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CAST STONE MATERIALS:

POROSITY DETERMINATION AND RELATIVE HUMIDITY-SATURATION RELATIONSHIPS

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RELATIONSHIPS**

June 15, 2016

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and

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EXECUTIVE SUMMARY

This document reports on the results of an investigation to characterize the moisture-humidity relationships of prototypical cast stone materials (CSMs) under study for immobilization of Hanford low-activity waste. The three materials described in this report [i.e., CSM-6 (Ave), CSM-19 (Hi Al), and CSM-21 (Hi SO₄)] were selected from the 26 materials created by Savannah River National Laboratory for a 2013 screening evaluation of cast stone blends led by Pacific Northwest National Laboratory (Westsik et al, 2013). The primary difference between these materials was their associated low-activity waste simulants which were derived from the Hanford Tank Waste Operations Simulator at the “average,” “high aluminum and chloride,” and “high sulfate” simulant compositions (Russel et al., 2013).

Since porosity is an integral component of the moisture-humidity relationship, this study refined the approach for estimating effective porosity of cast stone materials through experiment and analysis. Four methods of preparing CSMs for gravimetric analysis of porosity through over-drying were evaluated in parallel including (i) water-saturation, (ii) porewater exchange with 2-propanol, (iii) porewater exchange with ethanol, and (iv) equilibration at 100% relative humidity (RH). For each preparation method, the mass lost to oven-drying was assumed to be due to water evaporation and the pore volume was calculated by relating that mass loss to a volume of pore solution. For methods that involve porewater exchange with alcohol, the mass lost to drying was corrected for the ratios of the densities of alcohol and water. In addition to gravimetric analysis, a backscattered image analysis approach based on scanning electron microscopy was conducted.

Although each porosity method has its advantage and limitations, the recommended routine approach for estimating porosity of porous solids containing a high salt content remains oven-drying to constant mass. However, prior to drying at 105 °C, nearly- or fully-saturated cast stone (e.g., molded samples maintained or equilibrated at high relative humidity) should be initially equilibrated to water vapor in a chamber at 100% RH. Dry, or relatively dry, materials should be prepared for oven-drying at 85 °C by exchanging the pore solution with 2-propanol for a sufficient time to ensure complete penetration. For porewater exchange, the mass of alcohol lost to drying should be corrected for the density differences between water and alcohol to obtain the equivalent mass of water that would have been lost to drying. In general, porosity should be estimated by correcting the measured water mass lost to oven-drying for the volumetric ratio of water in the pore solution. However, these corrections require a critical assumption regarding the properties of the pore solution. A practical and recommended approach for estimating pore solution properties is to directly measure fluid density and salt content of an extraction of crushed material at 0.5 L/kg according to U.S. EPA Method 1316.

Based on the recommended 100% RH equilibration approach, the reported porosity of CSM-6 (Ave) and CSM-19 (Hi Al) were 36% and 40%, respectively, while the porosity of CSM-21 (Hi SO₄) was significantly higher at 53%. These porosity values are 9-15% less than the values reported by Westsik et al., (2013), in part, due over-estimation of porosity in the 2013 report based on an assumption that the properties of the pore solution could be represented by the properties of the high salt, low water content low-activity waste simulant. Dry density estimates for the four preparation techniques indicate up to 20% matrix dissolution following water saturation and 9% dissolution for porewater replacement with ethanol relative to 100% RH equilibration. Porewater replacement with propanol resulted in only a 3% loss in dry density compared to 100% RH equilibrated samples.

Cast Stone Materials: Porosity and Relative Saturation

Although cast stone displays some degree of hygroscopic behavior due to the presence of salts, these materials react to the RH of their storage environment through the uptake and release of water vapor (capillary condensation and evaporation). The mean relative saturation at equilibrium was 90% for CSMs stored at 82 and 68% RH, but mean relative saturation decreased to 84% when samples were stored at 33% RH. The fact that equilibrium relative saturation remained high, but not fully saturated, over a broad range of environmental RH was attributed to the hygroscopic nature of the CSM pore solution that lowered the activity of water vapor in the pores. While two of the CSMs [CSM-6 (Ave), CSM-21 (Hi SO₄)] displayed very similar moisture-humidity behavior (i.e., equilibrium saturations within 2% of each other), the equilibrium relative saturations of the third CSM [CSM-19 (Hi Al)] were 4-5% higher at all levels of RH. Relative saturation was not a simple function of porosity, but a combination of pore connectivity and the composition of the pore water (i.e., hygroscopic behavior).

Recommended Material Properties for Cast Stone Materials

Material ID	Dry Bulk Density (g-dry/cm ³)	Effective Porosity, η (cm ³ _{pore} /cm ³)	Equilibrated Relative Saturation, Θ_{eq}		
			Θ_{eq} at 82% RH (%)	Θ_{eq} at 68% RH (%)	Θ_{eq} at 33% RH (%)
CSM-6 (Ave)	1.67	36	89	90	84
CSM-19 (Hi Al)	1.70	40	94	94	89
CSM-21 (Hi SO ₄)	1.38	53	91	90	84

The results provided in this report represent the porosity and saturation-humidity relationships for fresh cast stone materials. Over time, the loss of hygroscopic salts due to leaching will increase the porosity of the system and reduce the hygroscopic behavior of the pore network, resulting in lower relative saturation at the relative humidity values tested in this report. Based on these observations, it is unlikely that cast stone materials will remain saturated in natural environments over the intervals and conditions relevant for performance assessments. As a result, cast stone could be susceptible to ingress and reaction of oxygen and carbon dioxide from the disposal environment under relatively dry disposal conditions.

ACRONYMS AND ABBREVIATIONS

CSM(s)	cast stone material(s)
HTWOS	Hanford Tank Waste Operations Simulator
LAW	low activity waste
PNNL	Pacific Northwest National Laboratory (Richland, WA)
RH	relative humidity
SEM	scanning electron microscope
SRNL	Savannah River National Lab (Aiken, SC)
U.S. EPA	United States Environmental Protection Agency
VU	Vanderbilt University (Nashville, TN)
W/D	water-to-dry blend ratio
wt%	percent by mass
ε	total, or bulk, porosity
η	effective porosity
Θ_t	relative saturation as a function of time (t)
Θ_{eq}	relative saturation at equilibrium with RH

1. INTRODUCTION

This report presents the results of experiments to characterize the effective porosity and relative saturation in response to a range of relative humidity for three prototype cast stone materials (CSMs). The specific materials characterized in this report (i.e., CSM-6, CSM-19 and CSM-21) were three of the 26 CSMs created by Savannah River National Laboratory (SRNL) in fiscal year 2013 for a screening-level evaluation for immobilization of Hanford low-activity waste (LAW) in cast stone blends (Westsik et al., 2013). This evaluation, led by Pacific Northwest National Laboratory (PNNL), focused on material characterization for freshly mixed and cured CSMs as well as leaching behavior of simulant constituents from fully-saturated materials. The porosity of cured CSMs was reported based on oven-drying at 105 °C of “as cast” CSM samples with correction of the mass lost to drying for the properties of the simulant used in each CSM recipe. Although PNNL recognized that the traditional approach of initially water-saturating the sample prior to drying could lead to dissolution of salts from the CSM matrix, the impact of water-saturation on the measured porosity of CSMs was not studied.

In natural environments, porous materials gain or lose moisture due to gradients in the thermodynamic activity of water vapor (i.e., relative humidity, or RH) between the pore structure and the environment. If the RH of the external environment is less than the RH within the pore space, the relative saturation (i.e., fraction of the pore space that is occupied by water) will decrease. Conversely, if the external RH is greater than the RH in the pore space, the relative saturation will increase due to pore condensation. The internal pore RH, or the activity of water vapor in the pore, is in local equilibrium with the activity of the porewater which may move within the connected pore network by capillary forces and water diffusion. For porous media containing a high salt content, the internal RH is further influenced by the concentration of hygroscopic salts in the porewater which can lower the activity of water vapor under local equilibrium.

An understanding of CSM porosity and moisture behavior is critical for assessing the long-term performance of these materials since porosity and relative saturation may be used to represent the amount of pore vapor within a porous matrix in equilibrium with the RH of the disposal environment. Lower values of relative saturation will typically result in increased rates of ingress of atmospheric oxygen and carbon dioxide which will react with the cast stone matrix. Thus, while effective porosity and relative saturation are considered important for estimating leaching behavior under disposal scenarios, these material parameters also are essential for determining the potential for chemical and physical degradation of the porous matrix through reaction with atmospheric constituents (e.g., carbon dioxide, oxygen). Assuming that cementitious media remain saturated when stored in low RH environments is likely to under-predict the impact of oxidation and carbonation on retention of LAW or treated supplemental waste contaminants.

In this report, the moisture behavior of CSMs in response to storage at controlled RH was quantified based on mass loss or gain during storage. Since CSM porosity is integral to relative saturation calculations, this report includes the description of a study to identify a recommended approach for determining porosity of porous media containing a high content of soluble salts (e.g., CSMs). The impact of four sample preparation methods (i.e., water-saturation, 2-propanol exchange, ethanol exchange and equilibration at 100% RH) on the measured porosity of CSM samples was investigated. In parallel, CSM porosity was determined by a microscopy image analysis method that required drying as part of sample preparation. These various approaches were conducted in parallel to highlight the benefits and limitations

of each approach relative to the approach used to determine porosity as reported in the PNNL report (Westsik et al., 2013). The porosity values based on a recommended approach were used to parameterize the time-dependent mass loss data from RH-relative saturation experiments on CSM samples stored at 82, 68 and 33% RH. Subsequent rebound of relative saturation during pore condensation was studied by measuring mass gained by RH-equilibrated CSMs when stored at 100% RH. The relative saturation results were plotted as a function of storage time and the equilibrium relative saturation were tabulated as a function of CSM mix design and environmental RH.

The data contained in this report are intended (i) to improve the understanding of cast stone properties, (ii) to support of parameter estimation for modeling of CSM performance under environmental conditions with a range of external relative humidity, and (iii) to provide a basis for further evaluation of reactions of cast stone with oxygen and carbon dioxide. The document does not provide detailed interpretation of the moisture-density relationships for CSMs nor does it link the provided data to the leaching results from the 2013 evaluation.

2. CAST STONE MATERIALS

Monolithic samples of three cast stone blends were provided to Vanderbilt University (VU) by SRNL as 72-cm (3-inch) diameter by 145-cm (6-inch) long cylinders (Garrabrants et al, 2016). **Table 1** summarizes the pertinent mix design parameters for the cast stone materials studied in this report, including the material identifier, the waste simulant blend, the ratio of solidification components within the dry blend, and the water-to-dry blend ratio. The non-radioactive simulants used to create the CSMs were all based 7.8M sodium loading according to the Hanford Tank Waste Operations Simulator (HTWOS) model. These simulants represent the mean simulant concentration over the 1046-week estimated treatment plan (Average), the peak aluminum and chloride concentration estimated at Week 235 (High Al) and the peak sulfate concentration estimated at Week 672 (High SO₄). Simulant recipes and solution parameters are presented in Russell et al (2013) while simulant concentrations used in creating the CSMs are provided in Westsik et al (2013).

Table 1: Mix Design for Cast Stone Materials

Material ID	HTWOS Simulant	Simulant Sodium (moles/L)	Dry Blend Ratio (PC:FA:SC)	W/D*
CSM-6 (Ave)	Average	7.8	8:45:47	0.4
CSM-19 (Hi Al)	High Al	7.8	8:45:47	0.4
CSM-21 (Hi SO ₄)	High SO ₄	7.8	8:45:47	0.6

Note: * W/D represents the ratio of water to dry blend containing portland cement, fly ash and slag cement.

The CSM monoliths were cut into smaller parallelepipeds for determination of porosity and relative saturation experiments using drying cutting techniques. For these relative saturation experiments, a single sample cylinder of each CSM was cut into several replicate 2.0±0.1 cm test cubes. Prior to cutting the sample cubes, approximately 1.5 cm of material was removed from each end of the monolith so that end- and edge-effects were minimized. The bulk of the material was sliced into 2-cm disks and each disc segmented into six 2-cm cubes (see **Figure 1**, left). The initial mass and dimensions of each sample cube

were measured and recorded prior to storing the samples in a 100% RH environment for initial equilibration step of the relative saturation experiments. Fragments of material cut between samples were collected for initial moisture content assessment. In order to determine the apparent porosity of CSMs, sample cubes were subsequently cut into thin slices of approximately 0.2-cm thick (see **Figure 1**, right) to facilitate saturation/drying experiments and analysis by scanning electron microscopy (SEM).

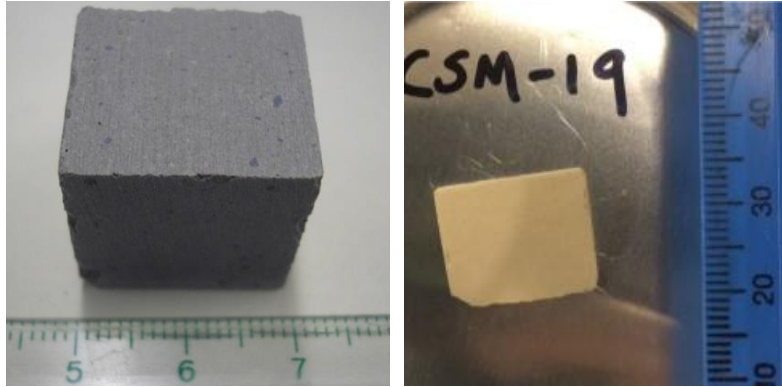


Figure 1: Samples for Humidity-Saturation (2-cm x 2-cm x 2-cm) and Porosity (2-cm x 2cm x 0.2 cm) Experiments.

