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Application of Small-angle Neutron Scattering Method to the Study of the Durability of Historic Brick and Mortar

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Small-angle neutron scattering measures the physical structure of materials in the 0.01-1000 nm range. lt yìelds the surface area, pore - size distribution, and the fractal dimensions (mass and surface) of the material over this size range. This technique is being used to study the durability of historic masonry made with pozzolanic mortars. Also brick and mortar deterioration processes caused by soluble salts or freeze - thaw damage are under investigation.

1. Introduction

lt is a widely accepted principle that the durability of bricks and other porous building materials depends in some way on the microstructure. However, the exact relationship is not yet completely understood. Part of the problem lies in finding an appropriate way to quantify the microstructure. Typically, the pore-size distribution or the integral of this distribution are used to predict durability according to some experimentally obtained correlation. These durability functions are all based on the hypothesis that smaller pores are more readily damaged by expansive forces of ice formation or salt precipitation than larger pores. However, the approach to specifying a critical pore-size distribution differs greatly.
The earliest durability functions simply used a single critical pore-size [1]. That is the percentage of the cumulative pore-size distribution below some specified value. This ranged from 1-2 μm all the way to 10 μm, although the values tended to cluster around 0.5 μm to 1 μm. Subsequently, Ravaglioli and Vecchi [2] proposed a two-point criteria based on a critical interval between 0.25 μm and 1.4 μm. In contrast, Maage [3] developed a function based on the combination of the total pore volume and the percentage of pore-sizes below 0.3 μm. These functions are all based on pore-size distributions obtained by mercury intrusion porosimetry. However, the durability test standards defined by materials testing societies such as the ASTM have been based on water absorption methods. For example, the widely used ASTM C216 standard [4] is based on the ratio of the mass of water absorbed during a 24-hr soaking in cold water to the amount absorbed alter 5 hrs in boiling water. Dimensional analysis shows that this corresponds roughly to the single critical pore-size approach, except that no single critical radius is actually specified. Instead, the fine pore-volume is approximated by the amount of water driven into the pores during the boiling test.

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These functions have been criticized by a number of investigators for various reasons including the way durability is actually measured, the pore-size distribution measurement methods, the extrapolation from a single type of test materials to others, etc. [1, 5, 6]. Moreover, Everett has pointed out that on the basis of thermodynamics the appropriate variable is not the cumulative pore-size distribution, but rather dA/dV, the derivative of the pore-surface area, A, with respect to the total volume of the solid, V [7]. A full critical review of these issues is beyond the scope of this paper.
Many of the concerns about the validity of these durability models arise from the limitations of the conventional techniques for quantifying the microstructure, i.e. mercury intrusion porosimetry and automated analysis of scanning electron microscope images. In this paper, we describe the application of small-angle neutron (SANS) and ultra-high resolution small-angle X-ray scattering (USAXS) to characterize the microstructure of historic brick and mortar at very fine length scales. These new tools may provide the basis for improved durability functions.

2. Conventional Measurement of Microstructure

The standard method for measuring the microstructures of bricks and mortar has been mercury intrusion porosimetry [8]. However, this has some inherent limitations. It can measure only pores that open to the outside. Also, ink-bottle pores with narrow necks may be incorrectly measured. Moreover, the reduction of the mercury intrusion volume data to a pore-size distribution is based on a simplified geometric model that assumes a cylindrical pore. This model also requires knowledge of the contact angle between the mercury and the material, which may be difficult to obtain. Finally, the finer the pores the greater the pressure required for intrusion, but these high pressures may cause deformation and microcracking of the material itself.
An alternative method is the automated image analysis of scanning electron microscope (SEM) images. This can provide information on the pore shape and orientation as well as size. However, this method observes only surfaces. Moreover, sample preparation and the vacuum required may alter hydrous phases that exist in mortar materials.

3. SANS/USAXS Techniques

The small-angle neutron scattering technique takes advantage of some special properties of the neutron. This atomic particle`s wavelength can be readily adjusted by passing it through materials at fixed temperatures. In the case of a cold neutron source chilled to 35 K, the resulting typical wavelengths range from 0.5 to 2.0 nm. Thus, they can probe material structure down to the molecular level. Moreover, the neutrons scatter very effectively from hydrogen-bearing materials such as those found in hydrated cement reaction products. Finally, compared to other probes of materials such as X-rays, neutrons can penetrate significant depths. This enables the neutrons to measure closed as well as open porosity.

