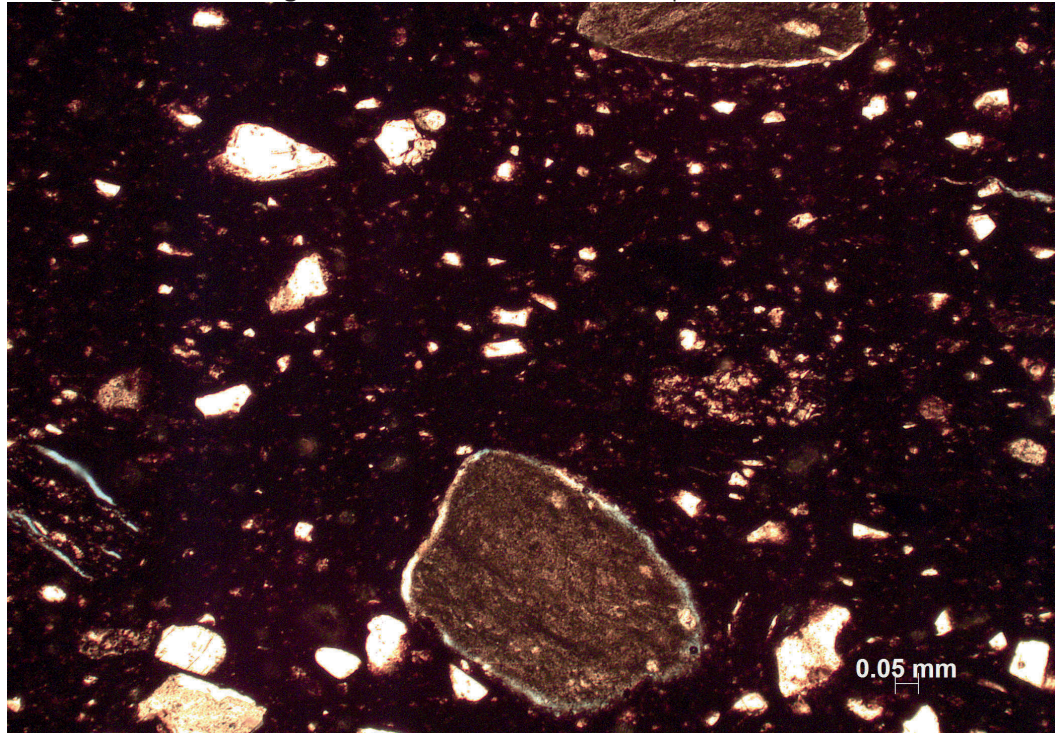


Mag: 25x Light: XPL Notes: Groundmass

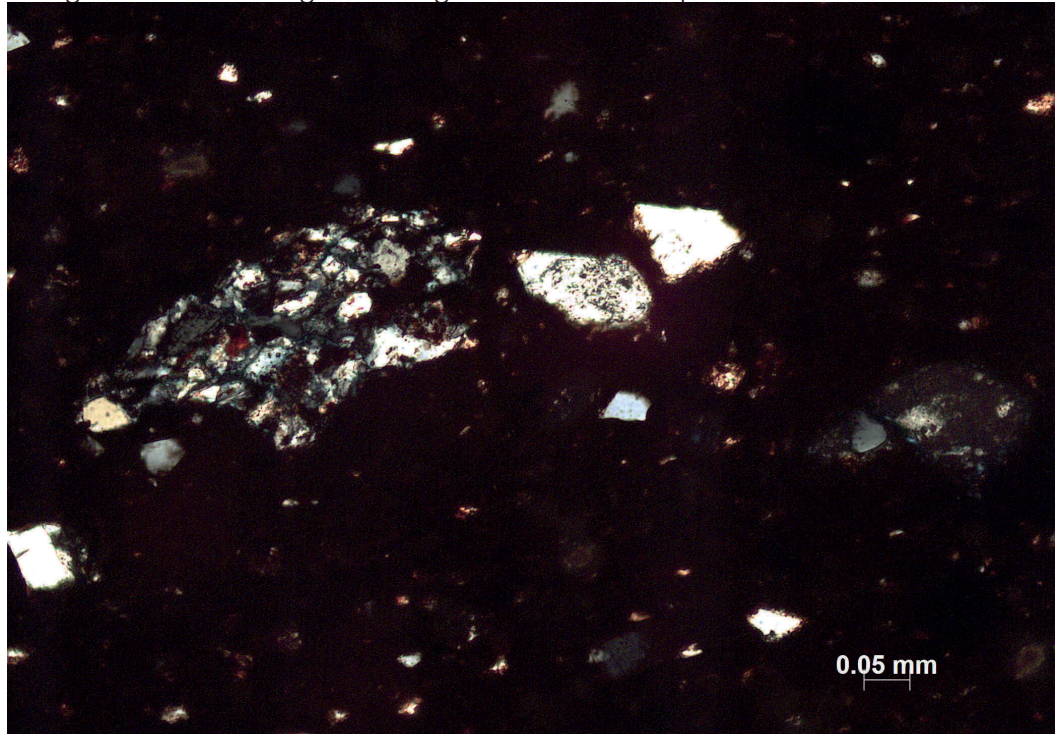


A Zeiss AxioScope A1 was used, and photomicrographs were taken using an AxioCam ICc3 with AxioVision SE64 software at the Ceramics Lab in the Center for the Analysis of Archaeological Materials.

Mag: 50x Light: PPL Notes: large shale inclusion used as temper

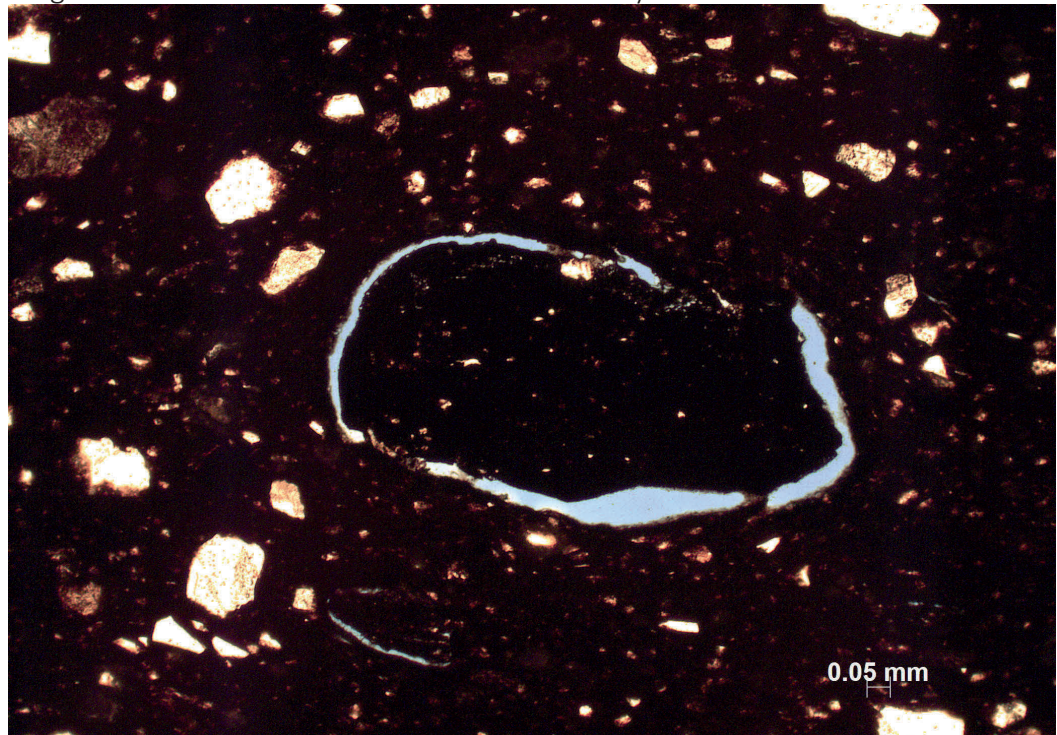


Mag: 100x Light: XPL Notes: large rock fragment used as temper

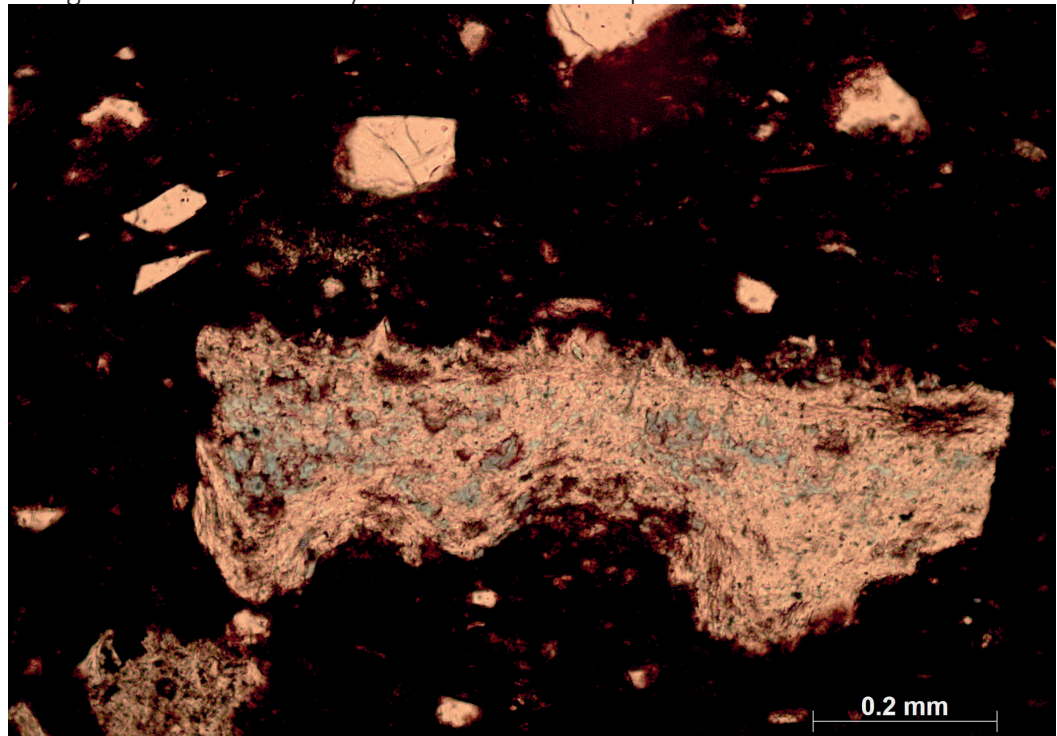


A Zeiss AxioScope A1 was used, and photomicrographs were taken using an AxioCam ICc3 with AxioVision SE64 software at the Ceramics Lab in the Center for the Analysis of Archaeological Materials.

Mag: 50x Light: PPL Notes: concentra[̄]on feature-iron clay nodule



Mag: 100x Light: PPL Notes: Salt crystal concentration in po e



A Zeiss AxioScope A1 was used, and photomicrographs were taken using an AxioCam ICc3 with AxioVision SE64 software at the Ceramics Lab in the Center for the Analysis of Archaeological Materials.

Appendix: C

Sample	Capillary Rise Raw Data											
	Tile 1				Tile 2				Tile 3			
Time	Face 1	Face 2	Face 3	Face 4	Face 1	Face 2	Face 3	Face 4	Face 1	Face 2	Face 3	Face 4
Min.	Rise (CM)	Rise (CM)	Rise (CM)	Rise (CM)	Rise (CM)	Rise (CM)	Rise (CM)	Rise (CM)	Rise (CM)	Rise (CM)	Rise (CM)	Rise (CM)
0	1	1	1	1	1	1	1	1	1	1	1	1
1	1.3	1	1.4	1	1.3	1	1.9	1	1.5	1.2	1.8	1
2	1.7	1	2.2	1	1.5	1	2.2	1	1.9	1.2	2.2	1
3	1.7	1	2.2	1	1.5	1	2.2	1	2	1.2	2.3	1
4	1.8	1	2.3	1	1.7	1	2.3	1	2	1.2	2.3	1
5	1.8	1	2.3	1	1.7	1	2.3	1	2.1	1.3	2.3	1
10	1.9	1.2	2.4	1	1.7	1	2.4	1	2.2	1.4	2.3	1.2
15	2	1.2	2.5	1	1.8	1.2	2.6	1	2.2	1.4	2.4	1.4
20	2	1.2	2.5	1	1.9	1.3	2.7	1.1	2.2	1.5	2.5	1.4
25	2	1.3	2.6	1	2	1.4	2.8	1.3	2.2	1.6	2.6	1.6
30	2.3	1.4	2.6	1.2	2.3	1.4	3	1.4	2.3	1.6	2.7	1.7
60	2.4	1.6	2.9	1.8	2.4	1.8	3.1	1.6	2.6	2	3	2
90	3	2.5	2.9	2.2	2.6	1.9	3.2	2	3	2	3.1	2.2
120	2.8	2.5	3	2.5	3.1	2.8	3.8	3	3	2.3	3.3	2.3
150	3.3	3.5	3.8	2.9	3	3.3	3.1	3	3.1	3	3.5	2.6
180	3.5	4	4	3.5	3	3.4	3.1	3	3.4	3	3.9	3

Appendix: C

Capillary Rise Raw Data								
Samples	Tile 4				Average			
Time	Face 1	Face 2	Face 3	Face 4	Right Face	Exterior Face	Left Face	Interior Face
Min.	Rise (CM)	Rise (CM)	Rise (CM)	Rise (CM)	Rise (CM)	Rise (CM)	Rise (CM)	Rise (CM)
0	1	1	1	1	1.00	1.00	1.00	1.00
1	1.5	1.2	1.5	1	1.40	1.10	1.65	1.00
2	1.6	1.2	1.7	1	1.68	1.10	2.08	1.00
3	1.6	1.2	1.8	1	1.70	1.10	2.13	1.00
4	1.6	1.2	1.8	1.1	1.78	1.10	2.18	1.03
5	1.7	1.3	1.9	1.2	1.83	1.15	2.20	1.07
10	1.8	1.4	2.1	1.3	1.90	1.25	2.30	1.17
15	2	1.4	2.2	1.5	2.00	1.30	2.43	1.30
20	2	1.4	2.2	1.5	2.03	1.35	2.48	1.30
25	2.1	1.4	2.2	1.6	2.08	1.43	2.55	1.40
30	2.2	1.5	2.3	1.8	2.28	1.48	2.65	1.57
60	2.4	1.7	2.6	2	2.45	1.78	2.90	1.93
90	2.7	2	2.9	2	2.83	2.10	3.03	2.13
120	2.8	2	3	2.5	2.93	2.40	3.28	2.43
150	2.9	2.7	3.2	2.5	3.08	3.13	3.40	2.67
180	3	3	3.4	3	3.23	3.35	3.60	3.17

Absorption Test Calculations																		
Salt	Code	H2O	(-wire)(M1)	Air (M2)	(-wire)(M2)	Va	Msat	Mp	Vp	Est. %	HSW Vp	HSW Va	Real Vol	Real Dens	Pr	Pa	Porosity	
								(g/cm3)		Porosity								
		g	g	g		cm3	g		cm3	%								cm3
NaCl	01cl	105.90	102.05	185.90	182.05	181.89	181.71	8.33	8.33	4.58	8.67	80.00	71.33	2.43	2.43	2.17	10.84	
NaCl	02cl	103.00	99.15	185.30	181.45	181.86	181.77	8.23	8.23	4.53	7.91	82.30	74.39	2.33	2.33	2.11	9.61	
NaCl	03cl	109.60	105.75	197.30	193.45	193.56	193.25	9.31	9.31	4.81	9.51	87.70	78.19	2.35	2.35	2.10	10.84	
NaCl	04cl	110.00	106.15	199.10	195.25	195.91	0.00	-183.61	-183.61	-93.72	11.64	89.10	77.46	2.37	2.37	2.06	13.06	
NaCl	05cl	103.80	99.95	187.80	183.95	184.28	184.16	11.01	11.01	5.97	10.80	84.00	73.20	2.37	2.37	2.06	12.86	
NaCl	06cl	110.40	106.55	195.00	191.15	195.09	195.03	10.02	10.02	5.14	6.14	84.60	78.46	2.36	2.36	2.19	7.26	
NaCl	07cl	110.50	106.65	198.80	194.95	195.70	195.38	11.78	11.78	6.02	11.35	88.30	76.95	2.39	2.39	2.08	12.85	
NaCl	08cl	106.70	102.85	199.50	195.65	196.58	196.19	10.90	10.90	5.54	10.36	92.80	82.44	2.25	2.25	2.00	11.16	
NaCl	09cl	106.75	102.90	190.00	186.15	186.95	186.77	9.62	9.62	5.15	9.00	83.25	74.25	2.39	2.39	2.13	10.81	
NaCl	10cl	111.00	107.15	200.30	196.45	197.51	0.00	-185.04	-185.04	-93.69	11.41	89.30	77.89	2.38	2.38	2.07	12.78	
NaCl	11cl	110.20	106.35	197.40	193.55	191.32	0.00	-183.56	-183.56	-95.94	9.99	87.20	77.21	2.38	2.38	2.11	11.46	
NaCl	12cl	110.00	106.15	194.30	190.45	191.23	190.97	8.43	8.43	4.41	7.91	84.30	76.39	2.39	2.39	2.17	9.38	
NaCl	13cl	116.00	112.15	212.40	208.55	209.73	209.07	12.89	12.89	6.15	12.37	96.40	84.03	2.33	2.33	2.04	12.83	
NaCl	14cl	112.50	108.65	201.80	197.95	198.81	198.40	11.00	11.00	5.53	10.55	89.30	78.75	2.38	2.38	2.10	11.81	
NaCl	15cl	111.20	107.35	200.00	196.15	196.94	196.69	11.26	11.26	5.72	10.72	88.80	78.08	2.37	2.37	2.09	12.07	
NaSO4	01so	106.50	102.65	191.50	187.65	188.17	188.07	11.25	11.25	5.98	10.83	85.00	74.17	2.38	2.38	2.08	12.74	
NaSO4	02so	108.50	104.65	192.35	188.50	189.09	0.00	-179.98	-179.98	-95.18	8.52	83.85	75.33	2.39	2.39	2.15	10.16	
NaSO4	03so	111.20	107.35	196.03	192.18	193.17	0.00	-184.63	-184.63	-95.58	7.55	84.83	77.28	2.39	2.39	2.18	8.90	
NaSO4	04so	95.70	91.85	170.80	166.95	168.21	0.00	-157.56	-157.56	-93.67	9.39	75.10	65.71	2.40	2.40	2.10	12.50	
NaSO4	05so	112.50	108.65	199.40	195.55	190.70	190.55	11.24	11.24	5.89	16.24	86.90	70.66	2.54	2.54	2.06	18.69	
NaSO4	06so	111.80	107.95	198.50	194.65	204.77	204.44	8.32	8.32	4.06	-1.47	86.70	88.17	2.22	2.22	2.26	-1.70	
NaSO4	07so	113.20	109.35	201.60	197.75	196.22	195.97	8.67	8.67	4.42	10.45	88.40	77.95	2.40	2.40	2.12	11.82	
NaSO4	08so	112.40	108.55	202.40	198.55	195.21	0.00	-185.72	-185.72	-95.14	12.83	90.00	77.17	2.41	2.41	2.06	14.26	
NaSO4	09so	112.00	108.15	201.30	197.45	198.50	198.33	12.05	12.05	6.07	11.17	89.30	78.13	2.38	2.38	2.09	12.51	
NaSO4	10so	112.80	108.95	202.20	198.35	199.42	199.02	11.78	11.78	5.91	11.11	89.40	78.29	2.39	2.39	2.09	12.43	
NaSO4	11so	111.10	107.25	199.60	195.75	196.59	196.36	12.74	12.74	6.48	12.13	88.50	76.37	2.40	2.40	2.07	13.71	
NaSO4	12so	110.30	106.45	198.10	194.25	194.86	0.00	-183.18	-183.18	-94.01	11.07	87.80	76.73	2.39	2.39	2.09	12.61	
NaSO4	13so	118.40	114.55	210.00	206.15	206.99	0.00	-197.54	-197.54	-95.43	8.61	91.60	82.99	2.38	2.38	2.16	9.40	
NaSO4	14so	110.00	106.15	195.00	191.15	191.76	191.36	7.90	7.90	4.12	7.69	85.00	77.31	2.37	2.37	2.16	9.05	
NaSO4	15so	119.00	115.15	214.40	210.55	211.12	0.00	-198.08	-198.08	-93.82	12.47	95.40	82.93	2.39	2.39	2.08	13.07	
NaSO4+NaCl	01lo	110.00	106.15	194.60	190.75	191.50	0.00	-183.29	-183.29	-95.71	7.46	84.60	77.14	2.38	2.38	2.17	8.82	
NaSO4+NaCl	02lo	105.30	101.45	187.00	183.15	183.82	0.00	-174.86	-174.86	-95.13	8.29	81.70	73.41	2.38	2.38	2.14	10.15	
NaSO4+NaCl	03lo	109.10	105.25	196.20	192.35	193.04	0.00	-181.55	-181.55	-94.05	10.80	87.10	76.30	2.38	2.38	2.08	12.40	
NaSO4+NaCl	04lo	120.00	116.15	215.80	211.95	213.04	0.00	-200.82	-200.82	-94.26	11.13	95.80	84.67	2.37	2.37	2.10	11.62	
NaSO4+NaCl	05lo	112.20	108.35	201.70	197.85	196.56	0.00	-187.02	-187.02	-95.15	10.83	89.50	78.67	2.38	2.38	2.09	12.10	
NaSO4+NaCl	06lo	105.50	101.65	188.60	184.75	194.59	0.00	-175.75	-175.75	-90.32	9.00	83.10	74.10	2.37	2.37	2.11	10.83	
NaSO4+NaCl	07lo	111.65	107.80	199.50	195.65	196.49	196.17	10.30	10.30	5.24	9.78	87.85	78.07	2.38	2.38	2.12	11.13	
NaSO4+NaCl	08lo	110.50	106.65	197.30	193.45	194.71	0.00	-184.48	-184.48	-94.75	8.97	86.80	77.83	2.37	2.37	2.13	10.33	

Appendix: C

NaSO4+NaCl	09lo	103.50	99.65	182.80	178.95	179.71	0.00	-171.89	-171.89	-95.65	7.06	79.30	72.24	2.38	2.38	2.17	8.90
NaSO4+NaCl	10lo	105.50	101.65	191.10	187.25	188.18	187.78	11.56	11.56	6.14	11.03	85.60	74.57	2.36	2.36	2.06	12.89
NaSO4+NaCl	11lo	100.00	96.15	178.80	174.95	175.85	0.00	-165.66	-165.66	-94.21	9.29	78.80	69.51	2.38	2.38	2.10	11.79
NaSO4+NaCl	12lo	110.00	106.15	197.10	193.25	194.13	0.00	-185.84	-185.84	-95.73	7.41	87.10	79.69	2.33	2.33	2.13	8.51
NaSO4+NaCl	13lo	113.90	110.05	204.50	200.65	202.38	0.00	-190.09	-190.09	-93.93	10.56	90.60	80.04	2.37	2.37	2.10	11.66
NaSO4+NaCl	14lo	105.25	101.40	187.80	183.95	184.41	184.31	9.42	9.42	5.11	9.06	82.55	73.49	2.38	2.38	2.12	10.98
NaSO4+NaCl	15lo	116.50	112.65	209.50	205.65	206.36	0.00	-193.99	-193.99	-94.01	11.66	93.00	81.34	2.38	2.38	2.09	12.54
H2O	01CC	108.50	195.90	192.05	193.02	0.00	-181.15	-181.15	-93.85	10.90	87.40	76.50	2.37	2.37	2.07	12.47	
H2O	02CC	100.50	178.00	174.15	174.76	0.00	-166.10	-166.10	-95.04	8.05	77.50	69.45	2.39	2.39	2.14	10.39	
H2O	03CC	103.70	183.70	179.85	180.90	0.00	-172.54	-172.54	-95.38	7.31	80.00	72.69	2.37	2.37	2.16	9.14	

Appendix: C

Evaporation	Test:	Raw Data							Weight Gain (g) Over Time (days)										
Salt	Code	Dry Wt	After Soak	1 Day	2 Days	3 Days	4 Days	5 Days	6 Days	7 Days	9 Days	11 Days	13 Days	15 Days	17 Days	20 Days	23 Days	26 Days	
NaCl	01ns	183.31	195.14	190.36	188.97	188.20	187.62	187.11	186.86	186.48	186.10	185.69	185.37	185.23	185.05	184.86	184.74	184.74	
NaCl	02ns	174.94	185.07	180.71	179.67	179.15	178.75	178.38	178.19	177.94	177.62	177.24	177.02	176.86	176.67	176.44	176.26	176.20	
NaCl	03ns	176.88	189.35	183.60	182.08	181.35	180.84	180.37	180.12	179.78	179.42	178.97	178.73	178.59	178.42	178.27	178.20	178.23	
NaCl	Control	178.38	189.85	184.89	183.57	182.90	182.40	181.95	181.72	181.40	181.05	180.63	180.37	180.23	180.05	179.86	179.73	179.72	
NaCl	04ns	176.53	186.60	181.45	180.41	179.93	179.57	179.23	179.05	178.81	178.58	178.28	178.10	178.01	177.88	177.74	177.65	177.65	
NaCl	05ns	155.88	164.02	159.86	159.11	158.74	158.45	158.16	158.02	157.80	157.62	157.35	157.22	157.13	157.01	156.91	156.81	156.81	
NaCl	06ns	178.61	187.22	183.39	182.56	182.16	181.86	181.57	181.43	181.21	181.00	180.73	180.56	180.44	180.30	180.11	179.96	179.88	
NaCl	Na4Fe(CN)6	170.34	179.28	174.90	174.03	173.61	173.29	172.99	172.83	172.61	172.40	172.12	171.96	171.86	171.73	171.59	171.47	171.45	
NaCl	07ns	198.91	208.81	203.93	202.97	202.51	202.17	201.82	201.67	201.42	201.21	200.92	200.76	200.64	200.49	200.33	200.19	200.10	
NaCl	08ns	172.22	184.16	177.29	176.08	175.52	175.11	174.71	174.53	174.24	174.03	173.76	173.63	173.57	173.48	173.47	173.45	173.45	
NaCl	09ns	183.45	193.21	188.39	187.30	186.81	186.46	186.12	185.96	185.71	185.50	185.21	185.04	184.94	184.81	184.67	184.57	184.56	
NaCl	k4Fe(CN)6	184.86	195.39	189.87	188.78	188.28	187.91	187.55	187.39	187.12	186.91	186.63	186.48	186.38	186.26	186.16	186.07	186.04	
NaCl	10ns	177.53	187.59	182.63	181.54	181.03	180.64	180.27	180.10	179.82	179.62	179.31	179.16	179.06	178.93	178.80	178.71	178.71	
NaCl	11ns	165.17	173.55	169.47	168.63	168.23	167.94	167.65	167.54	167.31	167.13	166.87	166.73	166.64	166.51	166.36	166.24	166.20	
NaCl	12ns	172.22	181.82	176.74	175.80	175.34	174.99	174.65	174.50	174.25	174.05	173.77	173.66	173.56	173.44	173.35	173.26	173.26	
NaCl	k4Fe(CN)6 + (NaPO3)6	171.64	180.99	176.28	175.32	174.87	174.52	174.19	174.05	173.79	173.60	173.32	173.18	173.09	172.96	172.84	172.74	172.72	
NaCl	13ns	181.43	192.51	186.58	185.49	185.02	184.64	184.28	184.11	183.85	183.63	183.33	183.17	183.07	182.92	182.80	182.69	182.65	
NaCl	14ns	193.10	205.55	199.76	198.29	197.62	197.10	196.59	196.35	196.00	195.68	195.26	195.02	194.90	194.75	194.60	194.52	194.52	
NaCl	15ns	197.66	209.38	203.12	201.89	201.30	200.85	200.43	200.23	199.90	199.70	199.38	199.22	199.15	199.03	198.96	198.90	198.90	
NaCl	Na4Fe(CN)6 + (NaPO3)6	190.73	202.48	196.49	195.22	194.65	194.20	193.77	193.56	193.25	193.00	192.66	192.47	192.37	192.23	192.12	192.04	192.02	
NaSO4	01nc	180.11	190.78	186.65	185.54	184.97	184.47	183.99	183.78	183.40	183.08	182.64	182.39	182.22	182.00	181.76	181.60	181.56	
NaSO4	02nc	186.74	198.52	193.90	192.63	192.00	191.48	190.97	190.71	190.28	189.92	189.42	189.14	188.96	188.73	188.49	188.34	188.33	
NaSO4	03nc	174.78	185.01	181.28	180.26	179.78	179.39	179.00	178.80	178.45	178.15	177.73	177.47	177.29	177.06	176.77	176.54	176.40	
NaSO4	Control	180.54	191.44	187.28	186.14	185.58	185.11	184.65	184.43	184.04	183.72	183.26	183.00	182.82	182.60	182.34	182.16	182.10	
NaSO4	04nc	183.66	196.90	191.45	189.84	189.20	188.57	187.95	187.64	187.15	186.75	186.25	185.97	185.80	185.60	185.44	185.35	185.38	
NaSO4	05nc	196.85	211.35	205.43	203.60	202.79	202.10	201.42	201.09	200.55	200.10	199.53	199.23	199.07	198.87	198.75	198.69	198.72	
NaSO4	06nc	167.35	177.66	173.47	172.40	171.88	171.42	171.02	170.83	170.48	170.17	169.76	169.53	169.38	169.19	168.94	168.78	168.73	
NaSO4	Na4Fe(CN)6	182.62	195.30	190.12	188.61	187.96	187.36	186.80	186.52	186.06	185.67	185.18	184.91	184.75	184.55	184.38	184.27	184.28	
NaSO4	07nc	189.26	203.37	197.67	195.79	194.96	194.27	193.55	193.25	192.75	192.33	191.81	191.54	191.40	191.22	191.11	191.07	191.09	
NaSO4	08nc	198.28	214.08	207.85	205.71	204.77	203.93	203.13	202.76	202.18	201.70	201.12	200.81	200.64	200.44	200.32	200.28	200.30	
NaSO4	09nc	172.94	184.03	179.96	178.80	178.31	177.85	177.37	177.14	176.73	176.39	175.92	175.63	175.44	175.20	174.90	174.69	174.57	
NaSO4	k4Fe(CN)6	186.83	200.49	195.16	193.43	192.68	192.02	191.35	191.05	190.55	190.14	189.62	189.33	189.16	188.95	188.78	188.68	188.65	
NaSO4	10nc	173.45	186.31	180.77	179.30	178.51	177.90	177.30	177.02	176.55	176.18	175.69	175.44	175.30	175.13	175.05	175.00	175.01	
NaSO4	11nc	177.00	189.27	184.24	182.80	182.08	181.50	180.93	180.66	180.23	179.88	179.43	179.18	179.04	178.85	178.66	178.55	178.56	
NaSO4	12nc	188.35	198.26	194.40	193.40	192.92	192.54	192.14	191.96	191.65	191.36	190.98	190.75	190.50	190.38	190.10	189.91	189.81	
NaSO4	k4Fe(CN)6 + (NaPO3)6	179.60	191.28	186.47	185.17	184.50	183.98	183.46	183.21	182.81	182.47	182.03	181.79	181.61	181.45	181.27	181.15	181.13	
NaSO4	13nc	206.71	219.32	213.87	212.49	211.76	211.21	210.68	210.43	210.01	209.70	209.28	209.03	208.90	208.70	208.50	208.38	208.37	
NaSO4	14nc	177.41	186.53	182.99	182.08	181.66	181.30	180.93	180.77	180.48	180.25	179.92	179.74	179.62	179.45	179.24	179.08	179.00	
NaSO4	15nc	175.50	184.51	181.30	180.47	179.98	179.64	179.30	179.14	178.85	178.58	178.22	178.00	177.84	177.64	177.36	177.13	177.01	
NaSO4	Na4Fe(CN)6 + (NaPO3)6	186.54	196.79	192.72	191.68	191.13	190.72	190.30	190.11	189.78	189.51	189.14	188.92	188.79	188.60	188.37	188.20	188.13	
NaSO4+NaCl	01nn	190.97	199.99	196.29	195.53	195.14	194.84	194.57	194.43	194.21	193.97	193.66	193.48	193.35	193.17	192.93	192.74	192.62	

Appendix: C

NaSO4+NaCl	02nn	185.44	199.13	193.35	192.06	191.43	190.98	190.55	190.32	190.01	189.65	189.23	188.96	188.78	188.51	186.53	187.90	187.70
NaSO4+NaCl	03nn	183.63	196.52	191.58	190.46	189.87	189.43	189.00	188.78	188.45	188.10	187.68	187.38	187.17	186.92	187.35	186.25	186.05
NaSO4+NaCl	Control	186.68	198.55	193.74	192.68	192.15	191.75	191.37	191.18	190.89	190.57	190.19	189.94	189.77	189.53	188.94	188.96	188.79
NaSO4+NaCl	04nn	185.27	199.28	193.16	191.64	190.93	190.36	189.80	189.55	189.11	188.10	188.29	188.01	187.85	187.62	187.35	187.19	187.11
NaSO4+NaCl	05nn	187.00	200.85	193.89	192.54	191.93	191.42	190.93	190.74	190.36	190.09	189.69	189.46	189.35	189.15	188.95	188.83	188.82
NaSO4+NaCl	06nn	180.35	191.64	186.64	185.69	185.23	184.85	184.47	184.32	184.05	183.80	183.47	183.26	183.10	182.92	182.67	182.47	182.36
NaSO4+NaCl	Na4Fe(CN)6	184.21	197.26	191.23	189.96	189.36	188.88	188.40	188.20	187.84	187.33	187.15	186.91	186.77	186.56	186.32	186.16	186.10
NaSO4+NaCl	07nn	167.02	176.10	172.15	171.38	170.99	170.69	170.39	170.26	170.02	169.81	169.54	169.36	169.23	169.06	168.86	168.67	168.57
NaSO4+NaCl	08nn	191.33	205.01	198.86	197.70	197.11	196.65	196.17	195.97	195.60	195.29	194.84	194.55	194.36	194.11	193.77	193.54	193.40
NaSO4+NaCl	09nn	186.42	196.15	192.04	191.28	190.90	190.59	190.29	190.15	189.91	189.69	189.40	189.21	189.07	188.88	188.62	188.42	188.27
NaSO4+NaCl	k4Fe(CN)6	181.59	192.42	187.68	186.79	186.33	185.98	185.62	185.46	185.18	184.93	184.59	184.37	184.22	184.02	183.75	183.54	183.41
NaSO4+NaCl	10nn	173.55	185.96	179.36	178.08	177.53	177.08	176.65	176.45	176.12	175.92	175.62	175.48	175.41	175.28	175.25	175.18	175.21
NaSO4+NaCl	11nn	180.41	195.27	188.44	186.96	186.27	185.71	185.21	184.95	184.57	184.23	183.75	183.45	183.26	183.01	182.72	182.54	182.50
NaSO4+NaCl	12nn	183.92	196.61	191.20	190.06	189.46	188.98	188.54	188.32	187.97	187.67	187.22	186.92	186.73	186.49	186.17	185.94	185.84
NaSO4+NaCl	k4Fe(CN)6 + (NaPO3)6	179.29	192.61	186.33	185.03	184.42	183.92	183.47	183.24	182.89	182.61	182.20	181.95	181.80	181.59	181.38	181.22	181.18
NaSO4+NaCl	13nn	179.66	188.74	184.67	183.90	183.52	183.22	182.89	182.77	182.51	182.32	182.04	181.84	181.74	181.56	181.36	181.20	181.10
NaSO4+NaCl	14nn	179.38	193.24	186.40	184.94	184.28	183.76	183.23	183.03	182.67	182.39	181.98	181.76	181.63	181.48	181.32	181.25	181.22
NaSO4+NaCl	15nn	188.46	203.03	196.13	194.74	194.07	193.51	192.93	192.71	192.30	192.00	191.53	191.23	191.09	190.85	190.63	190.47	190.46
NaSO4+NaCl	Na4Fe(CN)6 + (NaPO3)6	182.50	195.00	189.07	187.86	187.29	186.83	186.35	186.17	185.83	185.57	185.18	184.94	184.82	184.63	184.44	184.31	184.26
H2O	01EE	180.44	193.50	184.77	183.51	182.58	182.20	181.66	181.18	180.78	180.58	180.56	180.51	180.53	180.49	180.50	180.53	180.53
H2O	02EE	171.23	181.77	174.72	173.69	172.96	172.64	172.23	171.86	171.53	171.36	171.31	171.27	171.27	171.23	171.25	171.29	171.29
H2O	03EE	181.94	184.88	185.67	184.35	183.48	183.14	182.71	182.36	182.09	182.02	182.04	182.00	182.00	181.98	181.98	182.02	182.02
	H2O Control	177.87	186.72	181.72	180.52	179.67	179.33	178.87	178.47	178.13	177.99	177.97	177.93	177.93	177.90	177.91	177.95	177.95

Durability Tests: Raw Data Key

Durability Test 1: Raw Data Key

Dry Weight (g)	M0 (g)
Dry weight after salt contamination	M1 (g)
Weight of salt in tile (g)	M1-M0 (g)
Weight loss after 4-week weathering	M3
Amount of weight loss (g)	M1-M3 (g)
Amount of salt loss (g)	(M1-M3)-M4 (g)
% loss of salt	M8 (%)
% Total weight loss	M6(%)
Weight of spalled material	M4 (g)
% Weight loss of spalled material	M7(%)

Durability Test 2: Raw Data Key

Amount of weight loss (g)	N0-N3 (g)
Amount of salt loss (g)	(M1-M3)-M4 (g)
% loss of salt	N6 (%)
% Total weight loss	N5(%)
Weight of spalled material	N4 (g)
% Weight loss of spalled material	N7(%)

NaCl Cohort

Durability Test 1: Raw Data

Tile	M0 (g)	M1 (g)	M1-M0 (g)	M3	M1-M3 (g)	(M1-M3)-N	M8 (%)	M6(%)	M4 (g)	M7(%)
01C	161.17	164.49	3.32	-	-	-	-	-	-	-
02C	192.43	195.72	3.29	-	-	-	-	-	-	-
03C	172.52	175.77	3.25	-	-	-	-	-	-	-
04C	192.93	197.08	4.15	-	-	-	-	-	-	-
05C	191.89	195.96	4.07	193.36	2.60				1.33	
06C	180.44	184.48	4.04	182.16	2.32				1.26	
09C	188.38	192.77	4.39	190.20	2.57				1.33	
10C	188.75	193.17	4.42	190.55	2.62				1.36	
Avg	187.37	191.60	4.23	189.07	2.53	1.44	0.74		1.32	1.09
11C	192.70	196.39	3.69	194.20	2.19				1.12	
12C	169.38	173.00	3.62	172.61	0.39				0.23	
13C	166.95	171.22	4.27	168.47	2.75				1.61	
14C	187.12	190.47	3.35	188.20	2.27				1.19	
Avg	179.04	182.77	3.73	180.87	1.90	1.06	0.57		1.03	0.84
17C	196.93	199.21	2.28	196.88	2.33				1.17	
18C	176.10	179.51	3.41	177.10	2.41				1.34	
20C	174.20	178.08	3.88	175.21	2.87				1.61	
Avg	182.41	185.60	3.19	183.06	2.54	1.83	0.99		1.37	0.71
21C	190.93	194.56	3.63	192.22	2.34				1.20	
22C	175.05	178.55	3.50	176.33	2.22				1.24	
25C	171.96	175.43	3.47	173.24	2.19				1.25	
26C	184.95	189.02	4.07	186.57	2.45				1.30	
Avg	180.72	184.39	3.67	182.09	2.30	1.38	0.75		1.25	0.92
27C	192.32	196.44	4.12	194.00	2.44				1.24	
28C	178.10	181.76	3.66	179.28	2.48				1.36	
29C	171.26	174.97	3.71	170.61	4.36				2.49	
30C	171.56	174.44	2.88	172.74	1.70				0.97	
Avg	178.31	181.90	3.59	179.16	2.74	2.58	1.43		1.52	0.16