3. POROSITY OF CSM SAMPLES

The total porosity (ε) of a matrix represents the fraction of the total or bulk material volume (V_b) that consists of pore space or void volume (V_p):

$$\varepsilon = \frac{V_p}{V_b} \quad \text{Equation 1}$$

where V_p is the volume of the pore space (cm^3).

This total porosity includes both the open pores and those pores which are closed with respect to the continuous pore network. Since many porosity techniques only quantify the volume of the open, or continuous, pore network, the effective porosity (η) provided by the technique will always be less than the total porosity.

Environmental applications usually rely on definition of the effective porosity rather than total porosity. While closed pores are important in terms of macroscopic properties (e.g., bulk density, mechanical strength, etc.), the effective porosity is crucial for accurate modeling of leaching, mass transport, and material degradation processes. In nuclear waste applications, such as the containment of LAW in saltstone or cast stone¹, the mass transport and long-term performance of a material may have significant impact on the risks associated with potential release of radionuclides.

¹ The terminology, “cast stone” and “saltstone,” refers to cementitious waste forms for high-salt waste streams at DOE facilities in Richland, WA and Aiken, SC, respectively. Although the dry blends of cementitious components in these materials are similar, these materials differ in the composition of the waste streams incorporated into the matrix. However, both materials are essentially high-porosity porous mortars with significant potential for dissolution of the matrix when contacted with water.

Determination of porosity by gravimetric measurement typically is based on the mass of a porous matrix in three saturation states – a water-saturated state (m_{sat}), an oven-dried state (m_{dry}), and as a submerged matrix in a fluid bath (m_{sub}). The effective porosity may be calculated according to the following general equation:

$$\eta = \frac{V_p}{V_b} = \frac{(m_{sat} - m_{dry})}{\rho_{fluid(dry)}} \left| \frac{\rho_{fluid(sub)}}{(m_{sat} - m_{sub})} \right. \quad \text{Equation 2}$$

where $\rho_{fluid(dry)}$ is the density of the fluid lost to oven drying (g/cm^3),

$\rho_{fluid(sub)}$ is the density of the fluid bath used in the submersion measurement (g/cm^3),

m_{sat} is the mass of a fluid-saturated sample (g),

m_{dry} is the dried mass of the sample (g), and

m_{sub} is the measured mass of the sample submerged in the fluid bath (g).

Traditional approaches for structural cements and concretes, such as ASTM C642 (ASTM, 2013), sequence the collection of data such that the material is first oven-dried (m_{dry}), then saturated (m_{sat}) and submerged (m_{sub}) in a single fluid (e.g. water). When the density of the fluid lost to oven-drying ($\rho_{fluid(dry)}$) and the fluid used in the submersion measurement ($\rho_{fluid(sub)}$) are equal, Equation 2 is simplified to:

$$\eta = \frac{(m_{sat} - m_{dry})}{(m_{sat} - m_{sub})} \quad \text{Equation 3}$$

However, in the 2013 screening study, PNNL noted that these traditional saturation-based approaches might not be inappropriate for CSMs due to the potential to dissolve some of the matrix during water-saturation or immersion (Westsik et al, 2013). Therefore, PNNL determined porosity based on water loss to oven-drying (105 °C) of “as cast” samples without any procedure to saturate the samples. The bulk volume (V_b) in the effective porosity equation (Equation 2) was based on the geometric dimensions of regularly-shaped CSM samples.

PNNL did not attempt to quantify the impact of water-saturation versus “as cast” drying on porosity measurements; however, some porosity was probably not accounted for in the drying approach since it is unlikely that the “as cast” material was fully-saturated. The reported range of porosity for 26 CSMs in the screening report was 51-65% which seems to be relatively high compared to the 15-30% porosity reporting for slag cement blends (Ramezani pour and Malhotra, 1995) or to the average of 37% found by helium pycnometry for cast stone with up to 2.5 M sodium loading (Chung et al, 2013).

PNNL assumed that the mass lost to drying was due to water and related the pore space volume with an equivalent volume of pore solution assumed to have the density of the simulant used in each CSM. The volume of the pore solution was determined by dividing the mass loss by the density of water and the volume fraction of water in the original simulant solution.

$$\eta = \frac{V_p}{V_b} = \frac{(m_{sat} - m_{dry})_{water}}{V_b \cdot \rho_{water}} \left| \frac{v_{sim}}{v_{water}} \right. \quad \text{Equation 4}$$

where ρ_{water} is the density of water at the experiment temperature (g/cm^3),
 v_{sim} is the a unit volume of the simulant used for each CSM (cm^3), and
 v_{water} is the volume of water in a unit volume of simulant (cm^3).

The volume fraction of water in the simulant solution was determined by calculation using the recipe for creation of each simulant (Russell et al, 2013). By assuming that the pore solution has the same solution properties as the simulant used to create the CSM, PNNL is, therefore, assuming that salt solution used in preparation of the CSMs is unaltered by the chemical and physical changes associated with curing of the CSM.

3.1. POROSITY BY GRAVIMETRIC ANALYSIS

Following the general methodology of PNNL, porosity measurements of the three CSMs were based on the mass lost during oven-drying. However, unlike the PNNL experiments, samples were water-saturated prior to drying. In parallel, oven-drying was conducted on samples after alcohol exchange of pore water and with 2-propanol or ethanol (Aligizaki, 2006).

3.1.1. Water-Saturation Method

The testing sequence of ASTM C642 (e.g., drying, saturating, submerging) was modified to take advantage of the fact that CSM samples are largely saturated in their “as cast” state. Therefore, samples were initially saturated in reagent water for minimal time (~17 days) to achieve constant mass² and ensure complete water-saturation. The submerged mass of the saturated sample was measured using a hanging balance. Then the sample was oven-dried at 105 °C until a constant mass was recorded.

For most cementitious materials, water saturation is not considered to significantly damage the matrix; however, the CSM-21 (Hi SO₄) sample broke apart without intervention upon exposure to water (**Figure 4**, left). Degradation is likely due to dissolution of soluble sulfate salts in the pore structure as indicated by the degradation ring about an intact core on some of the pieces in the lower left of the figure. While CSM-6 (Ave) sample (**Figure 4**, right) did not break apart directly from water saturation, minor handling to remove surficial water prior to measurement of saturated mass was sufficient to break the sample into several pieces. Since some force was required to break the material and no degradation zone for CSM-6 (Ave) can be seen in the figure, the extent of degradation for CSM-6 (Ave) was considered less than for CSM-21 (Hi SO₄).

² “Constant mass” is defined in this document as a difference of less than 0.5% in successive mass measurements.



Figure 2: Degradation of CSM-21 (Hi SO4) and CSM-6 (Ave) after Water-Saturation.

3.1.2. Porewater Exchange/Saturation Methods

Since CSM sample showed a vulnerability to degradation upon water saturation, the oven-drying porosity method was repeated for all CSMs after porewater exchange with either 2-propanol or ethanol. During alcohol exchange, porewater is replaced with alcohol and allows for drying at lower temperatures (i.e., 85 °C rather than 105 °C) which may minimize damage to the matrix caused by high internal stress (Chung et al, 2013) or evaporation of waters of hydration of the mineral structure (Gallé, 2001). Samples were submerged in 2-propanol or ethanol the same interval used for water saturation (~17 days) until constant mass was achieved. Porosity was calculated in the same manner as for the water-saturated approaches with the additional step of adjusting the mass lost to drying for the density of alcohol.

3.1.3. Pore Solution Density Adjustment

Westsik et al. assumed that porosity could be evaluated by correcting the experimental mass loss due to drying by the density of water and the volume fraction of water in the simulant solution used to create the CSM (see Equation 4). A similar approach was taken by SIMCO Technologies, Inc. (SIMCO, 2010); however, the pore volume was calculated by correcting the water lost to drying for measurable properties of the pore solution, namely the solution density (ρ_{sol}) and salt content (c_{salt}):

$$\eta = \frac{V_p}{V_b} = \frac{(m_{sat} - m_{dry})_{water}}{V_b} \left| \frac{1}{(\rho_{sol} - c_{salt})} \right. \quad \text{Equation 5}$$

where ρ_{sol} is the density of water at the experiment temperature ($\text{g}_{sol}/\text{cm}^3_{sol}$), and c_{salt} is the a unit volume of the simulant used for each CSM ($\text{g}_{salt}/\text{cm}^3_{sol}$).

Since the pore solution is assumed to consist of water and dissolved salt, the $(\rho_{sol} - c_{salt})$ term directly relates the mass of water (g_{water}) to an equivalent volume of pore solution (cm^3_{sol}). Therefore, Equation 5 is numerically equal to Equation 4 by is based on measurable parameters of the pore solution. Based on Equation 5, a pore solution factor (F_{sol}) may be defined as:

$$F_{sol} = \frac{1}{(\rho_{sol} - c_{salt})} \quad \text{Equation 6}$$

This factor relates the measured mass lost to drying to a volume of pore solution and, thus, to the calculated effective porosity of the matrix. Although this approach is numerically equivalent to that used by PNNL, the choice of a solution assumed to represent the pore solution for this approach is very important. The effect of solution properties on the solution correction factor is shown in **Table 2** assuming various solutions represent the pore solution (e.g., assumptions by PNNL and SIMCO).

The ASTM C642 approach assumes that the pore solution is represented by reagent water and mass lost to drying is related to pore volume based on the density of water. Therefore, the pore solution factor (F_{sol}) is 1 when evaluated at room temperature (20 °C).

The PNNL assumption that CSM pore solutions have the same properties of their component simulants results in pore solution factors of 1.22 (Average), 1.24 (High Al), and 1.22 (High SO4) based on solution parameters for the cast stone simulants (Russell et al, 2013). In the SIMCO report, a 4M solution of sodium nitrate was assumed to represent pore solution and tabulated parameters (CRC, 1991) generated a pore solution factor of 1.20. The result of pore solution assumptions found in Westsik et al. (2013) and SIMCO (2010) result in a 14 to 24% increase in calculated porosity over the ASTM C642 approach.

Table 2. The Effect of Assumed Pore Solutions on the Solution Parameters and Solution Correction Factor for the Porosity Equation

Parameter	As measured	PNNL ^a			SIMCO ^b	VU ^c
	Water	Average	High Al	High SO4	4M NaNO ₃	L/S 0.5
ρ_{sol} (g _{sol} /cm ³ _{sol})	1.00	1.34	1.36	1.32	1.17	1.10
c_{salt} (g _{salt} /cm ³ _{sol})	-	0.52	0.55	0.44	0.34	0.15
F_{sol} (cm ³ _{sol} /g _{water})	1.00	1.22	1.24	1.14	1.20	1.05

Notes:

^a Simulant solution parameters from Russell et al, 2013.

^b Solution parameters reported for a 4M NaNO₃ solution (SIMCO, 2010).

^c Porewater solution parameters measured from L/S 0.5 mL/g extraction of CSM-21 following Method 1316 (EPA, 2013).

In the current study, VU considered the pore solution to be represented by a batch leaching extraction of crushed CSM at a low liquid-to-solid ratio (L/S) according to the United States Environmental Protection Agency (U.S. EPA) Method 1316 (EPA, 2013). Solution parameters are provided by direct measurement of solution density and total dissolved solids of an extraction of crushed CSM at L/S of 5 mL/g. The resultant pore solution factor of 1.05 is considerably less than the factors calculated according to the SIMCO or PNNL assumptions.

3.1.4. Adjustment for Exchange Fluid Density

For the porewater exchange experiments, the fluid density used in the drying experiments (e.g., ethanol, 2-propanol) is different than the fluid density assumed in the bulk volume determination (water). Therefore, the combined Equation 5 and Equation 6 need to be adjusted for the density of the alcohol used in the drying experiment:

$$\eta = \frac{V_p}{V_b} = \frac{(m_{sat} - m_{dry})_{alcohol}}{V_b} \left| \frac{F_{sol}}{\rho_{alcohol}} \right| \frac{\rho_{water}}{\rho_{alcohol}} \quad \text{Equation 7}$$

and the ratio between the density of water and the exchange fluid becomes an exchange fluid density correction factor (F_{exch}).

$$F_{exch} = \frac{\rho_{water}}{\rho_{alcohol}} \quad \text{Equation 8}$$

Using tabulated density values at 20 °C (CRC, 1991), the correction factors for the porewater exchange fluid density are:

$$F_{exch} = \frac{\rho_{water}}{\rho_{ethanol}} = \frac{0.99821}{0.7893} = 1.26 \text{ for ethanol and}$$

$$F_{exch} = \frac{\rho_{water}}{\rho_{2-propanol}} = \frac{0.99821}{0.7855} = 1.27 \text{ for 2-propanol.}$$

3.1.5. Overall Porosity Expression

The porosity of a CSM from drying experiments may be calculated by applying the pore solution correction factor (F_{sol}) and the fluid exchange correct factor (F_{exch}) to the basic porosity expression (Equation 2):

$$\eta = \frac{V_p}{V_b} = \frac{(m_{sat} - m_{dry})}{V_b} \cdot F_{sol} \cdot F_{exch} \quad \text{Equation 9}$$

3.2. DETERMINATION OF POROSITY BASED ON 2-D IMAGE ANALYSIS

In addition to gravimetric methods, the porosity of epoxy impregnated and polished CSM samples were estimated using SEM image analysis (Scrivener et al., 1986). This technique involves analysis of a grey-scale histogram based on a series of at least 200 backscattered 2-dimensional images (1024 x 896 pixels) of a polished surface. At the scan resolution, each pixel represents approximately 0.25 μm. The histogram is reduced to a binary black and white image by applying a grey-scale threshold value to distinguish void space (white) from that of the solid material (black). The threshold is derived from regression of a Gaussian curved fitted to the grey-scale histogram. The porosity is calculated as a percentage of white space within the image.

