IMPROVED NEUTRON-BASED SYSTEM FOR NDE OF SALT CONTAMINATION AND MOISTURE IN HISTORIC MASONRY

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Cycles of soluble salt deliquescence and dehydration in historic brick masonry in response to cycles of fluctuating moisture levels are known to have damaging effects over time. Nondestructive determination of the depth and degree of salt contamination and determination of moisture content in historic masonry are among some of the measurements that are needed to design appropriate remedial action. The focus of the paper is on an improved portable nondestructive evaluation system based on prompt gamma neutron activation (PGNA). The system works by irradiating a section of a structure with neutrons from a portable neutron generator. The gamma rays of characteristic energies resulting from interaction with target elements such as hydrogen, chlorine, sulfur, sodium and potassium are detected. The results can be used to map the spatial distribution of soluble salts in the structure. Several case studies and applications of the improved nondestructive evaluation system are discussed. It is concluded that the improved portable nondestructive evaluation system is a useful tool for quantitative analysis of elements associated with moisture, salt and other materials in historic masonry structures.

Keywords: Nondestructive evaluation, historic masonry, brick masonry, gamma rays, salt contamination, neutron activation

INTRODUCTION

Several investigations have shown that soluble salts are one of the most important causes of stone and masonry deterioration. The crystallization of salts from solution is one of the main mechanisms of deterioration involving loss of substance (Watt and Colston 2000). There have been many reports on loss of substance; one example is the western part of Jutland in Denmark where dust and powder fall from medieval churches have been reported for many years (Larsen and Nielsen 1990). Water soluble salts may accumulate in the pores of bricks and stones and cause deterioration. This behavior of salification has been observed in historic as well as modern brick structures (Larsen and Nielsen 1990).

Several theories for salt decay of bricks and stones have been proposed but the most widespread explanation has been based on salt crystallization theory where formation of salt crystals produces pressure in the pore walls of bricks and stones (cryptoefflorescence). The pressure due to salt crystallization is a function of the type of salt and the size and arrangement of the pores. Loss of material may take place when the pressure exceeds the
internal strength. Loss of material may also take place when fluctuating moisture levels make the salt undergo cycles of crystallization and dissolution (Watt and Colston 2000). Other theories for salt decay have also been proposed. One theory proposes a mechanism where crystals grow from coarse pores into small adjoining pores; a second theory proposes that crystal shape varies depending on the relative humidity and these changes will exert stresses on the pore walls (Larsen and Nielsen 1990). Another theory that has been proposed for deterioration of bricks is that differences in salt content and a temperature gradient through a brick can combine to produce shear forces between the exposed surface and the interior part of the brick because of differences in thermal expansion (Larsen and Nielsen 1990). In general the effects of thermal cycling, moisture cycling, temperature, and relative humidity on the salts are important in understanding the pattern of deterioration.

Franke and Schumann (1998) studied causes and mechanisms of decay of historic brick buildings in northern Germany and concluded that the main causes of deterioration are either salt or frost damage or a combination of both. They concluded that the dominant salt causing damage to outdoor brick is gypsum. The mechanism is described as follows (Franke and Schumann 1998): “The mechanism of the formation of a gypsum crust proceeds as follows: Potentially aggressive pollutants, such as SO₂, CO₂, and NOₓ, in combination with humidity are the causes for this type of deterioration. They are transported to the brick, which usually contains minerals that are acid-sensitive, like calcite or feldspar. The acid solution dissolves these minerals and transports them towards the surface, where Ca²⁺ from calcite or feldspar precipitates together with SO₄²⁻ of the sulfuric acid as gypsum. Damage to the brick occurs as soon as the outer layer of pores is filled with gypsum. The pressure due to further crystallization leads to sanding off or flaking of the outer layer. Laboratory simulations of the procedure proved that the necessary calcium is taken from the brick and the sulfate is delivered by acid deposition. The comparatively high capillarity of the brick enables a progression of the aggressive solutions towards the inner part of the brick and thus guarantees the calcium supply necessary to cause damage over time.”