Na2SO4 Cohort				Durability Test 1: Raw Data						
Tile	M0 (g)	M1 (g)	M1-M0 (g)	M3	M1-M3 (g)	(M1-M3)-M4 (g)	M8 (%)	M6(%)	M4 (g)	M7(%)
01S	184.68	189.48	4.80	-	-	-	-	-	-	-
02S	194.03	200.33	6.30	-	-	-	-	-	-	-
03S	178.55	183.95	5.40	-	-	-	-	-	-	-
04S	174.36	179.62	5.26	-	-	-	-	-	-	-
05S	195.88	201.47	5.59	198.33	3.14			1.56		
06S	179.46	184.09	4.63	181.65	2.44			1.33		
09S	171.71	176.90	5.19	173.26	3.64			2.06		
10S	178.68	184.86	6.18	181.28	3.58			1.94		
Avg	181.43	186.83	5.40	183.63	3.20	3.00	1.61	1.72	0.20	0.11
11S	181.12	186.30	5.18	183.22	3.08			1.65		
12S	171.11	174.85	3.74	172.57	2.28			1.30		
13S	164.26	168.83	4.57	166.18	2.65			1.57		
14S	199.01	203.11	4.10	200.50	2.61			1.29		
Avg	178.88	183.27	4.40	180.62	2.66	2.52	1.38	1.45	0.14	0.08
17S	178.30	183.88	5.58	180.25	3.63			1.97		
18S	179.24	184.62	5.38	180.92	3.70			2.00		
19S	190.84	196.07	5.23	193.32	2.75			1.40		
20S	171.75	175.32	3.57	173.54	1.78			1.02		
Avg	180.03	184.97	4.94	182.01	2.97	2.80	1.51	1.60	0.17	0.09
21S	175.51	180.88	5.37	177.53	3.35			1.85		
22S	175.76	180.81	5.05	177.79	3.02			1.67		
25S	180.35	185.70	5.35	182.31	3.39			1.83		
26S	176.97	181.83	4.86	178.63	3.20			1.76		
Avg	177.15	182.31	5.16	179.07	3.24	3.06	1.68	1.78	0.18	0.10
27S	168.58	173.14	4.56	170.22	2.92			1.69		
28S	173.09	178.96	5.87	175.12	3.84			2.15		
29S	174.95	179.98	5.03	176.86	3.12			1.73		
30S	188.93	194.45	5.52	190.58	3.87			1.99		
Avg	176.39	181.63	5.08	178.20	3.44	3.26	1.79	1.89	0.18	0.10

NaCl/ Na2SO4	Cohort		Durability Test 1: Raw Data							
Tile	M0 (g)	M1 (g)	M1-M0 (g)	M3	M1-M3 (g)	(M1-M3)-N	M8 (%)	M6(%)	M4 (g)	M7(%)
01CS	166.27	175.40	9.13	-	-	-	-	-	-	-
02CS	168.64	178.76	10.12	-	-	-	-	-	-	-
03CS	188.07	195.94	7.87	-	-	-	-	-	-	-
04CS	185.46	195.44	9.98	-	-	-	-	-	-	-
05CS	179.94	191.27	11.33	186.35	4.92			2.57		
06CS	174.34	185.03	10.69	180.22	4.81			2.60		
09CS	174.16	184.00	9.84	180.31	3.69			2.01		
10CS	180.35	191.00	10.65	186.33	4.67			2.45		
Avg	177.20	187.83	10.63	183.30	4.52	3.67	1.95	2.41	0.85	0.45
11CS	168.12	175.80	7.68	170.43	5.37			3.05		
13CS	174.14	185.03	10.89	177.08	7.95			4.30		
14CS	169.31	177.24	7.93	171.18	6.06			3.42		
Avg	170.52	179.36	8.83	172.90	6.46	6.21	3.45	3.59	0.25	0.14
17CS	181.78	189.22	7.44	183.62	5.60			2.96		
18CS	167.22	175.86	8.64	169.28	6.58			3.74		
19CS	176.36	184.99	8.63	178.65	6.34			3.43		
20CS	182.43	191.71	9.28	184.76	6.95			3.63		
Avg	176.95	185.45	8.50	179.08	6.37	5.91	3.19	3.44	0.46	0.25
21CS	184.21	195.58	11.37	185.12	10.46			5.35		
22CS	187.26	197.32	10.06	187.08	10.24			5.19		
25CS	163.17	173.40	10.23	165.58	7.82			4.51		
26CS	187.83	198.31	10.48	190.32	7.99			4.03		
Avg	180.62	191.15	10.54	182.03	9.13	8.16	4.26	4.77	0.97	0.51
27CS	175.27	186.21	10.94	178.18	8.03			4.31		
28CS	182.77	193.74	10.97	189.47	4.27			2.20		
29CS	203.41	212.60	9.19	205.63	6.97			3.28		
30CS	190.80	200.26	9.46	193.04				0.00		
Avg	188.06	198.20	10.14	191.58	6.42	5.39	1.91	2.45	1.03	0.54

NaCl	Durability Test 2: Raw Data						
Cohort	N0 (g)	N0-M3 (g)	(N0-M3)-N4 (g)	N6 (%)	N5 (%)	N4 (g)	N7 (%)
01C	-	-	-	-	-	-	-
02C	-	-	-	-	-	-	-
03C	-	-	-	-	-	-	-
04C	-	-	-	-	-	-	-
05C	191.74	1.62				0.84	
06C	180.37	1.79				0.98	
09C	188.24	1.96				1.03	
10C	188.76	1.79				0.94	
Avg	187.28	1.79	1.02	0.54		0.95	0.77 0.41
11C	192.47	1.73				0.89	
12C	170.90	1.71				0.99	
13C	166.79	1.68				1.00	
14C	186.97	1.23				0.65	
Avg	179.28	1.59	1.45	0.80		0.88	0.14 0.08
17C	194.98	1.90				0.97	
18C	176.25	0.85				0.48	
20C	174.24	0.97				0.55	
Avg	181.82	1.24	1.19	0.65		0.68	0.05 0.03
21C	190.38	1.84				0.96	
22C	174.74	1.59				0.90	
25C	171.85	1.39				0.80	
26C	184.78	1.79				0.96	
Avg	180.44	1.65	1.65	0.91		0.91	0.00 0.00
27C	191.93	2.07				1.07	
28C	177.97	1.31				0.73	
29C	168.97	1.64				0.96	
30C	171.42	1.32				0.76	
Avg	177.57	1.59	1.41	0.78		0.88	0.18 0.10

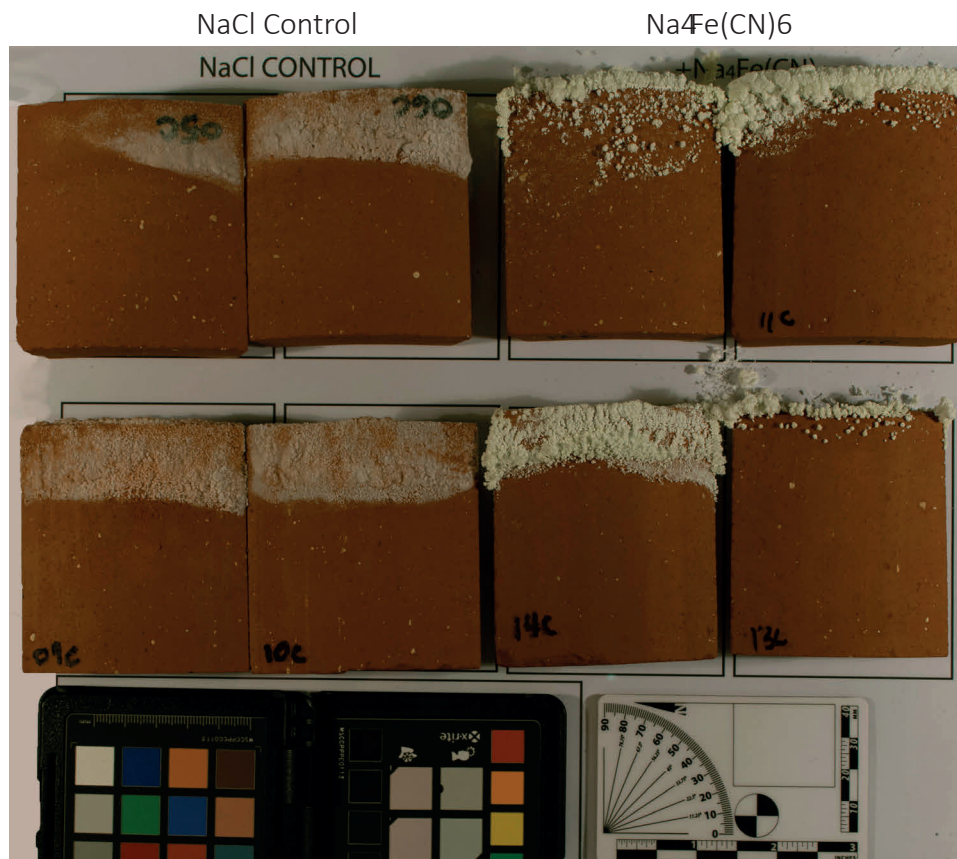
NaCl/	Na2SO4	Cohort	Durability Test 2: Raw Data				
Tile	N0 (g)	N0-M3 (g)	(N0-M3)-N4 (g)	N6 (%)	N5 (%)	N4 (g)	N7 (%)
01CS	-	-	-	-	-	-	-
02CS	-	-	-	-	-	-	-
03CS	-	-	-	-	-	-	-
04CS	-	-	-	-	-	-	-
05CS	180.70	5.65				3.03	
06CS	174.88	5.34				2.96	
09CS	174.83	5.48				3.04	
10CS	180.79	5.54				2.97	
Avg	177.80	5.50	3.77	2.06		3.00	1.73
11CS	168.07	2.36				1.38	
13CS	174.12	2.96				1.67	
14CS	169.36	1.82				1.06	
Avg	170.52	2.38	2.15	1.24		1.38	0.23
17CS	182.70	0.92				0.50	
18CS	167.31	1.97				1.16	
19CS	176.75	1.90				1.06	
20CS	183.32	1.44				0.78	
Avg	177.52	1.56	1.36	0.76		0.87	0.20
21CS	182.35	2.77				1.50	
22CS	186.76	0.32				0.17	
25CS	163.11	2.47				1.49	
26CS	188.01	2.31				1.21	
Avg	180.06	1.97	1.22	0.67		1.08	0.75
27CS	175.16	3.02				1.69	
28CS	186.76	2.71				1.43	
29CS	203.28	2.35				1.14	
30CS	190.46	2.58				1.34	
Avg	188.92	2.67		0.95		1.40	0.86

Appendix:C

Na2SO4	Cohort		Durability Test 2: Raw Data				
Tile	N0 (g)	N0-M3 (g)	(N0-M3)-N	N6 (%)	N5 (%)	N4 (g)	N7 (%)
01S	-	-	-	-	-	-	-
02S	-	-	-	-	-	-	-
03S	-	-	-	-	-	-	-
04S	-	-	-	-	-	-	-
05S	195.74	2.59			1.31		
06S	179.84	1.81			1.00		
09S	172.49	0.77			0.44		
10S	178.88	2.40			1.32		
Avg	181.74	1.89	1.35	0.74	1.03	0.54	0.29
11S	181.62	1.60			0.87		
12S	171.32	1.25			0.72		
13S	163.95	2.23			1.34		
14S	199.95	0.55			0.27		
Avg	179.21	1.41	0.91	0.50	0.78	0.50	0.28
17S	178.82	1.43			0.79		
18S	180.10	0.82			0.45		
19S	192.02	1.30			0.67		
20S	172.16	1.38			0.80		
Avg	180.78	1.23	0.89	0.49	0.68	0.34	0.19
21S	176.06	1.47			0.83		
22S	175.77	2.02			1.14		
25S	180.88	1.43			0.78		
26S	178.03	0.60			0.34		
Avg	177.69	1.38	0.81	0.45	0.77	0.57	0.32
27S	169.22	1.00			0.59		
28S	173.02	2.10			1.20		
29S	174.74	2.12			1.20		
30S	189.72	0.86			0.45		
Avg	176.68	1.52	1.01	0.57	0.85	0.51	0.29