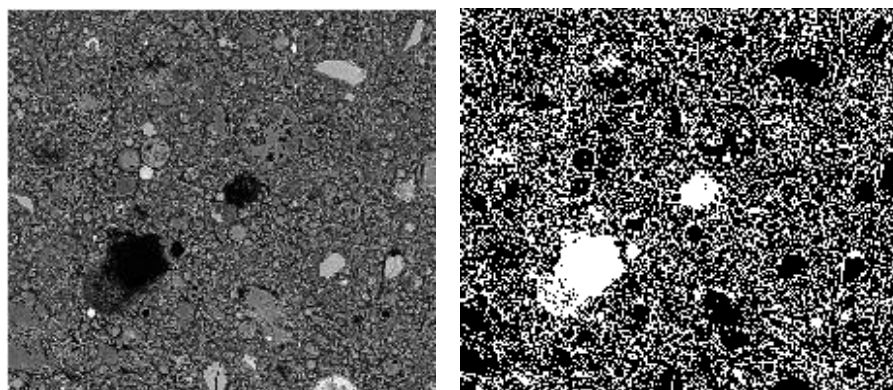


Figure 3. Example of 2-D Images (1024 x 896 pixels) Used in Porosity Determination of CSM-6 (Ave); grey-scale (left) and binary (right).

3.3. POROSITY RESULTS

The apparent porosity results for oven-drying techniques and SEM image analysis for the three study CSMs are shown in **Table 3** in comparison to the report porosity values (Westsik et al, 2013). The oven drying techniques included samples that were initially water-saturation or alcohol-exchanged with either 2-propanol or ethanol. SEM image analysis was not conducted on the CSM-21 (Hi SO₄) sample due to a high percentage of occlusions containing precipitated soluble salt which was considered to bias the imaging technique and result in artificially high porosity values.

Table 3. CSM Porosity (%) Based on Drying of Saturated Matrices, SEM Image Analysis.

Material	PNNL		Vanderbilt University				
	Reported ^a	Cast ^b	Water ^c	Propanol ^d	Ethanol ^d	SEM ^e	100%RH ^f
CSM-6 (Ave)	51.0	42.0	49.3	32.1	36.6	43.4	36.4
CSM-19 (Hi Al)	53.0	42.9	48.7	29.2	36.8	30.4	38.6
CSM-21 (Hi SO ₄)	62.2	54.8	60.1*	43.5*	52.0	NA	53.3

Notes:

- ^a Data reported in Westsik et al (2013) based on drying of cast materials to constant mass at 105 °C; mass lost to drying corrected for pore solution assuming properties of Average, High Al, or High SO₃ simulant (Russell et al, 2013).
- ^b PNNL data “back-corrected” for pore solution using F_{sol} to yield water mass lost to drying of cast material at 105 °C.
- ^c Saturation in DI water followed by drying to constant mass at 105 °C; mass lost to drying corrected for pore solution using measured properties of Method 1316 extractions at L/S 0.5 mL/g for each CSM.
- ^d Porewater exchange with alcohol (2-propanol or ethanol) followed by drying to constant mass at 85 °C; mass lost to drying corrected for pore solution using measured properties of Method 1316 extractions at L/S 0.5 mL/g for each CSM and for porewater exchange density.
- ^e Grey-scale histogram analysis of multiple 1024 x 896 pixel images; no corrections; * SEM analysis not conducted on CSM-21 sample due to significant number of occlusions containing soluble salt deposits.
- ^f Equilibration of cast material to water vapor at 100% RH followed by drying to constant mass at 105 °C.

NA Results “not available” as image analysis was not conducted due to sample degradation (i.e., breaking).

Of the five porosity techniques conducted by VU and presented in **Table 3**, the drying at 85 °C following porewater exchange with 2-propanol consistently provided the lowest estimate of apparent porosity. Conversely, initial saturation with water followed by oven-drying at 105 °C provided the highest porosity value for all CSMs. However, all VU methods were somewhat lower than the reported porosity for CSMs (Westsik et al, 2013), likely due to the assumption that CSM pore solution had the same properties as CSM simulant which led to large F_{sol} correction factors (**Table 2**). When the previously reported CSM porosity values were “back-corrected” using the associated F_{sol} values to the mass lost to drying at 105 °C, the PNNL values were still somewhat higher than corrected VU values derived from drying after water saturation but consistent with drying after ethanol exchange or equilibration to 100% RH. Image analysis using SEM provides reasonable results as well, but not enough data was recovered to comment on potential bias.

As mentioned in the 2013 screening program, water saturation of test samples likely results in dissolution of the CSM matrix which would bias the porosity measurement to a higher calculated value. The dry bulk density of the matrix as a function of material preparation method compared to the dry bulk density from equilibration to water vapor at 100% RH (**Table 4**) indicated a reduction in density of approximately 18%, 4%, and 9% for water-saturation, 2-propanol exchange and ethanol exchange, respectively. Thus, the values of porosity determined by oven-drying of initially equilibrated samples at 100% RH were considered the most appropriate for tested CSM samples.

Table 4. Dry Density as a Measure of CSM Matrix Dissolution

Material	100% RH	Water		2-Propanol		Ethanol	
	Density (g _{dry} /cm ³)	Density (g _{dry} /cm ³)	Mass Loss	Density (g _{dry} /cm ³)	Mass Loss	Density (g _{dry} /cm ³)	Mass Loss
CSM-6 (Ave)	1.67	1.40	16%	1.58	6%	1.51	10%
CSM-19 (Hi Al)	1.70	1.40	17%	1.66	2%	1.53	10%
CSM-21 (Hi SO ₄)	1.38	1.11	20%	1.40	-1%	1.28	7%

3.3.1. Check on Use of Method 1316 Extraction Data

One difference between the oven-drying techniques presented in this report and that used by PNNL in the 2013 screening program is the assumption of a representative pore solution. The data shown in **Table 3** for water-saturation and alcohol exchange are dependent on the assumption that the solution density and salt content of a low L/S extraction of each CSM could be used to the represent pore solution. Since these properties may be influenced by dilution (i.e. at higher L/S), the choice of the Method 1316 L/S used to represent pore water is important.

The L/S ratio of a fully-saturated porous matrix may be may be calculated as the ratio of the pore volume (V_p) to the mass of the solid matrix (M_m):

$$L/S = \frac{V_p}{M_m} = \frac{\eta \cdot V_b}{(1-\eta) \cdot V_b \cdot \rho_m} = \frac{\eta}{(1-\eta)} \left| \frac{(1-\eta)}{\rho_b - \rho_{sol} \cdot \eta} \right| = \frac{\eta}{\rho_b - \rho_{sol} \cdot \eta} \quad \text{Equation 10}$$

where η is the apparent porosity of the material ($\text{cm}^3_{\text{sol}}/\text{cm}^3$),
 V_b is the bulk volume of the solid matrix (cm^3),
 ρ_m is the density of the solid matrix or skeletal density ($\text{g}_{\text{matrix}}/\text{cm}^3_{\text{matrix}}$)
 ρ_b is the bulk density of the material (g/cm^3), and
 ρ_{sol} is the density of the pore solution ($\text{g}_{\text{sol}}/\text{cm}^3_{\text{sol}}$)

Therefore, the L/S of a fully-saturated sample of CSM-19 (bulk density of $192 \text{ g}/\text{cm}^3$, pore solution density of $1.08 \text{ g}/\text{cm}^3$, mean porosity of 36.4%) would be $0.24 \text{ mL}/\text{g}$. Similar calculations for CSM-6 and CSM-21 yield fully-saturated pore solution L/S values of 0.26 and 0.45, respectively. Therefore, an extraction at L/S of $0.5 \text{ mL}/\text{g}$ would be the most appropriate of the Method 1316 extraction points (which include 0.5, 1, 2, 5 and $10 \text{ mL}/\text{g}$) and would be expected to provide solution density and total dissolved solids parameters that, in general, approximate the pore solution of these CSMs. Alternatively, a sample of pore solution at an L/S of 0.2 may be obtained using the U.S. EPA Method 1314 column test (Garrabrants et al., 2016) and intermediate L/S values can be obtained through modification of either leaching test approach.

3.3.2. Selection of a Porosity Methodology

Each of the approaches used to determine porosity in **Table 3** have benefits and limitations as discussed in the following paragraphs.

PNNL Approach – The PNNL analysis was conducted on “as cast” samples, simplifying the procedure and eliminating the potential for dissolution of the matrix. However, the assumption that the pore structure of cast samples are water-filled meant that the approach would tend to under-estimate porosity. In addition, the further assumption that pore solution has the same properties as the CSM simulants leads to a 14 to 24% increase in porosity over that derived after 100% RH equilibration. Thus, corrections for the pore solution, which are required to relate water mass loss to a volume of pore solution, should be based on direct measurement of pore solution properties, if possible, or of low L/S extractions of CSMs.

Water-Saturation – The choice to saturate CSM samples in a water bath ensures a fully-saturated prior to oven-drying, but leads to up to 18% dissolution of CSM and subsequent over-estimation of porosity. This negates the possibility of water-saturation to ensure an initially water-filled porosity. The 5% correction for the pore solution based on extraction of CSMs at low L/S appears to be more realistic than the 14 to 24% corrections applied by PNNL (Westsik et al, 2013) or SIMCO (2010).

Porewater-Exchange with Alcohols – Soaking a sample of CSM in 2-propanol or ethanol has been considered to cause less damage to the CSM matrix because water-soluble salts may not be as soluble in alcohol. Additionally, porewater exchange with alcohol allows for lower oven temperature for drying so that damage to hydrated minerals may be minimized. However, the porosity values determined after porewater exchange with 2-propanol were consistently lower than all other techniques. These results are likely the result of less matrix dissolution (3% relative to 100% RH equilibrated samples) and incomplete penetration of 2-propanol into the pore structure. Porewater exchange with ethanol may provide better

alcohol penetration over the same contact period; however, the high degree of matrix dissolution (9%) and resultant high porosity value, especially for CSM-21 (Hi SO₄), may be an indication that the sulfate salts in the cast stone are soluble in ethanol.

Image Analysis – Analysis of SEM backscattered images provided a moderate porosity estimate between that of the two alcohol-exchange techniques. The benefits of this approach include the fact that the test materials has limited contact with fluids prior to analysis. However, materials need to be dried which can alter the pore structure of CSMs and polishing of samples requires a lubricant that is in contact with the test sample. Also, the image analysis approach requires critical selection of a proper threshold grey-scale value which could account for some of the difference between this and the other techniques. SEM images display limited resolution and, therefore, the image analysis methodology used in this report is likely to under-estimate porosity because large pores may not be captured in the SEM scan and very small pores that fall well within the pixel resolution may be neglected. Some benefit might be gained by combining the SEM technique for quantifying micro-porosity with other scanning approaches (e.g., CT scanning) that are better-suited to capture macro-porosity.

4. RELATIVE SATURATION-HUMIDITY RELATIONSHIPS

Relative saturation, Θ , represents the fraction of the total pore volume that is water-filled and in equilibrium with the relative humidity of the pore vapor. Used in conjunction with the material effective porosity ($\text{cm}^3_{\text{pore}}/\text{cm}^3$), the relative saturation ($\text{cm}^3_{\text{water}}/\text{cm}^3_{\text{pore}}$) provides a measure of the moisture content of the material ($\text{cm}^3_{\text{water}}/\text{cm}^3$) on an “as tested” basis.

$$MC = \Theta \cdot \eta \quad \text{Equation 11}$$

The relationship between atmospheric RH and relative saturation of a porous matrix can be determined by monitoring the mass loss or gain in a sample during storage under controlled RH. In the study reported here, samples of CSM were stored under controlled RH in air-tight containers and the mass of the samples were recorded as a function of time until constant mass was obtained. The relative saturation as a function of storage time (Θ_t) was calculated as the mass lost to drying from the experiment divided by the total mass lost if the material was completely dried.

$$\theta_t = \frac{(m_{sat} - m_t)}{(m_{sat} - m_{dry})} \quad \text{Equation 12}$$

where m_{sat} is the mass of a saturated sample (g),
 m_t is the measured mass of the sample as a function of storage time (g), and
 m_{dry} is the oven-dried mass of the sample (g).

Since the CSM samples were not structurally stable when water-saturated (see Section 3.1.1) or when oven-dried at 105 °C (see discussion below), the samples were initially equilibrated to a RH of 100% and the dried mass of the sample was calculated rather than measured. The dried mass of the sample was calculated by correcting the initially equilibrated sample mass (m_{sat}) for the mass of water in the pore space using the apparent porosity and the volume of the sample as follows:

$$m_{dry} = m_{sat} - \eta \cdot \rho_{water} \cdot V_b \quad \text{Equation 13}$$

where η is the apparent porosity of the sample ($\text{cm}^3_{\text{pore}}/\text{cm}^3$),

ρ_{water} is the density of liquid water, and

V_b is the bulk volume of the samples based on measured dimensions (cm^3).