For SANS the scattering processes involved are essentially elastic. Consequently, from the laws of conservation of energy and momentum, the scattering angle for a neutron of specified energy completely defines its interaction with a nucleus (Fig. 1).

In neutron scattering research, it is the practice to use wavevectors to describe the process. Consequently, instead of the scattering angle, 2θ, it is customary to use the scattering vector, Q, (see Fig. 2). The magnitude of Q is proportional to $\sin\theta$, and has the dimension of inverse length. The Q range for SANS studies is typically 0.01 to 10 nm^{-1}. This permits measurement of features in the size range of 1-100 nm.

In SANS studies, a monoenergetic beam of neutrons is selected by a helical velocity selector. This beam is highly collimated by leading it through a beam guide on the order of 8-15 m in length. The beam is then scattered off the sample and the scattered beam is measured with a position sensitive array of neutron detectors. For extremely small-angle scattering this detector array can be located as far as 15 m from the sample.

The interpretation of the neutron scattering data typically involves plotting the measured neutron intensity as a function of Q, i.e. I(Q) vs Q, usually on log/log scales. From fundamental theory of nuclear physics, this scattering function can be related to the spatial correlation function between individual scatters in the target material. From this, a number of characteristic microstructure parameters can be obtained. These include particle size, pore-size distribution, and fractal dimensions describing both spatial density and surface area.

Ultra-high resolution small-angle X-ray scattering (USAXS) yields similar results although at longer distance scales (50 nm - 1 µm). This technique is based on the Bonse-Hart double crystal diffraction method, here utilizing 0.124 nm X-rays, giving ultra-high small-angle scattering resolution [9].

Consequently, the two techniques can be used together to explore a greater range of length scales than either method alone.

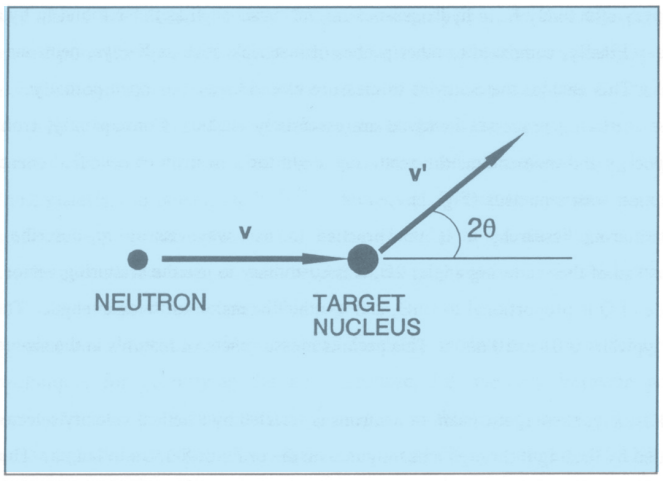

Figure 1. Basic neutron scattering process.

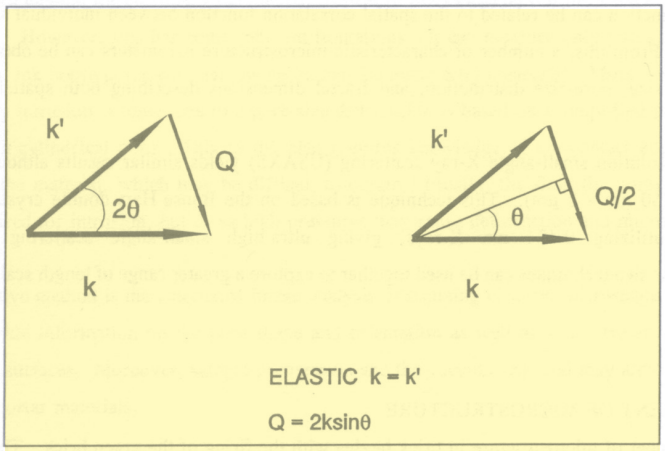

Figure 2. Relationship between scattering angle, 2θ, and scattering vector, Q.