Appendix D

2 Weeks



4 Weeks



Appendix D

2 Weeks

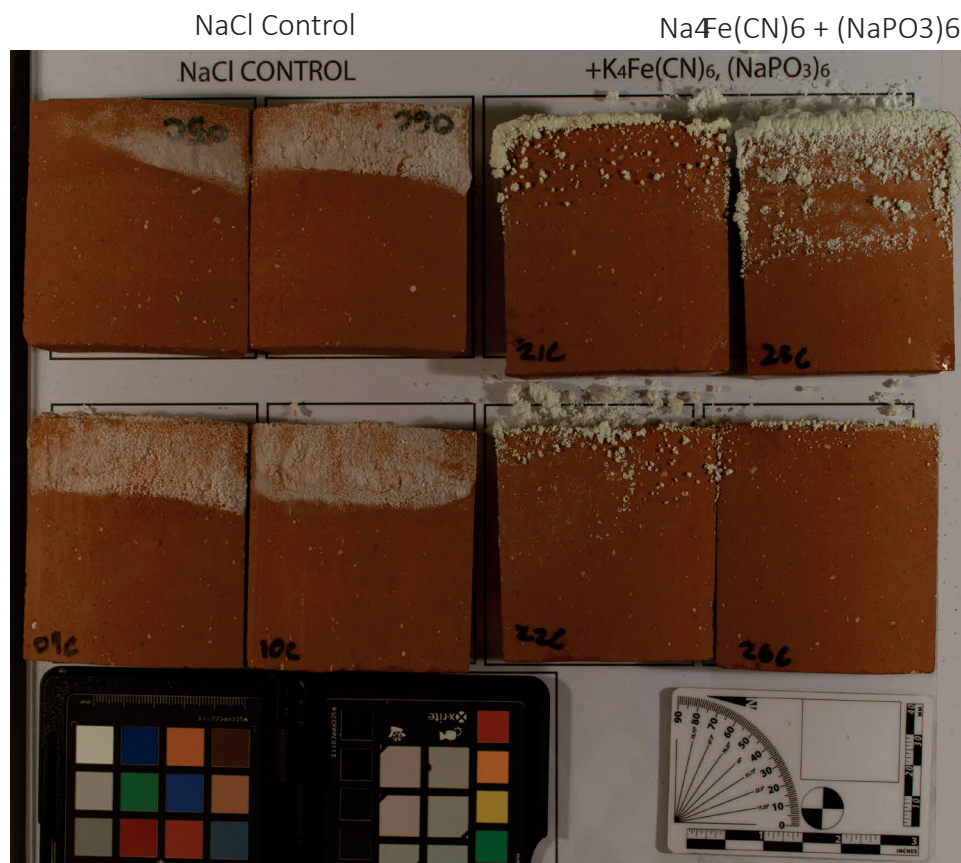


4 Weeks



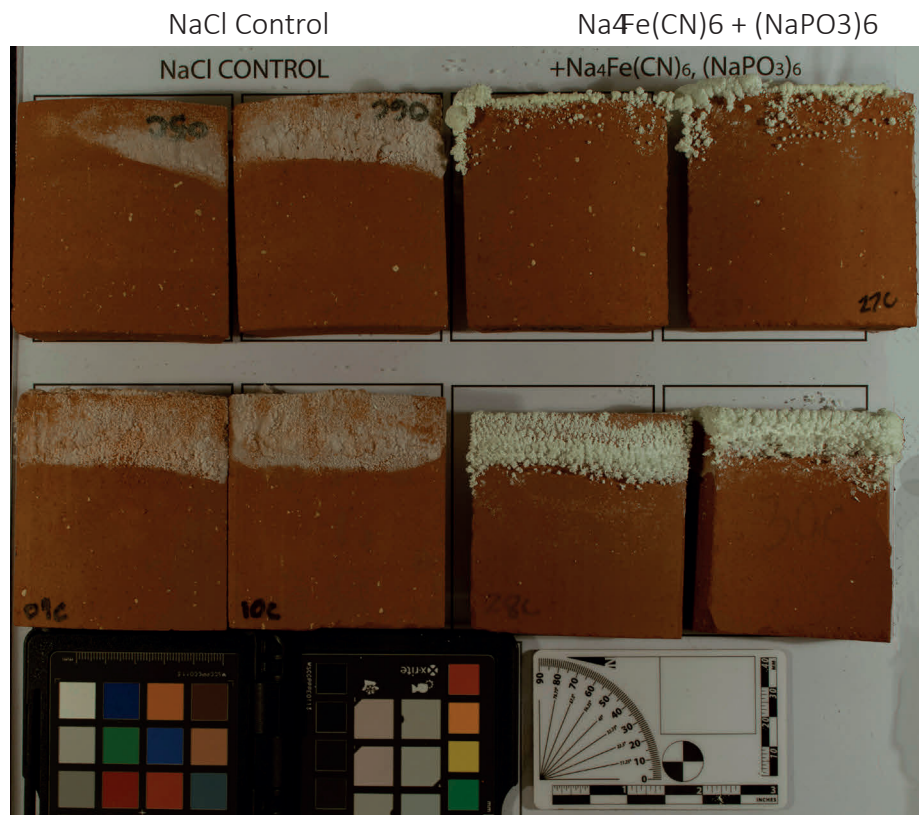
Appendix D

2 Weeks

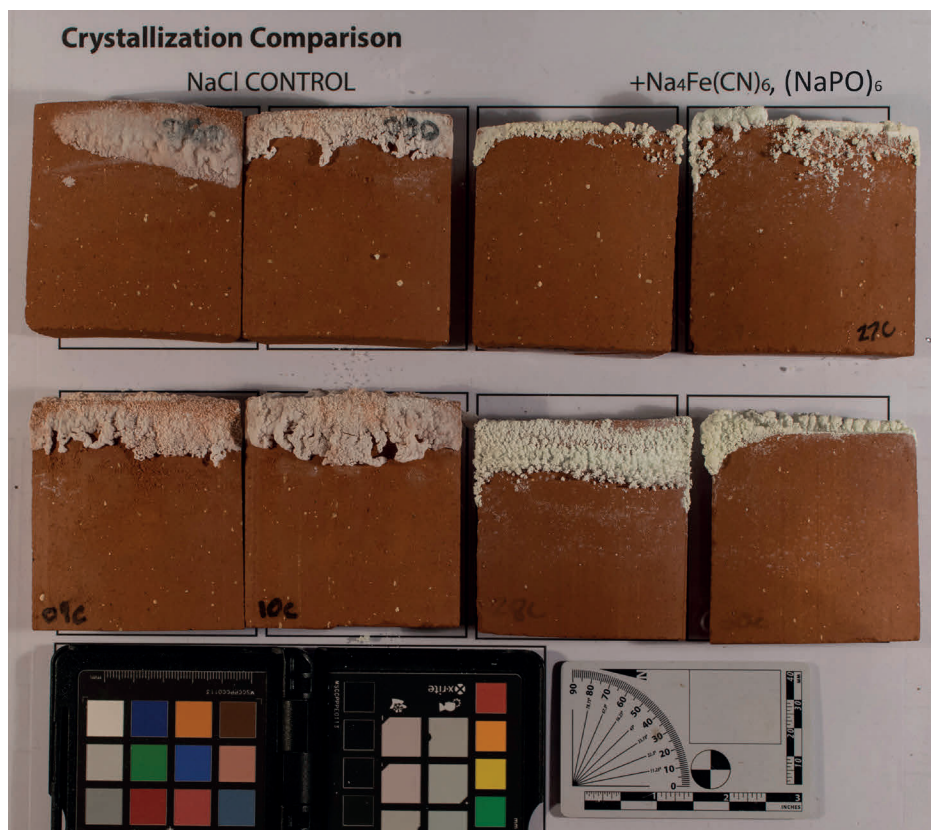


Appendix D

2 Weeks



4 Weeks



Appendix D

Na_2SO_4 Control

$\text{Na}_4\text{Fe}(\text{CN})_6$

2 Weeks

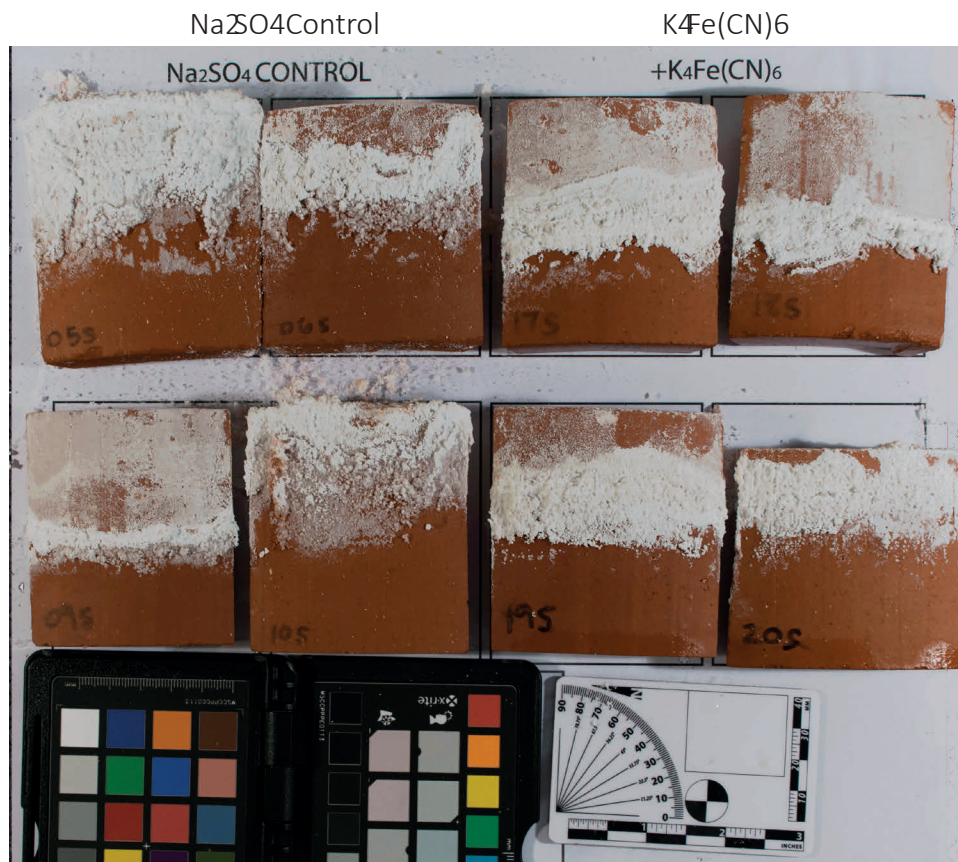


4 Weeks



Appendix D

2 Weeks

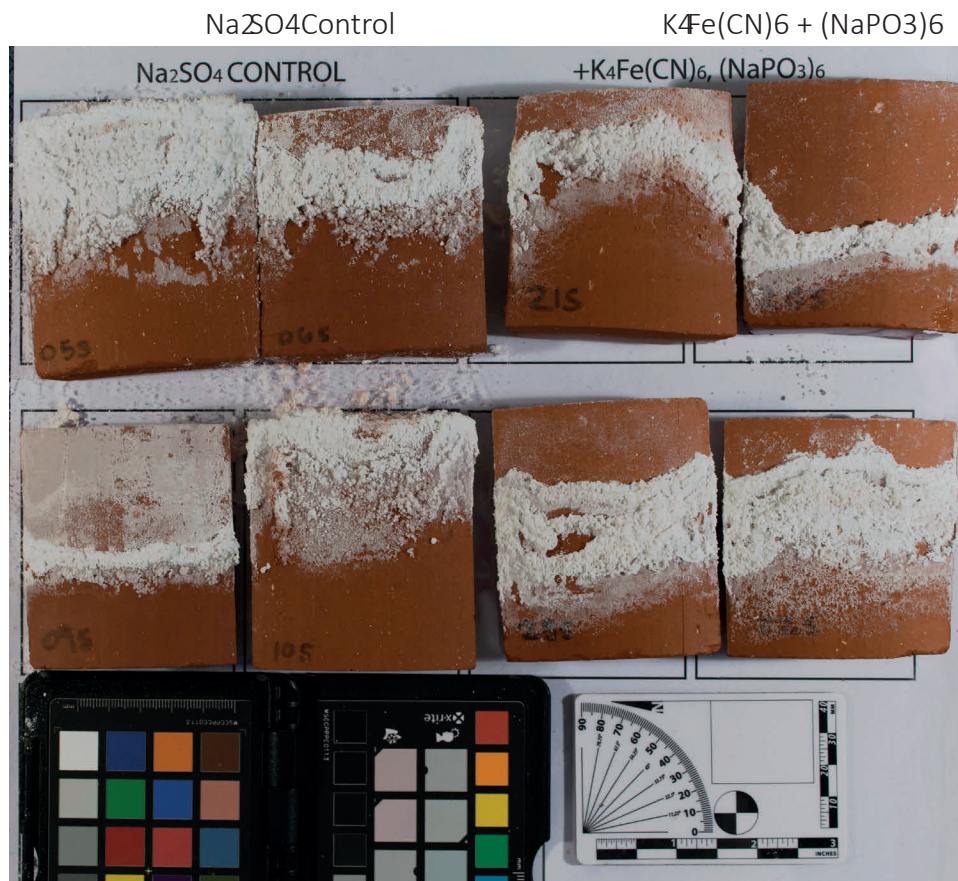


4 Weeks



Appendix D

2 Weeks



4 Weeks

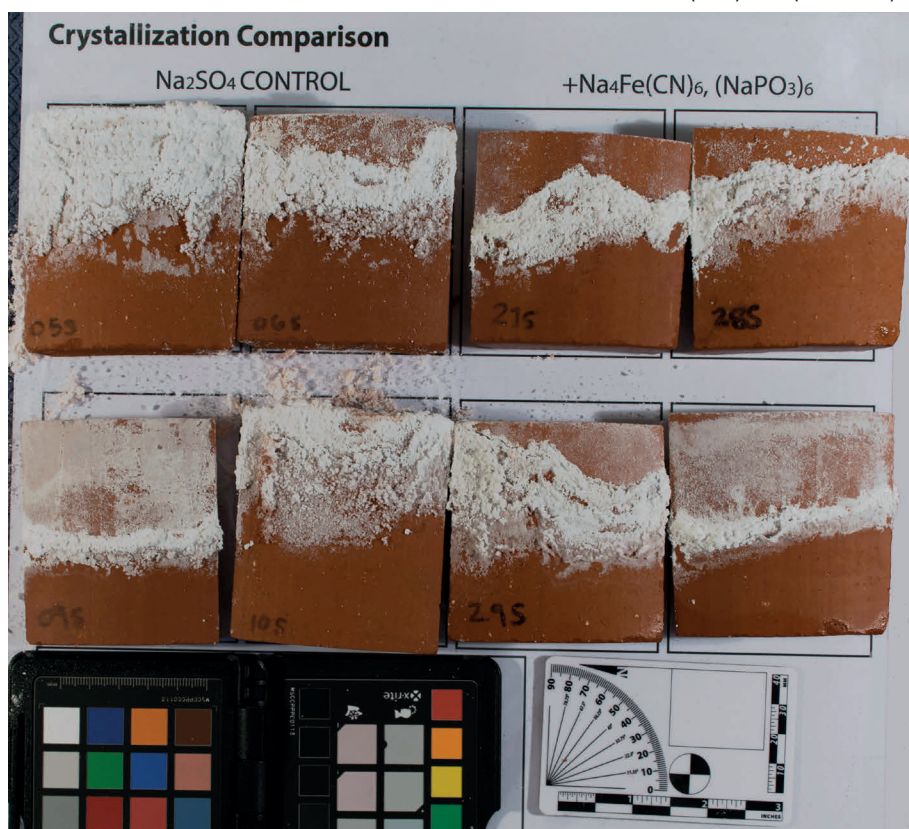


Appendix D

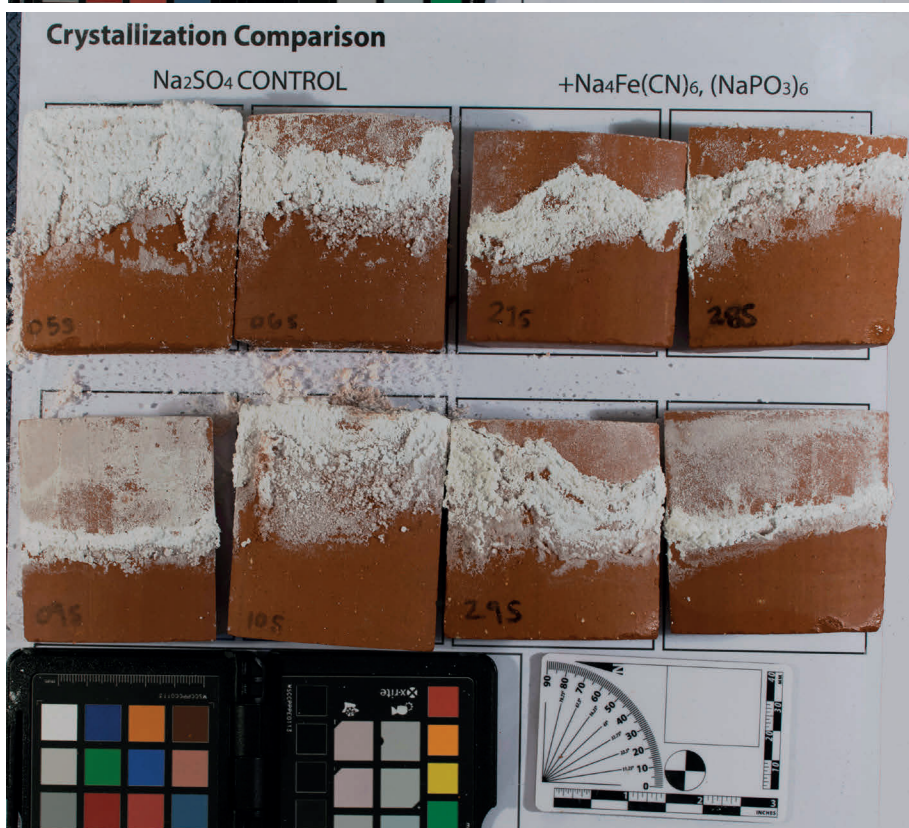
Na_2SO_4 Control

$\text{Na}_4\text{Fe}(\text{CN})_6 + (\text{NaPO}_3)_6$

2 Weeks



4 Weeks

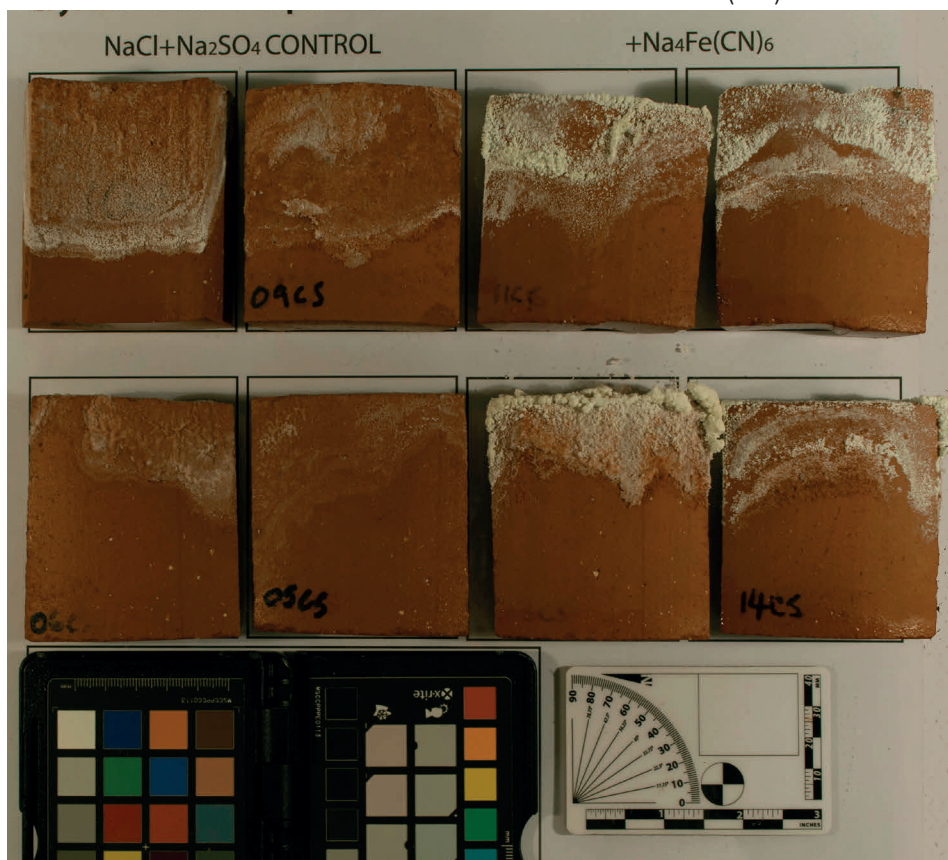


Appendix D

2 Weeks

NaCl/Na₂SO₄Control

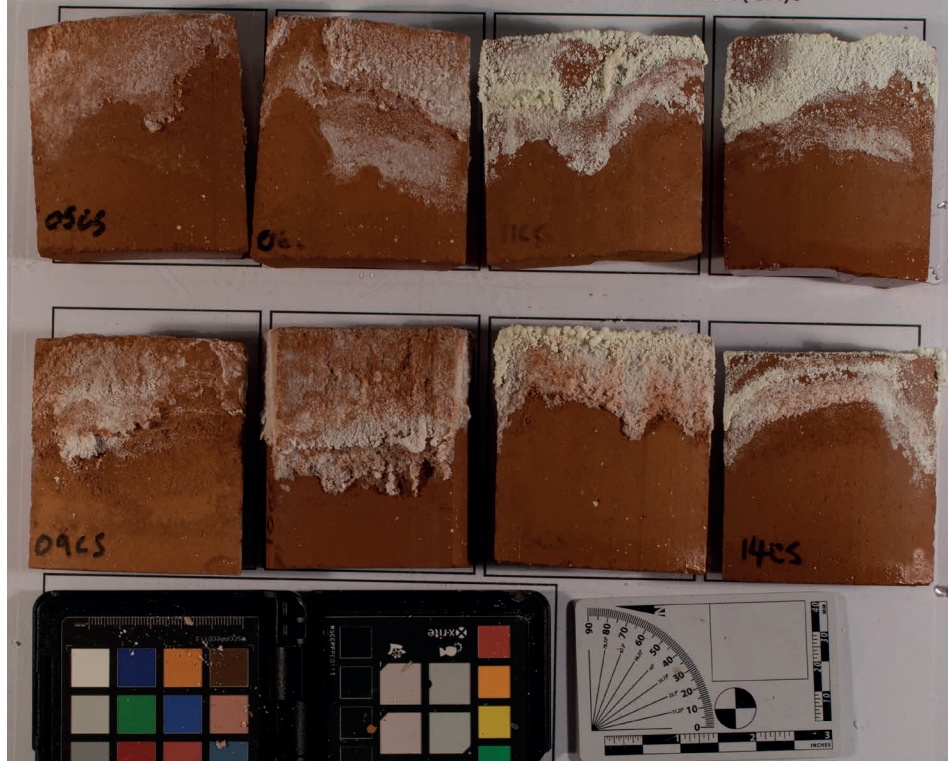
Na₄Fe(CN)₆



4 Weeks

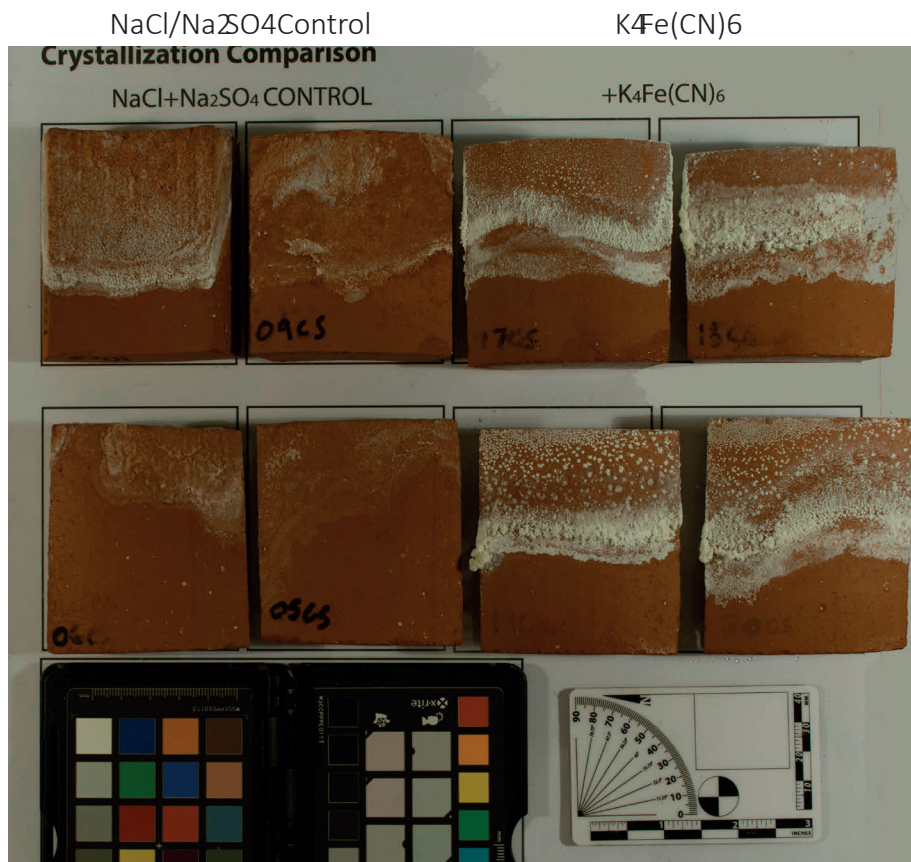
NaCl+Na₂SO₄ CONTROL

+Na₄Fe(CN)₆

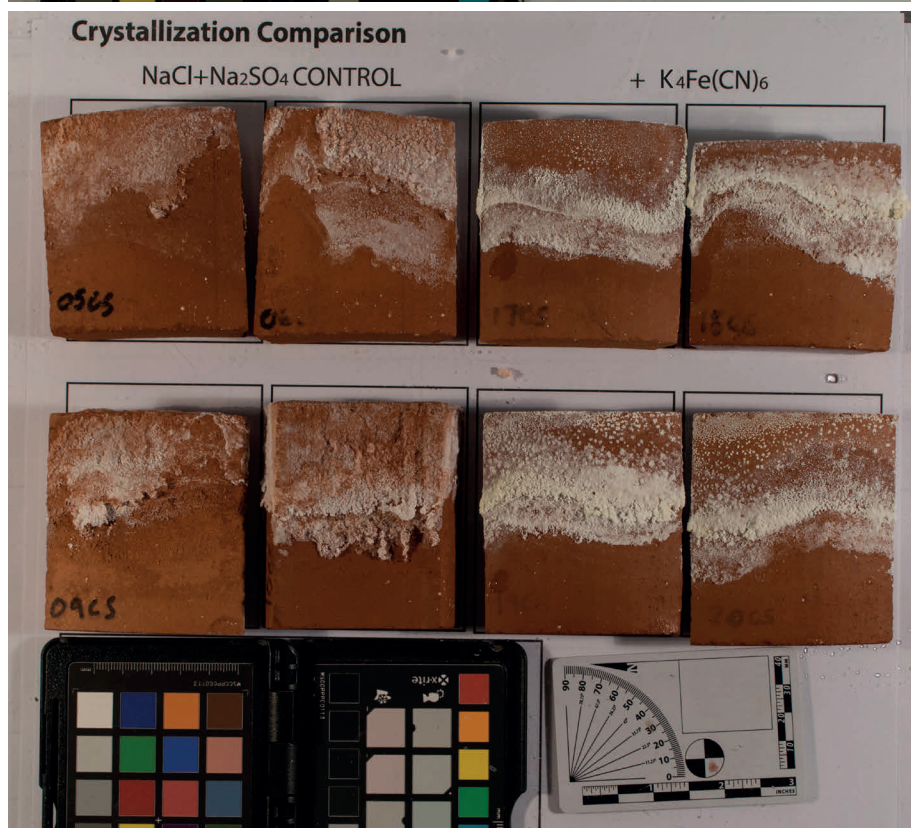


Appendix D

2 Weeks

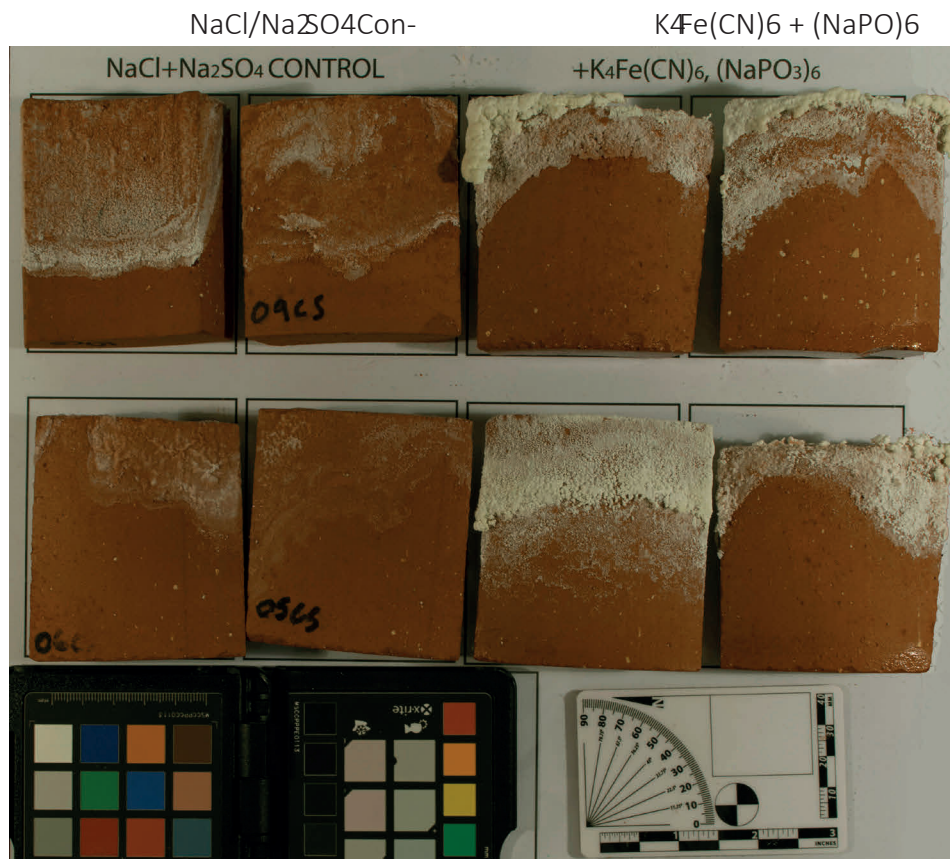


4 Weeks

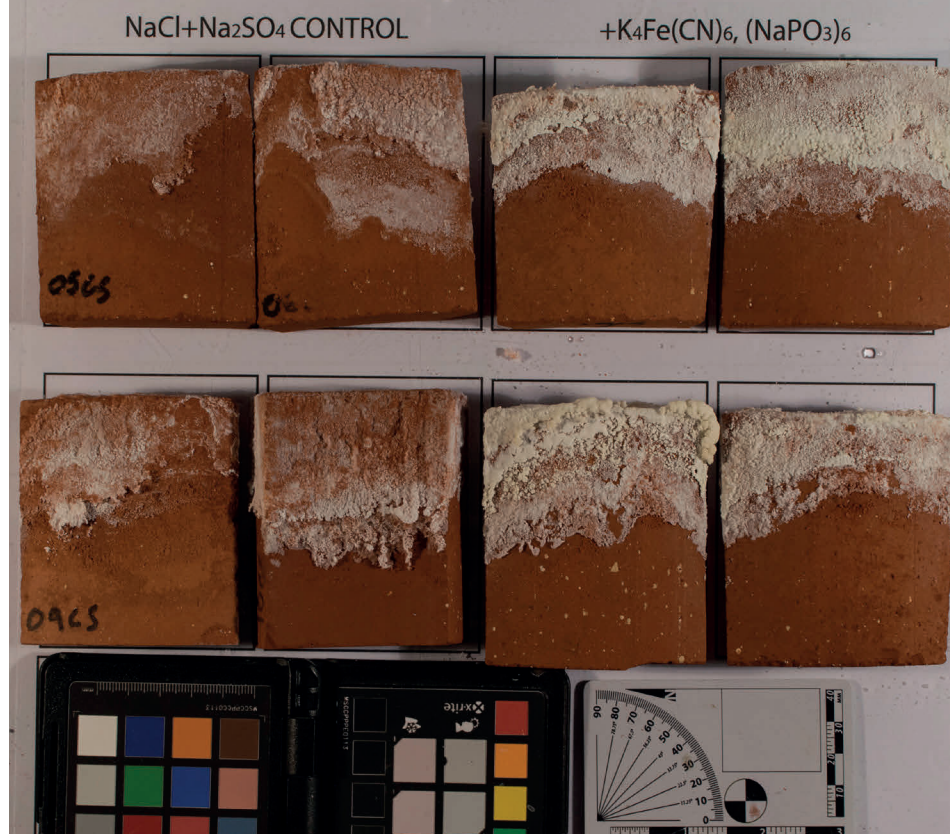


Appendix D

2 Weeks



4 Weeks

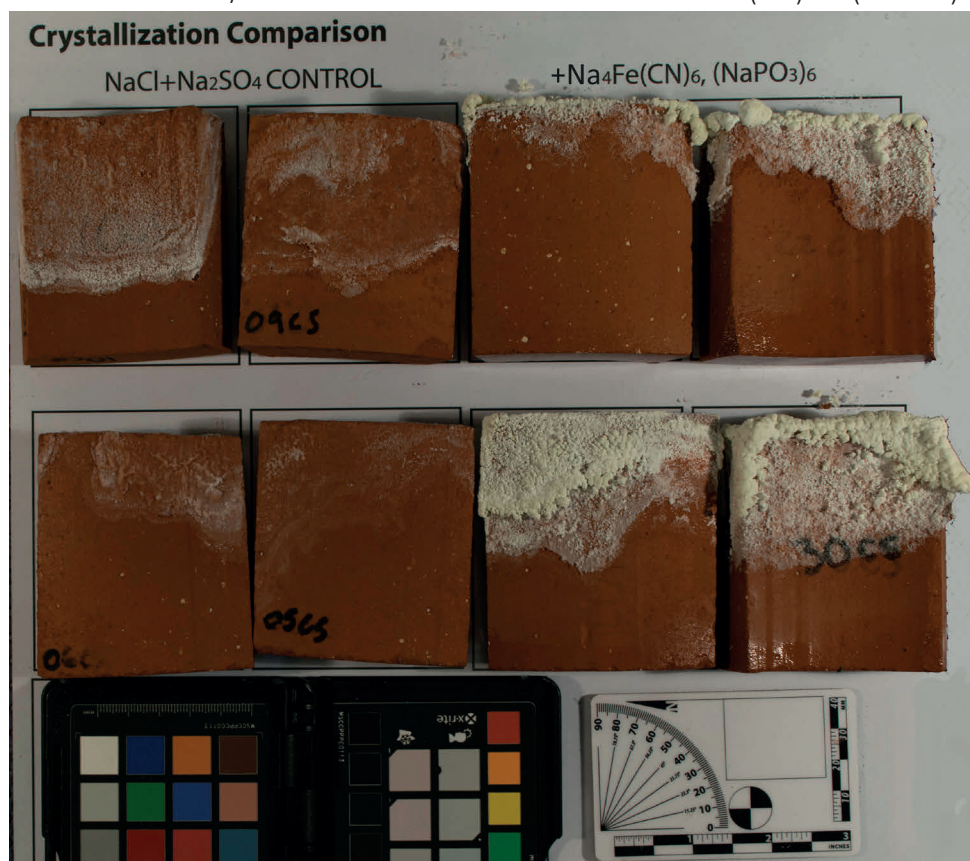


Appendix D

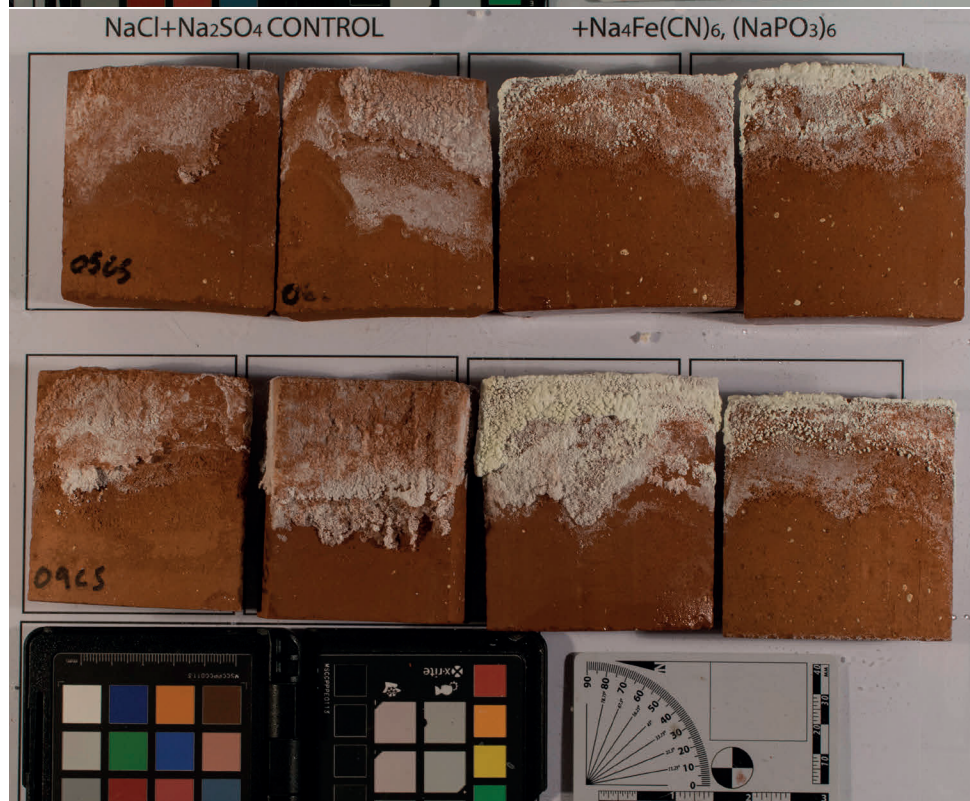
NaCl/Na₂SO₄Control

Na₄Fe(CN)₆ + (NaPO₃)₆

2 Weeks



4 Weeks



Appendix D
1 Week

NaCl Control

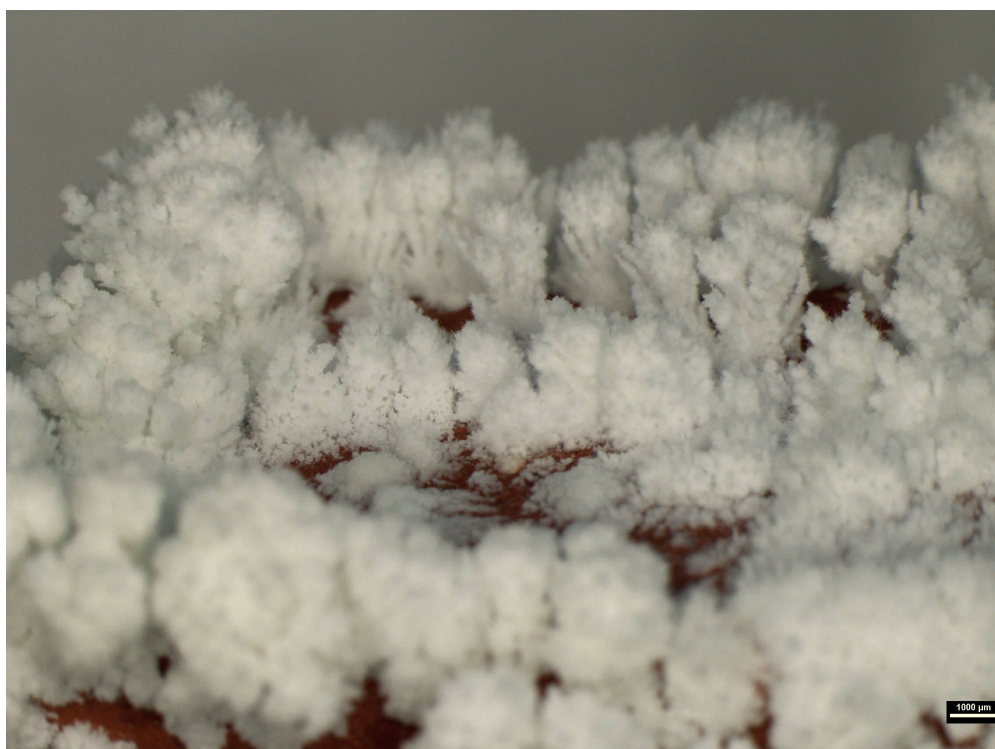


4 Weeks



Mag: 16x. A Leica MZ16a Microscope was used and photographs taken with a Nikon DS Fi-1 Camera with NIS Elements BR Software.

1 Week



4 Weeks



Mag: 16x. A Leica MZ16a Microscope was used and photographs taken with a Nikon DS Fi-1 Camera with NIS Elements BR Software.

Appendix D

1 Week



4 Weeks

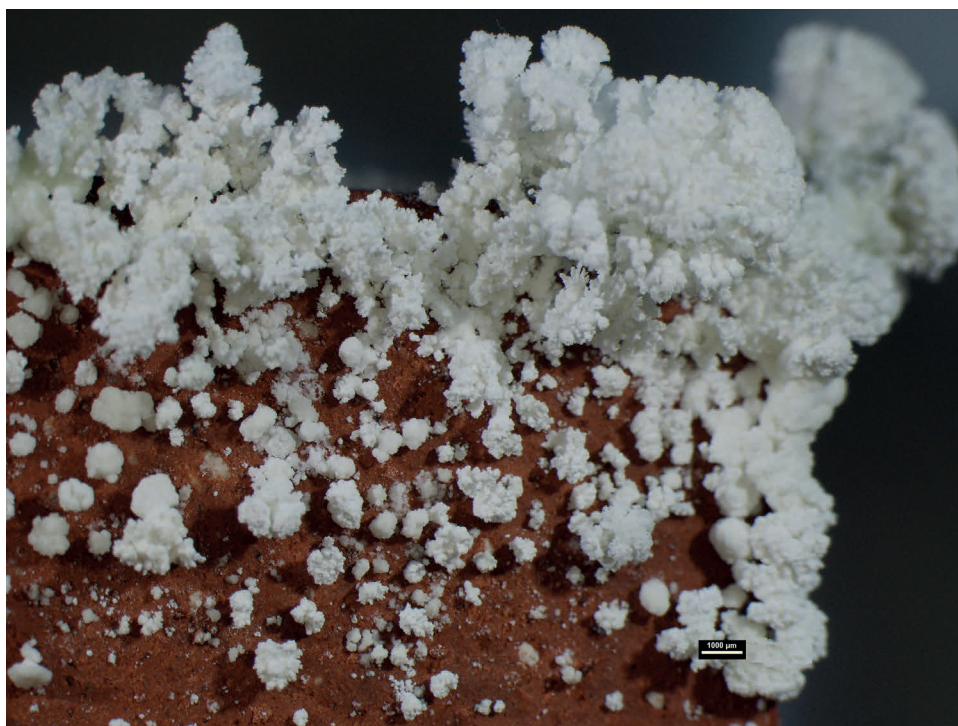


Mag: 40x and 16x. A Leica MZ16a Microscope was used and photographs taken with a Nikon DS Fi-1 Camera with NIS Elements BR Software.

1 Week

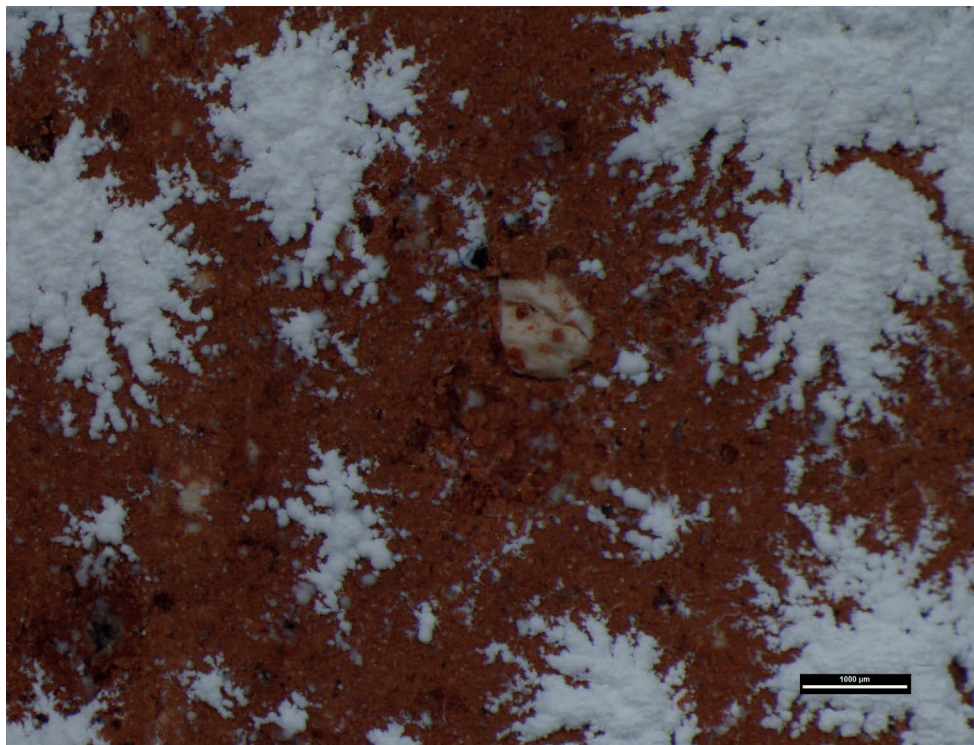


4 Weeks



Mag: 16x. A Leica MZ16a Microscope was used and photographs taken with a Nikon DS Fi-1 Camera with NIS Elements BR Software.

1 Week



4 Weeks



Mag: 40x. A Leica MZ16a Microscope was used and photographs taken with a Nikon DS Fi-1 Camera with NIS Elements BR Software.

1 Week



4 Weeks

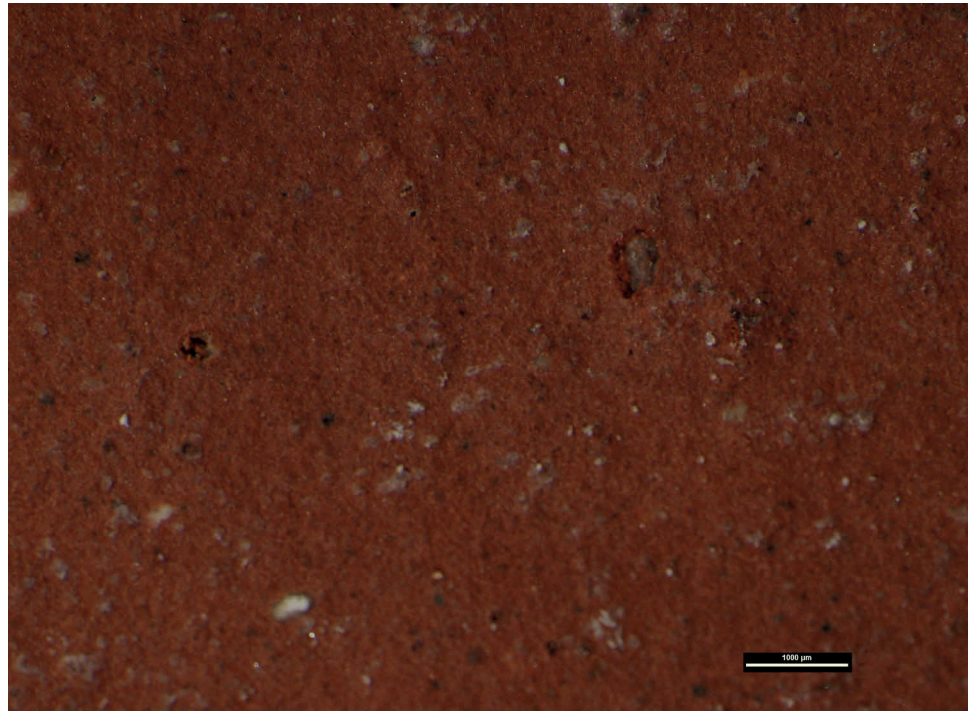


Mag: 16x. A Leica MZ16a Microscope was used and photographs taken with a Nikon DS Fi-1 Camera with NIS Elements BR Software.

Appendix D

Na₂SO₄ Control

1 Week

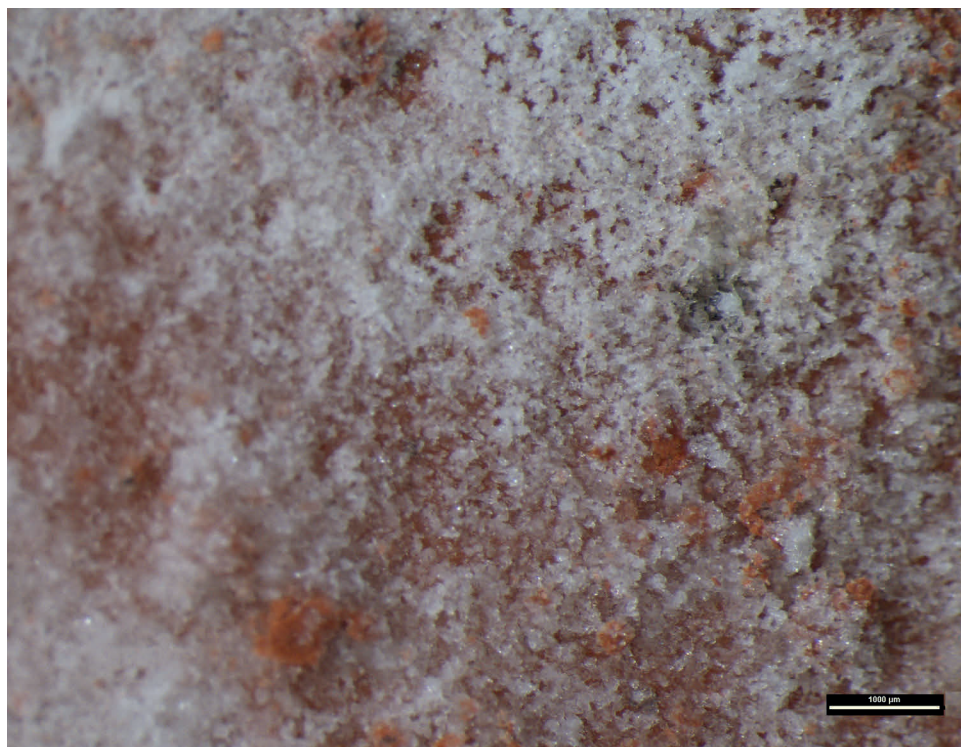


4 Weeks



Mag: 40x. A Leica MZ16a Microscope was used and photographs taken with a Nikon DS Fi-1 Camera with NIS Elements BR Software.

1 Week

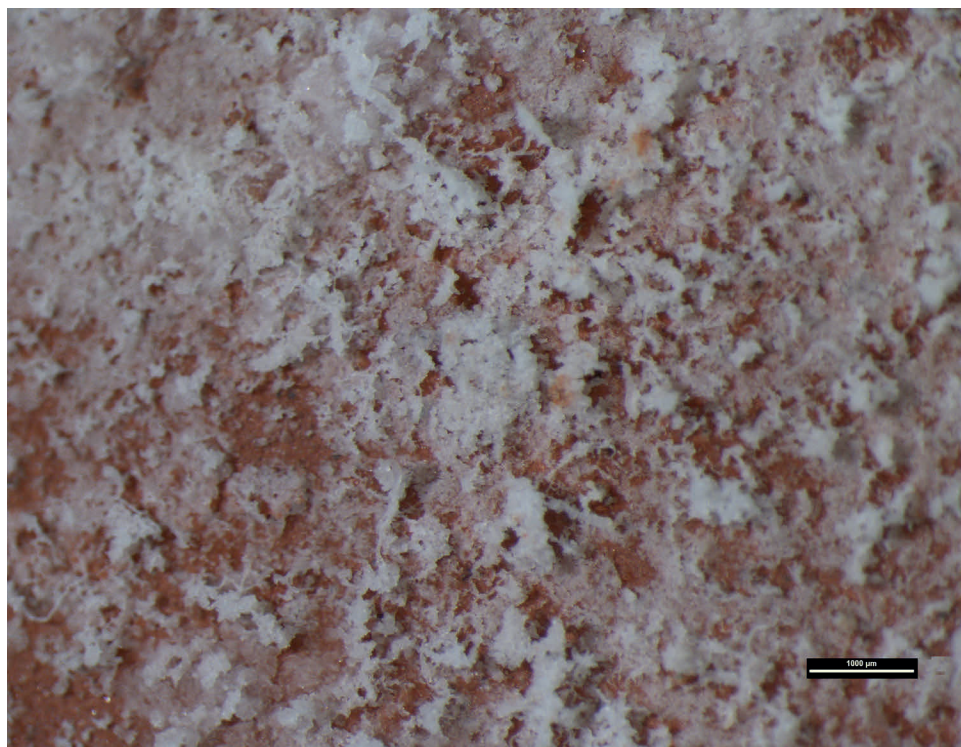


4 Weeks



Mag: 40x. A Leica MZ16a Microscope was used and photographs taken with a Nikon DS Fi-1 Camera with NIS Elements BR Software.

1 Week

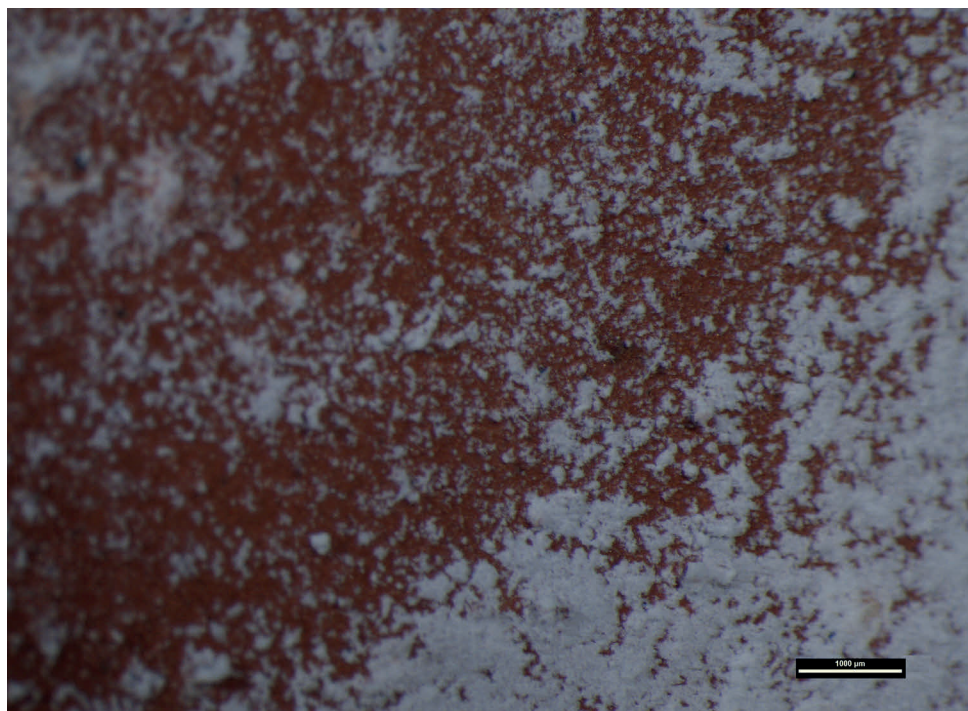


4 Weeks



Mag: 16x. A Leica MZ16a Microscope was used and photographs taken with a Nikon DS Fi-1 Camera with NIS Elements BR Software.

1 Week

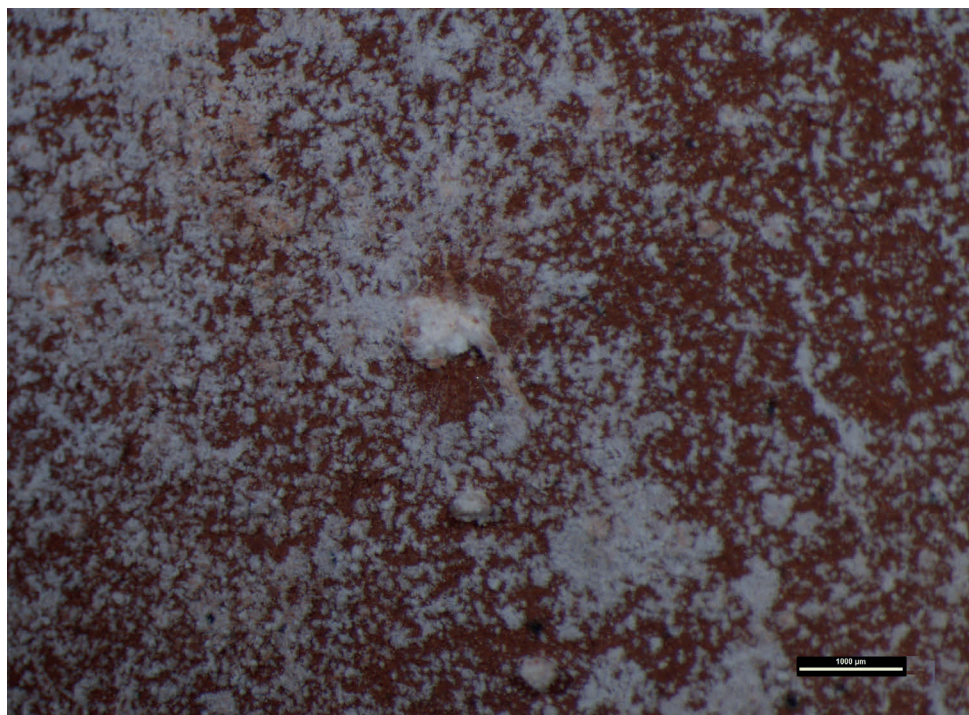


4 Weeks



Mag: 40x. A Leica MZ16a Microscope was used and photographs taken with a Nikon DS Fi-1 Camera with NIS Elements BR Software.

1 Week



4 Weeks

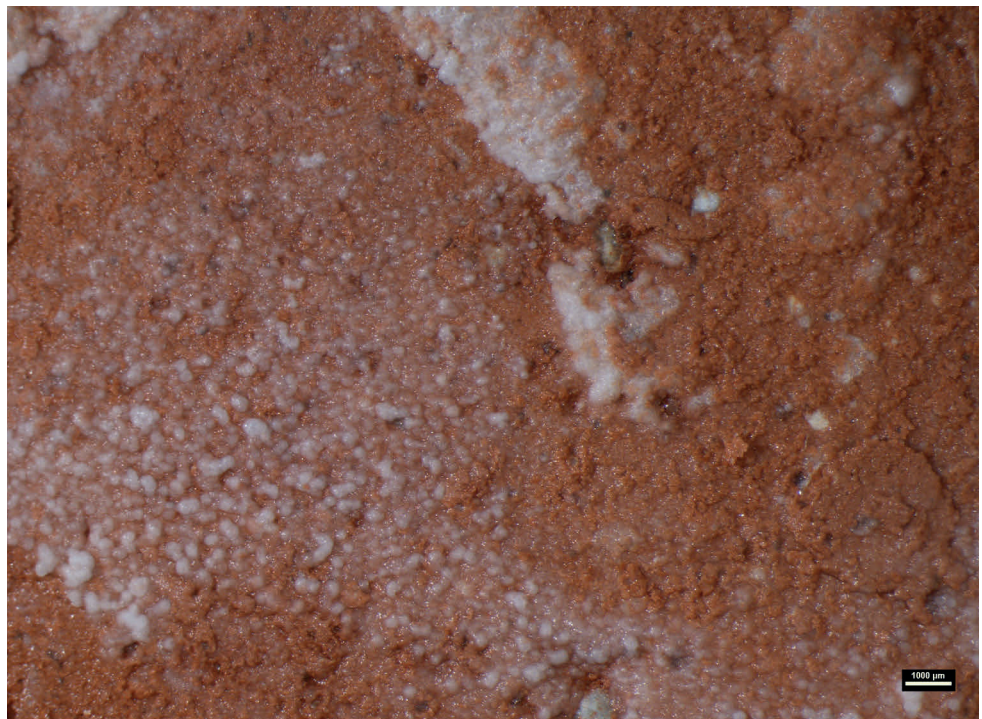


Mag: 40x. A Leica MZ16a Microscope was used and photographs taken with a Nikon DS Fi-1 Camera with NIS Elements BR Software.

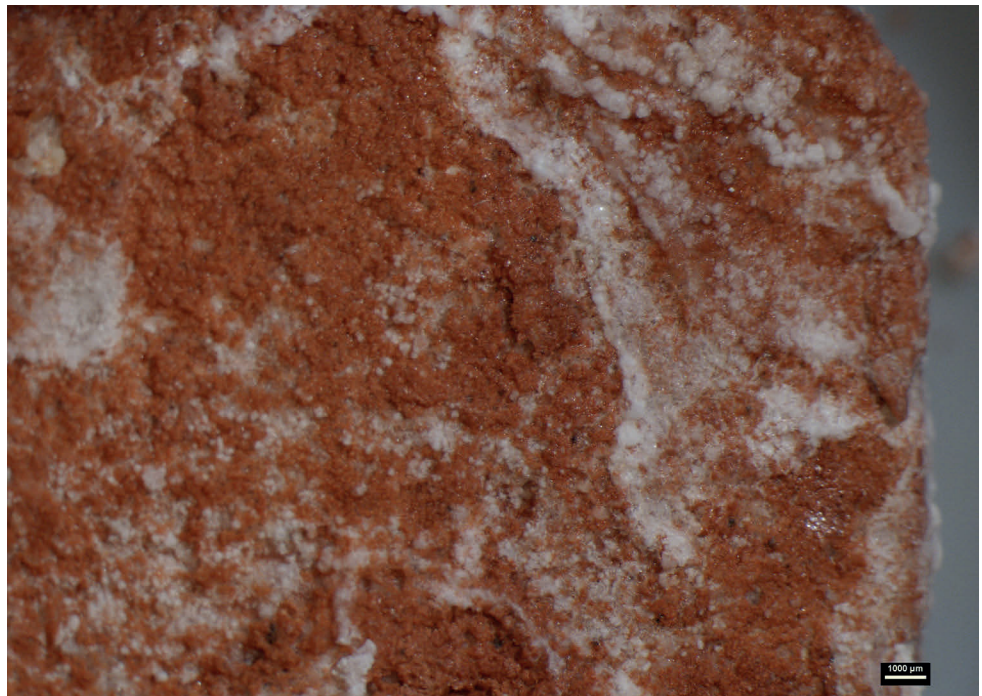
Appendix D

NaCl/Na₂SO₄ Control

1 Week



4 Weeks



Mag: 16x. A Leica MZ16a Microscope was used and photographs taken with a Nikon DS Fi-1 Camera with NIS Elements BR Software.

1 Week

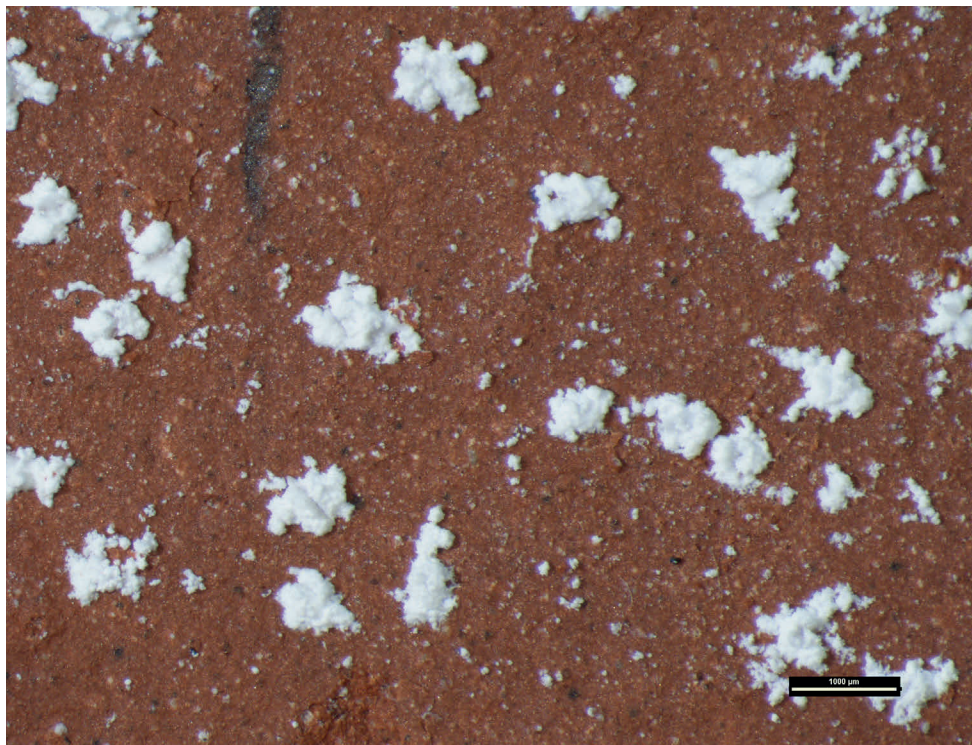


4 Weeks

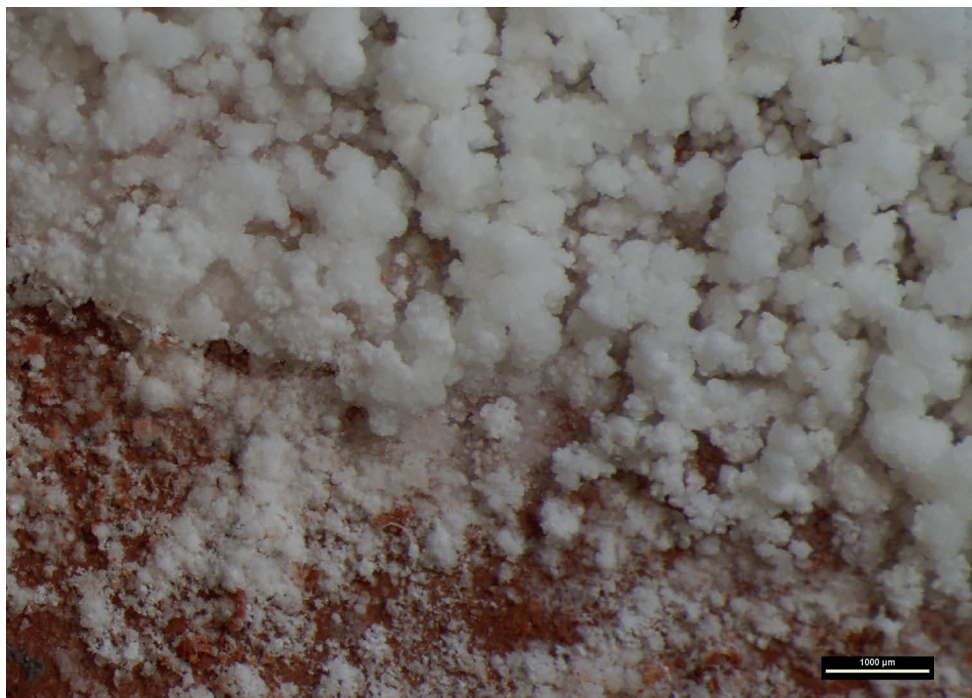


Mag: 16x. A Leica MZ16a Microscope was used and photographs taken with a Nikon DS Fi-1 Camera with NIS Elements BR Software.