4.1. EXPERIMENTAL METHODS

The relative saturation of 2-cm x 2-cm x 2-cm CSM samples as a function of RH was determined by equilibrating test samples in environments of controlled levels of RH using saturated hygroscopic salts (CRC, 1991; ASTM, 2007) at room temperature (20 ± 2 °C). The relative humidity in each RH-controlled container was monitored using a Fisher Scientific hygrometer (model 11-661-16). Rather than water saturation to ensure an initial relative saturation of 100%, samples were equilibrated to a 100% RH environmental to maximize initial relative saturation. The samples were then stored at 82%, 68% or 33% RH until a constant mass was recorded and equilibrium relative saturation based on the mass lost to storage.

4.1.1. Initial Equilibration at 100% RH

The CSM cubes were equilibrated in an air-tight container (15.7-cm length x 10.8-cm width x 5.7-cm height) maintained at 100% RH over a 50 mL reservoir of reagent water (**Figure 4**). Samples were placed on ceramic piers and Nikrothal (NiCr alloy) stilts to elevate the samples above the reservoir. The 100% RH environment was established in the sealed container for five days prior to introduction of test samples. During storage, the mass of the test samples were recorded daily for approximately 30 days until a constant mass was achieved for three consecutive recordings. For the purposes of the relative saturation calculations, these 100% RH equilibrated samples were considered to be initial condition for drying of samples at lower RH environments.

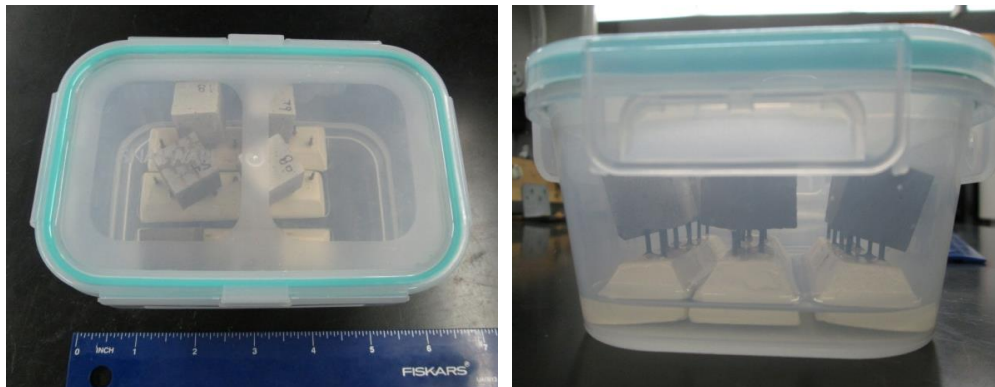


Figure 4: Equilibration of Cast Stone Cubes at 100% RH in Air-tight Containers Showing Ceramic Piers and Nikrothal Stilts for Elevating Sample Cubes

4.1.2. Drying in Controlled RH Environments

Relative humidity environments of 82%, 68% and 33% RH were established in small air-tight containers (10.8-cm length x 10.8-cm width x 6.4-cm height) using saturated salts of potassium bromide, sodium nitrate, magnesium chloride, respectively (CRC, 1991; ASTM, 2007). Approximately 30-mL of salt solution was poured into each container and sealed for five days prior to drying the test samples. The samples were placed on a plastic platform so that test samples were more than 1cm above the salt solution as shown in **Figures 5**. Once the relative humidity in each container was established, duplicate cubes of each CSM material were positioned on the platform. The mass of the cubes were recorded periodically until a constant mass was achieved for three consecutive recordings.



Figure 5: Storage of CSM Samples in a Controlled Environment at 33% RH.

4.1.3. Moisture Uptake from Dried Samples

The cubes that had equilibrated at 82%, 68% and 33% RH were returned to the 100% RH environment (see Section 4.1.1) to evaluate that uptake of moisture or “pore condensation” in the dried materials. The mass of the samples were monitored at regular intervals until at least three consecutive measurements of a constant mass.

4.1.4. Quality Assurance/Quality Control

For the relative humidity experiments, measures to ensure data quality control consisted mainly of regular calibration of laboratory equipment. Mass balances are calibrated bi-annually with the most recent calibration occurring one month prior to the start of these experiments. The hygrometer was calibrated at 97% RH using a saturated solution of potassium sulfate and at 43% RH using potassium carbonate (CRC, 1991; ASTM, 2007). For each calibration, a 1-cm layer of salt was placed in sealed container (10.8-cm length x 10.8-cm width x 6.4-cm height) and saturated with reagent water to the point that no more water could be absorbed into the salt layer. The container was sealed for 24 hours prior to measurement of the relative humidity. Three additional measurements were made daily to ensure constant relative humidity readings were achieved.

4.2. RELATIVE SATURATION RESULTS

The calculated relative saturation was plotted as a function of storage time for the experiments where CSM sample initially equilibrated at 100% RH were dried to RH values of 82%, 68% and 33% as well as

the subsequent pore condensation from those RH back to 100% RH. The laboratory data for moisture experiments of CSM samples is provided in **Appendix A** along with tables presenting the numerical results of relative saturation calculations. Select graphical results are presented in the following discussion while all graphical result are included in **Appendix B** of this report.

4.2.1. Relative Saturation during Drying

Figure 6 presents six graphs showing the change in relative saturation as a function of storage time as the CSM dried from an initially pore saturated state to equilibrium within the controlled RH environment. These relative saturation data are result of calculations using the lowest porosity derived from CSM saturation in 2-propanol. The three graphs at the top of the figure show the change in relative saturation as a function of storage time for each CSM with data series indicating the sample replicates and the three levels of relative humidity. The lower three graphs in the figure compare the same data for the three CSMs grouped by the RH of the storage environment. Duplicate analyses were conducted for all materials as shown in **Figure 6** for CSM-6 (Ave) and CSM-19 (Hi Al); however, one replicate of CSM-21 (Hi SO₄) cracked into fragments (similar to the pictures in **Figure 2**) during initial conditioning phase of the experiment at 100% RH.

4.2.2. Relative Saturation during Pore Condensation

The rebound in relative saturation during pore condensation at 100% RH of CSM samples initially equilibrated to 82%, 68% and 33% RH is presented in **Figure 7**. The layout of the figure is similar to that of **Figure 6** with the top three graphs showing the relative saturation at all initial RH conditions for each of the three CSMs and the lower three graphs showing the increase in relative saturation for all CSMs at each set of initial RH conditions.

When the dried CSM samples were placed back into the 100% RH environment, water was allowed to condense in the pore space until the material was in equilibrium with the high relative humidity environment. Pore condensation occurs with the similar behavior regardless of the initial degree of relative saturation (i.e., regardless of whether the sample was initially equilibrated at 82% RH or at 33% RH). As with the drying behavior, the final relative saturation during pore condensation of CSM materials initially equilibrated to 82% and 68% RH were approximately 97% meaning that the porous matrix does not return to full saturation. The final relative saturation for material initially equilibrated to 33% was slightly lower at approximately 95%. The fact that CSM samples that started the drying phase at a relative saturation of 100% (based on assumption that 100% RH equilibrated resulted in 100% saturation) did not return to 100% relative saturation after drying indicates potential for changes to the pore structure during the drying and humidification cycle.

4.2.3. Average Relative Saturation at Equilibrium

The average relative saturation at constant mass (\mathcal{O}_{eq}) for each CSM material is presented in **Table 4** for the drying and pore condensation phases of the experiment. At equilibrium, the mean relative saturation at equilibration (\mathcal{O}_{eq}) was 94% for CSM-19 (Hi Al) and 90% for CSM-6 (Ave) and CSM-21 (Hi SO₄). The similarity in relative saturation curves at high- and mid-level relative humidity is likely due to the hygroscopic nature of the salts contained in the CSM matrix. Drying in a low RH environment (i.e., 33%RH) yielded lower equilibrated relative saturation values of 84% for CSM-6 (Ave) and CSM-21 (Hi SO₄) and 89% for CSM-19 (Hi Al). Thus, the equilibrium relative saturation of CSM-19 (Hi Al) is 4-5% higher than the other CSMs for each level of RH examined.

Table 4. Mean Relative Saturation at Equilibrium (θ_{eq}) for CSMs.

Material	Drying		Pore Condensation	
	RH	θ_{eq}	RH	θ_{eq}
CSM-6 (Ave)	82%	89%	100%	95%
CSM-19 (Hi Al)		94%		96%
CSM-21 (Hi SO4)		91%		96%
CSM-6 (Ave)	68%	90%	100%	97%
CSM-19 (Hi Al)		94%		96%
CSM-21 (Hi SO4)		90%		95%
CSM-6 (Ave)	33%	84%	100%	91%
CSM-19 (Hi Al)		89%		94%
CSM-21 (Hi SO4)		83%		93%

If equilibrium relative saturation was dependent solely on porosity, the equilibrium relative saturation for the material with the high porosity, CSM-21 (Hi SO4), would display the lowest relative saturation. However, the porosity of CSM-19 (Hi Al) was 39% which is not significantly higher than the 36% porosity of CSM-6 (Ave), but significantly lower than the 52% porosity of CSM-21 (Hi SO4). Conversely, since CSM-21 (Hi SO4) has the highest porosity, the pore solution likely has a higher content of sulfate salts which are not as hygroscopic as nitrate/nitrite salts (CRC, 1991). Thus, equilibrium relative humidity is likely dependent on a combination of the effective porosity, the connectivity of the pore structure allowing of moisture transport, and the content and composition of hygroscopic salts in the pore solution.

Cast Stone Materials: Porosity and Relative Saturation

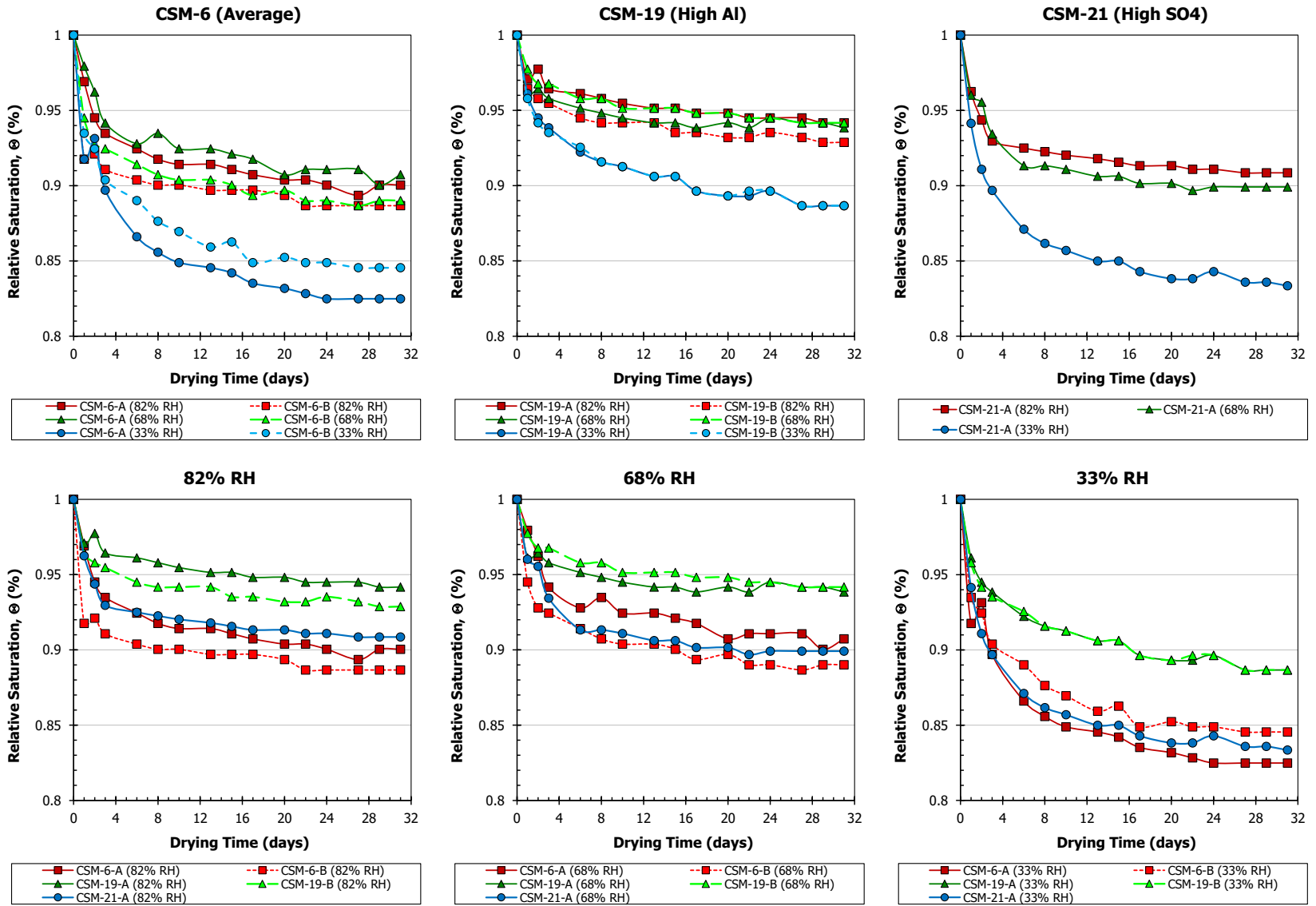


Figure 6: Relative Saturation (%) of CSM Samples during Drying Experiments at Controlled Relative Humidity.

