

Feasibility Study of Prompt Gamma Neutron Activation for NDT Measurement of Moisture in Stone and Brick

R.A. Livingston^a, M. Al-Sheikhly^a, C. Grissom^b, E. Aloiz^b and R. Paul^c

^a Materials Science & Engineering Dept., U. of Maryland, College Park MD 20742, USA

^b Museum Conservation Institute, Smithsonian Institution, Washington DC 20746, USA

^c Chemical Sciences Division, NIST, Gaithersburg MD 20899, USA

Abstract. The deterioration of stone and brick architecture or sculpture often involves damage caused by moisture. The feasibility of a non-destructive testing (NDT) method based on prompt gamma neutron activation (PGNA) for measuring the element hydrogen as an indication of water is being evaluated. This includes systematic characterization of the lithology and physical properties of seven building stones and one brick type used in the buildings of the Smithsonian Institution in Washington, D.C. To determine the required dynamic range of the NDT method, moisture-related properties were measured by standard methods. Cold neutron PGNA was also used to determine chemically bound water (CBW) content. The CBW does not damage porous masonry, but creates an H background that defines the minimum level of detection of damaging moisture. The CBW was on the order of 0.5 % by mass for all the stones. This rules out the measurement of hygric processes in all of the stones and hygric processes for the stones with fine scale pore-size distributions. The upper bound of moisture content, set by porosity through water immersion, was on the order of 5 %. The dynamic range is about 10-20. The H count rates were roughly 1-3 cps. Taking into account differences in neutron energies and fluxes and sample volume between cold PGNA and a portable PGNA instrument, it appears that it is feasible to apply PGNA in the field.

INTRODUCTION

Moisture can cause damage to works of art or architecture made of stone through a number of mechanisms such as direct chemical reaction, formation of expansive hydrous phases or freeze-thaw cycles [1]. For example, the weathering of the stone of the Sphinx is caused mainly by its sodium chloride content, which can deliquesce and recrystallize in response to atmospheric moisture cycles [2]. In order to develop effective conservation interventions, it is thus necessary to understand the source of the moisture and also the mechanisms by which it causes damage. This requires measurement of the moisture in the material and its spatial and temporal variations. However, nondestructive methods for measuring moisture within an object or structure based on electromagnetic techniques can be inaccurate and/or lacking in depth range [3]. The University of Maryland (UMD) and the Museum Conservation Institute (MCI) of the Smithsonian Institution are collaborating on a project to develop a nondestructive test method for measurement of moisture in stone using prompt gamma neutron activation (PGNA) to measure hydrogen (H). The proposed PGNA method is a second-generation system using an innovative electronic collimator with a portable neutron generator (see Fig. 1) [4].

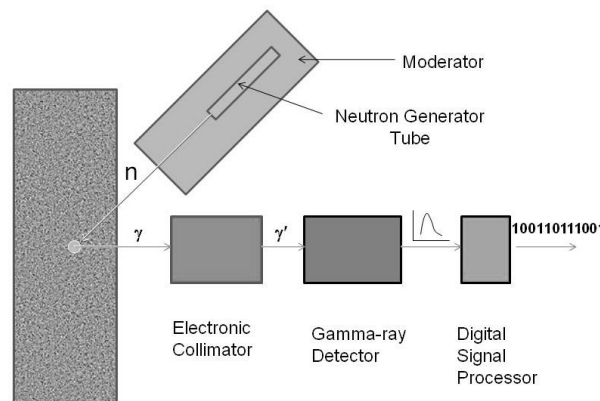


FIGURE 1. Schematic diagram of PGNA system for measuring moisture

The implementation of the PGNA system as a **non-destructive testing (NDT)** method involves the development of a calibration function. This in turn requires calibration specimens with known amounts of H. Since PGNA is an elemental analysis method that interacts only with the nucleus of an atom and not with the surrounding electron cloud, it is insensitive to the chemical state of the atom. Consequently, the calibration specimen does not have to replicate the actual mineralogy of the stone, just the number densities of the constituent elements. The specimen can thus be made of mixtures of powders of chemical compounds, typically oxides, in the correct proportions [5]. To avoid the difficulties of dealing with liquid water, the moisture content can be simulated by a solid containing H such as polyethylene or urea. The specification of the calibration specimens then raises a number of issues including dynamic range, minimum level of detection and the number of simulated stone types.