1 Week



4 Weeks



Mag: 40x. A Leica MZ16a Microscope was used and photographs taken with a Nikon DS Fi-1 Camera with NIS Elements BR Software.

1 Week



4 Weeks



Mag: 16x. A Leica MZ16a Microscope was used and photographs taken with a Nikon DS Fi-1 Camera with NIS Elements BR Software.

1 Week



4 Weeks



Mag: 16x. A Leica MZ16a Microscope was used and photographs taken with a Nikon DS Fi-1 Camera with NIS Elements BR Software.

Appendix D

NaCl Control

1 Week



4 Weeks



Appendix D

$\text{NaCl} + \text{Na}_4\text{Fe}(\text{CN})_6$

1 Week



4 Weeks



Appendix D



1 Week



4 Weeks



Appendix D



1 Week



4 Weeks



Appendix D



1 Week



4 Weeks



Appendix D

Na₂SO₄ Control

1 Week



4 Weeks



Appendix D

$\text{Na}_2\text{SO}_4/\text{Na}_4\text{Fe}(\text{CN})$

1 Week



4 Weeks



Appendix D



1 Week



4 Weeks



Appendix D



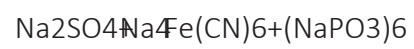
1 Week



4 Weeks



Appendix D



1 Week



4 Weeks



Appendix D

NaCl/Na₂SO₄Control

1 Week



4 Weeks



Appendix D

NaCl/Na₂SO₄/Na₄Fe(CN)₆

1 Week



4 Weeks



Appendix D

$\text{NaCl}/\text{Na}_2\text{SO}_4/\text{K}_4\text{Fe}(\text{CN})_6$

1 Week



4 Weeks



Appendix D

$\text{NaCl}/\text{Na}_2\text{SO}_4/\text{K}_4\text{Fe}(\text{CN})_6/(\text{NaPO}_3)_6$

1 Week



4 Weeks



Appendix D

$\text{NaCl}/\text{Na}_2\text{SO}_4/\text{K}_4\text{Fe}(\text{CN})_6 + (\text{NaPO}_3)_6$