Other studies on salt decay have identified sodium sulfate to be the most damaging of all the soluble salts. Sodium sulfate undergoes large amounts of volume change when hydrated, but even in cases where hydration did not take place, the resulting damage could be significant. Some studies have shown that the precipitation of the anhydrous phase, thenardite, could generate larger crystallization pressures and thus more damage than crystallization of mirabilite (Rodriguez-Navarro 2000). Other studies have presented contradictory conclusions (Rodriguez-Navarro et al. 2000); salt crystallization is a complex process and is not yet well understood (Caner-Saltik et al. 1998).

Unlike most studies on salt decay that have focused on alkali sulfates, Larson and Nielsen (1990) studied the role of sodium chloride (NaCl) in the deterioration of modern and medieval brick structures in Denmark. The authors found that NaCl constitutes the main part of water soluble salt in the medieval bricks that were investigated. Concentrations near the surface of bricks were 2 to 3 times the concentrations found in the interior. The salt was found in very small crystals in pores smaller than 15 μm. The study showed that NaCl influences the thermal expansion of modern as well as medieval bricks. NaCl of 2% by weight of brick was found to increase thermal expansion by 16%. Hygroscopic shrinkage of bricks also increases
with the amount of NaCl. The study also found that the amount of dusting and spalling appears to increase at relative humidities close to 75%, the crystallization point for NaCl.

Nondestructive determination of the depth and degree of salt contamination and determination of moisture content in historic masonry are among some of the measurements that are needed to design appropriate remedial action. The focus of this paper is on an improved portable nondestructive evaluation system based on prompt gamma neutron activation (PGNA). The system works by irradiating a section of a structure with neutrons from a portable neutron generator. The gamma rays of characteristic energies resulting from interaction with target elements such as hydrogen, chlorine, sulphur, sodium and potassium are detected. The results can be used to map the spatial distribution of soluble salts in the structure.

FIRST GENERATION NEUTRON-BASED SYSTEM
A portable system for detecting chlorides in concrete has been previously developed using prompt gamma neutron activation (PGNA) based on a $^{252}$Cf neutron source (Livingston & Saleh 1998; Saleh & Livingston 2000). In PGNA, neutrons are captured by nuclei in the target and gamma-rays of characteristic energy are emitted. A number of elements can be detected depending on the neutron capture cross section and the gamma-ray yield. A schematic diagram of the first generation chloride detection system is shown in Figure 1. The $^{252}$Cf radioisotope neutron source generates fast neutrons with typical energies in the 1-5 MeV range, while PGNA requires thermal neutrons ($2.57 \times 10^{-8}$ MeV). Therefore it is necessary to use a polyethylene moderator to slow down the neutrons to thermal energies. These thermalized neutrons enter the concrete and are captured by various nuclei including Cl. The

![Image of schematic diagram](image_url)
gamma rays emitted during capture are then detected by High Purity Germanium (HPGe) coaxial type gamma ray detector. However, the HPGe detector essentially detects gamma rays coming from any direction. This omnidirectional operation leaves some room for improvement:

1. The sampled volume in the concrete is relatively large ~100,000 cm$^3$ so that the spatial resolution is relatively coarse.
2. The chloride signal is averaged over depth, so it is not possible to measure the depth profile, which is important to assessing possible corrosion risk.
3. The detector is sensitive to gamma rays generated by the hydrogen content of the moderator around the source, which makes it impossible to measure water within the concrete itself, which is an important parameter.
4. The detector is also sensitive to the gamma-rays produced by PGNA of other elements in the moderator which adds significant background.

To overcome these drawbacks, a second-generation PGNA chloride measurement based on an electronic collimator has been developed and is currently being evaluated.

CONCEPTUAL DESIGN OF 2ND GENERATION SYSTEM

As discussed above, the current 1st generation system is omni-directional and thus samples a very large volume. In order to improve the spatial resolution, it is necessary to make the detector more directional by introducing a collimator to constrain the solid angle in which the gamma-rays are detected. In the laboratory this is usually done by a physical collimator, which consists of a shield of dense material such as lead around the detector, with an opening that defines the direction. However, the thickness of lead required to attenuate a 6.111 MeV gamma ray coming in the wrong direction by a factor of 100 would be about 10 cm. Consequently, the mass of the entire collimator would be about 250 lbs, which would be impractical for a system intended to be portable. An alternative approach employed here uses an electronic collimator based on the Compton telescope configuration (Livingston et al. 2010).