Cast Stone Materials: Porosity and Relative Saturation

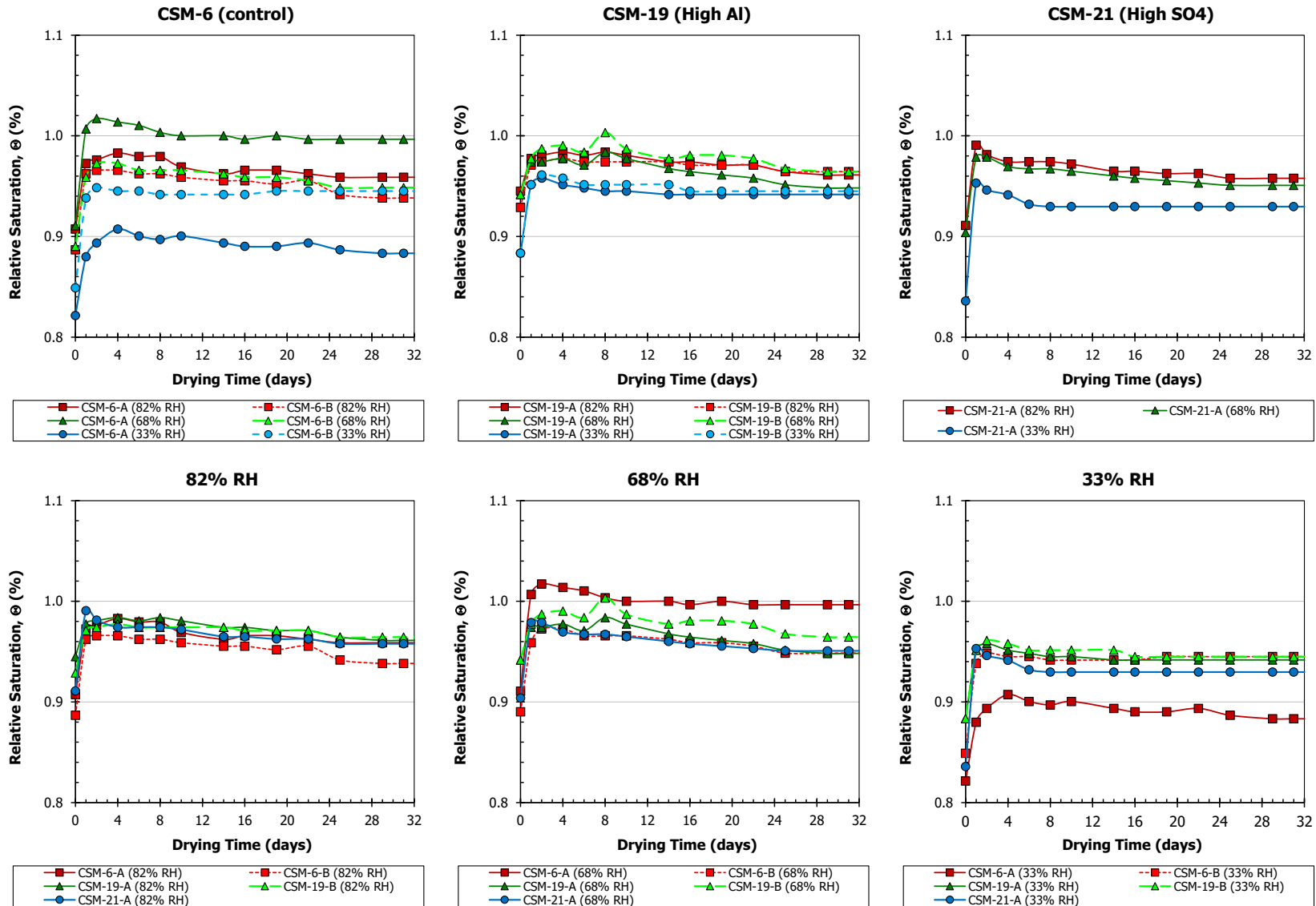


Figure 7: Relative Saturation (%) of CSM Samples during Drying Experiments at Controlled Relative Humidity.

5. CONCLUSIONS AND RECOMMENDATIONS

In this study, relationships between environmental relative humidity and relative saturation of three cast stone materials (CSMs) were determined by equilibrating saturated samples to relative humidity environments of 89%, 68% and 33% relative humidity. The rebound of relative saturation under pore condensation conditions was evaluated by storing samples, previous equilibrated to environments at low relative humidity, in a 100% relative humidity environment.

Since porosity is integral to the relative saturation evaluation, the methods for preparing a sample of CSM for gravimetric estimation of matrix porosity were investigated relative to the porosity estimates reported in a 2013 screening evaluation (Westsik et al., 2013). The four approaches for preparing CSM samples for oven-drying included (i) water-saturation, (ii) porewater exchange with 2-propanol, (iii) porewater exchange with ethanol, and (iv) equilibration to water vapor at 100% relative humidity. Samples of CSMs prepared using each of these methods were oven-dried and the porosity determined by correcting the mass lost to drying for pore solution properties. In addition, an image analysis approach for determining porosity based on backscattered scanning electron microscopy images was compared to gravimetric approaches.

Considering that, by nature, determination of porosity is estimate of a material property, all of the sample preparation methods provided reasonable porosity estimates for CSMs, but each approach has its limitations. The approach taken in the 2013 screening report was limited by its assumptions of an initially saturated “cast” material and that pore solution had the sample properties as the simulant used to create the CSM. These assumption lead to over-estimation of porosity by approximately 10-15% due to overly-strong corrections of the measured mass lost to drying. Approaches that involve porewater exchange with alcohol are susceptible to limited penetration of alcohol leading to incomplete exchange of porewater. The process of soaking a sample in alcohol to exchange pore solution is a balance between allowing for complete penetration and dissolution of alcohol-soluble salts. Based on comparison of dry bulk density after sample preparation, ethanol appeared to dissolved more of the matrix (9%) than 2-propanol (3%). Preparation of CSM samples for oven-drying by saturating in water dissolved as much 20% of the matrix, resulting in significant over-estimation of matrix porosity.

Based on the comparison presented in this study, an approach was recommend for estimating the effective porosity of porous material containing high content of soluble salts while minimizing degradation of the material. The recommended approach for fully- or nearly-saturated cast stone materials (e.g., laboratory materials storage at 100% RH) consists of initial equilibration of test samples in a controlled atmosphere of 100% RH, oven-drying of equilibrated samples at 105 °C, and correction of the measured mass lost based on the properties of the pore solution. The properties of the pore solution should be based on a 0.5 L/kg-dry extraction of crushed CSM material according to U.S. EPA Method 1316. If test samples are already mostly dried (e.g., recovered samples from relatively dry environments), the user should take advantage of that fact and porosity samples should be prepared by porewater exchange by soaking the samples in 2-propanol prior to oven-drying at a lower temperature of approximately 85 °C. The mass of 2-propanol lost to drying should be corrected to an equivalent mass of water using the ratio of water/propanol density and then corrected for pore solution properties based on the water extraction at 0.5 L/kg-dry, again, following U.S. EPA Method 1316.

Cast Stone Materials: Porosity and Relative Saturation

When CSM samples are stored under controlled relative humidity conditions, the relative saturation of the matrix (i.e., fraction of pore volume occupied by water) decreases when the relative humidity is less than 100%. Due to the hygroscopic nature of the pore solution, the moisture content of samples remains at nearly 90% even when stored at relatively low relative humidity of 68%. However, the relative saturation decreases to approximately 84% when samples are stored at low relative humidity. These observations imply that the CSM materials stored in the environment will lose moisture. Thus, CSMs will become susceptible to gaseous component penetration and reaction (e.g., oxidation and carbonation), and CSM performance will depend on the changes in material and leaching properties associated with these reactions.

6. REFERENCES

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Appendix A

Tabular Data for Relative Humidity/Relative Saturation Experiments

Cast Stone Materials: Porosity and Relative Saturation

Cast Stone Materials: Data for Relative Humidity

Drying

$$\text{Relative Saturation } \Theta = (m_{\text{sat}} - m_i) / (m_{\text{sat}} - m_{\text{dry}})$$

$$m_{\text{dry}} = m_{\text{sat}} - \eta * \rho_{\text{water}} * V_{\text{sample}}$$

	100%RH η	2-Prop η	SEM η
CSM-6	0.364	0.321	0.434
CSM-19	0.386	0.292	0.304
CSM-21	0.533	0.435	NA

"Saturated" CSM mass (M_{sat}) is actually mass equilibrated at 100% RH (pore condensation). Porosity values based on propanal saturation are from sample preparation of SEM samples (November 3, 2015). SEM porosity based on modified method of Scrivener K.L., HH Patel, PL Pratt and LJ Parrott, *Materials Research Society Proceedings*, 85, 1986.

Porosity Based on Water-saturation

Drying @ 82% RH (KBr)

Time (days)	Relative Saturation, Θ (%) as a Function of Time																Ave Θ_{eq}
	0	1	2	3	6	8	10	13	15	17	20	22	24	27	29	31	
CSM-6-A (82% RH)	1.00	0.97	0.95	0.93	0.92	0.92	0.91	0.91	0.91	0.91	0.90	0.90	0.90	0.89	0.90	0.90	0.89
CSM-6-B (82% RH)	1.00	0.92	0.92	0.91	0.90	0.90	0.90	0.90	0.90	0.90	0.89	0.89	0.89	0.89	0.89	0.89	0.89
CSM-19-A (82% RH)	1.00	0.97	0.98	0.96	0.96	0.96	0.95	0.95	0.95	0.95	0.95	0.94	0.94	0.94	0.94	0.94	0.94
CSM-19-B (82% RH)	1.00	0.96	0.96	0.95	0.94	0.94	0.94	0.94	0.94	0.94	0.93	0.93	0.94	0.93	0.93	0.93	0.93
CSM-21-A (82% RH)	1.00	0.96	0.94	0.93	0.92	0.92	0.92	0.92	0.92	0.91	0.91	0.91	0.91	0.91	0.91	0.91	0.91

Drying @ 68% RH (NaNO2)

Time (days)	Relative Saturation, Θ (%) as a Function of Time																Ave Θ_{eq}
	0	1	2	3	6	8	10	13	15	17	20	22	24	27	29	31	
CSM-6-A (68% RH)	1.00	0.98	0.96	0.94	0.93	0.93	0.92	0.92	0.92	0.92	0.91	0.91	0.91	0.91	0.90	0.91	0.90
CSM-6-B (68% RH)	1.00	0.95	0.93	0.92	0.91	0.91	0.90	0.90	0.90	0.89	0.90	0.89	0.89	0.89	0.89	0.89	0.89
CSM-19-A (68% RH)	1.00	0.96	0.96	0.96	0.95	0.95	0.94	0.94	0.94	0.94	0.94	0.94	0.94	0.94	0.94	0.94	0.94
CSM-19-B (68% RH)	1.00	0.98	0.97	0.97	0.96	0.96	0.95	0.95	0.95	0.95	0.95	0.94	0.94	0.94	0.94	0.94	0.94
CSM-21-A (68% RH)	1.00	0.96	0.96	0.93	0.91	0.91	0.91	0.91	0.91	0.90	0.90	0.90	0.90	0.90	0.90	0.90	0.90

Drying @ 33% RH (MgCl2)

Time (days)	Relative Saturation, Θ (%) as a Function of Time																Ave Θ_{eq}
	0	1	2	3	6	8	10	13	15	17	20	22	24	27	29	31	
CSM-6-A (33% RH)	1.00	0.92	0.93	0.90	0.87	0.86	0.85	0.85	0.84	0.84	0.83	0.83	0.82	0.82	0.82	0.82	0.84
CSM-6-B (33% RH)	1.00	0.93	0.92	0.90	0.89	0.88	0.87	0.86	0.86	0.85	0.85	0.85	0.85	0.85	0.85	0.85	0.85
CSM-19-A (33% RH)	1.00	0.96	0.94	0.94	0.92	0.92	0.91	0.91	0.91	0.90	0.89	0.89	0.90	0.89	0.89	0.89	0.89
CSM-19-B (33% RH)	1.00	0.96	0.94	0.94	0.93	0.92	0.91	0.91	0.91	0.90	0.89	0.90	0.90	0.89	0.89	0.89	0.89
CSM-21-A (33% RH)	1.00	0.94	0.91	0.90	0.87	0.86	0.86	0.85	0.85	0.84	0.84	0.84	0.84	0.84	0.84	0.84	0.83

Cast Stone Materials: Porosity and Relative Saturation

Cast Stone Materials: Data for Relative Humidity

Drying

$$\text{Relative Saturation } \Theta = (m_{\text{sat}} - m_t) / (m_{\text{sat}} - m_{\text{dry}})$$

$$m_{\text{dry}} = m_{\text{sat}} - \eta * \rho_{\text{water}} * V_{\text{sample}}$$

	100%RH η	2-Prop η	SEM η
CSM-6	0.364	0.321	0.434
CSM-19	0.386	0.292	0.304
CSM-21	0.533	0.435	NA

"Saturated" CSM mass (M_{sat}) is actually mass equilibrated at 100% RH (pore condensation). Porosity values based on propanol saturation are from sample preparation of SEM samples (November 3, 2015). SEM porosity based on modified method of Scrivener K.L., HH Patel, PL Pratt and LJ Parrott, *Materials Research Society Proceedings*, 85, 1986.