1 Week



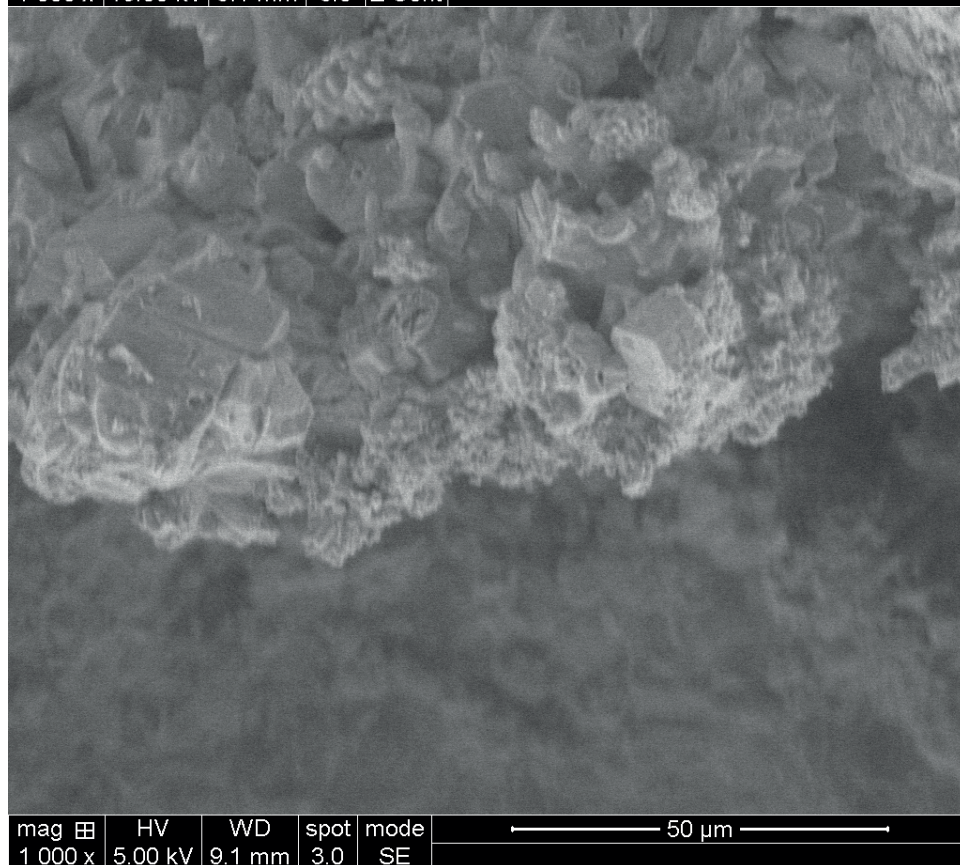
4 Weeks



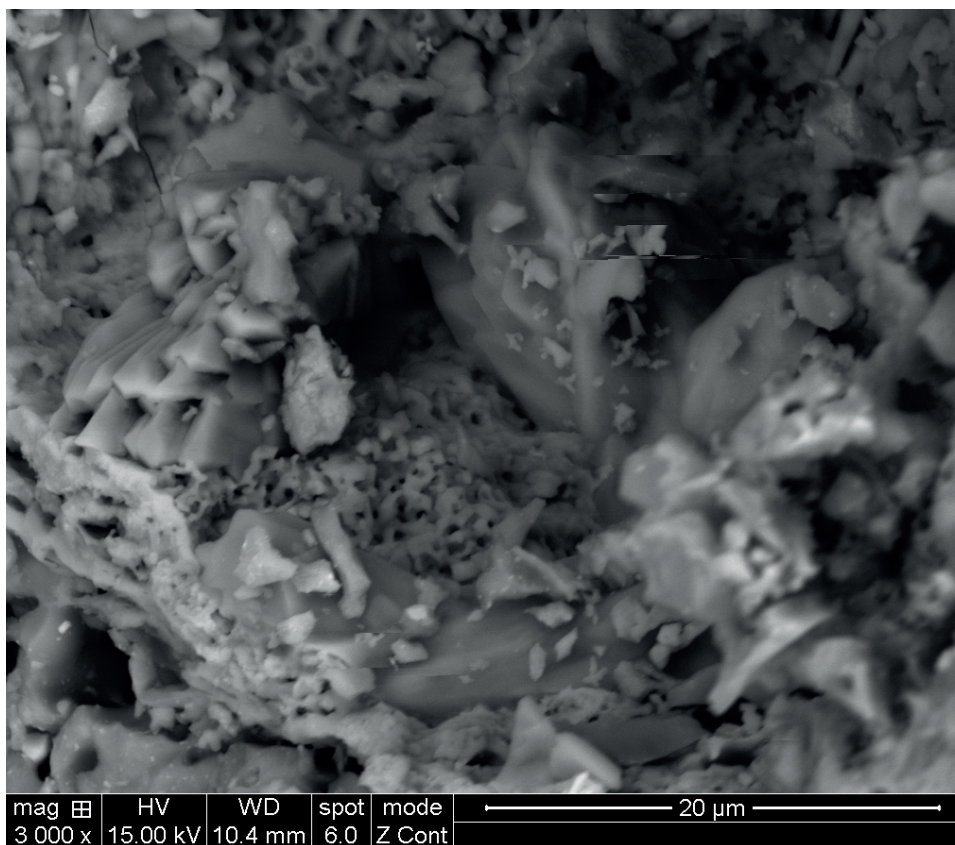
Appendix E
NaCl Control



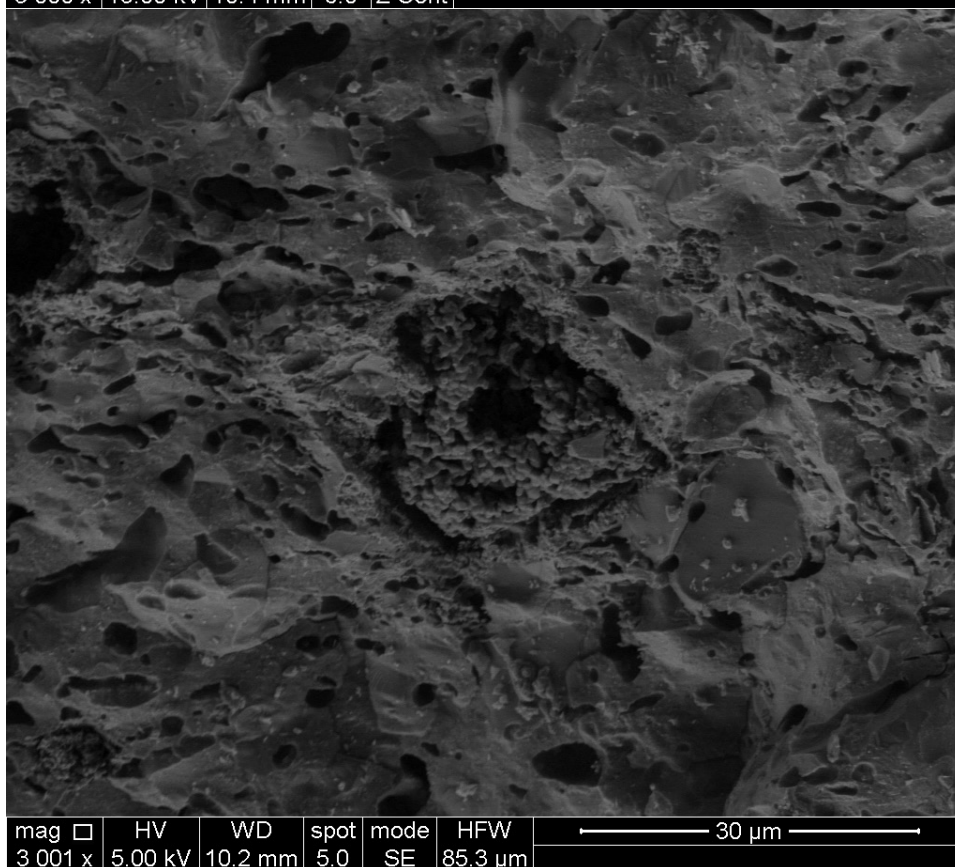
+Na₄Fe(CN)₆



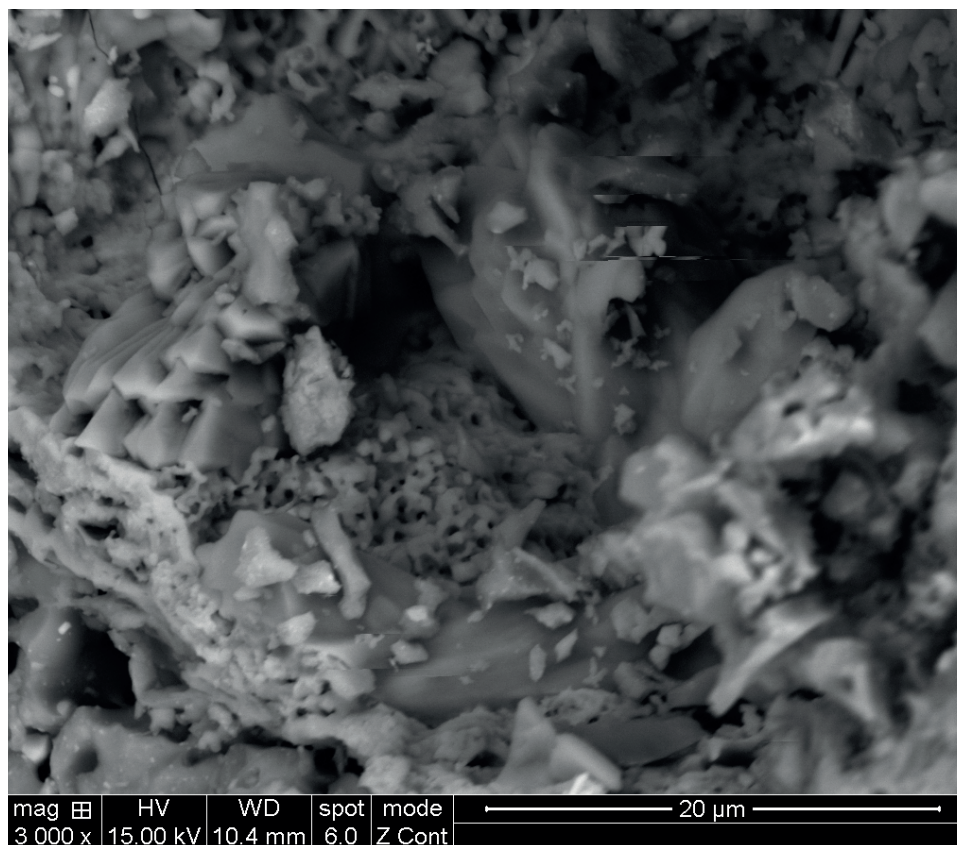
Appendix E
NaCl Control



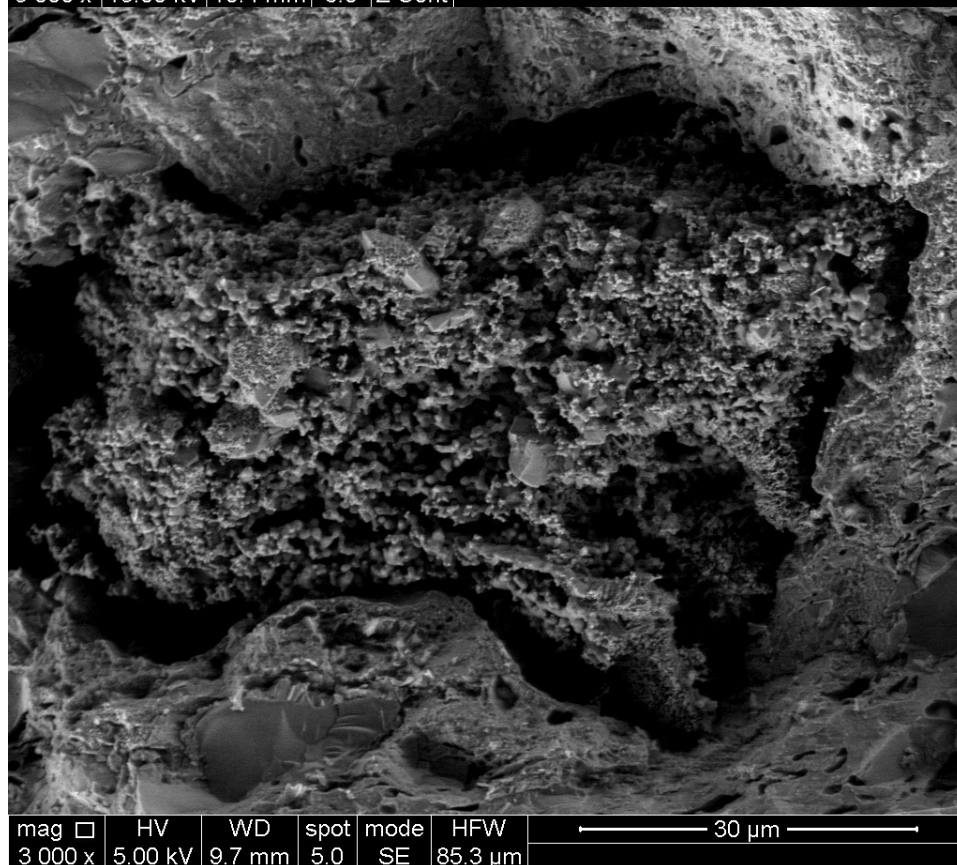
+K₄Fe(CN)₆



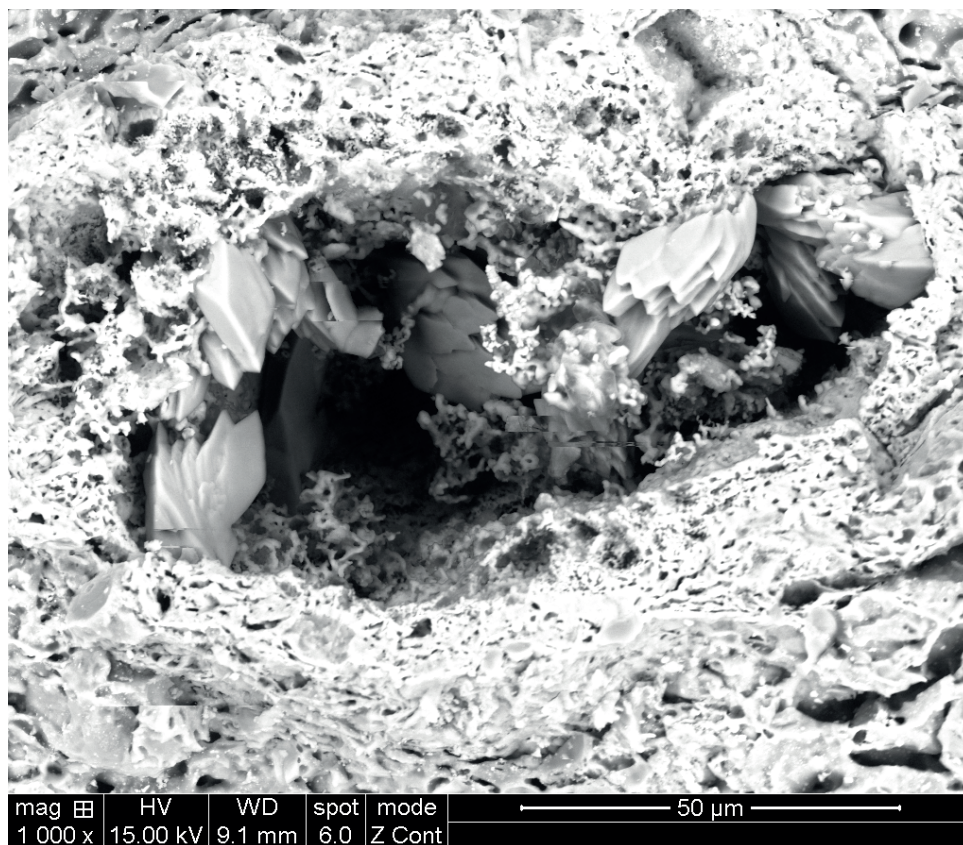
Appendix E
NaCl Control



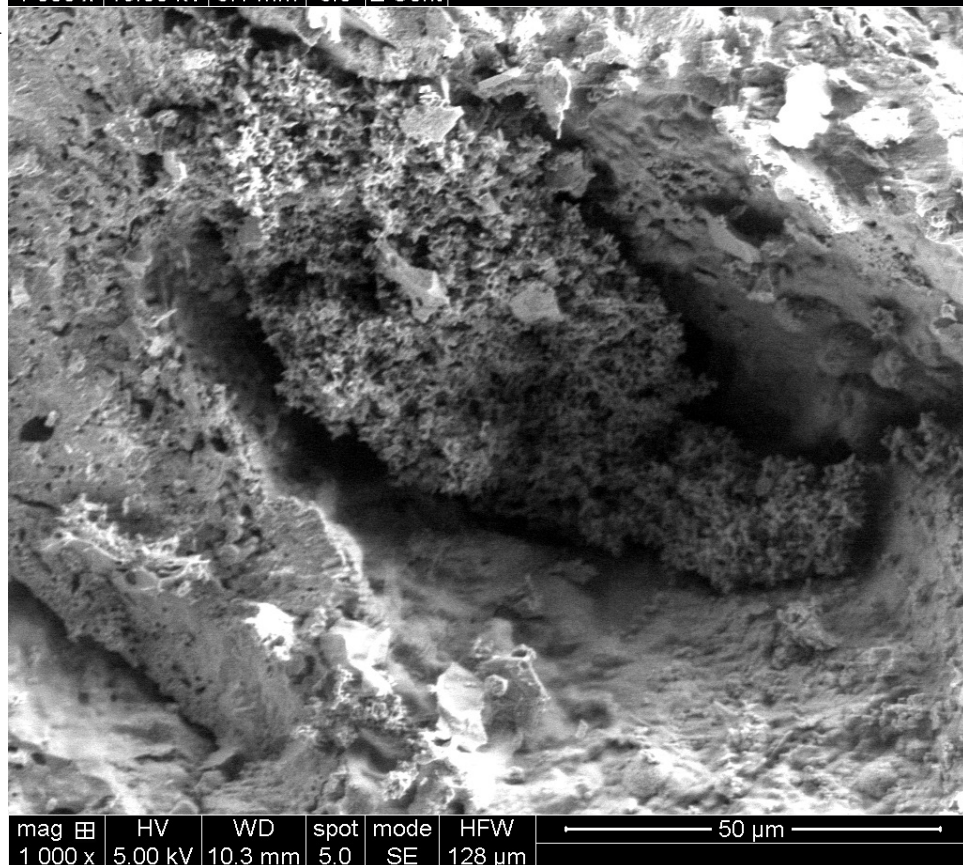
+K₄Fe(CN)₆ +
(NaPO₃)₆



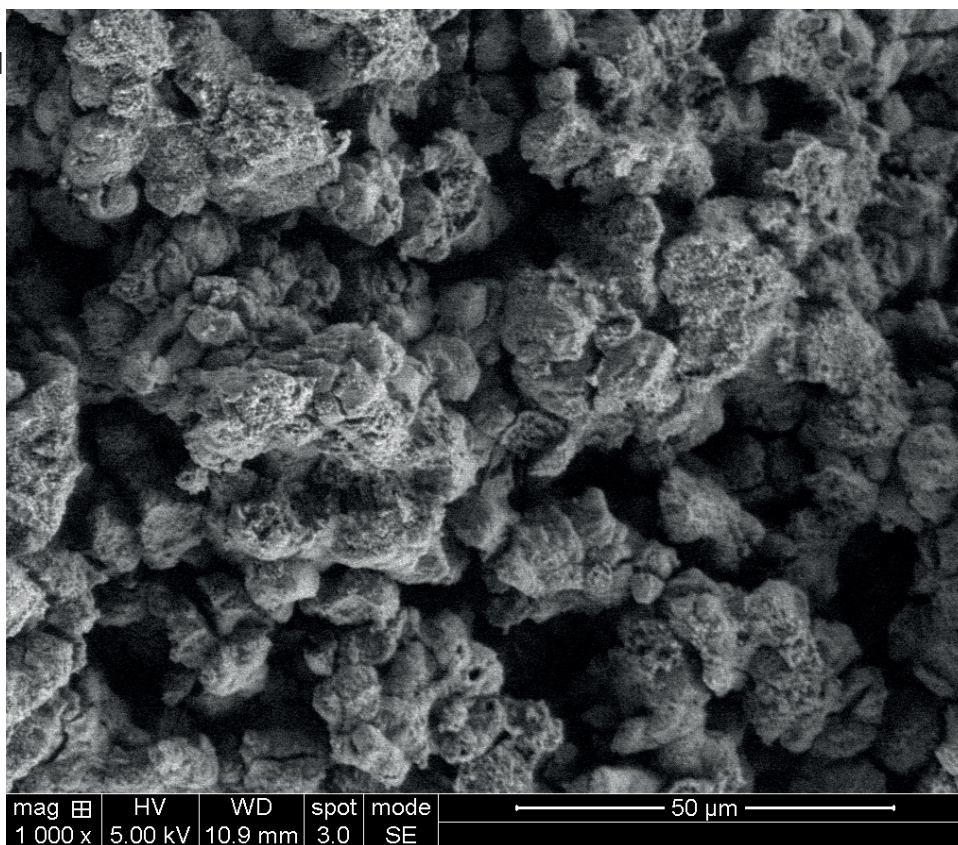
Appendix E
NaCl Control



+Na₄Fe(CN)₆ +
(NaPO₃)₆



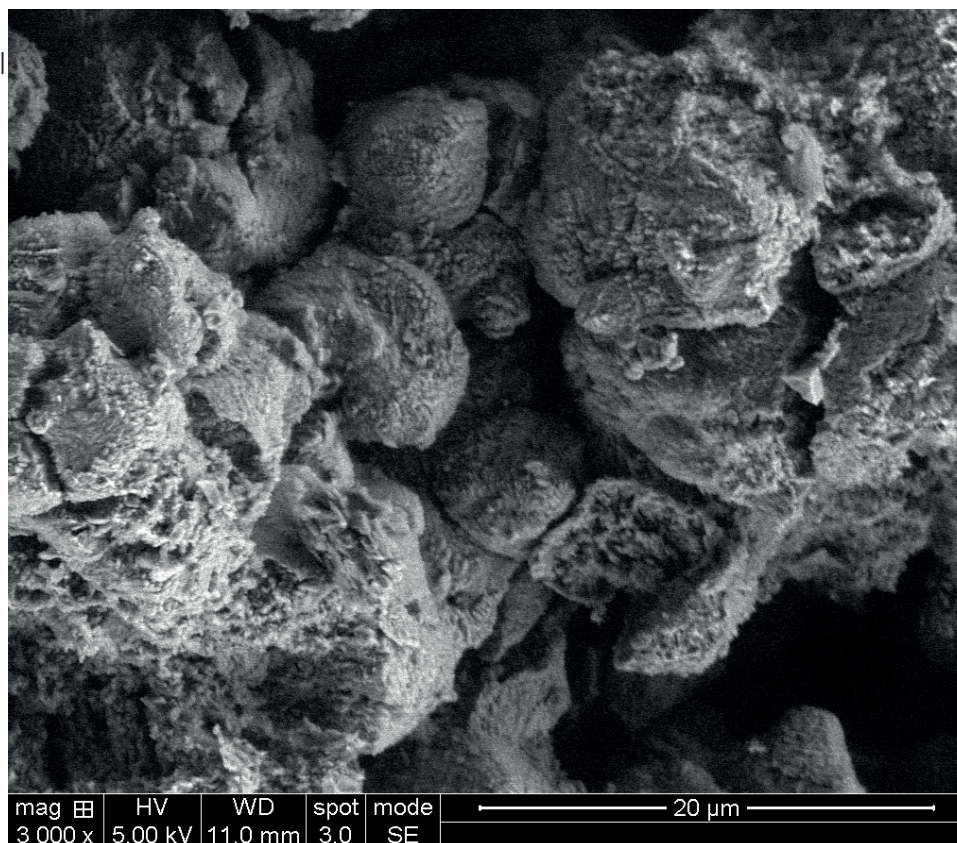
Appendix E
NaSO4 Control



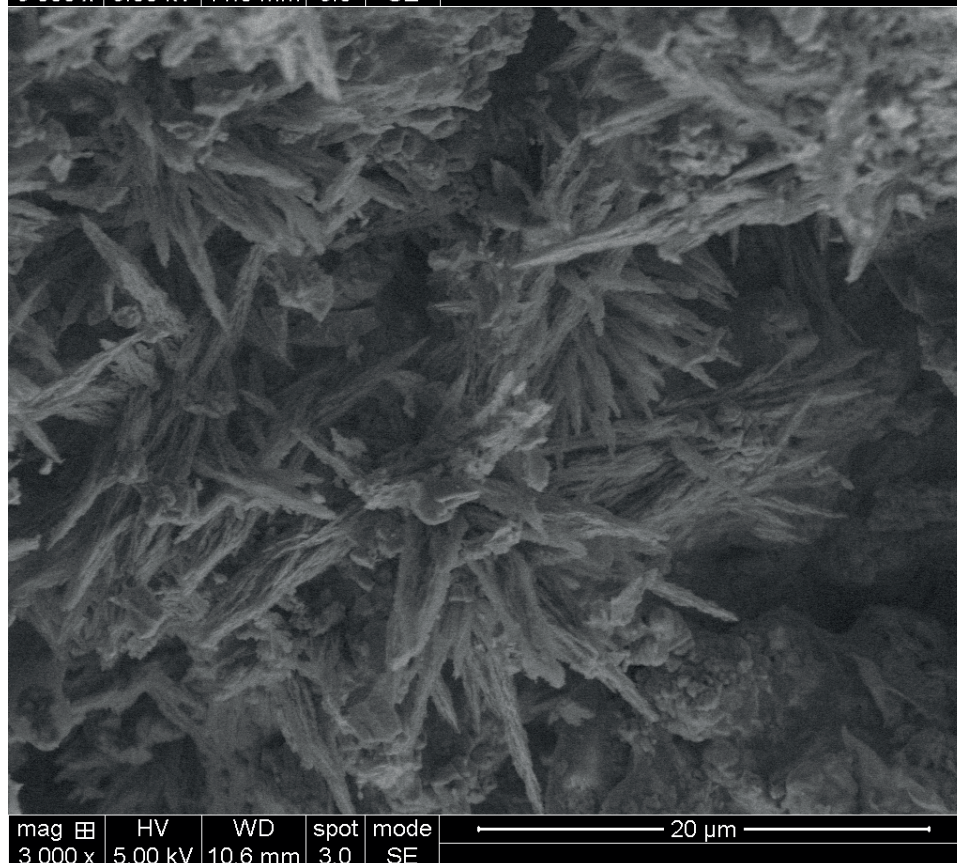
+Na4Fe(CN)6



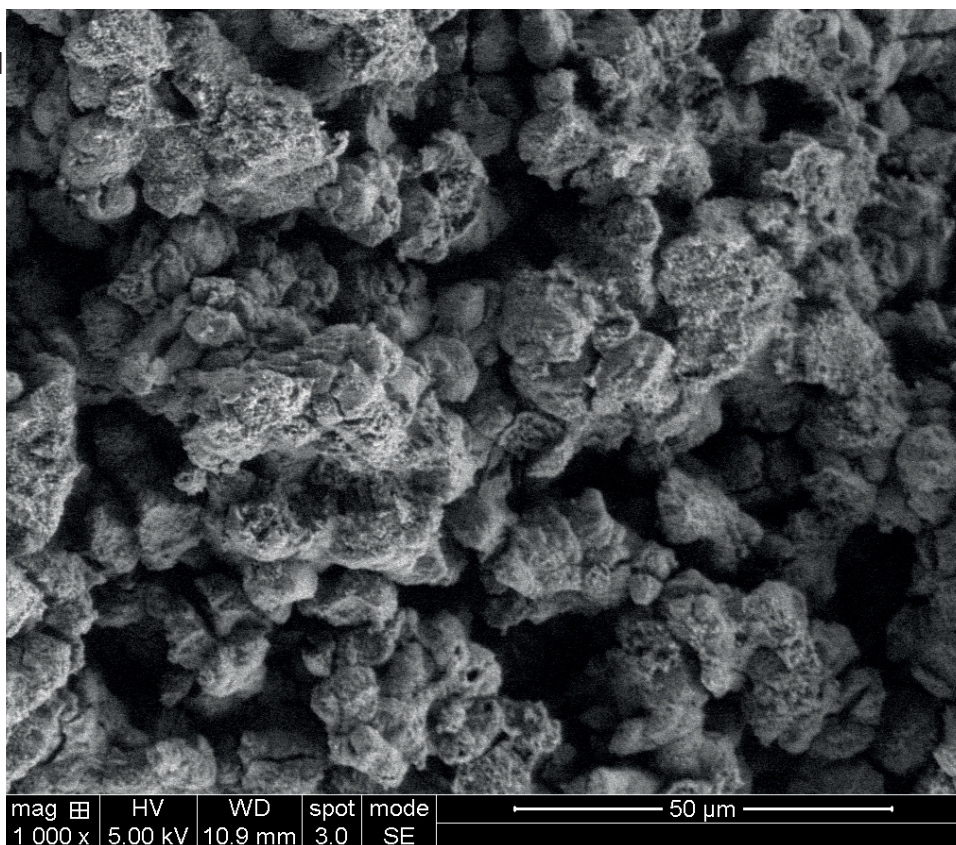
Appendix E
NaSO4 Control



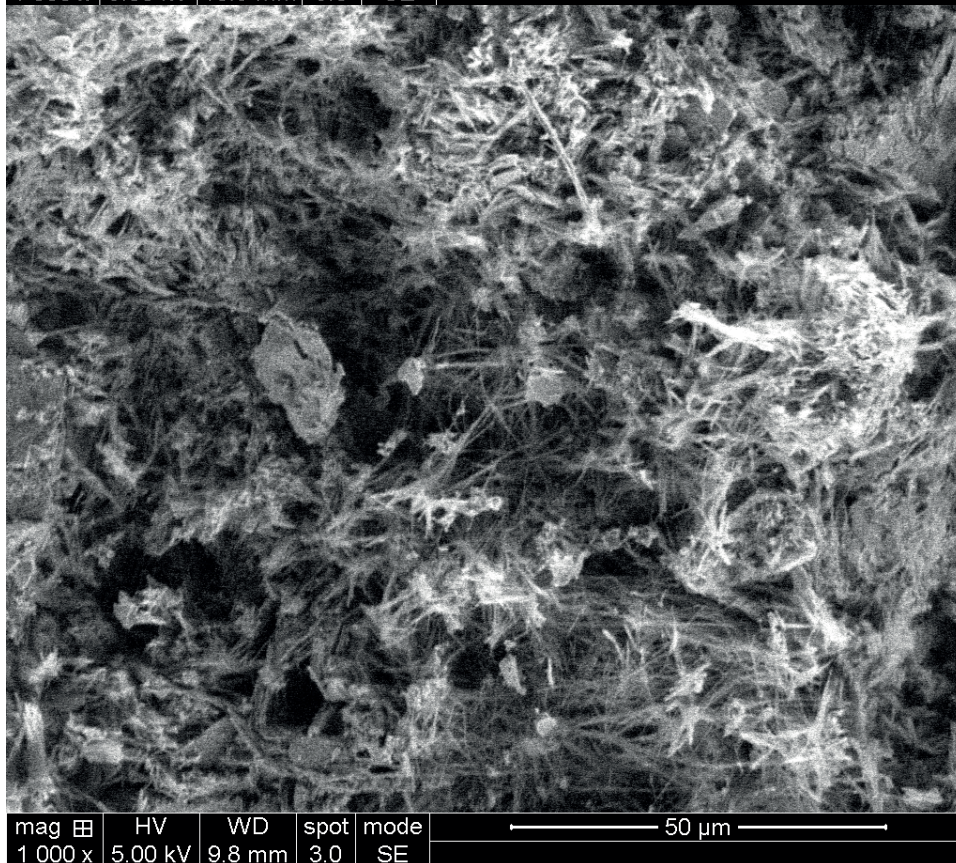
+K4Fe(CN)6



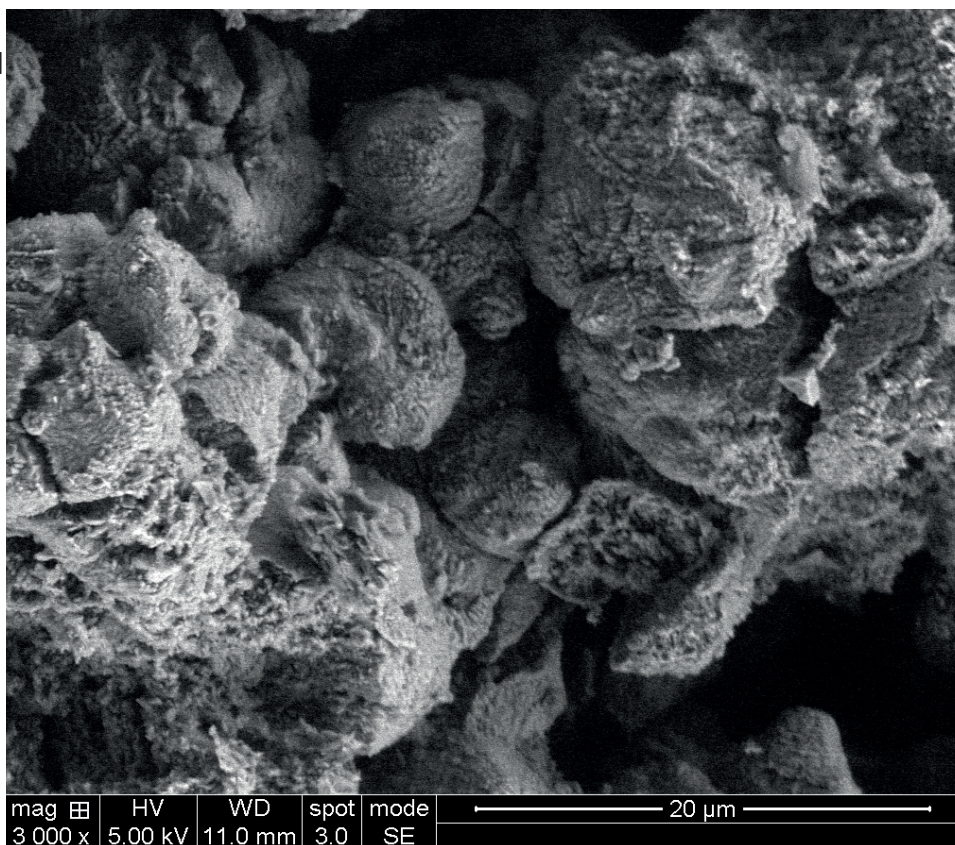
Appendix E
NaSO4 Control



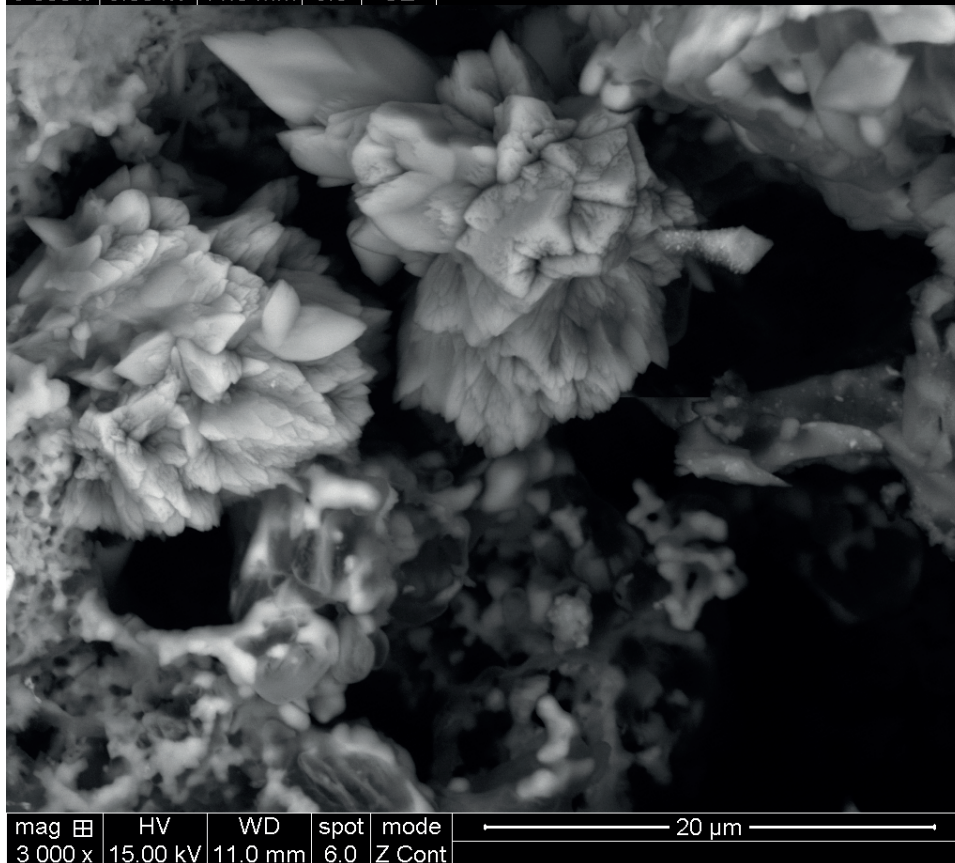
+K4Fe(CN)6+
(NaPO3)6



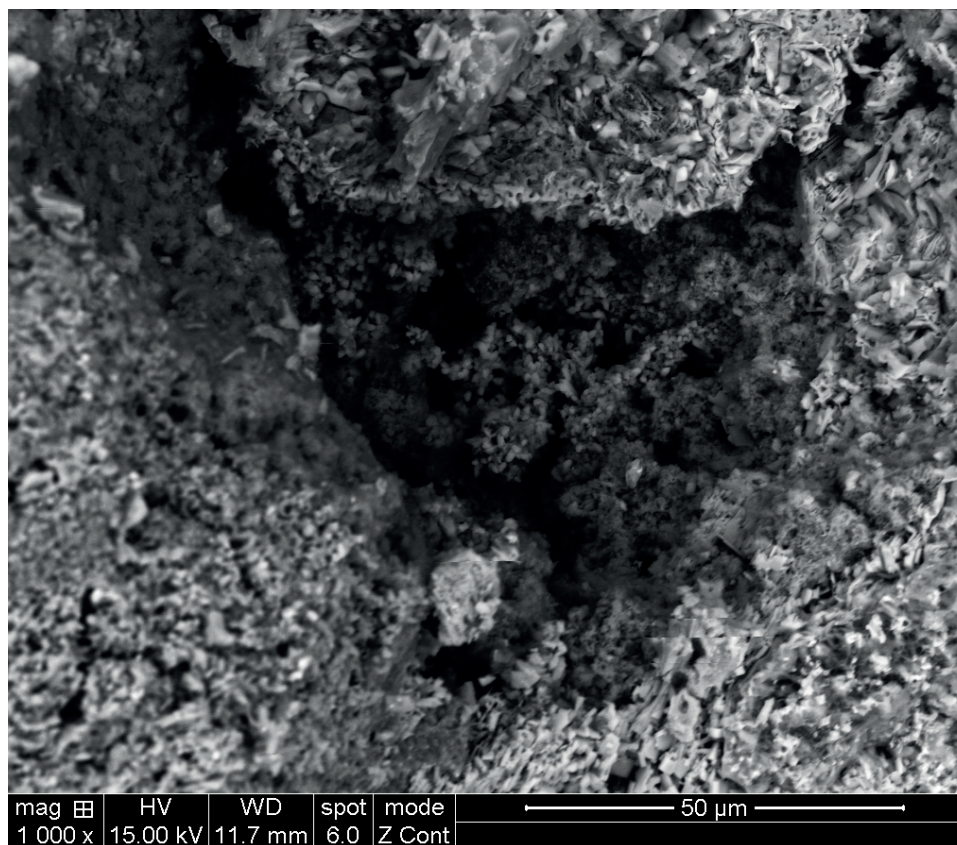
Appendix E
NaSO4 Control



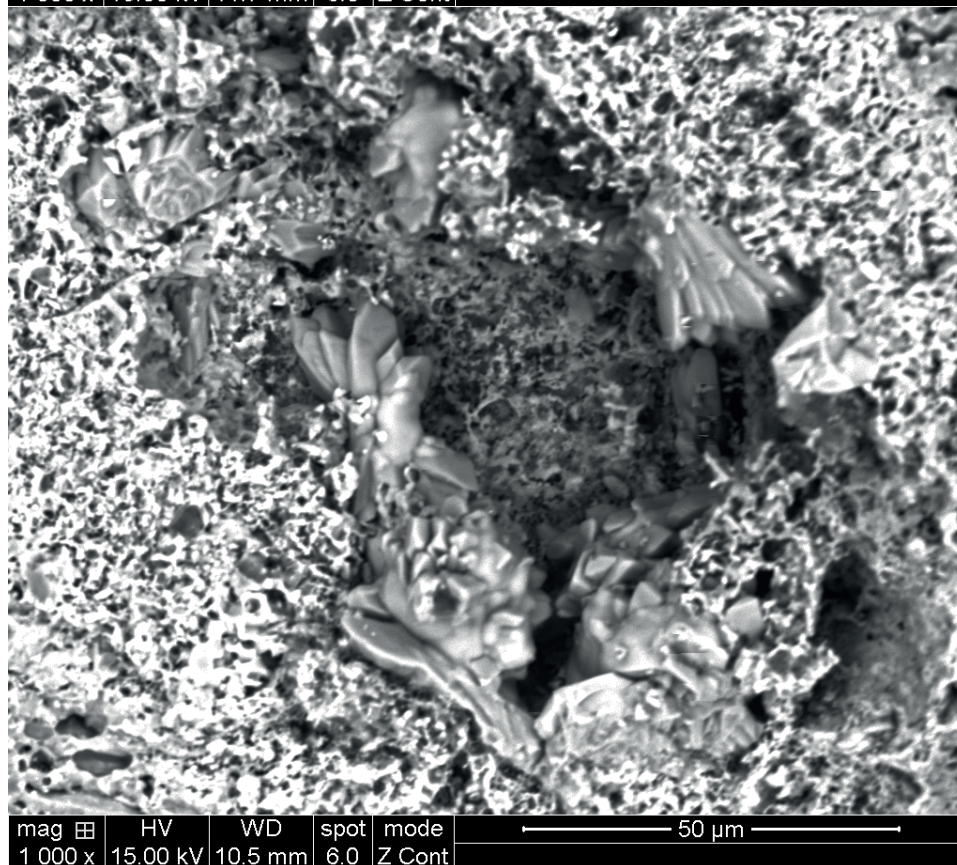
+K4Fe(CN)6+
(NaPO3)6



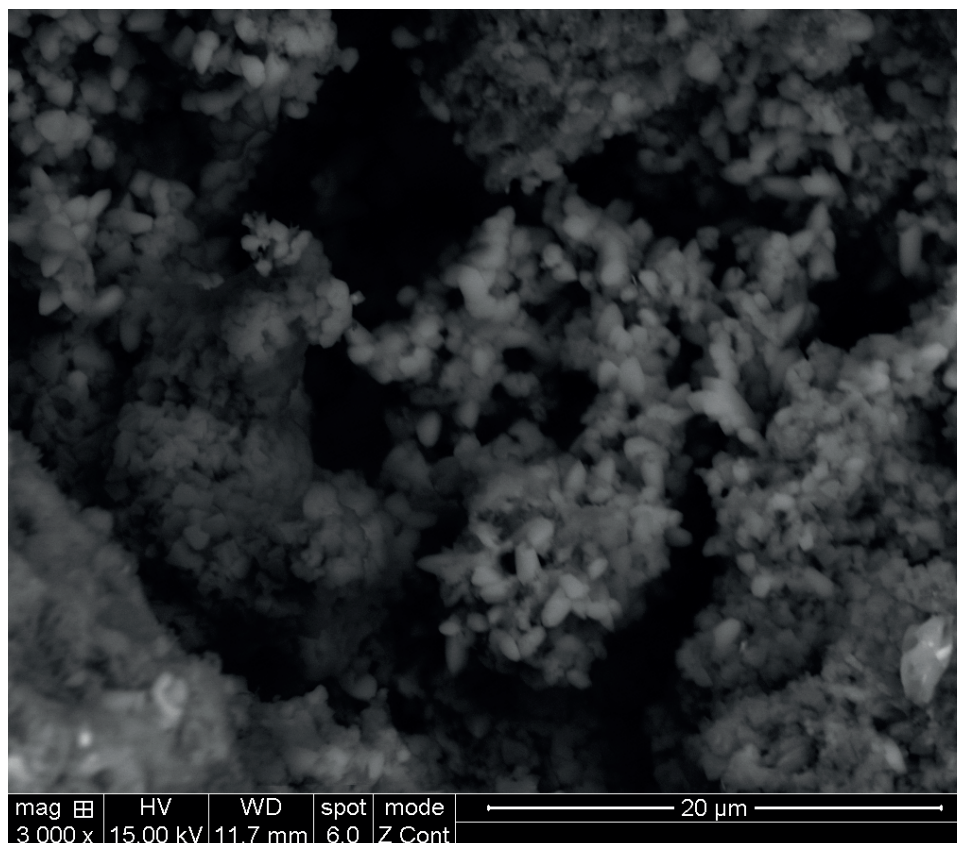
Appendix E
NaCl/ NaSO₄
Control



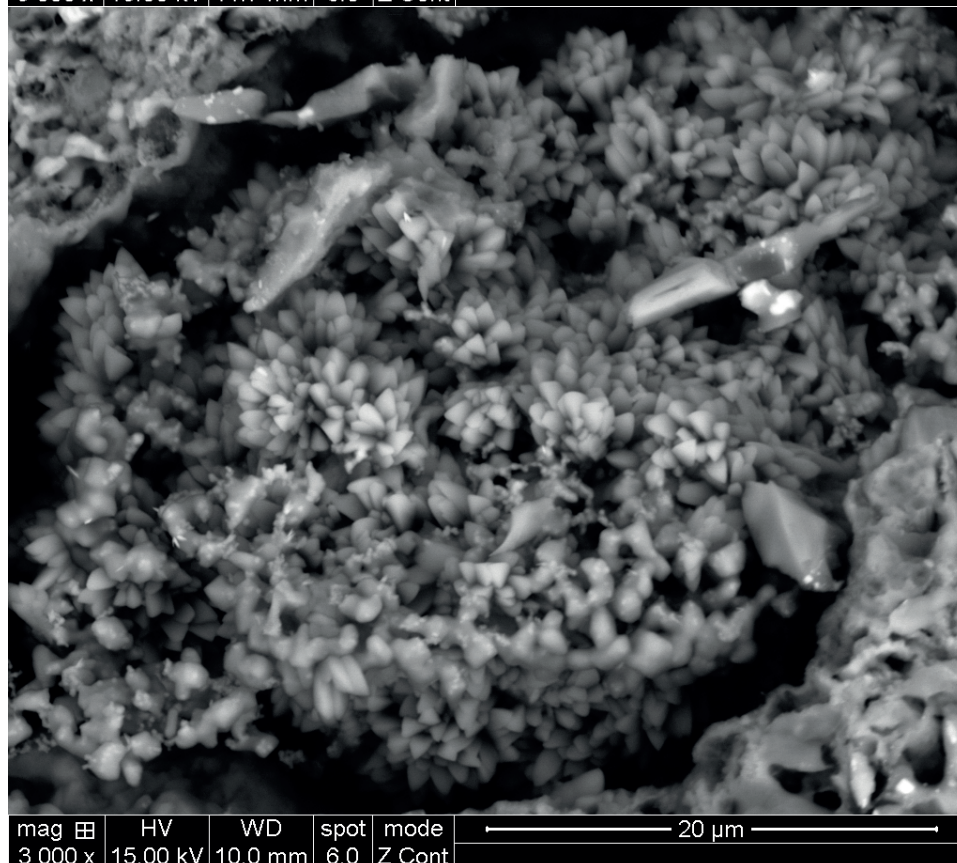
+Na₄Fe(CN)₆



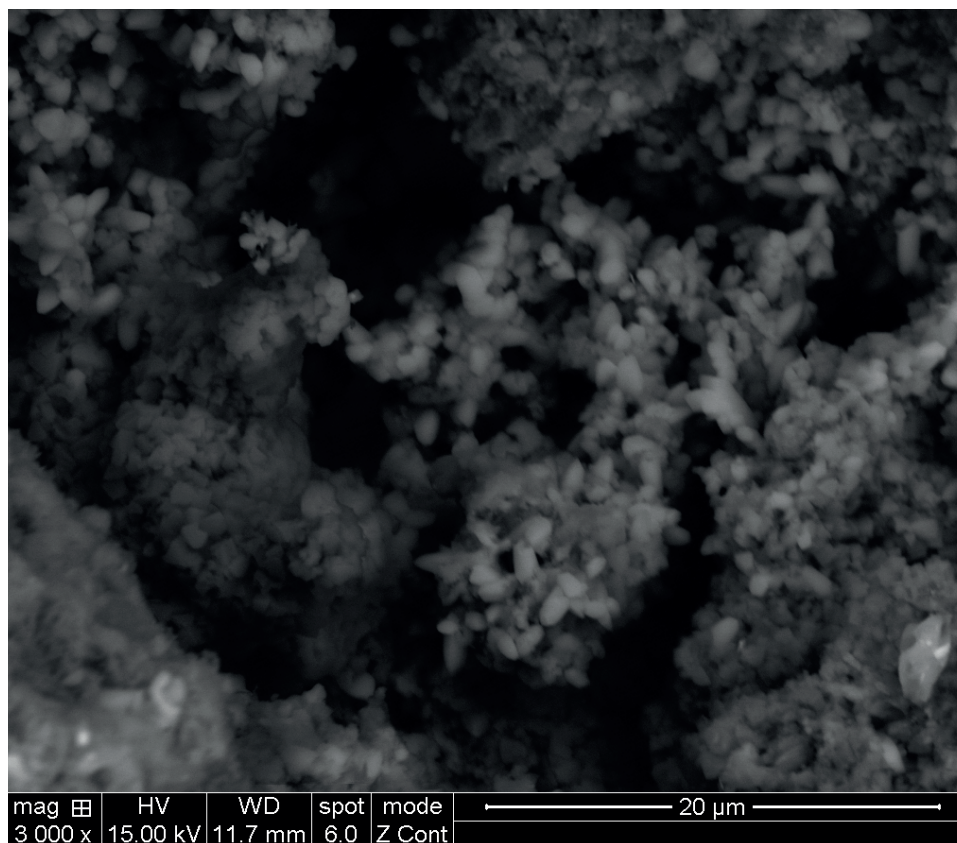
Appendix E
NaCl/ NaSO₄



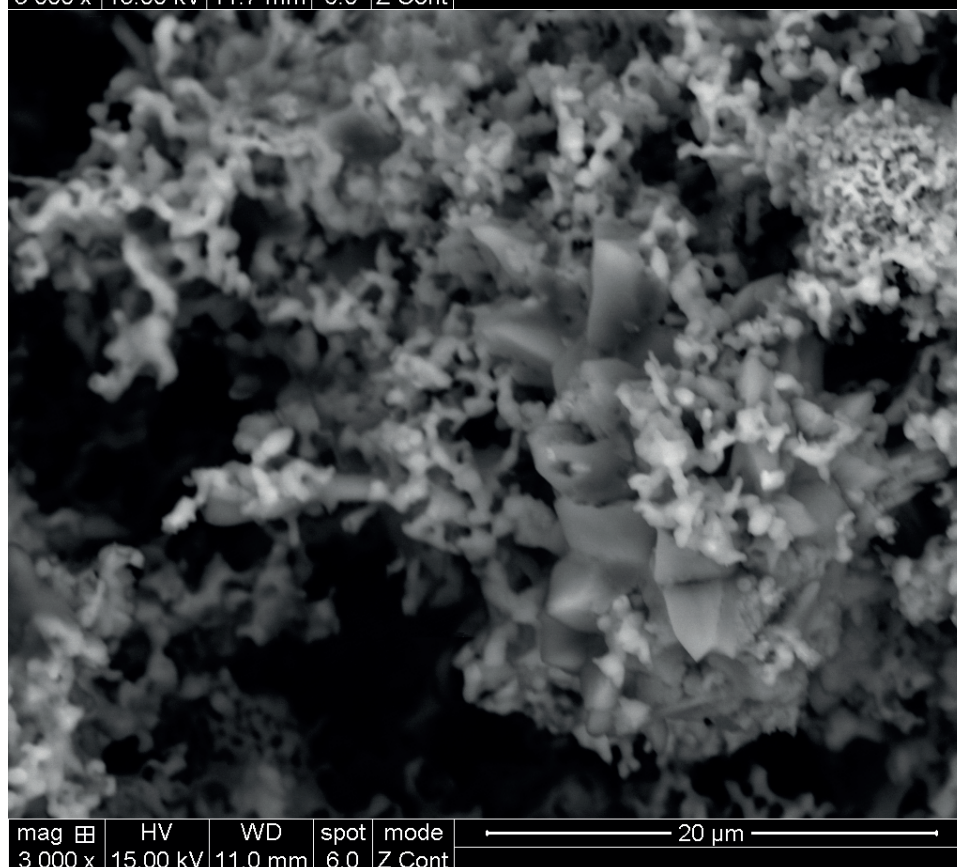
+K₄Fe(CN)₆



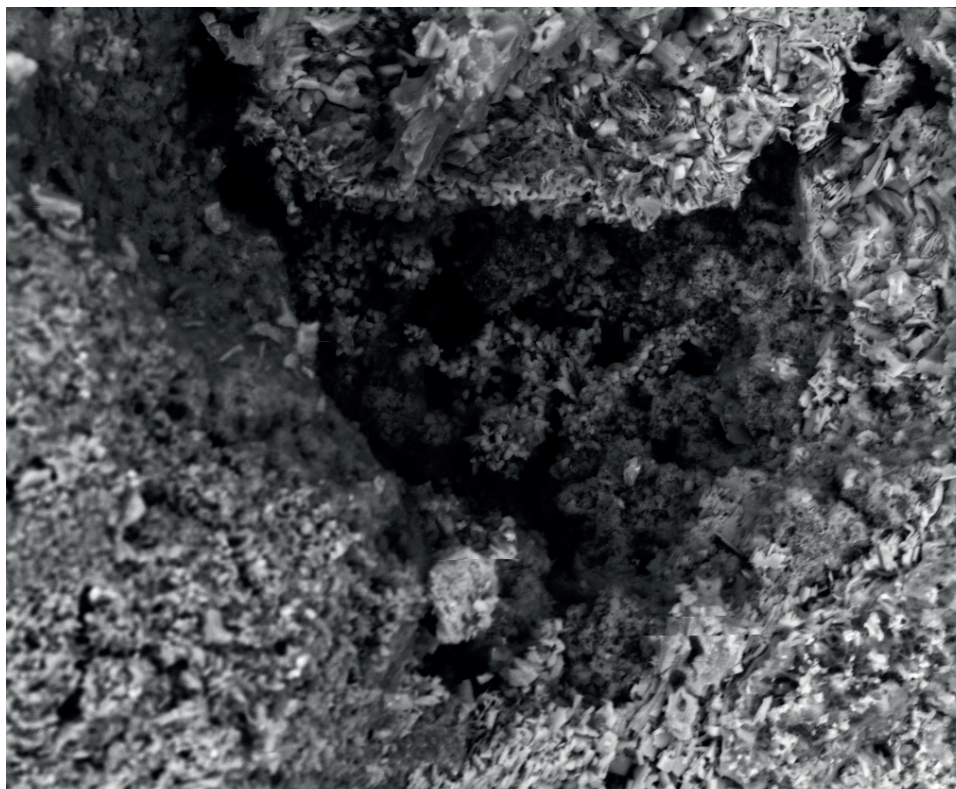
Appendix E
NaCl/ NaSO₄



+K₄Fe(CN)
6+(NaPO₃)₆



Appendix E
NaCl/ NaSO₄



mag	HV	WD	spot	mode	50 µm
1 000 x	15.00 kV	11.7 mm	6.0	Z Cont	

+Na₄Fe(CN)
6+(NaPO₃)₆



mag	HV	WD	spot	mode	50 µm
1 000 x	15.00 kV	9.6 mm	6.0	Z Cont	

Appendix F: ASTM & SDS Sheets



Standard Test Methods for Absorption and Bulk Specific Gravity of Dimension Stone¹

This standard is issued under the fixed designation C97/C97M; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 These test methods cover the tests for determining the absorption and bulk specific gravity of all types of dimension stone, except slate.

1.2 The values stated in either SI units or inch-pound units are to be regarded separately as standard. The values stated in each system may not be exact equivalents; therefore, each system shall be used independently of the other. Combining values from the two systems may result in non-conformance with the standard.

1.3 *This standard does not purport to address the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*²

C119 Terminology Relating to Dimension Stone

C1799 Guide to Dimension Stone Test Specimen Sampling and Preparation

3. Terminology

3.1 *Definitions*—All definitions are in accordance with Terminology C119.

4. Significance and Use

4.1 These test methods are useful in indicating the differences in absorption between the various dimension stones. These test methods also provide one element in comparing stones of the same type.

5. Sampling

5.1 The sample shall be selected to represent a true average of the type or grade of stone under consideration and shall be of the quality supplied to the market under the type designation to be tested. The sample may be selected by the purchaser or his authorized representative from the quarried stone or taken from the natural ledge and shall be of adequate size to permit the preparation of at least five test specimens. When perceptible variations occur, the purchaser may select as many samples as are necessary for determining the range in properties.

NOTE 1—Refer to Guide C1799 for additional information on selecting, preparing, and conditioning test specimens.

6. Test Specimens

6.1 The specimens may be cubes, prisms, cylinders, or any regular form with least dimension not under 2 in. [50 mm] and greatest dimension not over 3 in. [75 mm] but the ratio of volume to surface area shall not be less than 0.3 nor greater than 0.5 when measuring in inches [8 and 12.5 when measuring in millimetres]. All surfaces shall be reasonably smooth. Saw or core drill surfaces are considered satisfactory, but rougher surfaces shall be finished with No. 80 abrasive. No chisels or similar tools shall be used at any stage of preparing the specimens.

6.2 Prepare at least five specimens from each sample.

6.3 The same specimens may be used to determine both water absorption and bulk specific gravity. In this case, follow the procedures in 7.1 – 7.3 and 10.1, and issue a single report containing all information required in 9 and 13. Alternatively, separate specimens may be prepared from the same or different samples. In this case, follow the applicable procedure for separate determination and reporting of water absorption or bulk specific gravity, or both.

7. Procedure

7.1 Dry the specimens for 48 h in a ventilated oven at a temperature of $140 \pm 4^\circ\text{F}$ [$60 \pm 2^\circ\text{C}$]. At the 46th, 47th, and 48th hour, weigh the specimens to ensure that the weight is the same. If the weight continues to drop, continue to dry the specimens until there are three successive hourly readings with the same weight.

¹ These test methods are under the jurisdiction of ASTM Committee C18 on Dimension Stone and are the direct responsibility of Subcommittee C18.01 on Test Methods.

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² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

7.2 After drying, cool the specimens in the room for 30 min and weigh. When the specimens cannot be weighed immediately after cooling, store them in a desiccator. Determine the weights to the nearest 0.0005 oz [0.01 g].

7.3 Immerse the specimens completely in filtered or distilled water at $72 \pm 4^\circ\text{F}$ [$22 \pm 2^\circ\text{C}$] for 48 h. At the end of this period remove them from the water bath one at a time, surface dry with a damp cloth, and weigh to the nearest 0.0005 oz [0.01 g].

8. Calculation and Report

8.1 Calculate the weight percentage absorption (Note 2) for each specimen as follows:

$$\text{Absorption, weight \%} = [(B - A)/A] \times 100 \quad (1)$$

where:

A = weight of the dried specimen, oz [g], and

B = weight of the specimen after immersion, oz [g].

NOTE 2—If the percentage of absorption by volume is desired it will be necessary to determine the bulk specific gravity and multiply each value of percentage absorption by weight by the corresponding bulk specific gravity value.

8.2 Calculate the mean water absorption of the sample as the average of the weight percentage absorption for all specimens.

9. Report

9.1 The report shall contain the following information:

9.1.1 Identity of party providing the sample.

9.1.2 Name of stone.

9.1.3 Identity of sample.

9.1.4 Mean water absorption of sample.

9.1.5 Any variations to the procedure, including specimen dimensions, given in this standard

9.2 The report shall also contain the following information for each specimen:

9.2.1 Weight of dried specimen

9.2.2 Weight of soaked and surface-dried specimen in air.

9.2.3 Percentage water absorption by weight of specimen.

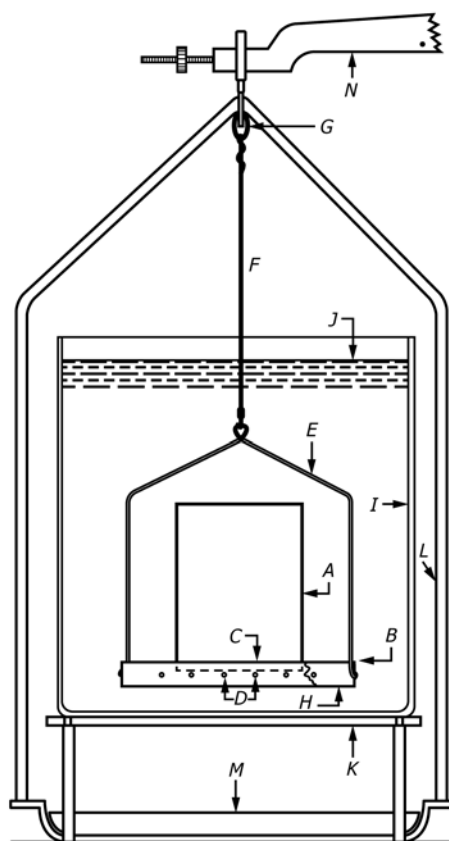
BULK SPECIFIC GRAVITY

10. Procedure

10.1 When both absorption and bulk specific gravity are to be determined on the same specimens, weigh the saturated specimens suspended in filtered or distilled water at $72 \pm 4^\circ\text{F}$ [$22 \pm 2^\circ\text{C}$] immediately after the absorption tests are completed. Determine the suspended weights to the nearest 0.0005 oz [0.01 g].

10.2 A satisfactory means of weighing specimens in water is to use a wire basket similar to that illustrated in Fig. 1 to suspend the specimen in a vessel of water. The water vessel shall be large enough so that only the suspending cable of the basket passes through the water surface. Ensure air bubbles are removed from the basket and specimen before recording the weight.

10.2.1 The water vessel can be supported on the balance pan with the basket suspended from a frame also supported on a



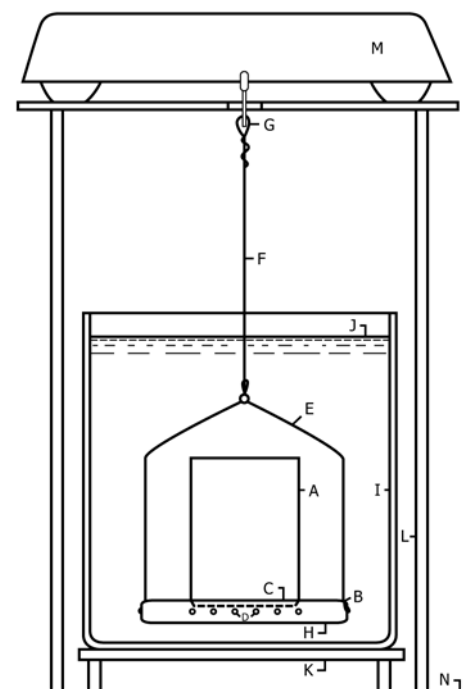
- | | |
|---|--|
| A—Specimen. | G—Loop for attachment to stirrup of balance. |
| B—Suspension basket. | H—Cutaway section of basket. |
| C—Brass ring. | I—Water jar. |
| D—Bottom of basket of No. 13 B & S gauge [1.8 mm] brass wire (all joints soldered). | J—Water level. |
| E—Bail of basket of No. 13 B & S gauge [1.8 mm] brass wire. | K—Water jar support. |
| F—Suspension wire of No. 20 B & S gauge [0.8 mm] brass wire. | L—Balance pan suspension rod. |
| | M—Balance pan. |
| | N—Beam of balance. |

FIG. 1 Bulk Specific Gravity Test Assembly: Water Vessel on Balance Pan

balance pan, as illustrated in Fig. 1. Determine the weight of the basket when suspended in water to the same depth as when weighing specimens therein. Subtract the weight of the basket to the nearest 0.0005 oz [0.01 g] from the combined weight of the specimen and basket.

10.2.2 The basket can be suspended beneath an electronic balance with the water vessel supported independently, as illustrated in Fig. 2. Zero the balance with the basket suspended in water to the same depth as when weighing specimens.

10.3 When the bulk specific gravity test is made on specimens other than those used for absorption, determine the dry weights as in 7.1 and 7.2. Immerse the specimens in filtered or distilled water at $72 \pm 4^\circ\text{F}$ [$22 \pm 2^\circ\text{C}$] for at least 1 h or until air bubbles do not form on the specimens within 5 min. Surface dry the specimens as in 7.3, weigh to the nearest 0.0005 oz [0.01 g], and return to the water bath. Determine the weights of the specimens suspended in water in accordance with 10.2 before the specimens have stood in the water more than 5 min.



- A—Specimen.
B—Suspension basket.
C—Brass ring.
D—Bottom of basket of No. 13 B & S gauge [1.8 mm] brass wire (all joints soldered).
E—Bail of basket of No. 13 B & S gauge [1.8 mm] brass wire.
F—Suspension wire of No. 20 B & S gauge [0.8 mm] brass wire.
G—Loop for attachment to stirrup of balance.
H—Cutaway section of basket.
I—Water jar.
J—Water level.
K—Water jar support.
L—Balance support.
M—Balance.
N—Benchtop.

FIG. 2 Bulk Specific Gravity Test Assembly: Water Vessel Below Balance

11. Calculation

11.1 Calculate the bulk specific gravity as follows:

$$\text{Bulk specific gravity} = A / (B - C) \quad (2)$$

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where:

- A = weight of the dried specimen, oz [g],
B = weight of the soaked and surface-dried specimen in air, oz [g], and
C = weight of the soaked specimen in water, oz [g].

11.2 Calculate the mean bulk specific gravity of the sample as the average of the bulk specific gravity for all specimens.

NOTE 3—The bulk specific gravity gives a convenient and accurate means of calculating the unit weight of the stone; for example, drystone weight per cubic foot [cubic metre] = bulk specific gravity × 62.4 [1000].

12. Report

12.1 The report shall contain the following information:

- 12.1.1 Identity of party providing the sample.
12.1.2 Name of stone.
12.1.3 Identity of sample.
12.1.4 Bulk specific gravity of sample.
12.1.5 Any variations to the procedure, including specimen dimensions, given in this standard.

12.2 The report shall also contain the following information for each specimen:

- 12.2.1 Weight of dried specimen.
12.2.2 Weight of soaked and surface-dried specimen in air.
12.2.3 Weight of soaked specimen suspended in water.
12.2.4 Bulk specific gravity of specimen.

13. Precision and Bias

13.1 Individual variations in a natural product may result in deviation from accepted values. A precision section will be added when sufficient data are available to indicate in repeatability and reproducibility.

14. Keywords

14.1 absorption; bulk specific gravity; dimension stone; stone; test



Standard Test Methods for Sampling and Testing Brick and Structural Clay Tile¹

This standard is issued under the fixed designation C67; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the U.S. Department of Defense.

1. Scope*

1.1 These test methods cover procedures for the sampling and testing of brick and structural clay tile. Although not necessarily applicable to all types of units, tests include modulus of rupture, compressive strength, absorption, saturation coefficient, effect of freezing and thawing, efflorescence, initial rate of absorption and determination of weight, size, warpage, length change, and void area. (Additional methods of test pertinent to ceramic glazed facing tile are included in Specification C126.)

1.2 The text of this standard references notes and footnotes which provide explanatory material. These notes and footnotes (excluding those in tables and figures) shall not be considered as requirements of the standard.

NOTE 1—The testing laboratory performing this test method should be evaluated in accordance with Practice C1093.

1.3 The values stated in inch-pound units are to be regarded as standard. The values given in parentheses are mathematical conversions to SI units that are provided for information only and are not considered standard.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 ASTM Standards:²

C126 Specification for Ceramic Glazed Structural Clay Facing Tile, Facing Brick, and Solid Masonry Units

C150 Specification for Portland Cement

¹ These test methods are under the jurisdiction of Committee C15 on Manufactured Masonry Units and is the direct responsibility of Subcommittee C15.02 on Brick and Structural Clay Tile.

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² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

C1093 Practice for Accreditation of Testing Agencies for Masonry

C1232 Terminology of Masonry

E4 Practices for Force Verification of Testing Machines

E6 Terminology Relating to Methods of Mechanical Testing

E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Terminology

3.1 *Definitions*—For definition relating to sampling and testing brick, refer to Terminology E6 and Terminology C1232.

4. Sampling

4.1 *Selection and Preparation of Test Specimens*—For the purpose of these tests, full-size brick, tile, or solid masonry units shall be selected by the purchaser or by the purchaser's authorized representative. Specimens shall be representative of the lot of units from which they are selected and shall include specimens representative of the complete range of colors, textures, and sizes. Specimens shall be free of or brushed to remove dirt, mud, mortar, or other foreign materials unassociated with the manufacturing process. Brushes used to remove foreign material shall have bristles of plastic (polymer) or horsehair. Wire brushes shall not be used for preparing specimens for testing. Specimens exhibiting foreign material that is not removed by brushing shall be discarded to ensure that damaged or contaminated specimens are not tested.

4.2 Number of Specimens:

4.2.1 *Brick*—For the modulus of rupture, compressive strength, abrasion resistance, and absorption determinations, at least ten individual brick shall be selected for lots of 1 000 000 brick or fraction thereof. For larger lots, five additional specimens shall be selected from each additional 500 000 brick or fraction thereof. Additional specimens are taken at the discretion of the purchaser.

4.2.2 *Structural Clay Tile*—For the weight determination and for compressive strength and absorption tests, at least five tile shall be selected from each lot of 250 tons (226.8 Mg) or fraction thereof. For larger lots, five additional specimens shall

*A Summary of Changes section appears at the end of this standard

be tested for each 500 tons (453.6 Mg) or fraction thereof. In no case shall less than five be taken. Additional specimens are taken at the discretion of the purchaser.

4.3 *Identification*—Each specimen shall be marked so that it is identifiable at any time. Markings shall cover not more than 5 % of the superficial area of the specimen.

5. Specimen Preparation

5.1 *Drying and Cooling:*

5.1.1 *Drying*—Dry the test specimens in a ventilated oven at 230 to 239°F (110 to 115°C) for not less than 24 h and until two successive weighings at intervals of 2 h show an increment of loss not greater than 0.2 % of the last previously determined weight of the specimen.

5.1.2 *Cooling*—After drying, cool the specimens in a drying room maintained at a temperature of 75 ± 15°F (24 ± 8°C), with a relative humidity between 30 and 70 %. Store the units free from drafts, unstacked, with separate placement, for a period of at least 4 h and until the surface temperature is within 5°F (2.8°C) of the drying room temperature. Do not use specimens noticeably warm to the touch for any test requiring dry units. The specimens shall be stored in the drying room with the required temperature and humidity maintained until tested.

5.1.2.1 An alternative method of cooling the specimens to approximate room temperature is permitted as follows: Store units, unstacked, with separate placement, in a ventilated room maintained at a temperature of 75 ± 15°F (24 ± 8°C), with a relative humidity between 30 and 70 % for a period of 4 h and until the surface temperature is within 5°F (2.8°C) of the ventilated room temperature, with a current of air from an electric fan passing over them for a period of at least 2 hours. The specimens shall be stored in the ventilated room with the required temperature and humidity maintained until tested.

5.2 *Weight Determination:*

5.2.1 Weigh five full size specimens that have been dried and cooled (see 5.1). The scale or balance used shall have a capacity of not less than 3000 g and shall be sensitive to 0.5 g.

5.2.2 Report results separately for each specimen to the nearest 0.1 g, with the average of all specimens tested to the nearest 0.1 g.

5.3 *Removal of Silicone Coatings from Brick Units*—The silicone coatings intended to be removed by this process are any of the various polymeric organic silicone compounds used for water-resistant coatings of brick units. Heat the brick at 950 ± 50°F (510 ± 28°C) in an oxidizing atmosphere for a period of not less than 3 hours. The rate of heating and cooling shall not exceed 300°F (149°C) per hour.

NOTE 2—Additional specimen preparation requirements for specific tests are indicated in the individual test methods.

6. Modulus of Rupture (Flexure Test)

6.1 *Test Specimens*—The test specimens shall consist of whole full-size units that have been dried and cooled (see 5.1). Five such specimens shall be tested.

6.2 *Procedure:*

6.2.1 Support the test specimen flatwise unless specified and reported otherwise (that is, apply the load in the direction of the depth of the unit) on a span approximately 1 in. (25.4 mm) less than the basic unit length and loaded at midspan. Specimens having recesses (panels or depressions) shall be placed so that such recesses are on the compression side. Apply the load to the upper surface of the specimen through a steel bearing plate ¼ in. (6.35 mm) in thickness and 1½ in. (38.10 mm) in width and of a length at least equal to the width of the specimen.

6.2.2 Make sure the supports for the test specimen are free to rotate in the longitudinal and transverse directions of the test specimen and adjust them so that they will exert no force in these directions.

6.2.3 *Speed of Testing*—The rate of loading shall not exceed 2000 lbf (8896 N)/min. This requirement is considered as being met when the speed of the moving head of the testing machine immediately prior to application of the load is not more than 0.05 in. (1.27 mm)/min.

6.3 *Calculation and Report:*

6.3.1 Calculate and report the modulus of rupture of each specimen to the nearest 1 psi (0.01 MPa) as follows:

$$S = 3W(l/2 - x)/bd^2 \quad (1)$$

where:

- S = modulus of rupture of the specimen at the plane of failure, lb/in.² (Pa),
- W = maximum load indicated by the testing machine, lbf (N),
- l = distance between the supports, in. (mm),
- b = net width, (face to face minus voids), of the specimen at the plane of failure, in. (mm),
- d = depth, (bed surface to bed surface), of the specimen at the plane of failure, in. (mm), and
- x = average distance from the midspan of the specimen to the plane of failure measured in the direction of the span along the centerline of the bed surface subjected to tension, in. (mm).

6.3.2 Calculate and report the average of the modulus of rupture determinations to the nearest 1 psi (0.01 MPa).

7. Compressive Strength

7.1 *Test Specimens:*

7.1.1 *Brick*—The test specimens shall consist of half brick units that have been dried and cooled (see 5.1), the full height and width of the unit, with a length equal to one half the full length of the unit ± 1 in. (25.4 mm), except as described below. When the test specimen, described above, exceeds the testing machine capacity, the test specimens shall consist of dry pieces of brick, the full height and width of the unit, with a length not less than one quarter of the full length of the unit, and with a gross cross-sectional area perpendicular to bearing not less than 14 in.² (90.3 cm²). Test specimens shall be obtained by any method that will produce, without shattering or cracking, a specimen with approximately plane and parallel ends. Five specimens shall be tested.

7.1.2 *Structural Clay Tile*—Test five tile specimens that have been dried and cooled (see 5.1) in a bearing bed length equal to the width ± 1 in. (25.4 mm); or test full-size units.

7.2 Capping Test Specimens:

7.2.1 All specimens shall be dry and cool within the meaning of 5.1.1 and 5.1.2 before any portion of the capping procedure is carried out.

7.2.2 Fill recessed or paneled surfaces that will become bearing surfaces during the compression test with a mortar composed of 1 part by weight of quick-hardening cement conforming to the requirements for Type III cement of Specification C150, and 2 parts by weight of sand. Age the specimens at least 48 h before capping them. Where the recess exceeds ½ in. (12.7 mm), use a brick or tile slab section or metal plate as a core fill. Cap the test specimens using one of the two procedures described in 7.2.3 and 7.2.4.

7.2.3 *Gypsum Capping*—Coat the two opposite bearing surfaces of each specimen with shellac and allow to dry thoroughly. Bed one of the dry shellacked surfaces of the specimen in a thin coat of neat paste of calcined gypsum (plaster of paris) that has been spread on an oiled nonabsorbent plate, such as glass or machined metal. The casting surface plate shall be plane within 0.003 in. (0.076 mm) in 16 in. (406.4 mm) and sufficiently rigid; and so supported that it will not be measurably deflected during the capping operation. Lightly coat it with oil or other suitable material. Repeat this procedure with the other shellacked surface. Take care that the opposite bearing surfaces so formed will be approximately parallel and perpendicular to the vertical axis of the specimen and the thickness of the caps will be approximately the same and not exceeding ⅛ in. (3.18 mm). Age the caps at least 24 h before testing the specimens.

NOTE 3—A rapid-setting industrial type gypsum is frequently used for capping.