The dynamic range in this case is ratio of the maximum expected value of the water concentration over the minimum **detectable** concentration. The minimum level of detection (MLD) is set by the H background. Finally the number of simulated stone types is determined by the variation in neutron transport properties as a function of the significant differences in the elemental composition of the stone types.

Specifying the dynamic range and MLD is complicated by the fact that the PGNA method measures total H, but the water in the stone can be found in several different states: free, capillary, adsorbed and chemically bound. Free water is found in saturated pores > 100 nm. Below this size, capillary effects become significant and water vapor can condense. This is a function of the RH as shown in Fig. 2.

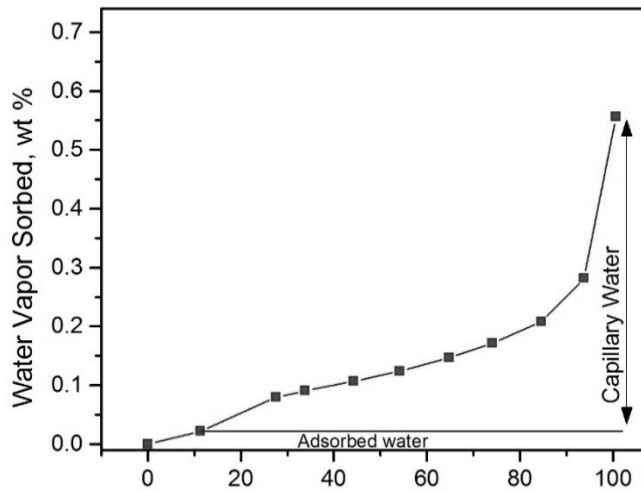


FIGURE 2. Moisture adsorption isotherm for Seneca sandstone

The relationship between RH and pore size, the adsorption isotherm, is given by the Kelvin-Thomson Equation:

$$\ln(RH) = \frac{2\sigma M_w}{r\rho_w RT}$$

where σ = air/water surface tension ; M_w = water mol. wt.; ρ_w = water density; r = pore radius; R = Universal Gas Constant and T = temperature, K. Since σ , M_w , and ρ_w are all properties of water, and not the stone, the adsorption isotherm essentially **represents** the stone's pore size distribution (PSD) multiplied by a known constant.

Adsorbed water is found on surfaces of fine pores measuring < 5 nm in diameter. As shown in Fig. 2, this water remains in the pores at an RH of 10 %. Since this low level of humidity is rarely reached in the ambient environment, this water is essentially nonevaporable. The evaporable water constituents, both bulk and capillary water, are mobile, moving through the stone by capillary attraction or concentration gradients. These are the primary agents of stone deterioration. Finally, the chemically bound water (CBW) includes water of hydration, interstitial water and the OH ion in crystal structures. This state of water does not cause damage but provides an H background that defines the **MLD** of evaporable water by PGNA.

There are also several categories of moisture deposition processes. Deposition in the liquid form, or "hygric" deposition, can occur through precipitation, flooding and leaking piping. It has the potential to completely saturate the pore space in the material [6]. Deposition of moisture from water vapor, or "hygric" deposition, occurs through capillary condensation as described above. This is limited to the volume of pores with radii between 5 nm and

100 nm. Finally, there are mixed deposition processes in which the source is water vapor, but potential pore spaces that could be saturated are not limited to just the capillary pores. These processes include soluble salt deliquescence as described above and psychrometric condensation, or dew formation, in which warm moist air comes in contact with stone having a temperature lower than the dew point.

Therefore, in order to get an estimate of the possible range of the values for the calibration specimens design, a systematic characterization was undertaken of the lithology and physical properties of seven representative types of building stones and a historic brick used in the monumental architecture of the Smithsonian Institution in Washington, D.C., from 1847 onward.

EXPERIMENTAL PROCEDURES

The Smithsonian building stones make up a representative sample of the American dimension stone industry with respect to style, quarrying techniques and geology: Holston marble (HM); Mt Airy granite (MG); two types of Vermont marble, Royal (RM) and Mountain White (MM); two samples of Seneca sandstone, from the Castle (CS) and DC Jail (DS); Mankato dolomite (MD); Salem limestone (SL) and historic brick from the Arts and Industries Building (AB). It was not necessary to take samples from the actual buildings, since in every case some surplus material was available for analysis. Although this collection also includes a brick, for convenience it will simply be called the Smithsonian stones in this paper.