Porosity Based on Propanol-saturation

Drying @ 82% RH (KBr)

Time (days)	Relative Saturation, Θ (%) as a Function of Time																Ave Θ_{eq}
	0	1	2	3	6	8	10	13	15	17	20	22	24	27	29	31	
CSM-6-A (82% RH)	1.00	0.96	0.94	0.93	0.91	0.91	0.90	0.90	0.90	0.89	0.89	0.89	0.89	0.88	0.89	0.89	0.88
CSM-6-B (82% RH)	1.00	0.91	0.91	0.90	0.89	0.89	0.89	0.88	0.88	0.88	0.88	0.87	0.87	0.87	0.87	0.87	0.87
CSM-19-A (82% RH)	1.00	0.96	0.97	0.95	0.95	0.94	0.94	0.94	0.94	0.93	0.93	0.93	0.93	0.93	0.92	0.92	0.91
CSM-19-B (82% RH)	1.00	0.95	0.94	0.94	0.93	0.92	0.92	0.92	0.91	0.91	0.91	0.91	0.91	0.91	0.91	0.91	0.91
CSM-21-A (82% RH)	1.00	0.95	0.93	0.91	0.91	0.91	0.90	0.90	0.90	0.89	0.89	0.89	0.89	0.89	0.89	0.89	0.89

Drying @ 68% RH (NaNO2)

Time (days)	Relative Saturation, Θ (%) as a Function of Time																Ave Θ_{eq}
	0	1	2	3	6	8	10	13	15	17	20	22	24	27	29	31	
CSM-6-A (68% RH)	1.00	0.98	0.96	0.93	0.92	0.93	0.91	0.91	0.91	0.91	0.89	0.90	0.90	0.90	0.89	0.89	0.89
CSM-6-B (68% RH)	1.00	0.94	0.92	0.91	0.90	0.89	0.89	0.89	0.89	0.88	0.88	0.88	0.88	0.87	0.88	0.88	0.88
CSM-19-A (68% RH)	1.00	0.95	0.95	0.94	0.94	0.93	0.93	0.92	0.92	0.92	0.92	0.92	0.93	0.92	0.92	0.92	0.92
CSM-19-B (68% RH)	1.00	0.97	0.96	0.96	0.94	0.94	0.94	0.94	0.94	0.93	0.93	0.93	0.93	0.92	0.92	0.92	0.92
CSM-21-A (68% RH)	1.00	0.95	0.95	0.92	0.89	0.89	0.89	0.89	0.89	0.88	0.88	0.87	0.88	0.88	0.88	0.88	0.88

Drying @ 33% RH (MgCl2)

Time (days)	Relative Saturation, Θ (%) as a Function of Time																Ave Θ_{eq}
	0	1	2	3	6	8	10	13	15	17	20	22	24	27	29	31	
CSM-6-A (33% RH)	1.00	0.91	0.92	0.88	0.85	0.84	0.83	0.82	0.81	0.81	0.81	0.80	0.80	0.80	0.80	0.80	0.81
CSM-6-B (33% RH)	1.00	0.93	0.91	0.89	0.88	0.86	0.85	0.84	0.84	0.83	0.83	0.83	0.83	0.82	0.82	0.82	0.82
CSM-19-A (33% RH)	1.00	0.95	0.93	0.92	0.90	0.89	0.88	0.88	0.88	0.86	0.86	0.86	0.86	0.85	0.85	0.85	0.85
CSM-19-B (33% RH)	1.00	0.94	0.92	0.91	0.90	0.89	0.88	0.88	0.88	0.86	0.86	0.86	0.86	0.85	0.85	0.85	0.85
CSM-21-A (33% RH)	1.00	0.93	0.89	0.87	0.84	0.83	0.82	0.82	0.82	0.81	0.80	0.80	0.81	0.80	0.80	0.80	0.80

Cast Stone Materials: Porosity and Relative Saturation

Cast Stone Materials: Data for Relative Humidity

Pore Condensation

$$\text{Relative Saturation } \Theta = (m_{\text{sat}} - m_t) / (m_{\text{sat}} - m_{\text{dry}})$$

$$m_{\text{dry}} = m_{\text{sat}} - \eta * \rho_{\text{water}} * V_{\text{sample}}$$

	100%RH	2-Prop	SEM
	η	η	η
CSM-6	0.364	0.321	0.434
CSM-19	0.386	0.292	0.304
CSM-21	0.533	0.435	NA

"Saturated" CSM mass (M_{sat}) is actually mass equilibrated at 100% RH (pore condensation). Porosity values based on propanol saturation are from sample preparation of SEM samples (November 3, 2015). SEM porosity based on modified method of Scrivener K.L., HH Patel, PL Pratt and LJ Parrott, *Materials Research*

Porosity Based on Water-saturation

Pore Condensation from 82% RH

Time (days)	Relative Saturation, Θ (%) as a Function of Time															Ave Θ_{eq}	
	0	1	2	4	6	8	10	14	16	19	22	25	29	31	33		
CSM-6-A (82% RH)	0.91	0.97	0.98	0.98	0.98	0.98	0.97	0.96	0.97	0.97	0.96	0.96	0.96	0.96	0.96	0.96	0.95
CSM-6-B (82% RH)	0.89	0.96	0.97	0.97	0.96	0.96	0.96	0.96	0.96	0.95	0.96	0.94	0.94	0.94	0.94	0.94	0.94
CSM-19-A (82% RH)	0.94	0.98	0.98	0.98	0.98	0.98	0.98	0.97	0.97	0.97	0.97	0.96	0.96	0.96	0.96	0.96	0.96
CSM-19-B (82% RH)	0.93	0.97	0.97	0.98	0.97	0.97	0.97	0.97	0.97	0.97	0.97	0.96	0.96	0.96	0.96	0.96	0.96
CSM-21-A (82% RH)	0.91	0.99	0.98	0.97	0.97	0.97	0.97	0.96	0.96	0.96	0.96	0.96	0.96	0.96	0.96	0.96	0.96

Pore Condensation from 68% RH

Time (days)	Relative Saturation, Θ (%) as a Function of Time															Ave Θ_{eq}	
	0	1	2	4	6	8	10	14	16	19	22	25	29	31	33		
CSM-6-A (68% RH)	0.91	1.01	1.02	1.01	1.01	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.97
CSM-6-B (68% RH)	0.89	0.96	0.97	0.97	0.97	0.97	0.97	0.96	0.96	0.96	0.96	0.95	0.95	0.95	0.95	0.95	0.95
CSM-19-A (68% RH)	0.94	0.97	0.97	0.98	0.97	0.98	0.98	0.97	0.96	0.96	0.96	0.95	0.95	0.95	0.95	0.95	0.96
CSM-19-B (68% RH)	0.94	0.98	0.99	0.99	0.98	1.00	0.99	0.98	0.98	0.98	0.98	0.97	0.96	0.96	0.96	0.96	0.96
CSM-21-A (68% RH)	0.90	0.98	0.98	0.97	0.97	0.97	0.96	0.96	0.96	0.96	0.95	0.95	0.95	0.95	0.95	0.95	0.95

Pore Condensation from 33% RH

Time (days)	Relative Saturation, Θ (%) as a Function of Time															Ave Θ_{eq}	
	0	1	2	4	6	8	10	14	16	19	22	25	29	31	33		
CSM-6-A (33% RH)	0.82	0.88	0.89	0.91	0.90	0.90	0.89	0.89	0.89	0.89	0.89	0.89	0.88	0.88	0.88	0.88	0.91
CSM-6-B (33% RH)	0.85	0.94	0.95	0.95	0.95	0.94	0.94	0.94	0.94	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.95
CSM-19-A (33% RH)	0.88	0.95	0.96	0.95	0.95	0.94	0.94	0.94	0.94	0.94	0.94	0.94	0.94	0.94	0.94	0.94	0.94
CSM-19-B (33% RH)	0.88	0.95	0.96	0.96	0.95	0.95	0.95	0.95	0.94	0.94	0.94	0.94	0.94	0.94	0.94	0.94	0.94
CSM-21-A (33% RH)	0.84	0.95	0.95	0.94	0.93	0.93	0.93	0.93	0.93	0.93	0.93	0.93	0.93	0.93	0.93	0.93	0.93

Cast Stone Materials: Porosity and Relative Saturation

Cast Stone Materials: Data for Relative Humidity

Pore Condensation

$$\Theta = (m_{\text{sat}} - m_t) / (m_{\text{sat}} - m_{\text{dry}})$$

$$m_{\text{dry}} = m_{\text{sat}} - \eta * \rho_{\text{water}} * V_{\text{sample}}$$

	100%RH	2-Prop	SEM
	η	η	η
CSM-6	0.364	0.321	0.434
CSM-19	0.386	0.292	0.304
CSM-21	0.533	0.435	NA

"Saturated" CSM mass (M_{sat}) is actually mass equilibrated at 100% RH (pore condensation). Porosity values based on propanol saturation are from sample preparation of SEM samples (November 3, 2015). SEM porosity based on modified method of Scrivener K.L., HH Patel, PL Pratt and LJ Parrott, *Materials Research Society Proceedings*, 85, 1986.

Porosity Based on Propanol-saturation

Pore Condensation from 82% RH

Time (days)	Relative Saturation, Θ (%) as a Function of Time															Ave Θ_{eq}
	0	1	2	4	6	8	10	14	16	19	22	25	29	31	33	
CSM-6-A (82% RH)	0.89	0.97	0.97	0.98	0.98	0.98	0.96	0.96	0.96	0.96	0.96	0.95	0.95	0.95	0.95	0.94
CSM-6-B (82% RH)	0.87	0.96	0.96	0.96	0.96	0.96	0.95	0.95	0.95	0.95	0.95	0.93	0.93	0.93	0.93	0.93
CSM-19-A (82% RH)	0.93	0.97	0.97	0.98	0.97	0.98	0.97	0.97	0.97	0.96	0.96	0.95	0.95	0.95	0.95	0.95
CSM-19-B (82% RH)	0.91	0.96	0.97	0.97	0.97	0.97	0.97	0.97	0.96	0.96	0.96	0.95	0.95	0.95	0.95	0.95
CSM-21-A (82% RH)	0.89	0.99	0.98	0.97	0.97	0.97	0.97	0.96	0.96	0.95	0.95	0.95	0.95	0.95	0.95	0.95

Pore Condensation from 68% RH

Time (days)	Relative Saturation, Θ (%) as a Function of Time															Ave Θ_{eq}
	0	1	2	4	6	8	10	14	16	19	22	25	29	31	33	
CSM-6-A (68% RH)	0.90	1.01	1.02	1.02	1.01	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.97
CSM-6-B (68% RH)	0.88	0.95	0.97	0.97	0.96	0.96	0.96	0.96	0.95	0.95	0.95	0.94	0.94	0.94	0.94	0.94
CSM-19-A (68% RH)	0.92	0.97	0.97	0.97	0.96	0.98	0.97	0.96	0.95	0.95	0.94	0.94	0.93	0.93	0.93	0.94
CSM-19-B (68% RH)	0.92	0.97	0.98	0.99	0.98	1.00	0.98	0.97	0.97	0.97	0.97	0.96	0.95	0.95	0.95	0.95
CSM-21-A (68% RH)	0.88	0.97	0.97	0.96	0.96	0.96	0.96	0.95	0.95	0.95	0.94	0.94	0.94	0.94	0.94	0.94

Pore Condensation from 33% RH

Time (days)	Relative Saturation, Θ (%) as a Function of Time															Ave Θ_{eq}
	0	1	2	4	6	8	10	14	16	19	22	25	29	31	33	
CSM-6-A (33% RH)	0.80	0.86	0.88	0.89	0.89	0.88	0.89	0.88	0.88	0.88	0.88	0.87	0.87	0.87	0.87	0.90
CSM-6-B (33% RH)	0.83	0.93	0.94	0.94	0.94	0.93	0.93	0.93	0.93	0.94	0.94	0.94	0.94	0.94	0.94	0.94
CSM-19-A (33% RH)	0.85	0.94	0.94	0.94	0.93	0.93	0.93	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.93
CSM-19-B (33% RH)	0.85	0.94	0.95	0.94	0.94	0.94	0.94	0.94	0.93	0.93	0.93	0.93	0.93	0.93	0.93	0.93
CSM-21-A (33% RH)	0.80	0.94	0.93	0.93	0.92	0.91	0.91	0.91	0.91	0.91	0.91	0.91	0.91	0.91	0.91	0.91