7.2.4 *Sulfur-Filler Capping*—Use a mixture containing 40 to 60 weight % sulfur, the remainder being ground fire clay or other suitable inert material passing a No. 100 (150-μm) sieve with or without plasticizer. The casting surface plate requirements shall be as described in 7.2.3. Place four 1-in. (25.4-mm) square steel bars on the surface plate to form a rectangular mold approximately ½ in. (12.7 mm) greater in either inside dimension than the specimen. Heat the sulfur mixture in a thermostatically controlled heating pot to a temperature sufficient to maintain fluidity for a reasonable period of time after contact with the surface being capped. Take care to prevent overheating, and stir the liquid in the pot just before use. Fill the mold to a depth of ¼ in. (6.35 mm) with molten sulfur material. Place the surface of the unit to be capped quickly in the liquid, and hold the specimen so that its vertical axis is at right angles to the capping surface. The thickness of the caps shall be approximately the same. Allow the unit to remain undisturbed until solidification is complete. Allow the caps to cool for a minimum of 2 h before testing the specimens.

7.3 Procedure:

7.3.1 Test brick specimens flatwise (that is, the load shall be applied perpendicular to the bed surface of the brick with the brick in the stretcher position). Test structural clay tile specimens in a position such that the load is applied in the same direction as in service. Center the specimens under the spherical upper bearing within ⅛ in. (1.59 mm).

7.3.2 The testing machine shall conform to the requirements of Practices E4.

7.3.3 The upper bearing shall be a spherically seated, hardened metal block firmly attached at the center of the upper head of the machine. The center of the sphere shall lie at the center of the surface of the block in contact with the specimen. The block shall be closely held in its spherical seat, but shall be free to turn in any direction, and its perimeter shall have at least ¼ in. (6.35 mm) clearance from the head to allow for specimens whose bearing surfaces are not exactly parallel. The diameter of the bearing surface shall be at least 5 in. (127.00 mm). Use a hardened metal bearing block beneath the specimen to minimize wear of the lower platen of the machine. The bearing block surfaces intended for contact with the specimen shall have a hardness not less than HRC60 (HB 620). These surfaces shall not depart from plane surfaces by more than 0.001 in. (0.03 mm). When the bearing area of the spherical bearing block is not sufficient to cover the area of the specimen, place a steel plate with surfaces machined to true planes within ± 0.001 in. (0.03 mm), and with a thickness equal to at least one third of the distance from the edge of the spherical bearing to the most distant corner between the spherical bearing block and the capped specimen.

7.3.4 *Speed of Testing*—Apply the load, up to one half of the expected maximum load, at any convenient rate, after which, adjust the controls of the machine so that the remaining load is applied at a uniform rate in not less than 1 nor more than 2 min.

7.4 Calculation and Report:

7.4.1 Calculate and report the compressive strength of each specimen to the nearest 10 psi (69 kPa) as follows:

$$\text{Compressive strength, } C = W / A \quad (2)$$

where:

- C = compressive strength of the specimen, lb/in.² (or kg/cm²) (or Pa·10⁴),
- W = maximum load, lbf, (or kgf) (or N), indicated by the testing machine, and
- A = average of the gross areas of the upper and lower bearing surfaces of the specimen, in.² (or cm²).

NOTE 4—When compressive strength is to be based on net area (example: clay floor tile), substitute for A in the above formula the net area, in in.² (or cm²), of the fire clay in the section of minimum area perpendicular to the direction of the load.

7.4.2 Calculate and report the average of the compressive strength determinations to the nearest 10 psi (69 kPa).

8. Absorption

8.1 Accuracy of Weighings:

8.1.1 *Brick*—The scale or balance used shall have a capacity of not less than 2000 g, and shall be sensitive to 0.5 g.

8.1.2 *Tile*—The balance used shall be sensitive to within 0.2 % of the weight of the smallest specimen tested.

8.2 Test Specimens:

8.2.1 *Brick*—The test specimens shall consist of half brick conforming to the requirements of 7.1.1. Five specimens shall be tested.

8.2.2 *Tile*—The specimens for the absorption test shall consist of five tile or three representative pieces from each of

these five tiles. Two of the three representative pieces shall be taken from the shells and one from an interior web, the weight of each piece being not less than 227 g. The specimens shall have had their rough edges or loose particles ground off. Pieces taken from tile that have been subjected to compressive strength tests shall be free of cracks due to failure in compression.

8.3 5-h and 24-h Submersion Tests:

8.3.1 Procedure:

8.3.1.1 Dry and cool the test specimens in accordance with 5.1 and weigh each one in accordance with 5.2.

8.3.1.2 *Saturation*—Submerge the dry, cooled specimen, without preliminary partial immersion, in clean water (soft, distilled or rain water) at 60 to 86°F (15.5 to 30°C) for the specified time. Remove the specimen, wipe off the surface water with a damp cloth and weigh the specimen. Complete weighing of each specimen within 5 min after removing the specimen from the bath.

8.3.2 Calculation and Report:

8.3.2.1 Calculate and report the cold water absorption of each specimen to the nearest 0.1 % as follows:

$$\text{Absorption, \%} = 100(W_s - W_d)/W_d \quad (3)$$

where:

W_d = dry weight of the specimen, and

W_s = saturated weight of the specimen after submersion in cold water.

8.3.2.2 Calculate and report the average cold water absorption of all specimens to the nearest 0.1 %.

8.4 1-h, 2-h, and 5-h Boiling Tests:

8.4.1 *Test Specimens*—The test specimens shall be the same five specimens used in the 5-h or 24-h cold-water submersion test where required and shall be used in the state of saturation existing at the completion of that test.

8.4.1.1 Dry and cool the test specimens in accordance with 5.1 when performing the boiling water absorption test without previously conducting the cold water absorption test.

8.4.2 Procedure:

8.4.2.1 Return the specimen that has been subjected to the cold-water submersion to the bath, and subject it to the boiling test as described in 8.4.2.2.

8.4.2.2 Submerge the specimen in clean water (soft, distilled or rain water) at 60 to 86°F (15.5 to 30°C) in such a manner that water circulates freely on all sides of the specimen. Heat the water to boiling, within 1 h, boil continuously for specified time, and then allow to cool to 60 to 86°F (15.5 to 30°C) by natural loss of heat. Remove the specimen, wipe off the surface water with a damp cloth, and weigh the specimen. Complete weighing of each specimen within 5 min after removing the specimen from the bath.

8.4.2.3 When the tank is equipped with a drain so that water at 60 to 86°F (15.5 to 30°C) passes through the tank continuously and at such a rate that a complete change of water takes place in not more than 2 min, make weighings at the end of 1 hour.

8.4.3 Calculation and Report:

8.4.3.1 Calculate and report the boiling water absorption of each specimen to the nearest 0.1 % as follows:

$$\text{Absorption, \%} = 100(W_b - W_d)/W_d \quad (4)$$

where:

W_d = dry weight of the specimen, and

W_b = saturated weight of the specimen after submersion in boiling water.

8.4.3.2 Calculate and report the average boiling water absorption of all specimens to the nearest 0.1 %.

8.5 Saturation Coefficient:

8.5.1 Calculate and report the saturation coefficient of each specimen to the nearest 0.01 as follows:

$$\text{Saturation coefficient} = (W_{c(24)} - W_d)/(W_{b(5)} - W_d) \quad (5)$$

where:

W_d = dry weight of the specimen,

$W_{c(24)}$ = saturated weight of the specimen after 24-h submersion in cold water, and

$W_{b(5)}$ = saturated weight of the specimen after 5-h submersion in boiling water.

8.5.2 Calculate and report the average saturation coefficient of all specimens to the nearest 0.01.

9. Freezing and Thawing

9.1 Apparatus:

9.1.1 *Compressor, Freezing Chamber, and Circulator* of such design and capacity that the temperature of the air in the freezing chamber will not exceed 16°F (−9°C) 1 h after introducing the maximum charge of units, initially at a temperature not exceeding 90°F (32°C).

9.1.2 *Trays and Containers*, shallow, metal, having an inside depth of $1\frac{1}{2} \pm \frac{1}{2}$ in. (38.1 ± 12.7 mm), and of suitable strength and size so that the tray with a charge of frozen units is movable by one technician.

9.1.3 *Balance*, having a capacity of not less than 2000 g and sensitive to 0.5 g.

9.1.4 *Drying Oven* that provides a free circulation of air through the oven and is capable of maintaining a temperature between 230 and 239°F (110 and 115°C).

9.1.5 *Thawing Tank* of such dimensions as to permit complete submersion of the specimens in their trays. Adequate means shall be provided so that the water in the tank is kept at a temperature of $75 \pm 10^\circ\text{F}$ ($24 \pm 5.5^\circ\text{C}$).

9.1.6 *Drying Room*, maintained at a temperature of $75 \pm 15^\circ\text{F}$ ($24 \pm 8^\circ\text{C}$), with a relative humidity between 30 and 70 %, and free from drafts.

9.2 Test Specimens:

9.2.1 *Brick*—The test specimens shall consist of half brick with approximately plane and parallel ends. When necessary, smooth any rough ends by trimming off a thin section with a masonry saw. The specimens shall be free from shattering or unsoundness, visually observed, resulting from the flexure or from the absorption tests. Additionally, prepare specimens by removing all loosely adhering particles, sand or edge shards from the surface or cores. Test five specimens.

9.2.2 *Structural Clay Tile*—The test specimens shall consist of five tile or of a cell not less than 4 in. (101.6 mm) in length sawed from each of the five tile.

9.3 Procedure:

9.3.1 Dry and cool the test specimens in accordance with 5.1. Weigh and record the dry weight of each in accordance with 5.2.

9.3.2 Carefully examine each specimen for cracks. A crack is defined as a fissure or separation visible to a person with normal vision from a distance of one foot under an illumination of not less than 50 fc. Mark each crack its full length with an indelible felt marking pen.

9.3.3 Submerge the test specimens in the water of the thawing tank for $4 \pm \frac{1}{2}$ hour.

9.3.4 Remove the specimens from the thawing tank and stand them in the freezing trays with one of their head faces down. Head face is defined as the end surfaces of a whole rectangular brick (which have the smallest area). (See Note 5.) A space of at least $\frac{1}{2}$ in. (12.7 mm) shall separate the specimens as placed in the tray. Pour sufficient water into the trays so that each specimen stands in $\frac{1}{2}$ in. depth of water and then place the trays and their contents in the freezing chamber for 20 ± 1 hour.

NOTE 5—The dimensions of some brick may prevent specimens from standing without support on one of their head faces. In such a case, any suitable rack or support that will achieve the $\frac{1}{2}$ in. (12.7 mm) separation of specimens and the specimen standing in $\frac{1}{2}$ in. (12.7 mm) depth of water will suffice.

9.3.5 Remove the trays from the freezing chamber after 20 ± 1 h and totally immerse them and their contents in the water of the thawing tank for $4 \pm \frac{1}{2}$ hour.

9.3.6 Freeze the test specimens by the procedure in 9.3.4 one cycle each day of the normal work week. Following the $4 \pm \frac{1}{2}$ h thawing after the last freeze-thaw cycle of the normal work week, remove the specimens from the trays and store them for 44 ± 1 h in the drying room. Do not stack or pile units. Provide a space of at least 1 in. (25.4 mm) between all specimens. Following this period of air drying, inspect the specimens, submerge them in the water of the thawing tank for $4 \pm \frac{1}{2}$ h, and again subject them to a normal week of freezing and thawing cycles in accordance with 9.3.4 and 9.3.5. When a normal 5-day work week is interrupted, put specimens into a drying cycle, which meets or extends past the 44 ± 1 h drying time outlined in the procedures of this section.

9.3.7 Continue the alternations of drying and submersion in water for $4 \pm \frac{1}{2}$ h, followed by 5 cycles of freezing and thawing or the number of cycles needed to complete a normal work week, until a total of 50 cycles of freezing and thawing has been completed. Stop the test when the test specimen develops a crack as defined in 9.4.3, breaks, or appears to have lost more than 3 % of its original weight by disintegration as judged by visual inspection.

9.3.8 After completion of 50 cycles, or when the test specimen has been withdrawn from test as a result of disintegration, dry and weigh the specimen as prescribed in 9.3.1.

9.4 Calculations, Examination, Rating and Report:

9.4.1 *Calculation*—Calculate the loss in weight as a percentage of the original weight of the dried specimen.

9.4.2 *Examination*—Re-examine the surface of the specimens for cracks (see 9.3.2) and record the presence of any new cracks developed during the freezing-thawing testing procedure. Measure and record the length of the new cracks. Examine the specimens for disintegration during the freeze-thaw process.

9.4.3 *Rating*—A specimen is considered to fail the freezing and thawing test under any of the following circumstances:

9.4.3.1 *Breakage and Weight Loss*—A separation or disintegration resulting in a weight loss of greater than that permitted by the referenced unit specification for the appropriate classification

9.4.3.2 *Cracking*—A specimen develops a crack during the freezing and thawing procedure that exceeds the length permitted by the referenced unit standard for the appropriate classification. If none of the above circumstances occur, the specimens are considered to pass the freezing and thawing test.

9.4.4 *Report*—The report shall state whether the sample passed or failed the test. Any failures shall include the rating and the reason for classification as a failure and the number of cycles causing failure in the event failure occurs prior to 50 cycles.

10. Initial Rate of Absorption (Suction) (Laboratory Test)

10.1 Apparatus:

10.1.1 *Trays or Containers*—Watertight trays or containers, having an inside depth of not less than $\frac{1}{2}$ in. (12.7 mm), and of such length and width that an area of not less than 300 in.² (1935.5 cm²) of water surface is provided. The bottom of the tray shall provide a plane, horizontal upper surface, when suitably supported, so that an area not less than 8 in. (203.2 mm) in length by 6 in. (152.4 mm) in width will be level when tested by a spirit level.

10.1.2 *Supports for Brick*—Two noncorrodible metal supports consisting of bars between 5 and 6 in. (127.00 and 152.4 mm) in length, having triangular, half-round, or rectangular cross sections such that the thickness (height) will be approximately $\frac{1}{4}$ in. (6.35 mm). The thickness of the two bars shall agree within 0.001 in. (0.03 mm) and, when the bars are rectangular in cross section, their width shall not exceed $\frac{5}{16}$ in. (7.9 mm).

10.1.3 *Means for Maintaining Constant Water Level*—Suitable means for controlling the water level above the upper surface of the supports for the brick within ± 0.01 in. (0.25 mm) (see Note 6), including means for adding water to the tray at a rate corresponding to the rate of removal by the brick undergoing test (see Note 7). For use in checking the adequacy of the method of controlling the rate of flow of the added water, a reference brick or half brick shall be provided whose displacement in $\frac{1}{8}$ in. (3.18 mm) of water corresponds to the brick or half brick to be tested within ± 2.5 %. Completely submerge the reference brick in water for not less than 3 h preceding its use.

NOTE 6—A suitable means for obtaining accuracy in control of the water level is provided by attaching to the end of one of the bars two stiff metal wires that project upward and return, terminating in points; one of which is $\frac{1}{8} - 0.01$ in. (3.18 – 0.25 mm) and the other $\frac{1}{8} + 0.01$ in.

(3.18 ± 0.25 mm) above the upper surface or edge of the bar. Such precise adjustment is obtainable by the use of depth plates or a micrometer microscope. When the water level with respect to the upper surface or edge of the bar is adjusted so that the lower point dimples the water surface when viewed by reflected light and the upper point is not in contact with the water, the water level is within the limits specified. Any other suitable means for fixing and maintaining a constant depth of immersion shall be permitted when equivalent accuracy is obtained. An example of such other suitable means is the use of rigid supports movable with respect to the water level.

NOTE 7—A rubber tube leading from a siphon or gravity feed and closed by a spring clip will provide a suitable manual control. The so-called “chicken-feed” devices as a rule lack sensitivity and do not operate with the very small changes in water level permissible in this test.

10.1.4 *Balance*, having a capacity of not less than 3000 g, and sensitive to 0.5 g.

10.1.5 *Drying Oven*, conforming to the requirements of 9.1.4.

10.1.6 *Timing Device*—A suitable timing device, preferably a stop watch or stop clock, which shall indicate a time of 1 min to the nearest 1 s.

10.2 *Test Specimens*, consisting of whole brick. Five specimens shall be tested.

10.3 Procedure:

10.3.1 The initial rate of absorption shall be determined for the test specimen as specified either oven-dried or ambient air-dried. When not specified the initial rate of absorption shall be determined for the test specimens oven-dried. Dry and cool the test specimens in accordance with the applicable procedures 10.3.1.1 or 10.3.1.2. Complete the test procedure in accordance with 10.3.2, 10.3.3, and 10.3.4.

NOTE 8—There is no correlated relationship between the value of initial rate of absorption for ambient air-dried and oven-dried units. The test methods provide different information.

10.3.1.1 *Oven-dried Procedure*—Dry and cool the test specimens in accordance with 5.1.

10.3.1.2 *Ambient Air-dried Procedure*—Store units unstacked, with separate placement in a ventilated room maintained at a temperature of 75 ± 15°F (24 ± 8°C) with a relative humidity between 30 % and 70 % for a period of 4 h, with a current of air from an electric fan passing over them for a period of at least 2 hours. Continue until two successive weighings at intervals of 2 h show an increment of loss not greater than 0.2 % of the last previously determined weight of the specimen.

10.3.2 Measure to the nearest 0.05 in. (1.27 mm) the length and width of the flatwise surface of the test specimen of rectangular units or determine the area of other shapes to similar accuracy that will be in contact with the water. Weigh the specimen to the nearest 0.5 g.

10.3.3 Adjust the position of the tray for the absorption test so that the upper surface of its bottom will be level when tested by a spirit level, and set the saturated reference brick (10.1.3) in place on top of the supports. Add water until the water level is 1/8 ± 0.01 in. (3.18 ± 0.25 mm) above the top of the supports. When testing tile with scored bed surfaces, the depth of water level is 1/8 ± 0.01 in. plus the depth of scores.

10.3.4 After removal of the reference brick, set the test brick in place flatwise counting zero time as the moment of contact

of the brick with the water. During the period of contact (1 min ± 1 s) keep the water level within the prescribed limits by adding water as required. At the end of 1 min ± 1 s, lift the brick from contact with the water, wipe off the surface water with a damp cloth, and reweigh the brick to the nearest 0.5 g. Wiping shall be completed within 10 s of removal from contact with the water, and weighing shall be completed within 2 min.

NOTE 9—Place the brick in contact with the water quickly, but without splashing. Set the brick in position with a rocking motion to avoid the entrapping of air on its under surface. Test brick with frogs or depressions in one flatwise surface with the frog or depression uppermost. Test molded brick with the struck face down.

10.4 Calculation and Report:

10.4.1 The difference in weight in grams between the initial and final weighings is the weight in grams of water absorbed by the brick during 1-min contact with the water. When the area of its flatwise surface (length times width) does not differ more than ±0.75 in.² (4.84 cm²) (±2.5 %) from 30 in.² (193.55 cm²), report the gain in weight of each specimen to the nearest 0.1 g, as its initial rate of absorption in 1 min.

10.4.2 When the area of its flatwise surface differs more than ± 0.75 in.² (4.84 cm²) (±2.5 %) from 30 in.² (193.55 cm²), calculate the equivalent gain in weight from 30 in.² (193.55 cm²) of each specimen to the nearest 0.1 g as follows:

$$X = 30 W/LB \text{ (metric } X = 193.55 W/LB) \quad (6)$$

where:

X = gain in weight corrected to basis of 30 in.² (193.55 cm²) flatwise area,

W = actual gain in weight of specimen, g,

L = length of specimen, in., (cm), and

B = width of specimen, in., (cm).

10.4.3 Report the corrected gain in weight, X , of each specimen to the nearest 0.1 g, as the initial rate of absorption in 1 min.

10.4.4 When the test specimen is a cored brick, calculate the net area and substitute for LB in the equation given in 10.4.2. Report the corrected gain in weight, X , of each specimen to the nearest 0.1 g, as the initial rate of absorption in 1 min.

10.4.5 When the specimen is non-prismatic, calculate the net area by suitable geometric means and substitute for LB in the equation given in 10.4.2.

10.5 Calculate and report the average initial rate of absorption of all specimens tested to the nearest 0.1 g/min/30 in.² (193.55 cm²).

10.6 Report the method of drying as oven-dried (in accordance with 10.3.1.1) or ambient air-dried (in accordance with 10.3.1.2).

11. Efflorescence

11.1 Apparatus:

11.1.1 *Trays and Containers*—Watertight shallow pans or trays made of corrosion-resistant metal or other material that will not provide soluble salts when in contact with distilled water containing leachings from brick. The pan shall be of such dimensions that it will provide not less than a 1-in. (25.4-mm) depth of water. Unless the pan provides an area such that the total volume of water is large in comparison with the amount

evaporated each day, suitable apparatus shall be provided for keeping a constant level of water in the pan.

11.1.2 *Drying Room*, conforming to the requirements of 9.1.6.

11.1.3 *Drying Oven*, conforming to the requirements of 9.1.4.

11.1.4 *Brush*, a soft-bristle brush.

11.2 *Test Specimens*:

11.2.1 The sample shall consist of ten full-size brick.

11.2.2 The ten specimens shall be sorted into five pairs so that both specimens of each pair are similar in appearance.

11.3 *Preparation of Specimens*—Remove by brushing any adhering dirt so as not to mistake it for efflorescence. Dry and cool the specimens in accordance with 5.1.

11.4 *Procedure*:

11.4.1 Set one specimen from each of the five pairs, on end, partially immersed in distilled water to a depth of approximately 1 in. (25.4 mm) for 7 days in the drying room. When several specimens are tested in the same container, separate the individual specimens by a spacing of at least 2 in. (50.8 mm).

NOTE 10—Do not test specimens from different sources simultaneously in the same container, because specimens with a considerable content of soluble salts will contaminate salt-free specimens.

NOTE 11—Empty and clean the pans or trays after each test.

11.4.2 Store the second specimen from each of the five pairs in the drying room without contact with water.

11.4.3 At the end of 7 days, inspect the first set of specimens and then place both sets in the drying oven without contact with water for 24 hours.

11.5 *Examination and Rating*—After drying, examine and compare each pair of specimens, observing the top and all four faces of each specimen from a distance of 10 ft. (3 m) under an illumination of not less than 50 footcandles (538.2 lm/m²) by an observer with normal vision. When under these conditions no difference is noted, report the rating as “not effloresced.” When a perceptible difference due to efflorescence is noted under these conditions, report the rating as “effloresced.” Report the appearance and distribution of the efflorescence.

11.6 *Precision and Bias*—No information is presented about either the precision or bias of the test method for efflorescence because the test result is nonquantitative.

12. Weight per Unit Area

12.1 *Apparatus*—A scale or balance sensitive to within 0.2 % of the weight of the smallest specimen.

12.2 *Procedure*—Weigh in accordance with 5.2 five full size structural clay tile units that have been dried and cooled (see 5.1).

12.3 *Calculation and Report*:

12.3.1 Calculate the weight per unit area of each specimen as follows:

$$W_a = \frac{n W_d}{A_{fa1} + A_{fa2}} \quad (7)$$

where:

W_a = weight per unit area of the specimen, lb/ft² (kg/m²),
 n = number of faces of the specimen (1 for split tile units or 2 for all other units),

W_d = dry weight of the specimen, lb (kg),

A_{fa1} = area (height × length) of finished face of specimen, ft² (m²), and

A_{fa2} = area (height × length) of back face of specimen, ft² (m²).

12.3.2 Report the results of Eq 7 separately for each specimen to the nearest 1 g and the average to the nearest 1 g for all specimens tested.

13. Measurement of Size

13.1 *Apparatus*—Either a 1-ft (or metric) steel rule, graduated in 1/32-in. (or 1-mm) divisions, or a gage or caliper having a scale ranging from 1 to 12 in. (25 to 300 mm), and having parallel jaws, shall be used for measuring the individual units. Steel rules or calipers of corresponding accuracy and size required shall be used for measurement of larger brick, solid masonry units, and tile.

13.2 *Procedure*—Measure ten whole full-size units that have been dried and cooled (see 5.1). These units shall be representative of the lot and shall include the extremes of color range and size as determined by visual inspection. (It is permissible to use the same samples for determining efflorescence and other properties.)

13.3 *Individual Measurements of Width, Length, and Height*—Measure the width across both ends and both beds from the midpoints of the edges bounding the faces. Record these four measurements to the nearest 1/32 in. (1 mm) and record the average to the nearest 1/64 in. (0.5 mm) as the width. Measure the length along both beds and along both faces from the midpoints of the edges bounding the ends. Record these four measurements to the nearest 1/32 in. (1 mm) and record the average to the nearest 1/64 in. (0.5 mm) as the length. Measure the height across both faces and both ends from the midpoints of the edges bounding the beds. Record these four measurements to the nearest 1/32 in. (1 mm) and record the average to the nearest 1/64 in. (0.5 mm) as the height. Use the apparatus described in 13.1. Retest by the same method when required.

13.4 *Report*—Report the average width, length, and height of each specimen tested to the nearest 1/32 in. (1.0 mm).

14. Measurement of Warpage

14.1 *Apparatus*:

14.1.1 *Steel Straightedge*:

14.1.2 *Rule or Measuring Wedge*—A steel rule graduated from one end in 1/32-in. (or 1-mm) divisions, or alternatively, a steel measuring wedge 2.5 in. (60 mm) in length by 0.5 in. (12.5 mm) in width by 0.5 in. (12.5 mm) in thickness at one end and tapered, starting at a line 0.5 in. (12.5 mm) from one end, to zero thickness at the other end. The wedge shall be graduated in 1/32-in. (or 1-mm) divisions and numbered to show the thickness of the wedge between the base, AB, and the slope, AC, Fig. 1.

14.1.3 *Flat Surface*, of steel or glass, not less than 12 by 12 in. (305 by 305 mm) and plane to within 0.001 in. (0.025 mm).

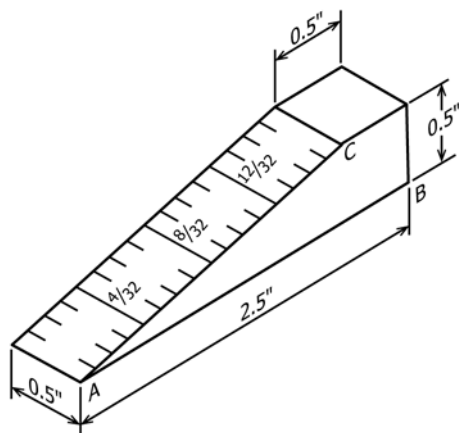


FIG. 1 Measuring Wedge

14.1.4 *Brush*, a soft-bristle brush.

14.2 *Sampling*—Use the sample of ten units selected for determination of size.

14.3 *Preparation of Samples*—Test the specimens as received, except remove any adhering dirt by brushing.

14.4 *Procedure*:

14.4.1 *Concave Surfaces*—Where the warpage to be measured is of a surface and is concave, place the straightedge lengthwise or diagonally along the surface to be measured, selecting the location that gives the greatest departure from straightness. Select the greatest distance from the unit surface to the straightedge. Using the steel rule or wedge, measure this distance to the nearest $\frac{1}{32}$ in. (1 mm), and record as the concave warpage of the surface. See Fig. 2.

14.4.2 *Concave Edges*—Where the warpage to be measured is of an edge and is concave, place the straightedge between the ends of the concave edge to be measured. Select the greatest distance from the unit edge to the straightedge. Using the steel rule or wedge, measure this distance to the nearest $\frac{1}{32}$ in. (1 mm), and record as the concave warpage of the edge.

14.4.3 *Convex Surfaces*—When the warpage to be measured is of a surface and is convex, place the unit with the convex surface in contact with a plane surface and with the corners approximately equidistant from the plane surface. Using the steel rule or wedge, measure the distance to the nearest $\frac{1}{32}$ in. (1 mm) of each of the four corners from the plane surface. Record the average of the four measurements as the convex warpage of the unit.

14.4.4 *Convex Edges*—Where the warpage to be measured is of an edge and is convex, place the straightedge between the ends of the convex edge. Select the greatest distance from the unit edge to the straightedge. Using the steel rule or wedge, measure this distance to the nearest $\frac{1}{32}$ in. (1 mm) and record as the convex warpage of the edge.

14.5 *Report*—Report all recorded warpage measurements of each specimen tested to the nearest $\frac{1}{32}$ in. (1.0 mm).

15. Measurement of Length Change

15.1 *Apparatus*—A dial micrometer or other suitable measuring device graduated to read in 0.0001-in. (or 0.001-mm) increments, mounted on a stand suitable for holding the specimen in such a manner that reproducible results are obtained, shall be used for measuring specimen length. Provisions shall be made to permit changing the position of the dial micrometer on its mounting rod so as to accommodate large variations in specimen size. The base of the stand and the tip of the dial micrometer shall have a conical depression to accept a $\frac{1}{4}$ -in. (6.35-mm) steel ball. A suitable reference instrument shall be provided for checking the measuring device.

15.2 *Preparation of Specimen*—Remove the ends of deeply textured specimens to the depth of the texture by cutting perpendicular to the length and parallel to each other. Drill a hole in each end of the specimen with a $\frac{1}{4}$ -in. (6.35-mm) carbide drill. Drill these holes at the intersection of the two diagonals from the corners. Place $\frac{1}{4}$ -in. (6.35-mm) steel balls in these depressions by cementing in place with a calcium aluminate cement. Any equivalent method for establishing the reference length is permissible.

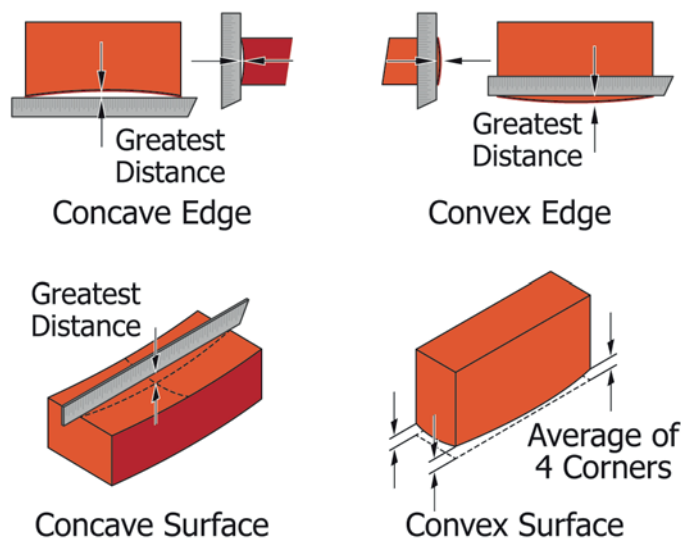


FIG. 2 Warpage Measurements

15.3 Procedure—Mark the specimen for identification and measure to the nearest 0.0001 in. (or 0.001 mm) in a controlled environment and make subsequent measurements in the same controlled environment, $\pm 2^{\circ}\text{F}$ ($\pm 1^{\circ}\text{C}$) and $\pm 5\%$ relative humidity. Record the temperature and relative humidity. Apply a reference mark to the specimen for orientation in the measuring device. Check the measuring device with the reference instrument before each series of measurements.

15.4 Report—When more than one specimen is tested, calculate and report the average length change of all specimens to the nearest 0.0001 in. (0.001 mm). The report shall include all individual recordings as well as the recorded laboratory temperature and relative humidity.

16. Initial Rate of Absorption (Suction)—Field Test

16.1 Scope—This test method is intended to serve as a volumetric means of determining the initial rate of absorption (IRA) of any size brick when weighing determination, described in Section 10 of these test methods, is impractical. This test method is applicable to assess the need for wetting the brick. This test method is performed on specimens taken from the field with no modification of moisture content, therefore, the IRA determined by this test method may differ from the IRA determined by the laboratory test method in Section 10, which requires drying the specimens.

16.2 Apparatus:

16.2.1 Absorption Test Pan—A watertight, rectangular pan, constructed of noncorroding material, with a flat rigid bottom and inside depth of about 1½ in. (38.1 mm). The inside length and width of the pan shall exceed the length and width of the tested brick by a minimum of 3 in. (76.2 mm) but not more than 5 in. (127.0 mm).

16.2.2 Brick Supports—Two noncorroding rectangular bars, ¼ in. (6.4 mm) in height and width and 1 in. (25.4 mm) shorter than the inside width of the pan in length. The brick supports shall be placed on the bottom of the pan just before the test or shall be permanently affixed to the bottom of the pan. The space between the supports shall be approximately 4 in. (101.6 mm) shorter than the length of the tested brick. A device indicating the desired water level shall be permanently attached to the end of one of the brick supports or shall be suspended from the top of the pan (see Fig. 3 (a) and (b)). Any other device of equivalent accuracy for controlling the required

water level, ⅛ in. (3.2 mm) above the brick supports, is permitted to be used in place of that depicted in Fig. 3.

16.2.3 Timing Device—A suitable timing device that shall indicate a time of 1 min to the nearest 1 s.

16.2.4 Squeeze Bottle—A plastic squeeze bottle, 100 mL capacity.

16.2.5 Graduated Cylinder—A plastic or glass graduated measuring cylinder, 100 mL capacity.

16.3 Test Specimens—Select six whole brick in accordance with the requirements of Paragraph 4.1.

16.4 Procedure:

16.4.1 Completely immerse one brick specimen in a container of water for 2 hours.

16.4.2 Measure to the nearest ⅛ in. (1.6 mm) the length and width of the five remaining specimens at the surface that will be in contact with water. When the test specimens are cored, determine the area of the cores at the same surface.

16.4.3 Pre-wet and drain the absorption pan and place it on a flat level surface.

16.4.4 Remove the pre-wetted specimen from the container, shake off the surface water, and place the specimen on brick supports in the pan. Pour water into the pan until the water reaches a level ⅛ in. (3.2 mm) above the brick supports. (When using a pointed level water indicator, pour water into the pan until the water makes a minimum contact (dimpling effect).) Remove the pre-wetted brick, and tilt the brick sharply so that one corner serves as a drip point for clinging surface water to return to the pan. Gently shake the brick to make the last drop fall. Put the pre-wetted brick back into the container of water.

16.4.5 Using the graduated cylinder, fill the squeeze bottle with exactly 100 mL of water.

16.4.6 Set the first test specimen squarely on the brick supports, counting zero time as the moment the brick contacts the water. At the end of 1 min $\pm$ 1 s lift the test specimen from water and tilt the brick sharply so that one corner serves as a drip point for clinging surface water to return to the pan. Gently shake the brick to make the last drop fall.

16.4.6.1 Continue setting the remaining test specimens into the pan in the same way until all five specimens are tested. During the test add water to the pan, using the squeeze bottle, to keep the water level approximately constant at the ⅛ in. depth. Refill the squeeze bottle with 100 mL of water when empty, recording each refill.

16.4.6.2 After the last specimen is tested, place the pre-wetted brick back in the pan and restore the original level with water from the squeeze bottle.

NOTE 12—Place the brick in contact with the water quickly, but without splashing. Set the brick in position with a rocking motion to avoid the entrapping of air on its under surface. Test brick with frogs or depressions in one flatwise surface with the frog or depression uppermost. Test molded brick with the struck face down.

16.4.7 Using the graduated cylinder, measure the volume of water remaining in the squeeze bottle.

16.5 Calculation and Report:

16.5.1 The number of refill plus the first full bottle, times 100 mL, minus the volume of water remaining in the squeeze

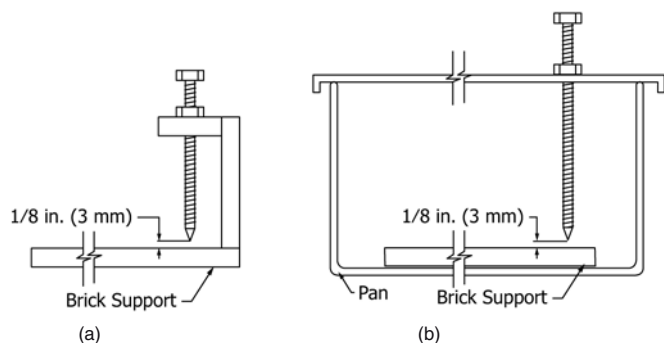


FIG. 3 Water Level Indicators

bottle, is the total measured volume of water in millilitres absorbed by the five specimens.

$$V_t = 100(n+1) - V_r \quad (8)$$

where:

V_t = total measured volume of water absorbed by all tested specimens, mL,

n = the number of squeeze bottle refills and

V_r = the volume of water remaining in the squeeze bottle, mL.

16.5.2 When the average net surface area in contact with water of a single specimen (sum of net surface areas divided by the number of specimens) differs by $\pm 0.75 \text{ in.}^2$ (4.84 cm^2) or less from 30 in.^2 (193.5 cm^2), report the total measured absorbed volume of water divided by five the number of tested specimens, as the IRA (Field) in g/min/30 in.²

$$\text{IRA (Field)} = \frac{V_t}{5} \quad (9)$$

16.5.3 When the average net surface area in contact with water differs by more than $\pm 0.75 \text{ in.}^2$ (4.84 cm^2) from 30 in.^2 (193.5 cm^2), calculate the equivalent volume in 1 min for 30 in.² (193.5 cm^2) of surface as follows:

$$V_c = \frac{30 V_t}{A_n} \left(\text{metric } V_c = \frac{193.5 V_t}{A_n} \right) \quad (10)$$

where:

V_c = average volume of absorbed water by a specimen, corrected to basis of 30 in.^2 (193.5 cm^2) of surface, mL, and

A_n = sum of net surface areas in contact with water of all tested specimens, in.² (cm^2).

16.5.4 *Report*—Report the corrected volume (V_c) as the IRA (Field) in g/l min/30 in.²

16.6 *Precision and Bias*—Insufficient data is currently available for a precision and bias statement.

17. Measurement of Void Area in Cored Units

17.1 Apparatus:

17.1.1 *Steel Rule or Calipers*—As described in 13.1.

17.1.2 *Graduated Cylinder*—A glass cylinder with a capacity of 500 mL.

17.1.3 *Paper*—A sheet of smooth, hard-finish paper not less than 24 by 24 in. (610 by 610 mm).

17.1.4 *Sand*—500 mL of clean, dry sand.

17.1.5 *Steel Straightedge*.

17.1.6 *Flat Surface*—A level, flat smooth, clean dry surface.

17.1.7 *Brush*—A soft-bristle brush.

17.1.8 *Neoprene Mat*—24 by 24 in. (610 by 610 mm) open-cell neoprene sponge ¼ in. (6.4 mm) in thickness.

17.1.9 *Balance*—See 10.1.4.

17.2 *Test Specimens*—Use of a sample of ten units selected as described for the determination of size. (It is permissible to use the samples taken for the determination of size.)

17.3 *Preparation of Samples*—Test the specimens as received, except remove any adhering dirt by brushing.

17.4 Procedure:

17.4.1 Measure and record the length, width, and depth of the unit as described for the determination of size.

17.4.2 Place the unit to be tested bed down (cores vertical) on the sheet of paper that has been spread over the neoprene mat on the flat surface.

17.4.3 Fill the cores with sand, allowing the sand to fall naturally. Do not work the sand into the cores. Using the steel straightedge, bring the level of the sand in the cores down to the top of the unit. With the brush, remove all excess sand from the top of the unit and from the paper sheet.

17.4.4 Lifting the unit up, allow all of the sand in the cores to fall on the sheet of paper.

17.4.5 Transfer the sand from the sheet of paper to the balance, weighing and recording to the nearest 0.5 g.

17.4.6 With a separate portion of the sand, fill a 500 mL cylinder to the exact 500 mL graduation by allowing the sand to fall naturally and without shaking or vibrating the cylinder. Transfer this sand to the balance, weighing and recording to the nearest 0.5 g.

17.5 Calculation and Report:

17.5.1 Determine the volume of sand held in the test unit as follows:

$$V_s = \frac{500 \text{ mL}}{S_c} \times S_u \quad (11)$$

where:

V_s = volume of sand held in test unit,

S_c = weight, in grams, of 500 mL sand contained in graduated cylinder, and

S_u = weight in grams of sand held in test unit.

17.5.2 Determine the percentage of void as follows:

$$\% \text{ Void area} = \frac{V_s}{V_u} \times \frac{1}{16.4} \times 100 \quad (12)$$

where:

V_s = volume of sand determined in 17.5.1, mL, and

V_u = length $\times$ width $\times$ depth recorded in 17.4.1, in.³

17.5.3 Report the results of Eq 12 in 17.5.2 for each specimen to the nearest 1 %, as the unit's percentage of void area.