Elemental Composition

The elemental composition of each type of stone was analyzed by Instrumental Neutron Activation Analysis (INAA) at the Missouri University Research Reactor. This detected 32 elements, but not Si, which was calculated by difference. From these data, the macroscopic thermal neutron scattering and capture cross-sections were calculated (Fig. 3). These are consistent with experimental values for whole rock specimens of limestones, marbles and sandstones measured in previous work by Czubek [7].

The macroscopic capture cross-sections, Σ_c , fall in the range of 0.65 m^{-1} to 1.04 m^{-1} . This corresponds to a neutron mean free path of 0.96 m to 1.5 m , which is an indication of the depth of penetration of the PGNA system. The values group into two relatively tight clusters, one for the silicate stones and the other for the carbonates. This suggests that number of different types of reference stone compositions could be reduced to just two, or perhaps 3 with the brick as a special case of silicate compositions. However, for each composition there would have to be several specimens containing different levels of H.

Evaporable Water

The maximum amount of water that could be taken up by a given stone, the saturated porosity, was determined by total immersion [8], and the range of capillary water was measured by means of an adsorption isotherm [9]. The results are plotted in Fig. 4. Overall, the lowest value for the end of the capillary range, for the Vt Royal marble, is $10 \mu\text{g/g}$, and the highest value of saturated porosity, 8 % for the A&I brick. This implies an overall dynamic range

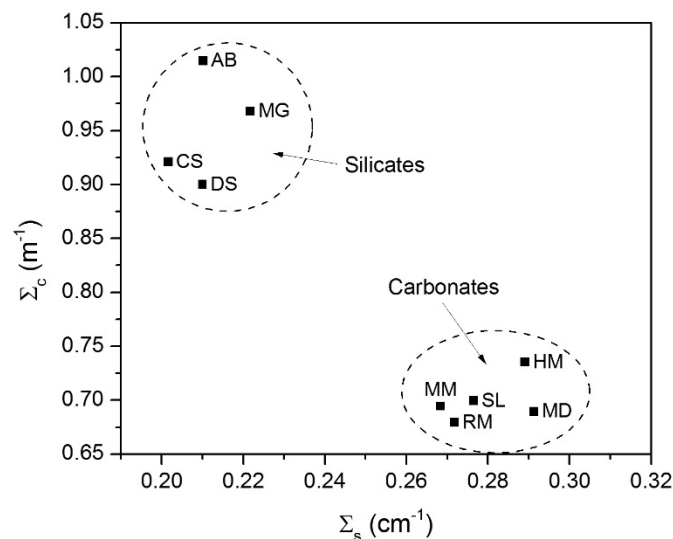


FIGURE 3. Macroscopic neutron cross-sections for Smithsonian stones

of 10^4 . However, the dynamic range for any individual stone is smaller, ranging from 184 for Seneca sandstone to 480 for Mankato dolomite.

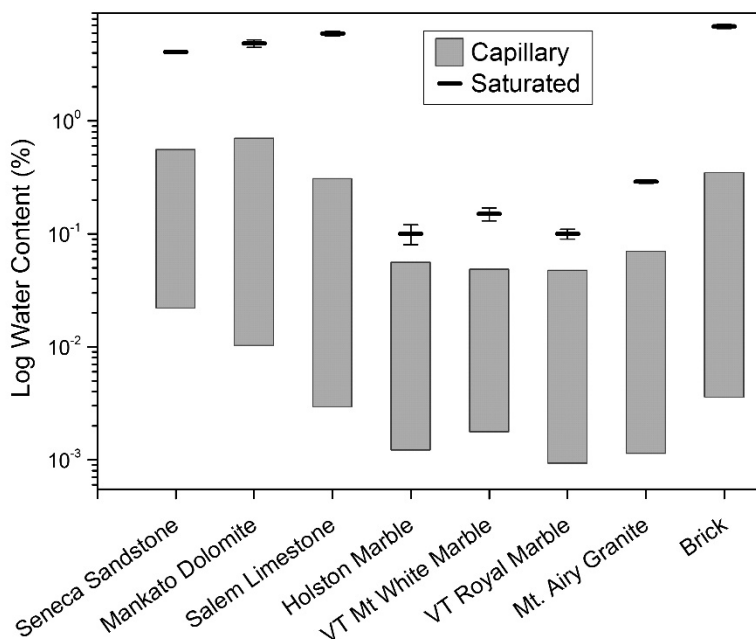


FIGURE 4. Capillary water range and saturated porosity. Precision of capillary water data is ± 0.1 mg