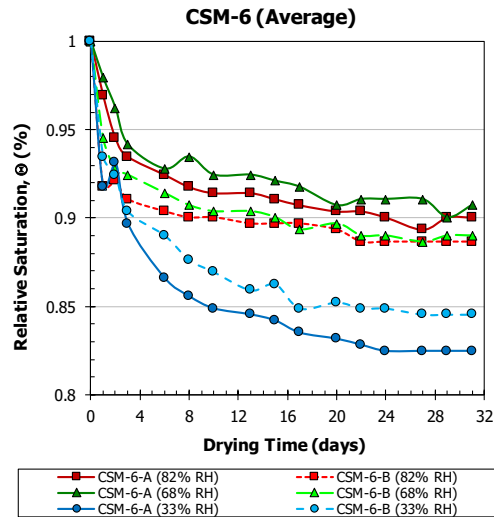
Appendix B

Graphical Data for Relative Humidity/Relative Saturation Experiments

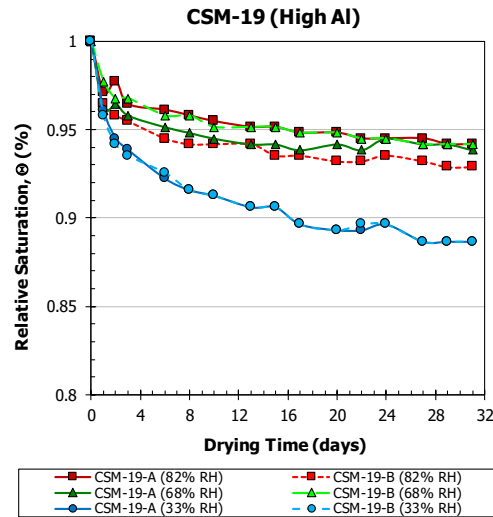
Cast Stone Materials: Porosity and Relative Saturation

Porosity Based on 100% RH Equilibration

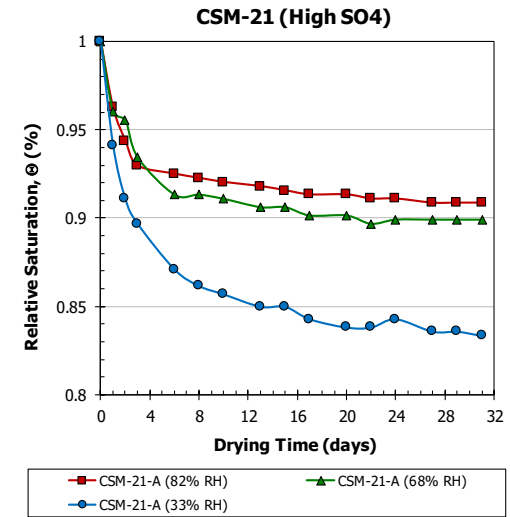
Cast Stone Material: Control



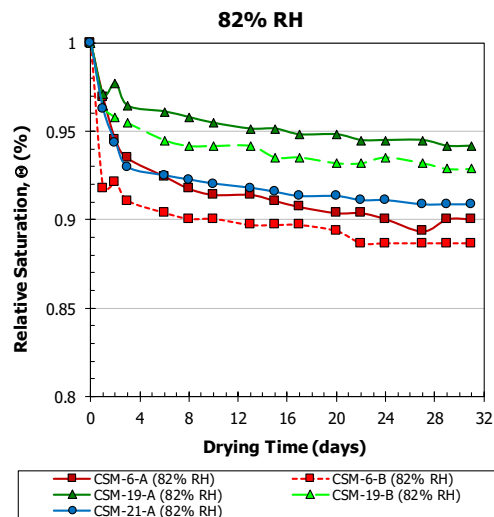
Cast Stone Material: High Al



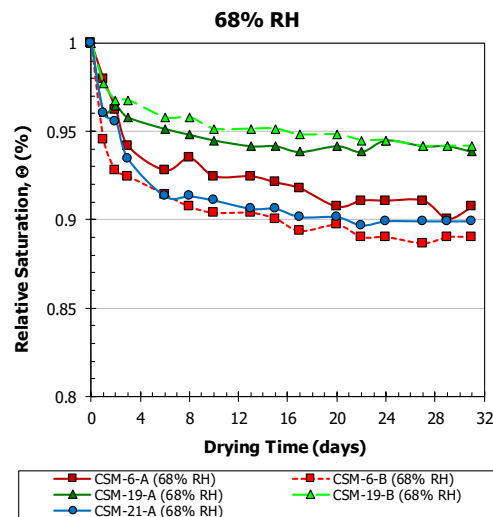
Cast Stone Material: High S



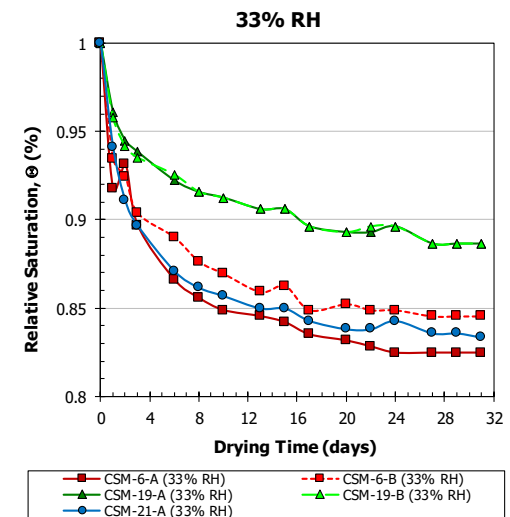
Cast Stone Material: 82% RH



Cast Stone Material: 68% RH



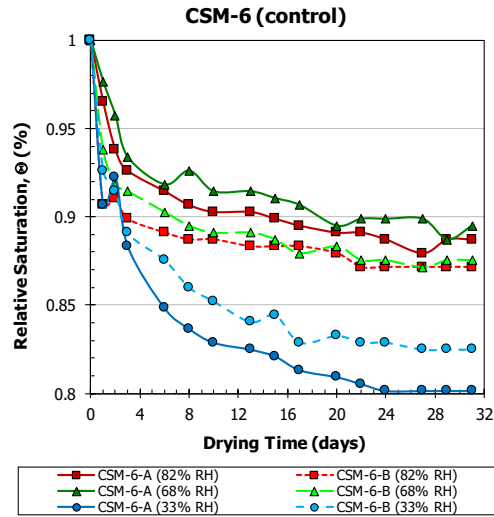
Cast Stone Material: 33% RH



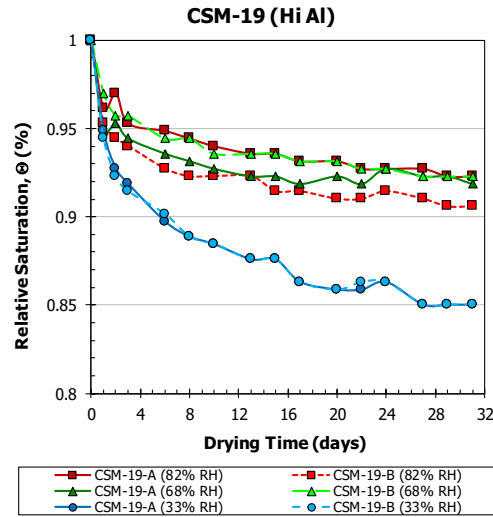
Cast Stone Materials: Porosity and Relative Saturation

Porosity Based on Propanol Saturation

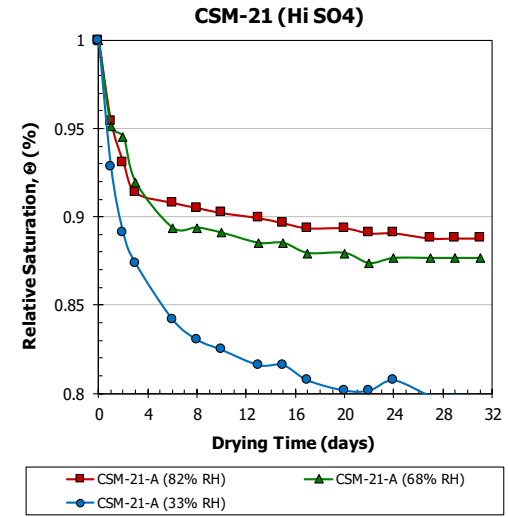
Cast Stone Material: Control



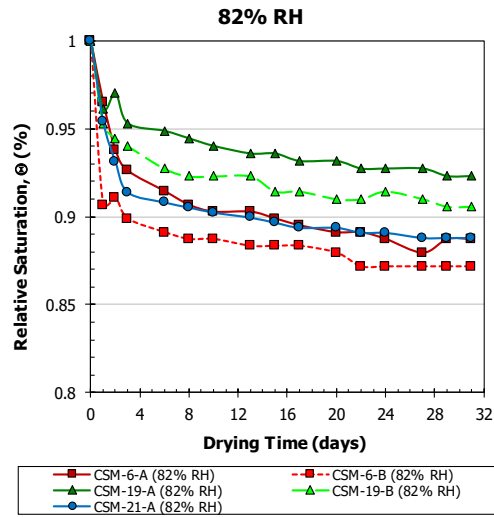
Cast Stone Material: High Al



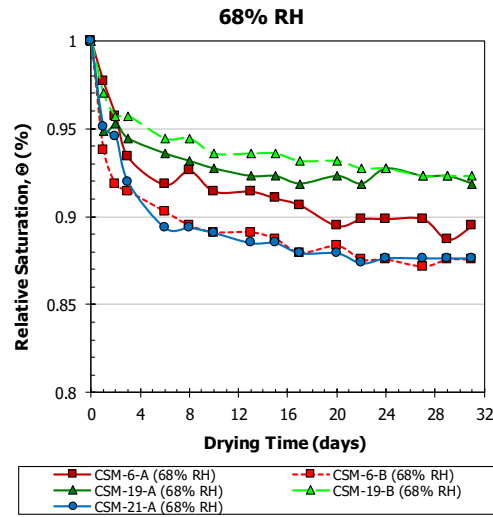
Cast Stone Material: High S



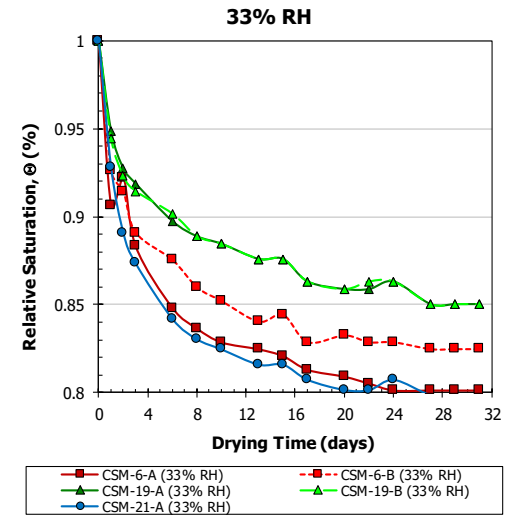
Cast Stone Material: 82% RH



Cast Stone Material: 68% RH



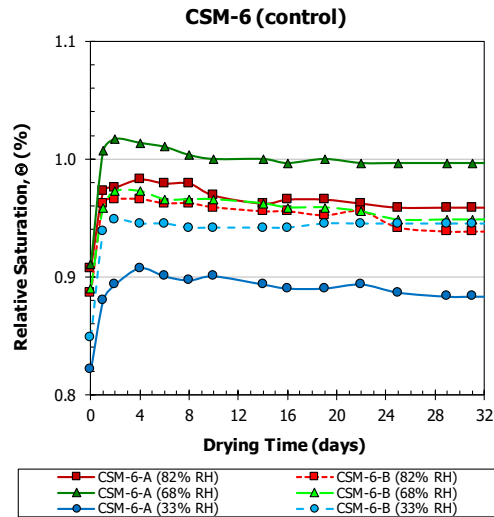
Cast Stone Material: 33% RH



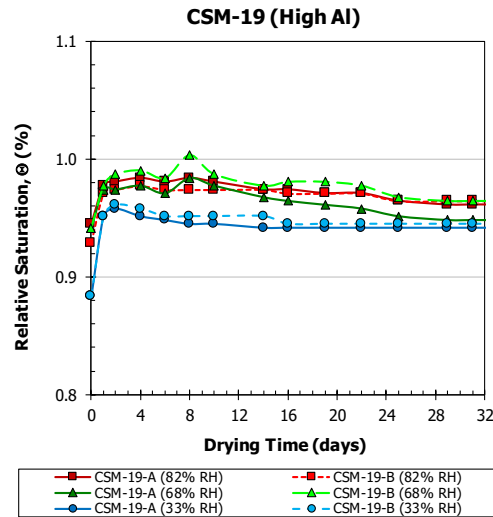
Cast Stone Materials: Porosity and Relative Saturation