18. Measurement of Void Area In Deep Frogged Units

NOTE 13—The area measured corresponds to a section located ¾ in. (9.5 mm) distant from the voided bed of the units.

18.1 Apparatus:

18.1.1 *Steel Rule or Gage or Calipers* (inside and outside)—as described in 13.1.

18.1.2 *Steel Straightedge*.

18.1.3 *Marking Pen or Scribe*.

18.1.4 *Brush*, a soft-bristle brush.

18.2 *Test Specimens*—Use a sample of 10 units selected as described for the determination of size. (It is permissible to use the samples taken for the determination of size.)

18.3 *Preparation of Sample*—Test the specimens as received except remove any adhering dirt by brushing.

18.4 Procedure:

18.4.1 Measure the length along both faces and the width along both ends at a distance of $\frac{3}{8}$ in. (9.5 mm) down from the bed containing the deep frogs. Record the measurements to the nearest $\frac{1}{32}$ in. (1 mm). Record the average of the two length measurements to the nearest $\frac{1}{32}$ in. (1 mm) as the length of the unit and the average of the two width measurements to the nearest $\frac{1}{32}$ in. (1 mm) as the width of the unit.

18.4.2 With the steel straightedge parallel to the length of the unit and centered over the deep frog or frogs, inscribe a mark on both faces of the frog $\frac{3}{8}$ in. (9.5 mm) below the underside of the steel straightedge (mark 1 on Fig. 4). With the steel straightedge parallel to the width of the unit and centered over the deep frog, inscribe a mark on both faces of each frog $\frac{3}{8}$ in. (9.5 mm) below the underside of the steel straightedge (mark 2 on Fig. 4).

18.4.3 Measure and record to the nearest $\frac{1}{32}$ in. (1 mm) the distance between the inscribed marks on a line parallel to the length of the unit for each frog, and measure and record to the nearest $\frac{1}{32}$ in. (1 mm) the distance between the inscribed marks on a line parallel to the width of the unit for each frog.

18.5 Calculations and Report:

18.5.1 Using the recorded length and width measurements calculate the gross area of the unit (A_u) in the plane of the unit $\frac{3}{8}$ in. (9.5 mm) down from the frogged bed.

18.5.2 Using the distance between the inscribed marks calculate the inside area of each deep frog (A_f) in the plane of the unit $\frac{3}{8}$ in. (9.5 mm) down from the frogged bed (see Fig. 4).

18.5.3 Determine the percentage of void as follows:

$$\% \text{ Void area} = \frac{\sum A_f \times 100}{A_u} \quad (13)$$

where:

$\sum A_f$ = sum of the inside area of the deep frogs, and
 A_u = gross area of unit.

18.5.4 Report the results of the equation in 18.5.3 for each specimen to the nearest 1 %, as the unit's percentage of void area.

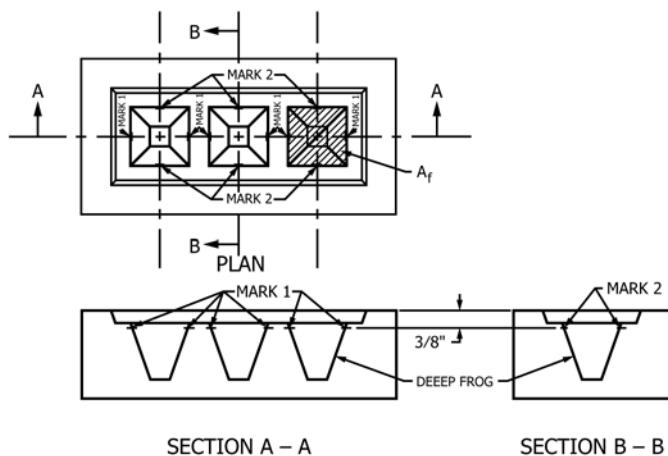


FIG. 4 Deep Frogged Units

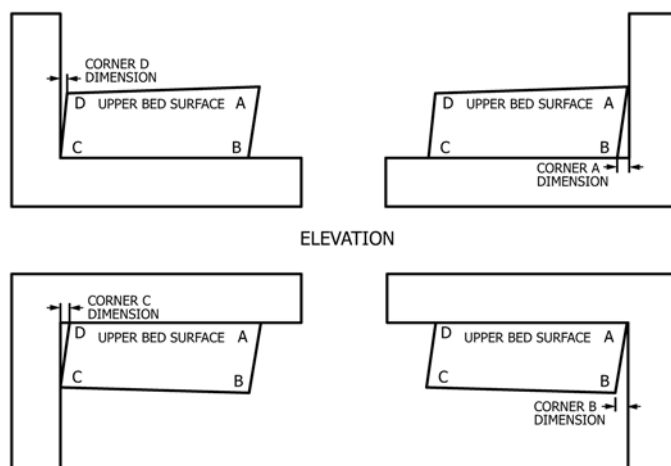


FIG. 5 Out-of-Square Measurements

19. Measurement of Out of Square

19.1 Apparatus:

19.1.1 Steel Rule or Calipers, as described in 13.1.

19.1.2 Steel Carpenter's Square.

19.2 Test Specimens—Use a sample of ten units selected as described for the measurement of size (see 13.2). (Samples taken for the measurement of size may be used in their as received state.)

19.3 Procedure:

19.3.1 Place one leg of a carpenter's square adjacent to the length of the unit when laid as a stretcher. Align the leg of the square parallel to the length of the unit by having the corners of the face of the unit in contact with the leg of the square. Locate the square parallel to and at or within $\frac{1}{4}$ in. (6.4 mm) of the face to be exposed. See Fig. 6.

19.3.2 Measure the deviation due to the departure from the 90° angle at each corner of the exposed face of the unit. Record the measurement to the nearest $\frac{1}{32}$ in. (1.0 mm) for each corner. See Fig. 5.

19.4 Report—Report the recorded measurements for each specimen tested to the nearest $\frac{1}{32}$ in. (1.0 mm) as the unit's deviation from square.

20. Measurement of Shell and Web Thickness

20.1 Apparatus—A caliper rule graduated in not more than $\frac{1}{64}$ in. (0.4 mm) divisions and having parallel jaws not less than $\frac{1}{2}$ in. (12.7 mm) in length.

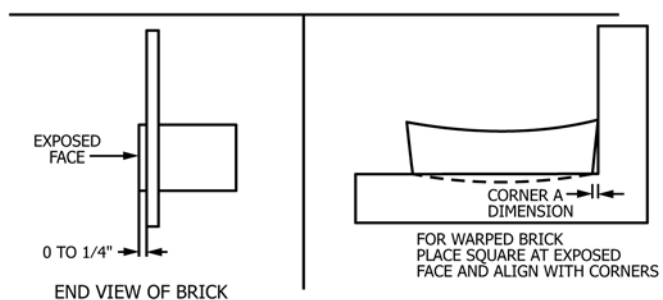


FIG. 6 Location of Carpenter's Square

20.2 *Test Specimens*—Use a sample of five units as described for the measurement of size (see 13.2). (Samples taken for the measurement of size may be used in their as received state.)

20.3 *Preparation of Samples*—Remove any shards or other projections interfering with measurement of the minimum parallel distance of two surfaces.

20.4 *Procedure*—For each unit, measure the shell thicknesses and, when required, the web thicknesses at the thinnest point of each element $\frac{1}{2}$ in. (12.7 mm) into the unit from either direction and record to the nearest division of the caliper.

NOTE 14—Current ASTM specification for solid masonry units from clay or shale do not include minimum web thickness requirements.

21. Breaking Load

21.1 *Test Specimens*—The test specimens shall consist of whole full-size units that have been dried and cooled (see 5.1). Five such specimens shall be tested.

21.2 Procedure:

21.2.1 Unless specified and reported otherwise, support the test specimen flatwise (that is, apply the load in the direction of the height of the unit). The load shall be placed at the midspan, within $\frac{1}{16}$ in. (2 mm) of the center. If the specimens have frogs or depressions, place the specimen so that the frogs or depressions are on the underside of the specimen. The supports for the specimen shall be solid steel rods $1 \pm \frac{3}{8}$ in. (25.4 $\pm$ 10 mm) in diameter placed $\frac{1}{2} \pm \frac{1}{16}$ in. (12.7 $\pm$ 2 mm) from each end. The length of each support shall be at least equal to the width of the specimen. See Fig. 7.

21.2.2 Apply the load to the upper surface of the specimen through a steel bearing plate $\frac{1}{4}$ in. (6.4 mm) in thickness and $1\frac{1}{2}$ in. (38.1 mm) in width and of a length at least equal to the width of the specimen.

21.2.3 *Speed of Testing*—The rate of loading shall not exceed 2000 lbf (8896 N)/min. This requirement shall be considered as being met when the speed of the moving head of the testing machine immediately prior to application of the load is not more than 0.05 in. (1.27 mm)/min.

21.3 Report:

21.3.1 Record the unit dimensions and span length.

21.3.2 Record the transverse breaking load, P , of each unit to the nearest lb (N).

21.3.3 Calculate and record the breaking load per width of unit as $p = P/w$ for each unit, lb/in. (N/mm). Report the average of the breaking loads per width of all the specimens tested as the breaking load of the lot.

22. Precision and Bias³

22.1 The precision of this test method is based on an interlaboratory study of C67, Standard Test Methods for Sampling and Testing Brick and Structural Clay Tile, conducted in 2013. Eight laboratories (one with five different operators) tested a total of eleven different brick sample types (molded brick, cored brick, and paver). Every “test result” represents an individual determination. All labs were asked to report either five or ten replicates for each of eight different parameters. Practice E691 was followed for the design and analysis of the data; the details are given in ASTM Research Report No. C15-1001.

22.1.1 *Repeatability (r)*—The difference between repetitive results obtained by the same operator in a given laboratory applying the same test method with the same apparatus under constant operating conditions on identical test material within short intervals of time would in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in 20.

22.1.1.1 Repeatability can be interpreted as maximum difference between two results, obtained under repeatability conditions, that is accepted as plausible due to random causes under normal and correct operation of the test method.

22.1.1.2 Repeatability limits are listed in Tables 1-8.

³ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:C15-1001. Contact ASTM Customer Service at service@astm.org.

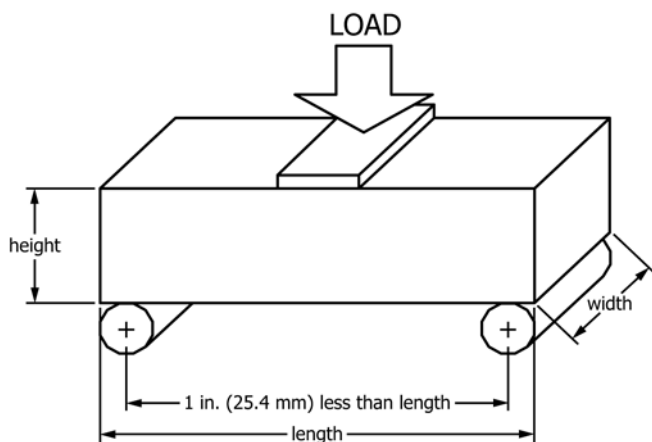


FIG. 7 Breaking Load Configuration



TABLE 1 Length (inches)

Material	$\bar{x}$	S_r	S_R	r	R	$CV\%_r$	$CV\%_R$
EB-01	7.693378	0.02437	0.035278	0.07	0.10	0.89	1.28
EB-02	7.723708	0.024315	0.03564	0.07	0.10	0.88	1.29
EB-03	7.631634	0.014489	0.025544	0.04	0.07	0.53	0.94
EB-04	7.629784	0.0313	0.038373	0.09	0.11	1.15	1.41
EB-05	7.668162	0.016222	0.024649	0.05	0.07	0.59	0.90
MB-01	7.667293	0.036841	0.045472	0.10	0.13	1.35	1.66
MB-02	7.659246	0.044106	0.057935	0.12	0.16	1.61	2.12
PB-01	7.993776	0.084608	0.087455	0.24	0.24	2.96	3.06
PB-02	7.9592	0.026266	0.035697	0.07	0.10	0.92	1.26
PB-03	8.00103	0.009367	0.021024	0.03	0.06	0.33	0.74
PB-04	8.001194	0.011771	0.025145	0.03	0.07	0.41	0.88

where:

- $\bar{x}$ = the average of all results for each material
 S_r = repeatability standard deviation (within a laboratory)
 S_R = reproducibility standard deviation (between laboratories)
 r = 95 % repeatability limit (within a laboratory)
 R = 95 % reproducibility limit (between laboratories)
 $CV\%_r$ = repeatability coefficient of variation in percent (within a Laboratory)
 $CV\%_R$ = reproducibility coefficient of variation in percent (between Laboratories)

TABLE 2 Width (inches)

Material	$\bar{x}^A$	S_r	S_R	r	R	$CV\%_r$	$CV\%_R$
EB-01	3.624156	0.024468	0.030720	0.07	0.09	1.89	2.37
EB-02	3.432901	0.017253	0.026957	0.05	0.08	1.41	2.20
EB-03	3.609135	0.011606	0.017123	0.03	0.05	0.90	1.33
EB-04	3.437376	0.037862	0.042200	0.11	0.12	3.08	3.44
EB-05	3.614303	0.01263	0.021261	0.04	0.06	0.98	1.65
MB-01	3.783171	0.024269	0.036198	0.07	0.10	1.80	2.68
MB-02	3.656117	0.043585	0.050470	0.12	0.14	3.34	3.87
PB-01	4.039485	0.006184	0.019114	0.02	0.05	0.43	1.32
PB-02	3.944122	0.018174	0.030109	0.05	0.08	1.29	2.14
PB-03	3.956498	0.015245	0.023093	0.04	0.06	1.08	1.63
PB-04	3.97225	0.016478	0.029843	0.05	0.08	1.16	2.10

^AThe average of the laboratories' calculated averages.

TABLE 3 Height (inches)

Material	$\bar{x}$	S_r	S_R	r	R	$CV\%_r$	$CV\%_R$
EB-01	2.2366	0.00948	0.020236	0.03	0.06	1.19	2.53
EB-02	2.256891	0.022257	0.026973	0.06	0.08	2.76	3.35
EB-03	2.272865	0.027648	0.033697	0.08	0.09	3.41	4.15
EB-04	2.237728	0.014144	0.018495	0.04	0.05	1.77	2.31
EB-05	2.27741	0.012882	0.021095	0.04	0.06	1.58	2.59
MB-01	2.261417	0.047147	0.050325	0.13	0.14	5.84	6.23
MB-02	2.279498	0.034447	0.042876	0.10	0.12	4.23	5.27
PB-01	2.298212	0.016566	0.021836	0.05	0.06	2.02	2.66
PB-02	2.266451	0.010608	0.020595	0.03	0.06	1.31	2.54
PB-03	2.275074	0.00693	0.02439	0.02	0.07	0.85	3.00
PB-04	2.248645	0.010667	0.028422	0.03	0.08	1.33	3.54

TABLE 4 Extruded Brick Void (%)

Material	$\bar{x}$	S_r	S_R	r	R	$CV\%_r$	$CV\%_R$
EB-01	23.22204	0.26897	1.761015	0.75	4.93	3.24	21.23
EB-02	20.25539	0.276236	0.639816	0.77	1.79	3.82	8.84
EB-03	23.53303	0.250746	0.615741	0.70	1.72	2.98	7.33
EB-04	26.52619	0.330939	0.735075	0.93	2.06	3.49	7.76
EB-05	19.56588	0.684706	0.936874	1.92	2.62	9.80	13.41

TABLE 5 Initial Rate of Absorption (g/30 in.²/minute)

Material	xbar	S _r	S _R	r	R	CV% _r	CV% _R
EB-01	17.56184	2.474341	2.651728	6.93	7.42	39.45	42.28
EB-02	52.13948	4.845499	6.547225	13.57	18.33	26.02	35.16
EB-03	2.491312	0.368364	0.467549	1.03	1.31	41.40	52.55
EB-04	7.33741	1.722662	1.933014	4.82	5.41	65.74	73.76
EB-05	9.231923	1.483979	1.814061	4.16	5.08	45.01	55.02
MB-01	9.921256	1.290575	1.5606	3.61	4.37	36.42	44.04
MB-02	50.64984	3.910687	5.340851	10.95	14.95	21.62	29.53

TABLE 6 24-hour Cold Water Absorption (%)

Material	xbar	S _r	S _R	r	R	CV% _r	CV% _R
EB-01	6.790671	0.2871	0.382429	0.80	1.07	11.84	15.77
EB-02	11.11266	0.407625	0.654685	1.14	1.83	10.27	16.50
EB-03	4.348747	0.227747	0.277342	0.64	0.78	14.66	17.86
EB-04	3.895394	0.608813	0.687843	1.70	1.93	43.76	49.44
EB-05	5.810543	0.533602	0.555338	1.49	1.55	25.71	26.76
MB-01	4.62871	0.160917	0.188072	0.45	0.53	9.73	11.38
MB-02	7.729764	0.81252	0.764114	2.28	2.14	29.43	27.68
PB-01	1.719857	0.106696	0.190757	0.30	0.53	17.37	31.06
PB-02	4.523482	0.542672	0.65029	1.52	1.82	33.59	40.25
PB-03	7.222433	0.698413	1.344528	1.96	3.76	27.08	52.12
PB-04	4.260449	0.282324	0.345213	0.79	0.97	18.55	22.69

TABLE 7 5-hour Boil Absorption (%)

Material	xbar	S _r	S _R	r	R	CV% _r	CV% _R
EB-01	9.714049	0.209283	0.284883	0.59	0.80	6.03	8.21
EB-02	17.28317	0.513757	0.731456	1.44	2.05	8.32	11.85
EB-03	4.920221	0.270294	0.339112	0.76	0.95	15.38	19.30
EB-04	4.890991	0.937264	1.06388	2.62	2.98	53.66	60.91
EB-05	9.014489	0.578729	0.60829	1.62	1.70	17.98	18.89
MB-01	7.976241	0.326698	0.399738	0.91	1.12	11.47	14.03
MB-02	12.13562	0.695373	0.663461	1.95	1.86	16.04	15.31
PB-01	2.11331	0.116154	0.203582	0.33	0.57	15.39	26.97
PB-02	6.143766	0.507478	0.602678	1.42	1.69	23.13	27.47
PB-03	10.47515	0.72069	1.479149	2.02	4.14	19.26	39.54
PB-04	7.451895	0.316024	0.326908	0.88	0.92	11.87	12.28

TABLE 8 Saturation Coefficient (dimensionless)

Material	xbar ^A	S _r	S _R	r	R	CV% _r	CV% _R
EB-01	0.698748	0.017078	0.025791	0.05	0.07	6.84	10.33
EB-02	0.642826	0.012131	0.023137	0.03	0.06	5.28	10.08
EB-03	0.885389	0.023326	0.047923	0.07	0.13	7.38	15.16
EB-04	0.803674	0.038595	0.050333	0.11	0.14	13.45	17.54
EB-05	0.643601	0.021621	0.028202	0.06	0.08	9.41	12.27
MB-01	0.579928	0.009373	0.018492	0.03	0.05	4.53	8.93
MB-02	0.636051	0.043261	0.041406	0.12	0.12	19.04	18.23
PB-01	0.814034	0.015706	0.049919	0.04	0.14	5.40	17.17
PB-02	0.733164	0.028237	0.036980	0.08	0.10	10.78	14.12
PB-03	0.682578	0.040127	0.062406	0.11	0.17	16.46	25.60
PB-04	0.571284	0.013808	0.031256	0.04	0.09	6.77	15.32

^AThe average of the laboratories' calculated averages.

22.1.2 *Reproducibility (R)*—The difference between two single and independent results obtained by different operators applying the same test method in different laboratories using different apparatus on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in 20.

22.1.2.1 Reproducibility can be interpreted as maximum difference between two results, obtained under reproducibility conditions, that is accepted as plausible due to random causes under normal and correct operation of the test method.

22.1.2.2 Reproducibility limits are listed in **Tables 1-8**.

22.1.3 The terms *repeatability limit* and *reproducibility limit* are used as specific in Practice **E177**.

22.1.4 Any judgment in accordance with statements 22.1.1 and 22.1.2 would have an approximate 95 % probability of being correct.

22.2 *Bias*—At the time of the study, there was no accepted reference material suitable for determining the bias for this test method, therefore no statement on bias is being made.

22.3 The precision statement was determined through statistical examination of 6579 test results, from 8 laboratories, on 11 types of brick material. The brick materials tested were described as:

EB-01: Extruded Modular Brick provided by ACME Brick Company
 EB-02: Extruded Modular Sawdust Brick provided by Borai Brick
 EB-03: Extruded Modular Brick provided by Endicott Clay Products Company
 EB-04: Extruded Modular Brick provided by General Shale
 EB-05: Extruded Modular Brick provided by Interstate Brick
 MB-01: Molded Modular Brick provided by The Belden Brick Company
 MB-02: Molded Modular Brick provided by Redland Brick
 PB-01: Nibless Extruded 4 × 8 Clay Paver provided by The Belden Brick Company
 PB-02: Nibless Extruded 4 × 8 Shale Paver provided by General Shale
 PB-03: Nibless Extruded 4 × 8 Clay/Shale Paver provided by Pine Hall Brick
 PB-04: Nibless Extruded 4 × 8 Shale Paver provided by Pine Hall Brick

22.3.1 To judge the equivalency of two test results, it is recommended to choose the brick material type closest in characteristics to the test material.

22.4 *Precision and Bias Statements for Other Test Methods:*

22.4.1 *Efflorescence*—No information is presented about either the precision or bias of the efflorescence test method since the test result is nonquantitative.

22.4.2 *Freezing and Thawing*—No information is presented about either the precision or bias of the Freezing and Thawing test method because part of the result is nonquantitative.

22.4.3 *Warpage, Out of Square, Shell and Web Thickness—Precision*—No information is presented about the precision of

the Warpage, Out of Square, Shell and Web Thickness test methods. These test methods will be the subject of an upcoming work item focusing on dimensional measurement and is anticipated to be completed in 2015.

22.4.4 *Warpage, Out of Square, Shell and Web Thickness—Bias*—There was no accepted reference material suitable for determining the bias for these test methods, therefore no statement on bias is being made.

22.4.5 *Compressive Strength, Breaking Load, Modulus of Rupture—Precision*—No information is presented about the precision of the Compressive Strength, Breaking Load, Modulus of Rupture test methods. These test methods will be the subject of an upcoming work item focusing on destructive testing and is anticipated to be completed in 2016.

22.4.6 *Compressive Strength, Breaking Load, Modulus of Rupture—Bias*—There was no accepted reference material suitable for determining the bias for these test methods, therefore no statement on bias is being made.

22.4.7 *Length Change—Precision*—No information is presented about the precision of the Length Change test method. This test method will be the subject of an upcoming work item and is anticipated to be completed in 2017.

22.4.8 *Length Change—Bias*—There was no accepted reference material suitable for determining the bias for this test method, therefore no statement on bias is being made.

23. Keywords

23.1 absorption; compressive strength; efflorescence; freezing and thawing; initial rate of absorption; length change; modulus of rupture; out-of-square; sampling; size; void area; warpage

SUMMARY OF CHANGES

Committee C15 has identified the location of selected changes to this standard since the last issue (C67 – 13a) that may impact the use of this standard. (July 1, 2014)

(1) Added Precision and Bias section (Section 22).

Committee C15 has identified the location of selected changes to this standard since the last issue (C67 – 13) that may impact the use of this standard. (December 1, 2013)

(1) Revised specimen preparation for test methods to clarify drying and cooling procedures.

Committee C15 has identified the location of selected changes to this standard since the last issue (C67 – 12) that may impact the use of this standard. (July 1, 2013)

(1) Wording in many sections was revised to conform with ASTM's Form and Style Manual.

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Safety Data Sheet

according to 29CFR1910/1200 and GHS Rev. 3

Effective date : 12.05.2014

Page 1 of 7

Sodium Chloride, Reagent Grade

SECTION 1 : Identification of the substance/mixture and of the supplier

Product name : Sodium Chloride, Reagent Grade

Manufacturer/Supplier Trade name:

Manufacturer/Supplier Article number: S25541A

Recommended uses of the product and uses restrictions on use:

Manufacturer Details:

AquaPhoenix Scientific
9 Barnhart Drive, Hanover, PA 17331

Supplier Details:

Fisher Science Education
15 Jet View Drive, Rochester, NY 14624

Emergency telephone number:

Fisher Science Education Emergency Telephone No.: 800-535-5053

SECTION 2 : Hazards identification

Classification of the substance or mixture:



Irritant

Eye irritation, category 2B

Eye Irritation 2

Signal word :Warning

Hazard statements:

Causes serious eye irritation

Precautionary statements:

If medical advice is needed, have product container or label at hand

Keep out of reach of children

Read label before use

Wear protective gloves/protective clothing/eye protection/face protection

Do not eat, drink or smoke when using this product

Wash skin thoroughly after handling

IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses if present and easy to do – continue rinsing

If eye irritation persists get medical advice/attention

Other Non-GHS Classification:

WHMIS

D2B



Safety Data Sheet

according to 29CFR1910/1200 and GHS Rev. 3

Effective date : 12.05.2014

Page 2 of 7

Sodium Chloride, Reagent Grade

NFPA/HMIS



NFPA SCALE (0-4)

Health	1
Flammability	0
Physical Hazard	1
Personal Protection	X

HMIS RATINGS (0-4)

SECTION 3 : Composition/information on ingredients

Ingredients:

CAS 7647-14-5

Sodium Chloride,ACS

100 %

Percentages are by weight

SECTION 4 : First aid measures

Description of first aid measures

After inhalation: Move exposed individual to fresh air. Loosen clothing as necessary and position individual in a comfortable position. Seek medical advice if discomfort or irritation persists. Remove to fresh air. Give artificial respiration if necessary. If breathing is difficult, give oxygen.

After skin contact: Wash affected area with soap and water. Rinse thoroughly. Seek medical attention if irritation or other symptoms persist. Wash affected area with soap and water. Rinse thoroughly. Seek medical attention if irritation persists or if concerned. Flush with water for 15 minutes.

After eye contact: Protect unexposed eye. Remove contact lens(es) if able to do so during rinsing. Seek medical attention if irritation persists or if concerned. Immediately flush eyes with water for at least 15 minutes. Immediately get medical assistance.

After swallowing: Rinse mouth thoroughly. Do not induce vomiting. Seek medical attention if irritation, discomfort or vomiting persists. Have exposed individual drink sips of water or milk. Seek medical attention.

Most important symptoms and effects, both acute and delayed:

Nausea, Headache, Shortness of breath. Irritation- all routes of exposure.;

Indication of any immediate medical attention and special treatment needed:

If seeking medical attention, provide SDS document to physician. Note to physician: Treat symptomatically.

SECTION 5 : Firefighting measures

Extinguishing media

Suitable extinguishing agents: If in laboratory setting, follow laboratory fire suppression procedures. Use appropriate fire suppression agents for adjacent combustible materials or sources of ignition

For safety reasons unsuitable extinguishing agents:

Special hazards arising from the substance or mixture:

Combustion products may include sodium oxides or other toxic vapors. Avoid generating dust; fine dust dispersed in air in sufficient concentrations, and in the presence of an ignition source is a potential dust explosion hazard

Advice for firefighters:

Safety Data Sheet

according to 29CFR1910/1200 and GHS Rev. 3

Effective date : 12.05.2014

Page 3 of 7

Sodium Chloride, Reagent Grade

Protective equipment: Use NIOSH-approved breathing equipment

Additional information (precautions): Move product containers away from fire or keep cool with water spray as a protective measure, where feasible. Use non-sparking equipment/tools

SECTION 6 : Accidental release measures

Personal precautions, protective equipment and emergency procedures:

Wear protective equipment. Avoid contact with skin and eyes. Avoid formation of dust and aerosols. Provide appropriate exhaust ventilation at places where dust is formed. Always obey local regulations. Avoid contact skin, eyes, and clothing. Use respiratory protective device against the effects of fumes/dust/aerosol. Keep unprotected persons away. Ensure adequate ventilation. Keep away from ignition sources. Protect from heat. Stop the spill, if possible. Contain spilled material by diking or using inert absorbent. Transfer to a disposal or recovery container.

Environmental precautions:

Prevent from reaching drains, sewer or waterway. Collect contaminated soil for characterization per Section 13. Should not be released into the environment.

Methods and material for containment and cleaning up:

If in a laboratory setting, follow Chemical Hygiene Plan procedures. Collect liquids using vacuum or by use of absorbents. Place into properly labeled containers for recovery or disposal. If necessary, use trained response staff/contractor. Dust deposits should not be allowed to accumulate on surfaces, as these may form an explosive mixture if they are released into the atmosphere in sufficient concentration. Avoid dispersal of dust in the air (i.e., clearing dust surfaces with compressed air). Always obey local regulations.

Reference to other sections:

SECTION 7 : Handling and storage

Precautions for safe handling:

Follow good hygiene procedures when handling chemical materials. Protect from freezing and physical damage. Keep away from sources of ignition. Store protected from moisture and direct sunlight. Do not eat, drink, smoke, or use personal products when handling chemical substances. If in a laboratory setting, follow Chemical Hygiene Plan. Use only in well ventilated areas. Avoid generation of dust or fine particulate. Avoid dispersal of dust in the air (i.e., clearing dust surfaces with compressed air). Routine housekeeping should be instituted to ensure that dusts do not accumulate on surfaces. Dry powders can build static electricity charges when subjected to the friction of transfer and mixing operations. Avoid contact with skin, eyes and clothing

Conditions for safe storage, including any incompatibilities:

Store in a cool location. Provide ventilation for containers. Avoid storage near extreme heat, ignition sources or open flame. Store away from foodstuffs. Store away from oxidizing agents. Store in cool, dry conditions in well sealed containers. Keep container tightly sealed. Protect from freezing and physical damage. Keep away from sources of ignition. Store protected from moisture and direct sunlight.

SECTION 8 : Exposure controls/personal protection



Control Parameters:

7647-14-5, ACGIH TLV TWA (inhalable particles), 10 mg/m³
7647-14-5, OSHA PEL TWA (Total Dust), 15 mg/m³ (50 mppcf*)
, , *mppcf = Millions of particles per cubic foot of air

Safety Data Sheet

according to 29CFR1910/1200 and GHS Rev. 3

Effective date : 12.05.2014

Page 4 of 7

Sodium Chloride, Reagent Grade

Appropriate Engineering controls:	Emergency eye wash fountains and safety showers should be available in the immediate vicinity of use/handling. Provide exhaust ventilation or other engineering controls to keep the airborne concentrations of vapor or dusts (total/respirable) below the applicable workplace exposure limits (Occupational Exposure Limits-OELs) indicated above. Ensure that dust-handling systems (such as exhaust ducts, dust collectors, vessels, and processing equipment) are designed in a manner to prevent the escape of dust into the work area (i.e., there is no leakage from the equipment)
Respiratory protection:	Not required under normal conditions of use. Use suitable respiratory protective device when high concentrations are present. Use suitable respiratory protective device when aerosol or mist is formed. For spills, respiratory protection may be advisable.
Protection of skin:	The glove material has to be impermeable and resistant to the product/ the substance/ the preparation being used/handled. Selection of the glove material on consideration of the penetration times, rates of diffusion and the degradation. Wear protective clothing
Eye protection:	Safety glasses with side shields or goggles.
General hygienic measures:	The usual precautionary measures are to be adhered to when handling chemicals. Keep away from food, beverages and feed sources. Immediately remove all soiled and contaminated clothing. Wash hands before breaks and at the end of work. Do not inhale gases/fumes/dust/mist/vapor/aerosols. Avoid contact with the eyes and skin.

SECTION 9 : Physical and chemical properties

Appearance (physical state,color):	White solid	Explosion limit lower:	Not determined
		Explosion limit upper:	Not determined
Odor:	Odorless	Vapor pressure:	1 mmHg @ 865°C
Odor threshold:	Not determined	Vapor density:	>1
pH-value:	Not determined	Relative density:	Not determined
Melting/Freezing point:	801°C	Solubilities:	Soluble in water
Boiling point/Boiling range:	1461°C	Partition coefficient (n-octanol/water):	Not determined
Flash point (closed cup):	Not determined	Auto/Self-ignition temperature:	Not determined
Evaporation rate:	Not determined	Decomposition temperature:	Not determined
Flammability (solid,gaseous):	Not determined	Viscosity:	a. Kinematic: Not determined b. Dynamic: Not determined
Density: Not determined Specific Gravity: 2.165 Molecular Weight: 58.44 g/mol			

SECTION 10 : Stability and reactivity

Reactivity: Material is hygroscopic.

Chemical stability: No decomposition if used and stored according to specifications.

Safety Data Sheet

according to 29CFR1910/1200 and GHS Rev. 3

Effective date : 12.05.2014

Page 5 of 7

Sodium Chloride, Reagent Grade

Possible hazardous reactions:None under normal processing

Conditions to avoid:Store away from oxidizing agents, strong acids or bases.Incompatible materials, dust generation, combustible materials, exposure to moist air or water

Incompatible materials:Metals. Strong oxidizers. Strong acids.Strong bases.Incompatible materials, dust generation, combustible materials, exposure to moist air or water.

Hazardous decomposition products:May evolve chlorine gas when in contact with strong acids. Sodium/sodium oxides. Hydrogen chloride gas

SECTION 11 : Toxicological information

Acute Toxicity:		
Dermal:	> 10gm/kg	LD50 dermal-rabbit (7647-14-5)
Oral:	3000 mg/kg bw	LD50 oral-rat (7647-14-5)
Inhalation:	42 g/m3	LC50 inhalation-rat (1h) (7647-14-5)
Chronic Toxicity: No additional information.		
Corrosion Irritation: No additional information.		
Sensitization:	No additional information.	
Single Target Organ (STOT):	No additional information.	
Numerical Measures:	No additional information.	
Carcinogenicity:	No additional information.	
Mutagenicity:	No additional information.	
Reproductive Toxicity:	No additional information.	

SECTION 12 : Ecological information

Ecotoxicity

Fish (acute 7647-14-5): 96 Hr LC50 Lepomis macrochirus: 5560 - 6080 mg/L [flow-through]; 96 Hr LC50 Lepomis macrochirus: 12946 mg/L [static]; 96 Hr LC50 Pimephales promelas: 6020 - 7070 mg/L [static]; 96 Hr LC50 Pimephales promelas: 7050 mg/L [semi-static]; 96 Hr LC50 Pimephales promelas: 6420 - 6700 mg/L [static]; 96 Hr LC50 Oncorhynchus mykiss: 4747 - 7824 mg/L [flow-through]

Crustacea (acute 7647-14-5): : 48 Hr EC50 Daphnia magna: 1000 mg/L; 48 Hr EC50 Daphnia magna: 340.7 - 469.2 mg/L [Static]

Persistence and degradability: Can attenuate over time; large amounts can persist in the environment.

Bioaccumulative potential:

Mobility in soil: Soluble in water; thus mobile along soil/water interface

Other adverse effects: Should not be released into environment

SECTION 13 : Disposal considerations

Waste disposal recommendations:

Product/containers must not be disposed together with household garbage. Do not allow product to reach sewage system or open water.It is the responsibility of the waste generator to properly characterize all waste materials according to applicable regulatory entities (US 40CFR262.11). Consult federal state/ provincial and local regulations regarding the proper disposal of waste material that may incorporate some amount of this

Safety Data Sheet

according to 29CFR1910/1200 and GHS Rev. 3

Effective date : 12.05.2014

Page 6 of 7

Sodium Chloride, Reagent Grade

product.

SECTION 14 : Transport information

UN-Number

Not Regulated.

UN proper shipping name

Not Regulated.

Transport hazard class(es)

Packing group:Not Regulated

Environmental hazard:

Transport in bulk:

Special precautions for user:

SECTION 15 : Regulatory information

United States (USA)**SARA Section 311/312 (Specific toxic chemical listings):**

Acute

SARA Section 313 (Specific toxic chemical listings):

None of the ingredients is listed

RCRA (hazardous waste code):

None of the ingredients is listed

TSCA (Toxic Substances Control Act):

All ingredients are listed.

CERCLA (Comprehensive Environmental Response, Compensation, and Liability Act):

None of the ingredients is listed

Proposition 65 (California):**Chemicals known to cause cancer:**

None of the ingredients is listed

Chemicals known to cause reproductive toxicity for females:

None of the ingredients is listed

Chemicals known to cause reproductive toxicity for males:

None of the ingredients is listed

Chemicals known to cause developmental toxicity:

None of the ingredients is listed

Canada**Canadian Domestic Substances List (DSL):**

All ingredients are listed.

Canadian NPRI Ingredient Disclosure list (limit 0.1%):

None of the ingredients is listed

Canadian NPRI Ingredient Disclosure list (limit 1%):

None of the ingredients is listed

Safety Data Sheet

according to 29CFR1910/1200 and GHS Rev. 3

Effective date : 12.05.2014

Page 7 of 7

Sodium Chloride, Reagent Grade

SECTION 16 : Other information

This product has been classified in accordance with hazard criteria of the Controlled Products Regulations and the SDS contains all the information required by the Controlled Products Regulations. Note: The responsibility to provide a safe workplace remains with the user. The user should consider the health hazards and safety information contained herein as a guide and should take those precautions required in an individual operation to instruct employees and develop work practice procedures for a safe work environment. The information contained herein is, to the best of our knowledge and belief, accurate. However, since the conditions of handling and use are beyond our control, we make no guarantee of results, and assume no liability for damages incurred by the use of this material. It is the responsibility of the user to comply with all applicable laws and regulations applicable to this material.

GHS Full Text Phrases:

Abbreviations and acronyms:

IMDG: International Maritime Code for Dangerous Goods
PNEC: Predicted No-Effect Concentration (REACH)
CFR: Code of Federal Regulations (USA)
SARA: Superfund Amendments and Reauthorization Act (USA)
RCRA: Resource Conservation and Recovery Act (USA)
TSCA: Toxic Substances Control Act (USA)
NPRI: National Pollutant Release Inventory (Canada)
DOT: US Department of Transportation
IATA: International Air Transport Association
GHS: Globally Harmonized System of Classification and Labelling of Chemicals
ACGIH: American Conference of Governmental Industrial Hygienists
CAS: Chemical Abstracts Service (division of the American Chemical Society)
NFPA: National Fire Protection Association (USA)
HMIS: Hazardous Materials Identification System (USA)
WHMIS: Workplace Hazardous Materials Information System (Canada)
DNEL: Derived No-Effect Level (REACH)

Effective date : 12.05.2014

Last updated : 03.24.2015

Safety Data Sheet

according to 29CFR1910/1200 and GHS Rev. 3

Effective date : 12.21.2014

Page 1 of 6

Aluminum Sodium Sulfate

SECTION 1 : Identification of the substance/mixture and of the supplier

Product name : Aluminum Sodium Sulfate

Manufacturer/Supplier Trade name:

Manufacturer/Supplier Article number: S25136

Recommended uses of the product and uses restrictions on use:

Manufacturer Details:

AquaPhoenix Scientific
9 Barnhart Drive, Hanover, PA 17331

Supplier Details:

Fisher Science Education
15 Jet View Drive, Rochester, NY 14624

Emergency telephone number:

Fisher Science Education Emergency Telephone No.: 800-535-5053

SECTION 2 : Hazards identification

Classification of the substance or mixture:

Not classified for physical or health hazards under GHS.

Hazard statements:

Precautionary statements:

Combustible Dust Hazard: :

May form combustible dust concentrations in air (during processing).