Chemically Bound Water

To determine the typical amounts of CBW that might be encountered, thermogravimetric analysis (TGA) was initially used. This consists of measuring the mass loss as the sample is progressively heated up to 900 °C [10]. However, there were some drawbacks to using TGA. Among them is the very small sample size, ~ 20 μg . Since several of the stones were somewhat heterogeneous, a sample this small may not be representative. This could explain the relatively large standard deviations that were observed. Also, the resolution of the instrument was limited to 0.01 % mass change, and several of the stones, e.g. Mt. Airy Granite, had CBW that were close to that limit. Finally, the TGA data can be ambiguous concerning the chemical compositions of the volatiles. The method only measures total mass loss. In some cases of the carbonate rocks, this could include CO_2 as well as H_2O . Moreover, some of the stones can contain organic matter, which can release a combination of CO_2 and H_2O upon heating. In contrast, PGNA makes direct measurement of H, down to 1 $\mu\text{g/g}$ to 10 $\mu\text{g/g}$. Moreover, it can handle larger samples, on the order of grams, which should be more representative. Therefore, it was decided to re-measure CBW in the stones using the Cold Neutron PGNA station at the National Institute of Standards and Technology (NIST).

Sample Preparation

The stone samples were crushed into powders to create a uniform particle size for PGNA analysis. The powders were placed in an oven at 65 °C and dried for 5 d to drive off evaporable water. At NIST, approximately 0.5 g of each powder was compressed into a pellet, which was then sealed in a Teflon bag. Because the brick, sandstones, dolomite, granite and Holston marble powders were found not to pelletize well, graphite was added to them before compression. Three replicates of each stone were analyzed.

In addition to the stone samples, several standards were also prepared and analyzed. The H background was analyzed with an empty Teflon bag in air or in vacuum. Since the graphite was also found to have H, a standard pellet of graphite alone was also prepared and analyzed. To compensate for variations in sample mass, geometric effects and neutron flux variations, the H peak counts were normalized by the Si peak counts or the Ca peak counts

depending on whether the sample was a silicate or a carbonate. Thus it was necessary to analyze samples of pure silica sand and precipitated calcium carbonate chalk. Finally in order to develop calibration factors, samples of silica and chalk were prepared with known amounts of H. This was provided by adding urea to the standards. Approximately 10 % urea by mass was added. Three replicates of each of these standards were also analyzed.

Irradiation

Each pellet was irradiated with cold neutrons. The thermal neutron equivalent flux was approximately $8 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$. In all, 27 samples of stone, 8 standards and 2 background samples were analyzed, generating a total of 37 spectra. The time required to collect enough counts of hydrogen for an uncertainty of under 2 % varied with each sample. At the shortest, the standards collected enough counts within an hour, while the royal marbles took over 16 h to achieve an uncertainty of 2.2 % to 2.1 %.

Data Analysis

The spectra were analyzed using the VMS peak search function of the Canberra Genie 2000 MCA software. The peak used for H was 2.222 MeV, the only one available for this element. For Si and Ca, the 3.538 MeV and the 1.942 MeV peaks respectively were used.

For calculating the H concentrations, the H count rate was first ratioed by either the Ca count rate or the Si count rate, depending on the mineralogy of the stone being measured, to correct for the effects of neutron self-shielding, scattering and fluence rate variation [11]. The formula for converting the gamma-rays counts ratio data to the H concentration in the stone is given by:

$$H = x_{Ca} b_{Ca} \frac{(\gamma_H - \gamma_{H_b})}{\gamma_{Ca}}$$

or

$$H = x_{Si} b_{Si} \frac{(\gamma_H - \gamma_{H_b})}{\gamma_{Si}}$$

where x_i is the concentration of Si or Ca in the stone, b_i is the calibration factor, γ_H is the H count rate of the sample, γ_{H_b} is the H background and γ_{Ca} and γ_{Si} are the Ca and Si count rates, respectively. The x_i can be obtained from the PGNA spectra itself, but to save time, the values determined previously by Instrumental Neutron Activation Analysis (INAA) were used instead.