Porosity Based on 100% RH Equilibration

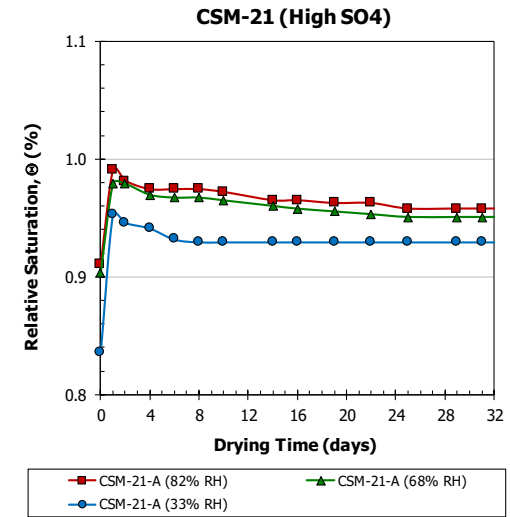
Cast Stone Material: Control



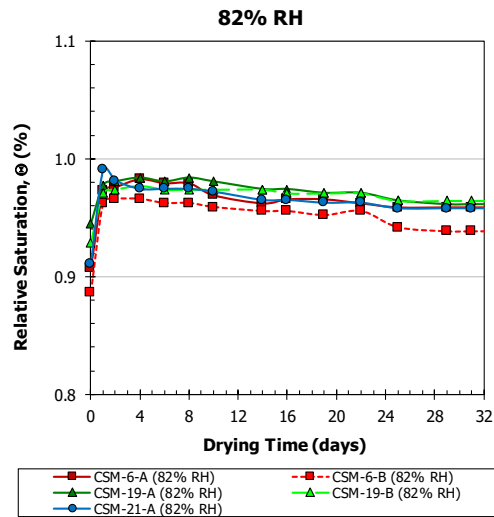
Cast Stone Material: High Al



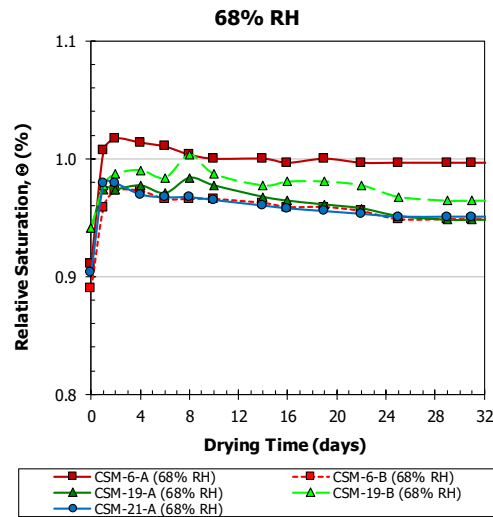
Cast Stone Material: High S



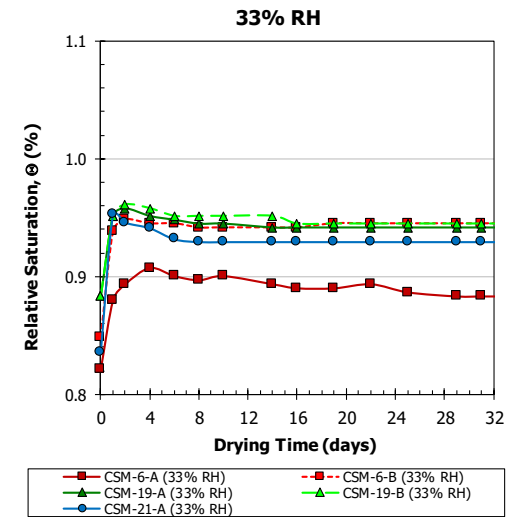
Cast Stone Material: 82% RH



Cast Stone Material: 68% RH



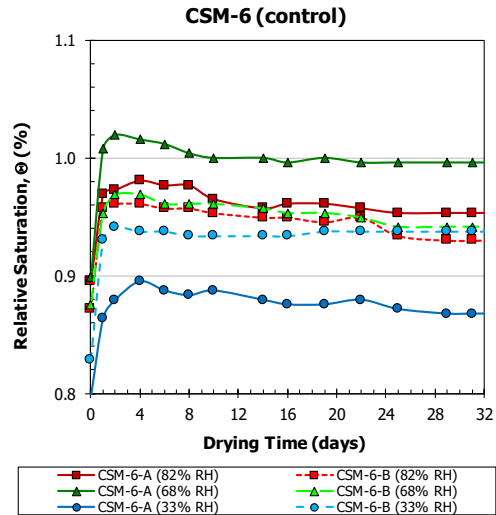
Cast Stone Material: 33% RH



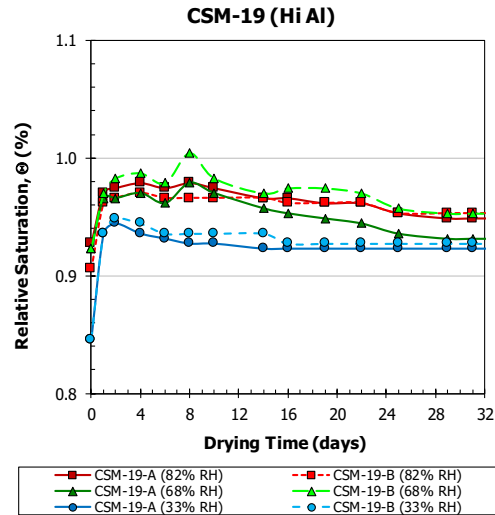
Cast Stone Materials: Porosity and Relative Saturation

Porosity Based on Propanol Saturation

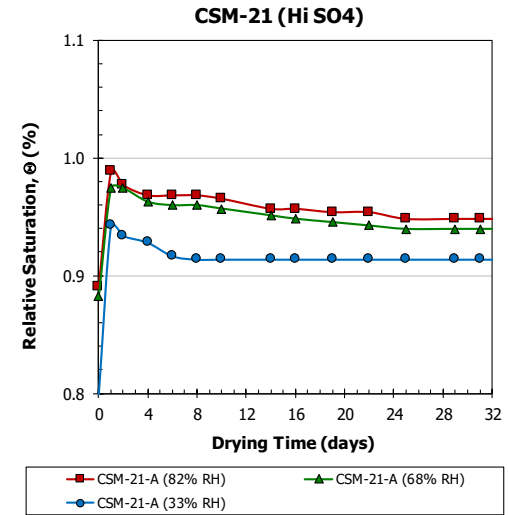
Cast Stone Material: Control



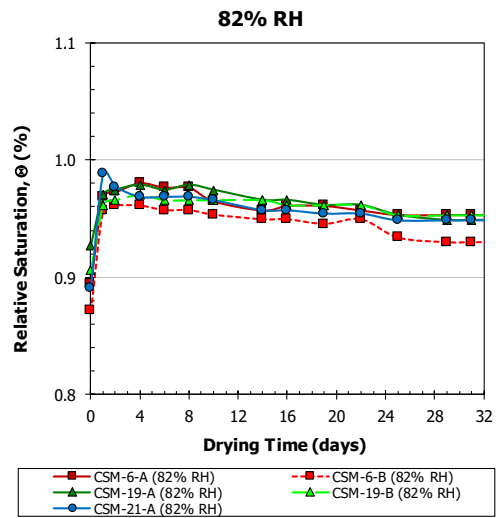
Cast Stone Material: High Al



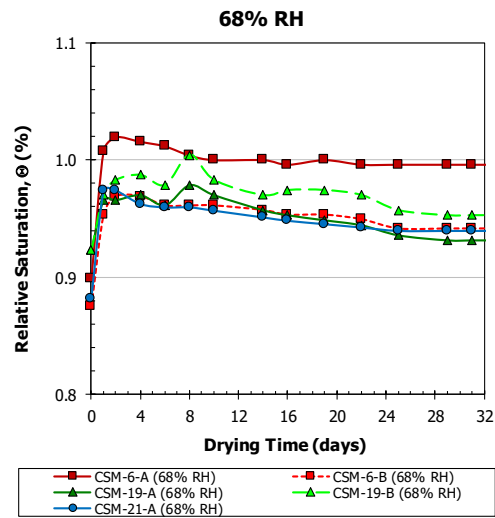
Cast Stone Material: High S



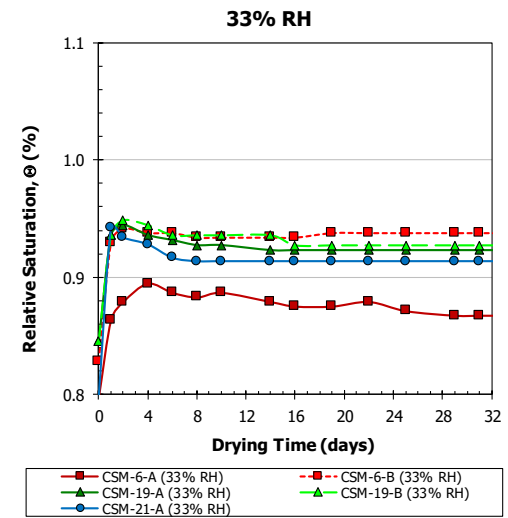
Cast Stone Material: 82% RH



Cast Stone Material: 68% RH

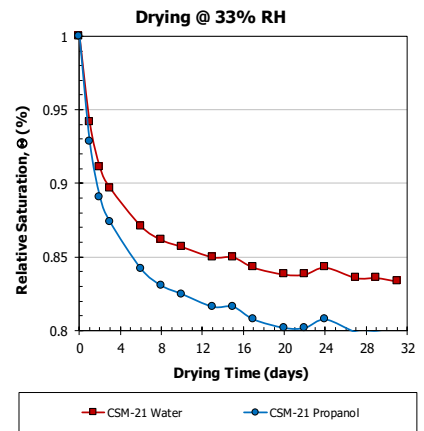
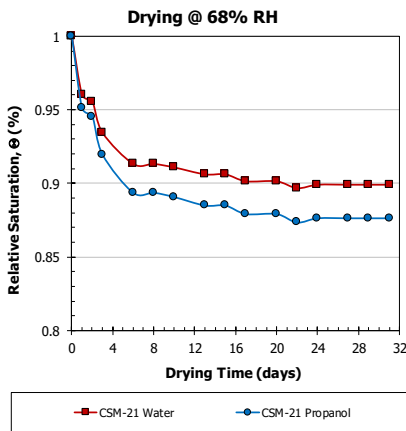
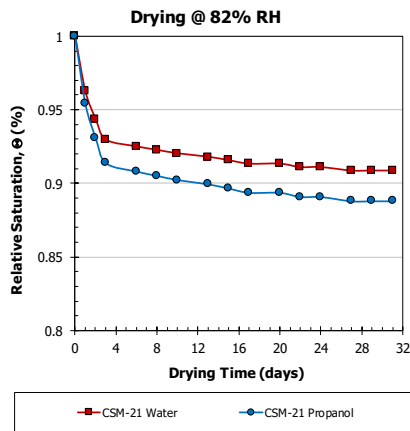
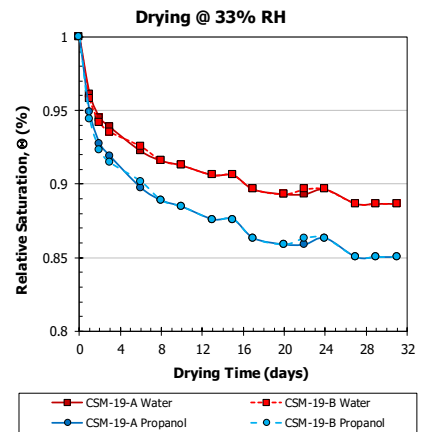
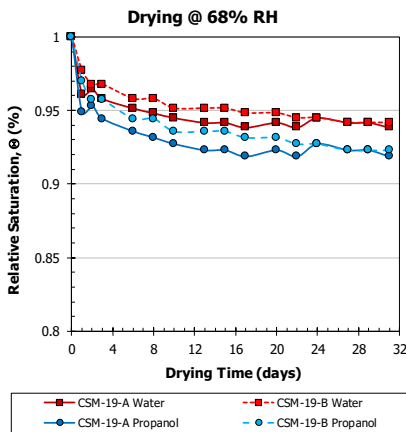
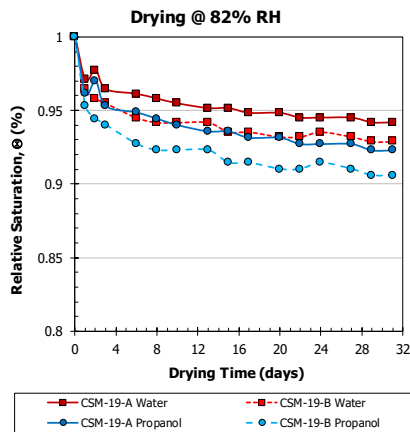
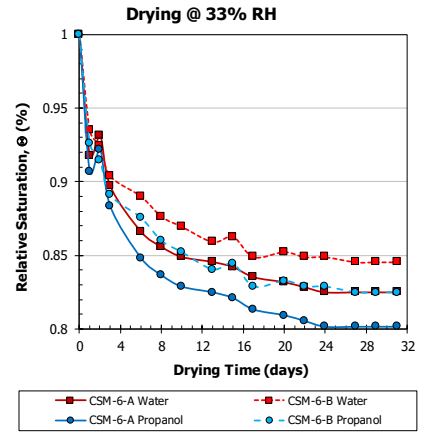
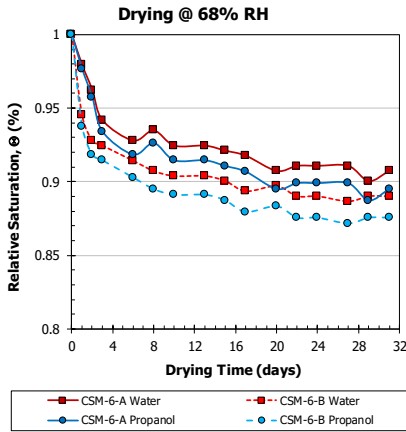
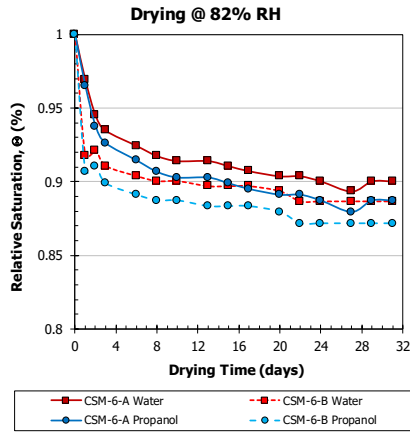


Cast Stone Material: 33% RH



Cast Stone Materials: Porosity and Relative Saturation

Comparison of Drying for 100% RH and Propanol-based Porosity



Cast Stone Materials: Porosity and Relative Saturation

Comparison of Pore Condensation for 100% RH and Propanol-based Porosity