Other Non-GHS Classification:

WHMIS



NFPA/HMIS



NFPA SCALE (0-4)

Health	2
Flammability	0
Physical Hazard	0
Personal Protection	X

HMIS RATINGS (0-4)

Safety Data Sheet

according to 29CFR1910/1200 and GHS Rev. 3

Effective date : 12.21.2014

Page 2 of 6

Aluminum Sodium Sulfate

SECTION 3 : Composition/information on ingredients

Ingredients:

CAS 10102-71-3	Aluminum Sodium Sulfate	100 %
Percentages are by weight		

SECTION 4 : First aid measures

Description of first aid measures

After inhalation: Loosen clothing as necessary and position individual in a comfortable position. Remove to fresh air. Give artificial respiration if necessary. If breathing is difficult give oxygen. Do not perform mouth-to-mouth on an unconscious person.

After skin contact: Wash affected area with soap and water. Seek medical attention if irritation persists or if concerned.

After eye contact: Protect unexposed eye. Rinse or flush exposed eye gently using water for 15-20 minutes. Remove contact lenses while rinsing. Occasionally lift the upper and lower eyelids while rinsing. Immediately get medical assistance.

After swallowing: Rinse mouth thoroughly. Do not induce vomiting. Immediately get medical assistance. Provide SDS document to physician.

Most important symptoms and effects, both acute and delayed:

Irritation. Nausea. Headache. Shortness of breath.;

Indication of any immediate medical attention and special treatment needed:

If seeking medical attention provide SDS document to physician.

SECTION 5 : Firefighting measures

Extinguishing media

Suitable extinguishing agents: Use water, dry chemical, chemical foam, or alcohol-resistant foam.

For safety reasons unsuitable extinguishing agents:

Special hazards arising from the substance or mixture:

Advice for firefighters:

Protective equipment: Wear protective eyewear, gloves, and clothing.

Additional information (precautions): Ensure adequate ventilation. Avoid contact with skin, eyes, and clothing.

SECTION 6 : Accidental release measures

Personal precautions, protective equipment and emergency procedures:

Use spark-proof tools and explosion-proof equipment. Avoid contact with skin, eyes and clothing. Ensure adequate ventilation.

Environmental precautions:

Should not be released into environment. Collect contaminated soil for characterization per Section 13 .

Methods and material for containment and cleaning up:

Follow Chemical Hygiene Plan. Avoid dispersal of dust in the air. Do not clear dust on surfaces with compressed air. Vacuum or sweep up material and place into a suitable disposal container. Clean up spills immediately. Observe precautions for protective equipment. Always obey local regulations. If necessary use trained response staff or contractor.

Safety Data Sheet

according to 29CFR1910/1200 and GHS Rev. 3

Effective date : 12.21.2014

Page 3 of 6

Aluminum Sodium Sulfate

Reference to other sections:

SECTION 7 : Handling and storage

Precautions for safe handling:

Dust deposits should not be allowed to accumulate on surfaces. Dust may form an explosive mixture if sufficient concentration is released into the atmosphere. Follow Chemical Hygiene Plan. Do not inhale gases, fumes, dust, mist, vapor, and aerosols. Wash hands after handling. Avoid contact with skin, eyes and clothing. Dry powders can build static electricity charges when subjected to the friction of transfer and mixing operations. Follow good hygiene procedures when handling chemical materials. Do not eat, drink, smoke, or use personal products when handling chemical substances. Use only in well ventilated areas.

Conditions for safe storage, including any incompatibilities:

Keep container tightly closed in a cool, dry, and well-ventilated area. Store away from incompatible materials. Keep away from food, beverages, and feed sources.

SECTION 8 : Exposure controls/personal protection



Control Parameters:

No applicable occupational exposure limits

Appropriate Engineering controls:

It is recommended that all dust control equipment such as local exhaust ventilation and material transport systems involved in handling of this product contain explosion relief vents or an explosion suppression system or an oxygen deficient environment. Emergency eye wash fountains and safety showers should be available in the immediate vicinity of use or handling. Normal ventilation is adequate.

Respiratory protection:

Not required under normal conditions of use.

Protection of skin:

Select glove material impermeable and resistant to the substance. Select glove material based on rates of diffusion and degradation.

Eye protection:

Safety glasses with side shields or goggles.

General hygienic measures:

The usual precautionary measures are to be adhered to when handling chemicals. Wash hands before breaks and at the end of work. Wash hands and exposed skin with soap and plenty of water. Keep away from food, beverages, and feed sources.

SECTION 9 : Physical and chemical properties

Appearance (physical state,color):	Clear colorless crystals	Explosion limit lower: Explosion limit upper:	Non Explosive Non Explosive
Odor:	Odorless	Vapor pressure:	Not Applicable
Odor threshold:	Not Applicable	Vapor density:	Not Applicable
pH-value:	7 (1% aqueous solution)	Relative density:	Not Applicable
Melting/Freezing point:	61°C	Solubilities:	Soluble in water
Boiling point/Boiling range:	Decomposes	Partition coefficient (n-octanol/water):	Not Applicable

Safety Data Sheet

according to 29CFR1910/1200 and GHS Rev. 3

Effective date : 12.21.2014

Page 4 of 6

Aluminum Sodium Sulfate

Flash point (closed cup):	Not Applicable	Auto/Self-ignition temperature:	Not Applicable
Evaporation rate:	Not Applicable	Decomposition temperature:	No Information
Flammability (solid,gaseous):	No Information	Viscosity:	a. Kinematic:Not Applicable b. Dynamic: Not Applicable
Density: No Information			

SECTION 10 : Stability and reactivity

Reactivity:

Chemical stability:Stable under normal conditions.

Possible hazardous reactions:

Conditions to avoid:Excessive heat.

Incompatible materials:

Hazardous decomposition products:

SECTION 11 : Toxicological information

Acute Toxicity: No additional information.	
Chronic Toxicity: No additional information.	
Corrosion Irritation: No additional information.	
Sensitization:	No additional information.
Single Target Organ (STOT):	No additional information.
Numerical Measures:	No additional information.
Carcinogenicity:	No additional information.
Mutagenicity:	No additional information.
Reproductive Toxicity:	No additional information.

SECTION 12 : Ecological information

Ecotoxicity Persistence and degradability:

Bioaccumulative potential:

Mobility in soil:

Other adverse effects:

SECTION 13 : Disposal considerations

Waste disposal recommendations:

Dilute with water and flush to sewer. Chemical waste generators must determine whether a discarded chemical is classified as a hazardous waste. Chemical waste generators must also consult local, regional, and national hazardous waste regulations. Ensure complete and accurate classification.

Safety Data Sheet

according to 29CFR1910/1200 and GHS Rev. 3

Effective date : 12.21.2014

Page 5 of 6

Aluminum Sodium Sulfate

SECTION 14 : Transport information

UN-Number

UN proper shipping name

Transport hazard class(es)

Packing group:

Environmental hazard:

Transport in bulk:

Special precautions for user:

SECTION 15 : Regulatory information

United States (USA)

SARA Section 311/312 (Specific toxic chemical listings):

None of the ingredients is listed

SARA Section 313 (Specific toxic chemical listings):

None of the ingredients is listed

RCRA (hazardous waste code):

None of the ingredients is listed

TSCA (Toxic Substances Control Act):

All ingredients are listed.

CERCLA (Comprehensive Environmental Response, Compensation, and Liability Act):

None of the ingredients is listed

Proposition 65 (California):

Chemicals known to cause cancer:

None of the ingredients is listed

Chemicals known to cause reproductive toxicity for females:

None of the ingredients is listed

Chemicals known to cause reproductive toxicity for males:

None of the ingredients is listed

Chemicals known to cause developmental toxicity:

None of the ingredients is listed

Canada

Canadian Domestic Substances List (DSL):

All ingredients are listed.

Canadian NPRI Ingredient Disclosure list (limit 0.1%):

None of the ingredients is listed

Canadian NPRI Ingredient Disclosure list (limit 1%):

None of the ingredients is listed

SECTION 16 : Other information

This product has been classified in accordance with hazard criteria of the Controlled Products Regulations and the

Safety Data Sheet

according to 29CFR1910/1200 and GHS Rev. 3

Effective date : 12.21.2014

Page 6 of 6

Aluminum Sodium Sulfate

SDS contains all the information required by the Controlled Products Regulations. Note: The responsibility to provide a safe workplace remains with the user. The user should consider the health hazards and safety information contained herein as a guide and should take those precautions required in an individual operation to instruct employees and develop work practice procedures for a safe work environment. The information contained herein is, to the best of our knowledge and belief, accurate. However, since the conditions of handling and use are beyond our control, we make no guarantee of results, and assume no liability for damages incurred by the use of this material. It is the responsibility of the user to comply with all applicable laws and regulations applicable to this material.

GHS Full Text Phrases:

Abbreviations and acronyms:

IMDG: International Maritime Code for Dangerous Goods

PNEC: Predicted No-Effect Concentration (REACH)

CFR: Code of Federal Regulations (USA)

SARA: Superfund Amendments and Reauthorization Act (USA)

RCRA: Resource Conservation and Recovery Act (USA)

TSCA: Toxic Substances Control Act (USA)

NPRI: National Pollutant Release Inventory (Canada)

DOT: US Department of Transportation

IATA: International Air Transport Association

GHS: Globally Harmonized System of Classification and Labelling of Chemicals

ACGIH: American Conference of Governmental Industrial Hygienists

CAS: Chemical Abstracts Service (division of the American Chemical Society)

NFPA: National Fire Protection Association (USA)

HMIS: Hazardous Materials Identification System (USA)

WHMIS: Workplace Hazardous Materials Information System (Canada)

DNEL: Derived No-Effect Level (REACH)

Effective date : 12.21.2014

Last updated : 03.19.2015

1 Identification

Product identifier

Product name: Sodium hexacyanoferrate(II) decahydrate

Stock number: 39660

CAS Number:

14434-22-1

EC number:

237-081-9

Relevant identified uses of the substance or mixture and uses advised against.

Identified use: SU24 Scientific research and development

Details of the supplier of the safety data sheet

Manufacturer/Supplier:

Alfa Aesar

Thermo Fisher Scientific Chemicals, Inc.

30 Bond Street

Ward Hill, MA 01835-8099

Tel: 800-343-0660

Fax: 800-322-4757

Email: tech@alfa.com

www.alfa.com

Information Department: Health, Safety and Environmental Department

Emergency telephone number:

During normal business hours (Monday-Friday, 8am-7pm EST), call (800) 343-0660. After normal business hours, call Carechem 24 at (866) 928-0789.

2 Hazard(s) identification

Classification of the substance or mixture in accordance with 29 CFR 1910 (OSHA HCS)

The substance is not classified according to the Globally Harmonized System (GHS).

Hazards not otherwise classified No information known.

Label elements

GHS label elements Not applicable

Hazard pictograms Not applicable

Signal word Not applicable

Hazard statements Not applicable

WHMIS classification Not controlled

Classification system

HMIS ratings (scale 0-4)

(Hazardous Materials Identification System)

HEALTH 1 Health (acute effects) = 1

FIRE 1 Flammability = 1

REACTIVITY 1 Physical Hazard = 1

Other hazards

Results of PBT and vPvB assessment

PBT: Not applicable.

vPvB: Not applicable.

3 Composition/information on ingredients

Chemical characterization: Substances

CAS# Description:

14434-22-1 Sodium hexacyanoferrate(II) decahydrate

Identification number(s):

EC number: 237-081-9

Additional information:

CAS# for anhydrous form:

13601-19-9

4 First-aid measures

Description of first aid measures

After inhalation

Supply fresh air. If required, provide artificial respiration. Keep patient warm.

Seek immediate medical advice.

After skin contact

Immediately wash with water and soap and rinse thoroughly.

Seek immediate medical advice.

After eye contact Rinse opened eye for several minutes under running water. Then consult a doctor.

After swallowing Seek medical treatment.

Information for doctor

Most important symptoms and effects, both acute and delayed No further relevant information available.

Indication of any immediate medical attention and special treatment needed No further relevant information available.

5 Fire-fighting measures

Extinguishing media

Suitable extinguishing agents Product is not flammable. Use fire-fighting measures that suit the surrounding fire.

Special hazards arising from the substance or mixture If this product is involved in a fire, the following can be released:

Advice for firefighters

Protective equipment:

Wear self-contained respirator.

Wear fully protective impervious suit.

6 Accidental release measures

Personal precautions, protective equipment and emergency procedures

Wear protective equipment. Keep unprotected persons away.

Ensure adequate ventilation

Environmental precautions: Do not allow material to be released to the environment without proper governmental permits.

Methods and material for containment and cleaning up: Pick up mechanically.

Product name: Sodium hexacyanoferrate(II) decahydrate

(Contd. of page 1)

Prevention of secondary hazards: No special measures required.
Reference to other sections
See Section 7 for information on safe handling
See Section 8 for information on personal protection equipment.
See Section 13 for disposal information.

7 Handling and storage

Handling
Precautions for safe handling
Keep container tightly sealed.
Store in cool, dry place in tightly closed containers.
Ensure good ventilation at the workplace.
Information about protection against explosions and fires: No information known.
Conditions for safe storage, including any incompatibilities
Storage
Requirements to be met by storerooms and receptacles: No special requirements.
Information about storage in one common storage facility: No information known.
Further information about storage conditions:
Keep container tightly sealed.
Store in cool, dry conditions in well sealed containers.
Specific end use(s) No further relevant information available.

8 Exposure controls/personal protection

Additional information about design of technical systems:
Properly operating chemical fume hood designed for hazardous chemicals and having an average face velocity of at least 100 feet per minute.

Control parameters
Components with limit values that require monitoring at the workplace:

Iron salts, soluble (as Fe)
mg/m³
ACGIH TLV 1
Finland TWA 1
Korea TLV 1
Norway TWA 1
Switzerland MAK-W 1
United Kingdom LTEL 1; 2-STEL
Additional information: No data

Exposure controls
Personal protective equipment
General protective and hygienic measures
The usual precautionary measures for handling chemicals should be followed.
Keep away from foodstuffs, beverages and feed.
Remove all soiled and contaminated clothing immediately.
Wash hands before breaks and at the end of work.
Maintain an ergonomically appropriate working environment.
Breathing equipment: Use suitable respirator when high concentrations are present.
Protection of hands:
Impervious gloves
Check protective gloves prior to each use for their proper condition.
The selection of suitable gloves not only depends on the material, but also on quality. Quality will vary from manufacturer to manufacturer.
Eye protection: Safety glasses
Body protection: Protective work clothing.

9 Physical and chemical properties

Information on basic physical and chemical properties

General Information

Appearance:

Form: Powder
Color: Light yellow
Odor: Odorless
Odor threshold: Not determined.

pH-value: Not applicable.

Change in condition
Melting point/Melting range: 82 °C (180 °F)
Boiling point/Boiling range: Not determined
Sublimation temperature / start: Not determined

Flash point: Not applicable
Flammability (solid, gaseous): Not determined.
Ignition temperature: Not determined
Decomposition temperature: Not determined
Auto igniting: Not determined.

Danger of explosion: Product does not present an explosion hazard.

Explosion limits:
Lower: Not determined
Upper: Not determined
Vapor pressure: Not applicable.
Density at 20 °C (68 °F): 1.458 g/cm³ (12.167 lbs/gal)
Relative density: Not determined.
Vapor density: Not applicable.
Evaporation rate: Not applicable.
Solubility in / Miscibility with
Water at 20 °C (68 °F): 318.5 g/l
Soluble

Partition coefficient (n-octanol/water): Not determined.
Viscosity:
dynamic: Not applicable.
kinematic: Not applicable.

(Contd. on page 3)
USA

Product name: **Sodium hexacyanoferrate(II) decahydrate**

(Contd. of page 2)

Other information

No further relevant information available.

10 Stability and reactivity

Reactivity No information known.
Chemical stability Stable under recommended storage conditions.
Thermal decomposition / conditions to be avoided: Decomposition will not occur if used and stored according to specifications.
Possibility of hazardous reactions Reacts with acids
Conditions to avoid No further relevant information available.
Incompatible materials:
Oxidizing agents
No information known.
Hazardous decomposition products:
Nitrogen oxides
Carbon monoxide and carbon dioxide
Toxic metal compounds
Hydrogen cyanide

11 Toxicological information

Information on toxicological effects
Acute toxicity: No effects known.
LD/LC50 values that are relevant for classification: No data
Skin irritation or corrosion: May cause irritation
Eye irritation or corrosion: May cause irritation
Sensitization: No sensitizing effects known.
Germ cell mutagenicity: No effects known.
Carcinogenicity: No classification data on carcinogenic properties of this material is available from the EPA, IARC, NTP, OSHA or ACGIH.
Reproductive toxicity: No effects known.
Specific target organ system toxicity - repeated exposure: No effects known.
Specific target organ system toxicity - single exposure: No effects known.
Aspiration hazard: No effects known.
Subacute to chronic toxicity:
Iron compounds may cause vomiting, diarrhea, pink urine, black stool, and liver damage. May cause damage to the kidneys. Irritating to the respiratory tract, they may cause pulmonary fibrosis if dusts are inhaled.
Subacute to chronic toxicity: No effects known.
Additional toxicological information: To the best of our knowledge the acute and chronic toxicity of this substance is not fully known.

12 Ecological information

Toxicity
Aquatic toxicity: No further relevant information available.
Persistence and degradability No further relevant information available.
Bioaccumulative potential No further relevant information available.
Mobility in soil No further relevant information available.
Ecotoxicological effects:
Remark: Harmful to aquatic organisms
Additional ecological information:
General notes:
Do not allow material to be released to the environment without proper governmental permits.
Do not allow undiluted product or large quantities to reach ground water, water course or sewage system.
May cause long lasting harmful effects to aquatic life.
Avoid transfer into the environment.
Harmful to aquatic organisms
Results of PBT and vPvB assessment
PBT: Not applicable.
vPvB: Not applicable.
Other adverse effects No further relevant information available.

13 Disposal considerations

Waste treatment methods
Recommendation Consult state, local or national regulations to ensure proper disposal.
Uncleaned packagings:
Recommendation: Disposal must be made according to official regulations.
Recommended cleansing agent: Water, if necessary with cleansing agents.

14 Transport information

Not a hazardous material for transportation.

UN-Number
DOT, IMDG, IATA None

UN proper shipping name
DOT, IMDG, IATA None

Transport hazard class(es)
DOT, ADR, IMDG, IATA
Class None

Packing group
DOT, IMDG, IATA None

Environmental hazards: Not applicable.

Special precautions for user Not applicable.

Transport in bulk according to Annex II of MARPOL73/78 and the IBC Code Not applicable.

Transport/Additional information: Not dangerous according to the above specifications.

DOT
Marine Pollutant (DOT): No

Product name: **Sodium hexacyanoferrate(II) decahydrate**

(Contd. of page 3)

15 Regulatory information

Safety, health and environmental regulations/legislation specific for the substance or mixture

GHS label elements Not applicable

Hazard pictograms Not applicable

Signal word Not applicable

Hazard statements Not applicable

National regulations

All components of this product are listed in the U.S. Environmental Protection Agency Toxic Substances Control Act Chemical substance Inventory.

All components of this product are listed on the Canadian Domestic Substances List (DSL).

SARA Section 313 (specific toxic chemical listings) Substance is not listed.

California Proposition 65

Prop 65 - Chemicals known to cause cancer Substance is not listed.

Prop 65 - Developmental toxicity Substance is not listed.

Prop 65 - Developmental toxicity, female Substance is not listed.

Prop 65 - Developmental toxicity, male

14434-22-1 Sodium hexacyanoferrate(II) decahydrate

Information about limitation of use:

For use only by technically qualified individuals.

This product is subject to the reporting requirements of section 313 of the Emergency Planning and Community Right to Know Act of 1986 and 40CFR372.

Other regulations, limitations and prohibitive regulations

Substance of Very High Concern (SVHC) according to the REACH Regulations (EC) No. 1907/2006. Substance is not listed.

The conditions of restrictions according to Article 67 and Annex XVII of the Regulation (EC) No 1907/2006 (REACH) for the manufacturing, placing on the market and use must be observed.

Substance is not listed.

Annex XIV of the REACH Regulations (requiring Authorisation for use) Substance is not listed.

Chemical safety assessment: A Chemical Safety Assessment has not been carried out.

16 Other information

Employers should use this information only as a supplement to other information gathered by them, and should make independent judgement of suitability of this information to ensure proper use and protect the health and safety of employees. This information is furnished without warranty, and any use of the product not in conformance with this Material Safety Data Sheet, or in combination with any other product or process, is the responsibility of the user.

Department issuing SDS: Global Marketing Department

Date of preparation / last revision 11/24/2015 / -

Abbreviations and acronyms:

RID: Règlement international concernant le transport des marchandises dangereuses par chemin de fer (Regulations Concerning the International Transport of Dangerous Goods by Rail)

IATA-DGR: Dangerous Goods Regulations by the "International Air Transport Association" (IATA)

ICAO: International Civil Aviation Organization

ICAO-TI: Technical Instructions by the "International Civil Aviation Organization" (ICAO)

IMDG: International Maritime Code for Dangerous Goods

DOT: US Department of Transportation

IATA: International Air Transport Association

EINECS: European Inventory of Existing Commercial Chemical Substances

CAS: Chemical Abstracts Service (division of the American Chemical Society)

HMIS: Hazardous Materials Identification System (USA)

WHMIS: Workplace Hazardous Materials Information System (Canada)

LC50: Lethal concentration, 50 percent

LD50: Lethal dose, 50 percent

vPvB: very Persistent and very Bioaccumulative

ACGIH: American Conference of Governmental Industrial Hygienists (USA)

OSHA: Occupational Safety and Health Administration (USA)

NTP: National Toxicology Program (USA)

IARC: International Agency for Research on Cancer

EPA: Environmental Protection Agency (USA)

USA

Safety Data Sheet

according to 29CFR1910/1200 and GHS Rev. 3

Effective date : 12.16.2014

Page 1 of 7

Potassium Ferrocyanide

SECTION 1 : Identification of the substance/mixture and of the supplier

Product name : Potassium Ferrocyanide

Manufacturer/Supplier Trade name:

Manufacturer/Supplier Article number: S25489

Recommended uses of the product and uses restrictions on use:

Manufacturer Details:

AquaPhoenix Scientific
9 Barnhart Drive, Hanover, PA 17331

Supplier Details:

Fisher Science Education
15 Jet View Drive, Rochester, NY 14624

Emergency telephone number:

Fisher Science Education Emergency Telephone No.: 800-535-5053

SECTION 2 : Hazards identification

Classification of the substance or mixture:



Toxic

Acute toxicity (oral, dermal, inhalation), category 2

Chronic hazards to the aquatic environment, category 3

AcTox Inhaln 2

AcAq Tox

Signal word : Danger

Hazard statements:

Harmful to aquatic life with long lasting effects

Precautionary statements:

If medical advice is needed, have product container or label at hand

Keep out of reach of children

Read label before use

Do not eat, drink or smoke when using this product

Do not breathe dust/fume/gas/mist/vapours/spray

Use only outdoors or in a well-ventilated area

Wear respiratory protection

IF INHALED: Remove victim to fresh air and keep at rest in a position comfortable for breathing

Immediately call a POISON CENTER or doctor/physician

Specific treatment is urgent (see ... on this label)

Store in a well ventilated place. Keep container tightly closed

Store locked up

Dispose of contents/container to ...

Combustible Dust Hazard: :

May form combustible dust concentrations in air (during processing).

Safety Data Sheet

according to 29CFR1910/1200 and GHS Rev. 3

Effective date : 12.16.2014

Page 2 of 7

Potassium Ferrocyanide

Other Non-GHS Classification:

WHMIS
NFPA/HMIS



NFPA SCALE (0-4)

Health	1
Flammability	
Physical Hazard	
Personal Protection	X

HMIS RATINGS (0-4)

SECTION 3 : Composition/information on ingredients

Ingredients:		
CAS 14459-95-1	Potassium Ferrocyanide,Trihydrate	100 %
Percentages are by weight		

SECTION 4 : First aid measures

Description of first aid measures

After inhalation: Loosen clothing as necessary and position individual in a comfortable position. If breathing difficult, give oxygen. Seek immediate medical attention. Remove to fresh air. Give artificial respiration if necessary.

After skin contact: Wash affected area with soap and water. Flush with water for 15 minutes. Seek immediate medical attention or advice.

After eye contact: Protect unexposed eye. Rinse/flush exposed eye(s) gently using water for 15-20 minutes. Remove contact lens(es) if able to do so during rinsing. Seek immediate medical attention or advice.

After swallowing: Rinse mouth thoroughly. Do not induce vomiting. Have exposed individual drink sips of water or milk. Seek immediate medical attention or advice.

Most important symptoms and effects, both acute and delayed:

Irritation, Nausea, Headache, Shortness of breath.;

Indication of any immediate medical attention and special treatment needed:

If seeking medical attention, provide SDS document to physician. Note to physician: Treat symptomatically.

SECTION 5 : Firefighting measures

Extinguishing media

Suitable extinguishing agents: If in laboratory setting, follow laboratory fire suppression procedures. Use appropriate fire suppression agents for adjacent combustible materials or sources of ignition

For safety reasons unsuitable extinguishing agents:

Special hazards arising from the substance or mixture:

Combustion products may include carbon oxides or other toxic vapors. Thermal decomposition can lead to release of irritating gases and vapors. Avoid generating dust; fine dust dispersed in air in sufficient concentrations, and in the presence of an ignition source is a potential dust explosion hazard.

Advice for firefighters:

Safety Data Sheet

according to 29CFR1910/1200 and GHS Rev. 3

Effective date : 12.16.2014

Page 3 of 7

Potassium Ferrocyanide

Protective equipment: Use NIOSH-approved respiratory protection/breathing apparatus.

Additional information (precautions): Move product containers away from fire or keep cool with water spray as a protective measure, where feasible. Use spark-proof tools and explosion-proof equipment.

SECTION 6 : Accidental release measures

Personal precautions, protective equipment and emergency procedures:

Wear protective equipment. Transfer to a disposal or recovery container. Avoid contact with skin and eyes, and clothing. Use spark-proof tools and explosion-proof equipment. Use respiratory protective device against the effects of fumes/dust/aerosol. Keep unprotected persons away. Ensure adequate ventilation. Keep away from ignition sources. Protect from heat. Stop the spill, if possible. Contain spilled material by diking or using inert absorbent.

Environmental precautions:

Prevent from reaching drains, sewer or waterway. Collect contaminated soil for characterization per Section 13. Should not be released into the environment.

Methods and material for containment and cleaning up:

If in a laboratory setting, follow Chemical Hygiene Plan procedures. Collect liquids using vacuum or by use of absorbents. Place into properly labeled containers for recovery or disposal. If necessary, use trained response staff/contractor. Dust deposits should not be allowed to accumulate on surfaces, as these may form an explosive mixture if they are released into the atmosphere in sufficient concentration. Avoid dispersal of dust in the air (i.e., clearing dust surfaces with compressed air). Clean up spills immediately. Always obey local regulations.

Reference to other sections:

SECTION 7 : Handling and storage

Precautions for safe handling:

Minimize dust generation and accumulation. Wash hands after handling. Avoid dispersal of dust in the air (i.e., clearing dust surfaces with compressed air). Use in chemical fume hood. Routine housekeeping should be instituted to ensure that dusts do not accumulate on surfaces. Dry powders can build static electricity charges when subjected to the friction of transfer and mixing operations. Follow good hygiene procedures when handling chemical materials. Do not eat, drink, smoke, or use personal products when handling chemical substances. If in a laboratory setting, follow Chemical Hygiene Plan. Use only in well ventilated areas. Avoid generation of dust or fine particulate. Avoid contact with eyes, skin, and clothing.

Conditions for safe storage, including any incompatibilities:

Store in a cool location. Provide ventilation for containers. Avoid storage near extreme heat, ignition sources or open flame. Store away from foodstuffs. Store away from oxidizing agents. Store in cool, dry conditions in well sealed containers. Keep container tightly sealed. Store away from direct sunlight.

SECTION 8 : Exposure controls/personal protection



Control Parameters:

13746-66-2, Potassium Ferrocyanide , ACGIH TLV: 1mm/m3
13746-66-2, Potassium Ferrocyanide, OSHA PEL: 5mg/m3

Safety Data Sheet

according to 29CFR1910/1200 and GHS Rev. 3

Effective date : 12.16.2014

Page 4 of 7

Potassium Ferrocyanide

- Appropriate Engineering controls:** Emergency eye wash fountains and safety showers should be available in the immediate vicinity of use/handling. Provide exhaust ventilation or other engineering controls to keep the airborne concentrations of vapor or dusts (total/respirable) below the applicable workplace exposure limits (Occupational Exposure Limits-OELs) indicated above. Use under a fume hood. It is recommended that all dust control equipment such as local exhaust ventilation and material transport systems involved in handling of this product contain explosion relief vents or an explosion suppression system or an oxygen deficient environment. Ensure that dust-handling systems (such as exhaust ducts, dust collectors, vessels, and processing equipment) are designed in a manner to prevent the escape of dust into the work area (i.e., there is no leakage from the equipment).
- Respiratory protection:** Not required under normal conditions of use. Use suitable respiratory protective device when high concentrations are present. Use suitable respiratory protective device when aerosol or mist is formed. For spills, respiratory protection may be advisable.
- Protection of skin:** The glove material has to be impermeable and resistant to the product/ the substance/ the preparation being used/handled. Selection of the glove material on consideration of the penetration times, rates of diffusion and the degradation.
- Eye protection:** Safety glasses with side shields or goggles.
- General hygienic measures:** The usual precautionary measures are to be adhered to when handling chemicals. Keep away from food, beverages and feed sources. Immediately remove all soiled and contaminated clothing. Wash hands before breaks and at the end of work. Do not inhale gases/fumes/dust/mist/vapor/aerosols. Avoid contact with the eyes and skin.

SECTION 9 : Physical and chemical properties

Appearance (physical state,color):	Yellow Solid	Explosion limit lower: Explosion limit upper:	Not determined Not determined
Odor:	Odorless	Vapor pressure:	negligible
Odor threshold:	Not determined	Vapor density:	Not determined
pH-value:	9.5	Relative density:	Not determined
Melting/Freezing point:	70°C	Solubilities:	Soluble in water
Boiling point/Boiling range:	Not determined	Partition coefficient (n-octanol/water):	Not determined
Flash point (closed cup):	Not determined	Auto/Self-ignition temperature:	Not determined
Evaporation rate:	Not determined	Decomposition temperature:	Not determined
Flammability (solid,gaseous):	Not determined	Viscosity:	a. Kinematic: Not determined b. Dynamic: Not determined
Density: Not determined Specific Gravity: 1.85			

SECTION 10 : Stability and reactivity

Safety Data Sheet

according to 29CFR1910/1200 and GHS Rev. 3

Effective date : 12.16.2014

Page 5 of 7

Potassium Ferrocyanide

Reactivity:

Chemical stability: No decomposition if used and stored according to specifications.

Possible hazardous reactions:

Conditions to avoid: Store away from oxidizing agents, strong acids or bases. Dust generation. High temperatures, incompatible materials, light, moisture, water, ignition sources.

Incompatible materials: Strong acids. Strong bases. Strong oxidizing agents. Strong reducing agents.

Hazardous decomposition products: Carbon oxides (CO, CO₂). Hydrogen cyanide. Nitrogen oxides

SECTION 11 : Toxicological information

Acute Toxicity:		
Oral:	3,613 mg/kg	LD50 Oral - rat
Chronic Toxicity: No additional information.		
Corrosion Irritation: No additional information.		
Sensitization:	No additional information.	
Single Target Organ (STOT):	No additional information.	
Numerical Measures:	No additional information.	
Carcinogenicity:	No additional information.	
Mutagenicity:	No additional information.	
Reproductive Toxicity:	No additional information.	

SECTION 12 : Ecological information

Ecotoxicity

AcTox : to daphnia and other aquatic invertebrates EC50 - Daphnia - 32 mg/l - 48 h

Persistence and degradability: Readily degradable in the environment.

Bioaccumulative potential:

Mobility in soil:

Other adverse effects:

SECTION 13 : Disposal considerations

Waste disposal recommendations:

Product/containers must not be disposed together with household garbage. Do not allow product to reach sewage system or open water. It is the responsibility of the waste generator to properly characterize all waste materials according to applicable regulatory entities (US 40CFR262.11). Consult federal state/ provincial and local regulations regarding the proper disposal of waste material that may incorporate some amount of this product.

SECTION 14 : Transport information

UN-Number

Not Regulated.

UN proper shipping name

Safety Data Sheet

according to 29CFR1910/1200 and GHS Rev. 3

Effective date : 12.16.2014

Page 6 of 7

Potassium Ferrocyanide

Not Regulated.

Transport hazard class(es)

Packing group:Not Regulated

Environmental hazard:

Transport in bulk:

Special precautions for user:

SECTION 15 : Regulatory information

United States (USA)

SARA Section 311/312 (Specific toxic chemical listings):

Reactive, Acute

SARA Section 313 (Specific toxic chemical listings):

None of the ingredients is listed

RCRA (hazardous waste code):

None of the ingredients is listed

TSCA (Toxic Substances Control Act):

All ingredients are listed.

CERCLA (Comprehensive Environmental Response, Compensation, and Liability Act):

None of the ingredients is listed

Proposition 65 (California):

Chemicals known to cause cancer:

None of the ingredients is listed

Chemicals known to cause reproductive toxicity for females:

None of the ingredients is listed

Chemicals known to cause reproductive toxicity for males:

None of the ingredients is listed

Chemicals known to cause developmental toxicity:

None of the ingredients is listed

Canada

Canadian Domestic Substances List (DSL):

All ingredients are listed.

Canadian NPRI Ingredient Disclosure list (limit 0.1%):

None of the ingredients is listed

Canadian NPRI Ingredient Disclosure list (limit 1%):

None of the ingredients is listed

SECTION 16 : Other information

This product has been classified in accordance with hazard criteria of the Controlled Products Regulations and the SDS contains all the information required by the Controlled Products Regulations. Note: The responsibility to provide a safe workplace remains with the user. The user should consider the health hazards and safety information contained herein as a guide and should take those precautions required in an individual operation to instruct employees and develop work practice procedures for a safe work environment. The information contained herein is,

Safety Data Sheet

according to 29CFR1910/1200 and GHS Rev. 3

Effective date : 12.16.2014

Page 7 of 7

Potassium Ferrocyanide

to the best of our knowledge and belief, accurate. However, since the conditions of handling and use are beyond our control, we make no guarantee of results, and assume no liability for damages incurred by the use of this material. It is the responsibility of the user to comply with all applicable laws and regulations applicable to this material.

GHS Full Text Phrases:

Abbreviations and acronyms:

IMDG: International Maritime Code for Dangerous Goods

PNEC: Predicted No-Effect Concentration (REACH)

CFR: Code of Federal Regulations (USA)

SARA: Superfund Amendments and Reauthorization Act (USA)

RCRA: Resource Conservation and Recovery Act (USA)

TSCA: Toxic Substances Control Act (USA)

NPRI: National Pollutant Release Inventory (Canada)

DOT: US Department of Transportation

IATA: International Air Transport Association

GHS: Globally Harmonized System of Classification and Labelling of Chemicals

ACGIH: American Conference of Governmental Industrial Hygienists

CAS: Chemical Abstracts Service (division of the American Chemical Society)

NFPA: National Fire Protection Association (USA)

HMIS: Hazardous Materials Identification System (USA)

WHMIS: Workplace Hazardous Materials Information System (Canada)

DNEL: Derived No-Effect Level (REACH)

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Last updated : 03.19.2015

KILN FIRING CHART

Firing converts ceramic work from weak greenware into a strong, durable form. As the temperature in a kiln rises, many changes take place in the clay; and understanding what happens during the firing can help you avoid problems. The following chart provides highlights of what happens when firing clay.

Temperature C° F°		Color	Cone (approx.)	Event
1400	2552	Brilliant white	14 13 12	End of porcelain range
1300	2372	White	11	End of stoneware range
		Yellow-white	9 7	
1200	2192	Yellow	5½ 4 2	End of earthenware (red clay) range
1100	2012	Yellow-orange	1	Between 1100-1200°C, mullite and cristobalite (two types of silica) form when clay starts converting to glass. Clay and ceramic particles start to melt together and form crystals. These changes make the material shrink as it becomes more dense. Soaking (holding the end temperature) increases the amount of fused matter and the amount of chemical action between the fluxes and the more refractory materials.
		Orange	04 05	
1000	1832	Red-orange	06 07 08	
900	1652	Cherry red	010 012 013	
800	1472	Dull red	015 016 017	Between 300-800°C, the temperature must be raised steadily and ample air must be present to permit the complete burning of carbonaceous materials (impurities in the clay along with paper, wax, etc.). After 800°C, the clay surface will start to seal off, trapping unburned carbonaceous materials and sulfides, which could cause bloating and black coring.
700	1292	Dark red	018 019 020	
600	1112	Dull red glow	021 022	
500	932	Black		Quartz inversion occurs at 573°C. When clay is refired for a glaze firing, quartz crystals change from an alpha (α) crystal structure to a beta (β) crystal structure. The inversion is reversed on cooling. This conversion creates stresses in the clay so temperature increase and decrease must be slow to avoid cracking the work.
400	752			Between 480-700°C chemical water (referred to as "water smoke") is driven off.
300	572			Upon cooling, cristobalite, a crystalline form of silica found in all clay bodies, shrinks suddenly at 220°C. Fast cooling at this temperature will cause ware to crack.
200	392			
100	212			Water boils and converts to steam. Trapped water will cause clay to explode so all water should be evaporated below 100°C. Begin a firing by keeping the kiln below 100°C until all water has evaporated.

PotteryMaking
Illustrated

Index

- absorption, 15, 32, 71, 72, 75, 77, 78, 103, 104, 106
conservation, 9, 10, 16, 17, 20, 47, 59, 109
deliquescence, 12, 20, 45, 57
Desalination, iv, 16, 36, 37, 88, 112, 114, 115, 118
efflorescence, 9, 10, 25, 26, 29, 40, 43, 58, 84, 85, 90, 91, 92, 94, 95, 96, 98, 99, 101, 102, 103, 104, 108, 109
EM Quant, viii, 59, 61, 62, 64
evaporation, viii, 10, 13, 14, 19, 20, 22, 24, 25, 26, 27, 29, 33, 36, 40, 45, 72, 76, 78, 80, 81, 82, 83, 98, 100, 102, 103, 104, 106, 107
fabric, 46, 68, 69, 70, 71
ferrocyanide, 9, 19, 39, 42, 43, 75, 101, 103, 106, 117
fireskin, 73
hexametaphosphate, 9, 43, 44, 75, 103
inhibitors, 9, 18, 20, 39, 42, 44, 58, 59, 75, 82, 89, 95, 97, 100, 102, 103, 104, 105, 106, 107, 108, 109
Kiln #8, v, viii, 52, 55, 56, 67
mirabilite, 14, 30, 34, 64, 101
nitrates, 11, 18, 26, 29, 32, 61, 63, 64, 65
nitrite, 32
nucleation, 9, 18, 19, 20, 39, 40, 41, 43, 44, 102, 103, 104, 108
Petrography, 67, 116
porosity, 11, 12, 23, 31, 66, 68, 69, 70, 72, 75, 77, 103, 104, 106, 107
potassium ferrocyanide, 9, 43
poulticing, 9, 16, 37, 38, 45
Sandkuhl, v, viii, 66, 69
sodium chloride, 9, 30, 43, 55, 63, 65, 67, 77, 100, 103, 104, 105
sodium ferrocyanide, 42
sodium hexametaphosphate, 9
sodium sulfate, 9, 29, 30, 34, 43, 63, 65, 67, 78, 82, 96, 97, 99, 100, 101, 103, 104, 105, 111
spall, viii, 14, 28, 34, 35, 84, 86, 89, 90, 95, 97, 100, 101, 103, 104, 108
Subflorescence, iv, 19, 27
supersaturation, 9, 13, 19, 31, 33, 39, 40, 41, 43, 71, 83, 84, 102, 104, 107, 108
Terracotta, iv, v, 21, 22, 23, 24, 28, 34, 60, 66, 114
thenardite, 14, 30, 34, 64, 101
thermodynamic modeling, 17
WCMC. *See* Western Clay Manufacturing Co.
Western Clay Manufacturing Company, 46, 50, 66, 116, 118