The overall H background at the PGNA station was measured by counting with just an empty Teflon bag in the beam. Two measurements were made, one in air and the other in a vacuum. The mean value was $0.08629 \pm 0.002682 \text{ counts s}^{-1}$ (1s uncertainty from counting statistics). For comparison, the lowest H count rate observed for the stone samples was about 2 cps. The calibration factors, b_i , were determined by measuring the H count rates on reference samples made of mixtures of urea with either pure calcium carbonate or silica standard. However, the calculations were more complicated for the silicates, the Holston marble and the Mankato dolomite because of the addition of graphite to the samples. It was necessary to make an additional correction for the H background contributed by the graphite. To correct for this background, it was necessary to modify Eqn (2).

The H concentrations were calculated using Eqn (2 or 3) for carbonate or silicate stones respectively. The results are presented in Fig. 5. The values are relatively tightly clustered in the range of 0.13 % to 0.57 % despite the significantly different types of mineralogy involved. The values for the two samples of Seneca sandstone are essentially the same within the range of uncertainties, which indicates that this sandstone is relatively uniform in composition. The value of 0.37 % for the Salem limestone falls within the range of 0.17 % to 0.43 % for H_2O^+ previously found by the Karl Fischer analysis of Salem limestone samples by the U.S. Geological Survey [12].

DISCUSSION

The data for the various states of water are summarized in Fig. 6. For the fine porosity stones, the marbles and the Mt. Airy granite, the CBW values all plot above the others. Thus PGNA would not be effective in measuring either

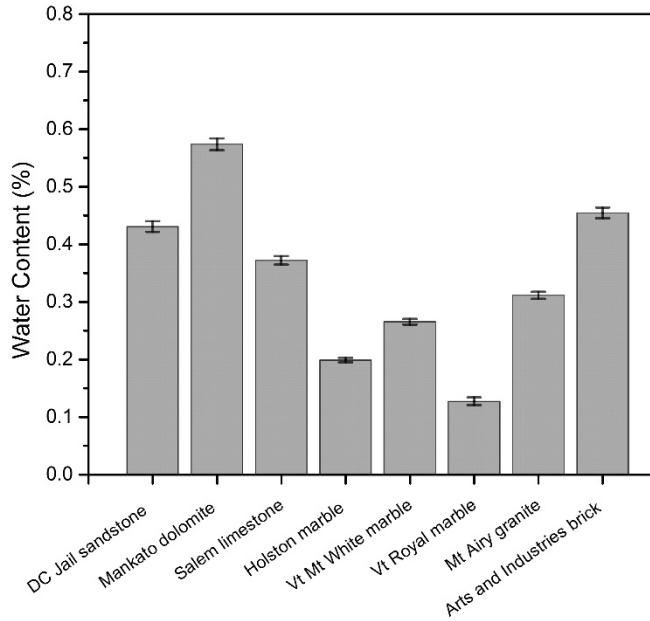


FIGURE 5. PGNA chemically bound water

the hydric or the hygric effects in these stones. For the other, coarser porosity stones, the CBW falls between the saturated pore value and the upper end of the capillary water range. Consequently, for these stones it also would not be possible to measure hygric effects, but it would be feasible to measure hydric and mixed processes. In addition, the dynamic ranges of these stones are restricted by their CBW to 10 to 20.