The significant features of this system are shown in Figure 2. In this system, a gamma-ray emitted from the brick first passes through the electronic collimator. If it is travelling in the right direction, i.e. from the brick, it is counted. In the process, the gamma-ray gives up a small amount of energy through Compton scattering. The gamma-ray leaving the collimator then enters a conventional HPGe detector where its remaining energy is measured. The output of the HPGe detector is an analog voltage pulse as shown in Figure 2. In conventional counting electronics, this pulse is integrated to give a total charge, which is then digitized for assignment to a specific counting bin or channel. In the 2nd generation system, another innovation is the introduction of a digital signal processor digitizes the actual shape of the analog pulse. This enables more precise determination of the gamma-ray particle’s energy.

The third innovation is the replacement of the $^{252}$Cf radioisotope source by a neutron generator. This is motivated by the fact that introducing the electronic collimator reduces the overall count rate. Commercially available portable neutron generators use the deuterium-deuterium (D-D) or deuterium-tritium (D-T) fusion reaction to generate the neutrons and can...
produce neutron currents as high as $3 \times 10^8$ n/s, which is about 30 times greater than the maximum from the $^{252}$Cf radioisotope source. In addition to providing a higher neutron flux, the use of the neutron generator would minimize the need for shielding requirements during transport.

In addition to the improved spatial resolution of the detector, background would be significantly reduced, thereby improving the counting statistics and reducing the time required to make a scan of an area. By eliminating the hydrogen signal from the moderator, it would also be possible to measure moisture in the brick. Also, the neutron generator can be operated in a pulsed mode. This makes it possible to measure additional elements by fast neutron activation and also to make time-of-flight measurements for depth profile measurement.

The introduction of the NaI detector into the PGNA system reduces the counting rate. To compensate for this, the $^{252}$Cf radioisotope source is replaced by a neutron generator which can give a higher neutron flux. The main components of the neutron generator are illustrated in Figure 3 (Chichester & Simpson 2004). It is actually a compact linear accelerator. The ion source is deuterium gas. The deuterons are stripped of electrons which gives them a positive charge. They are then accelerated by the large voltage difference between the ion source and the target. When the accelerated deuterons hit the target which can be either more deuterium (D-D) or tritium (D-T) fusion happens with the production of a helium atom and a neutron. This appears to be a highly complicated system that would be difficult to operate in the field, but in fact, commercial systems based on sealed tube design have been developed. These are simple to use and reliable. Consequently, they are now used in a number of applications in the field, such as petroleum detection and explosives detection (Chichester & Simpson 2004).
The main issue for the specification of the neutron generator is the selection of the type (D-D or D-T) of neutron generator tube. One consideration is the energy of the neutrons. The D-T fusion reaction produces a 14.1MeV neutron. The D-D reaction produces a lower energy neutron with 2.45 MeV. In comparison, $^{252}$Cf emits neutrons with a range of energies with the most probable value being about 2 MeV. Thus a larger volume of moderator than currently used would be required to slow the neutrons down to thermal energies. This would increase the bulk and weight of the overall system. On the basis of neutron energies it would appear that D-D type would be preferable since the neutron energies are relatively close to that of $^{252}$Cf. The neutron source strength must also be considered. The D-D nominal yield is $2.5 \times 10^6$ n/s while the D-T yield is $3.0 \times 10^8$ n/s. Thus the D-D system would produce fewer neutrons than the existing $^{252}$Cf source. Therefore the choice is the D-T system (Livingston et al 2011). The moderator has also been redesigned to maximize the delivery of thermal neutrons to the target while minimizing losses due to capture, and at the same time minimizing the radiation exposure to the operators.