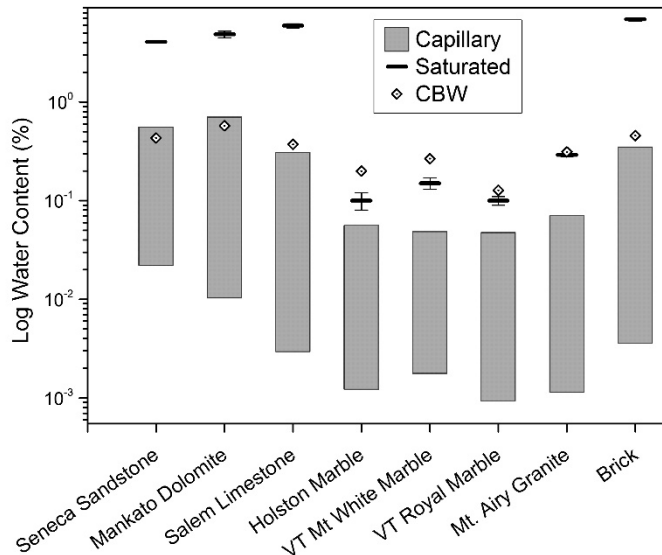


FIGURE 6: All states of water. Uncertainties for CBW are presented in Fig. 5

PROJECTED PGNA FIELD PERFORMANCE

The results of the NIST PGNA measurement of the CBW in the Smithsonian stones provide some data points that can be used to project the performance of the portable PGNA system being developed at the UMD for use in the field. Table 1 presents some PGNA parameters for the NIST CNR measurements compared to those for a field system based on a neutron generator. The H₂O concentration, 0.4 %, is taken from the Salem limestone CBW. This

would be the minimum value that would have to be detected in the field. It is the same for both cases, because it is a property of the stone, not the measurement system. On the other hand, the sample volumes differ significantly. For the CNR measurements, this was fixed by the pellet size. In the case of the field system, the volume is a function of the electronic collimator design and the details of the neutron and gamma ray transport in the material, which cannot be determined analytically. However, 1000 cm³ is a reasonable order of magnitude, based on previous work using Monte Carlo numerical simulations, which found a sample volume of 10⁵ for an uncollimated system [13]. The neutron flux also differs significantly, in the other direction. This reflects the fact that neutron sources for use in the field are limited to strengths less than about 10⁹ s⁻¹ to avoid the need for bulky and heavy shielding. The reactor-based value of 8x10⁸ n/cm²-sec is the thermal equivalent of the actual cold neutron flux. The gamma-ray detector efficiencies are the same, assuming that both measurement systems use the same design of HPGe detector. Then, for the observed H count rate of 35 cps for the reactor case, the equivalent count rate for the field system would be on the order of 1 cps. This is a reasonable rate for field measurement because it implies a data acquisition time of about 15 min to achieve 3 % uncertainty. It should also be noted that it is for the lowest expected H value. For the fully saturated Salem limestone, this would go up to about 15 cps (See Fig.6).

TABLE 1: Comparison of PGNA parameters

Parameter	Reactor, measured	Field, projected
H ₂ O concentration, %	0.4	0.4
Sample volume, cm ³	0.5	1000
Neutron flux, cm ⁻² ·s ⁻¹	8x10 ⁸	5x10 ³
Detector absolute efficiency, %	0.0268	0.0268
H Count rate, cps	35	~1

This estimate of the projected field performance does not take into account two hardware-based factors that would reduce the effective count rate. One is the H background, mainly from the hydrogenous moderator around the neutron generator. The other is the loss of detector efficiency due to the introduction of the electronic collimator. However, these can only be determined by actual measurement on a prototype PGNA system.

There are several options for dealing with these factors including increasing the sample volume by designing the electronic collimator; increasing the neutron flux by using a more advanced moderator design; and switching to a scintillator- type gamma ray detector, which would increase the efficiency but with a minor reduction in energy resolution.

CONCLUSIONS

Measurements on a collection of Smithsonian Institution building stones and brick have shown that the expected chemically bound water content is on the order of 0.5 % regardless of the stone mineralogy. This thus sets a lower limit for measurement in the field by PGNA. Consequently, PGNA would not be feasible for measuring either hygric or hydric moisture effects in materials with fine pore-size distribution. It would be feasible for measuring hydric and mixed effects in materials with coarser pores such as sedimentary rocks and brick. For these materials, the dynamic range is about 10. Only 3 types of calibration specimens are required: sandstone, carbonate and brick. The projected 1 cps H count rate for the field system is a practical value for data acquisition.

The identification of certain commercial equipment, instruments, or materials does not imply recommendation or endorsement by the National Institute of Standards and Technology. These identifications are made only in order to specify the experimental procedures in adequate detail.

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