FIELD AND LABORATORY APPLICATIONS

An older version of the PGNA system was used to investigate a brick structure suffering from severe salt deterioration. The structure was built around 1800 and was used as a smokehouse on the Benjamin Powell House in Colonial Williamsburg in the state of Virginia in the north eastern part of the United States. The small portable neutron source was placed next to the target material under investigation. The neutrons penetrate and interact with the nuclei of its constituent elements. This leads to scattering of high energy neutrons or capture of neutrons of thermal energy. In both cases the result can be shown as a gamma ray spectrum. Figure 4 shows part of a gamma ray spectrum taken at the smokehouse; elements detected in this energy range include aluminium, silicon, chlorine and potassium (Livingston & Taylor 1998). Each measuring point represents a volume and with spatial contouring software it is possible to interpolate values between the measurement points to provide contour maps of individual
elements in the wall. For example, for the chlorine gamma ray signal, the map can further be converted into concentration of sodium chloride based on calibration data obtained on specimens containing known amounts of salt. The results showed variable salt content with sharp decrease towards the ground level (Figure 5). To verify the PGNA results, cores were taken from areas of low Cl signal and high Cl signal. The destructive test results were consistent with the PGNA results.

To estimate the total amount of salt contained in the measured area of the wall, a set of experiments was conducted in the laboratory using simulated brick samples containing known amounts of salt to determine the calibration function that converts the gamma ray counts to the concentration of chloride (Livingston, 1992). Once this function was obtained, it was then possible to integrate over the contours of Fig. 5 to calculate the total salt content as $97 \pm 22$ lb. Subsequently, as a conservation treatment the Colonial Williamsburg Foundation removed the salt from the Smokehouse using poultices (Taylor & Jaworski, 2002). Analysis of the used poultices determined that the total salt content was 78.1 lbs, in good agreement with the PGNA results. A similar procedure was followed for determination of moisture content based on hydrogen gamma ray signals. The results showed variation between 2% to 11% which is consistent with moisture contents that are typically found in brick walls.

The improved PGNA system was recently used on concrete slab laboratory specimens. The neutron generator shown in Figure 3 was not ready to be used so instead the $^{252}$Cf neutron source was used. The first gamma-ray spectrum was done without the $^{252}$Cf neutron source in order to establish the radiation background in the lab. The only significant peak observed in the background was for $^{40}$K. This was expected since potassium is typically found in bricks.
Figure 5: Contours of sodium chloride for the north wall (white: lowest concentration)

previously placed on the center line of the concrete slabs (Figure 6). A stack of lead bricks were placed between the moderator and the detector. A spectrum was then acquired; several prominent lines were observed including the 2.223 MeV line for hydrogen. This is due to the hydrogen content in the concrete as well as in the moderator. Chlorine was also successfully detected at the characteristic 6.111 MeV peak along with other Cl lines at 5.089 and 5.598 MeV. In addition, several lines were observed for silicon. Since silicate coarse and fine aggregates were used to make the concrete slabs, it would be a dominant element. Finally, lines for Ca, Al and K were also observed. Part of the PGNA spectrum for 5-7.5 MeV is shown in Figure 7. This would make it possible to estimate the concrete mix design. The test was judged to be successful and the full data is currently being analyzed.

CONCLUSIONS
Cycles of soluble salt deliquescence and dehydration in historic brick masonry in response to cycles of fluctuating moisture levels are known to have damaging effects over time. Nondestructive determination of the depth and degree of salt contamination and determination of moisture content in historic masonry are among some of the measurements that are needed to design appropriate remedial action. An improved portable nondestructive evaluation system based on prompt gamma neutron activation (PGNA) is described. The system works by irradiating a section of a structure with neutrons from a portable neutron generator. The gamma rays of characteristic energies resulting from interaction with target elements such as hydrogen, chlorine, sulfur, sodium and potassium are detected. The results can be used to map the spatial distribution of soluble salts in the structure. Applications of the improved nondestructive evaluation system in the field as well as in the laboratory are discussed. The field specimen consisted of a historic brick structure that was constructed around 1800. The laboratory specimens consisted of concrete slabs with known amount of salt. The improved PGNA system was successfully used to measure the amount of salt and moisture in both the
field and laboratory specimens. Destructive tests conducted on cores taken from the historic brick structure were consistent with the PGNA test results for chlorine. It can be concluded that the improved portable nondestructive evaluation system is a useful tool for quantitative analysis of elements associated with moisture, salt and other materials in historic masonry structures.

Figure 6: PGNA test setup

Figure 7: PGNA spectrum, 5-7.5 MeV
REFERENCES