4. Development of Microstructure

The development of microstructure in brick begins with the firing of the green brick. This consists of quartz grains held together by a binder of clay minerals. During firing the clay minerals melt into a glassy matrix. This destroys the nanoscale texture characteristic of the clay platelets. At the same time, the quartz grains are sintered together slightly.

In contrast, a pure lime mortar, which does not contain Portland cement, possesses little or no structure at the nanoscale. The slaked lime consists of fine platelets of calcium hydroxide. The attraction between these platelets provides the initial set of the mortar.

In the case of a pozzolanic mortar the reaction of the pozzolans with $Ca(OH)_2$ yields colloidal panicles of calcium silicate hydrates (C-S-H), which have characteristic dimensions on the order of 5-10 nm. These particles aggregate into ramified structures which ultimately form a gel network giving the mortar its strength.

Once in place the brick and mortar undergo long term changes over the period of months to decades. In the brick, the glassy matrix can react with atmospheric moìsture to regenerate clay minerals. Also, exposure to cyclic stresses from temperature changes, soluble salts, etc. will induce microcracking in the brick. In the slaked lime mortar, the process of carbonation leads to the conversion of the fine-grained portlandite to coarser calcite crystals. In regions isolated from the atmosphere, the portlandite can remain unreacted. In the pozzolanic mortar, the carbonation reaction breaks down the C-S-H network, yielding calcite and amorphous silica. In summary, the brick should tend to develop fine-scale microstructure with time, while the mortar may tend to lose it.

5. Experimental Approach

SANS/SAXS measurements were carried out on two sets of historic masonry samples. One set consisted of specimens of brick, from a roughly one hundred year-old building in Hamburg, Germany [10]. Some coupons cut from this brick had been subjected to a number of salt crystallization cycles in a sodium sulfate bath.

The other set of samples came from the Hagia Sophia in Istanbul, Turkey, and was essentially a proto-concrete because it actually consisted of brick fragments in a pozzolanic mortar [11]. The Hagia Sophia was built ca 530 AD, but these samples were obtained from a repaired area of one of the great arches, and thus are probably only 1,000 years old.

For SANS analysis, the samples were cut to roughly rectangular shape 3 cm by 2 cm. The thickness was reduced to 1 mm by cutting on a microtome saw. It was necessary to limit the sample

thickness in order to minimize the amount of multiple neutron scattering.
The neutron scattering data were collected on the 30 m NIST/ Exxon/U.Minnesota SANS instrument at NIST, Gaithersburg. Measurements were made at three different detector distances in order to access the maximum range of Q values.
For the USAXS analysis the sample thickness had to be reduced to less than 150 μm. Since it was not feasible to slice the samples this thinly with the microtome, the samples were crushed to a powder in a hand mortar and sieved to a size less than 100 μm. The particles passing the sieve was then wrapped in polyimide plastic film, which is transparent to X-rays, and pressed to the specified thickness. The USAXS data were taken at the National Synchrotron Light Source at Brookhaven National Laboratory.

6. Data Interpretation

The plot of the Hagia Sophia mortar data is presented in Fig. 3. The SANS and USAXS data have been combined in a single plot covering six orders of magnitude of length. This extensive range of scales demonstrates one of the advantages of SANS/USAXS over SEM image analysis, which operates over a very limited length scale.
The data have also been transformed through multiplication by a factor of Q^4. This makes it easier to see differences among curves from various specimens. Moreover, it can be shown that this type of plot characterizes fractal surfaces. That is, if a material has relatively smooth pore surfaces, the resulting curve in this Q^4 plot will be essentially flat.
The plot of the Hagia Sophia data produced a curve that was convex upward (Fig. 3). It also tends to level off at higher Q^4 values, suggesting relatively little very fine pore surface area. This is characteristic of geological materials rather than manmade cementitious ones. For comparison, the SANS/USAXS data for a typical modern ordinary Portland cement paste have also been included. This curve is concave upward and the slope continues to increase with Q^4 indicating that there is a significant amount of nanoscale structure. Since the Hagia Sophia mortar was pozzolanic, it would also have had initially a microstructure with features like that of the Portland cement paste. However after 1,000 years of exposure, carbonation has apparently reduced the nanoscale structure and thus produced a microstructure resembling a limestone or a calcareous sandstone.
The Hamburg brick data show a more complex curve that is nearly level in the low Q^4 range, corresponding to length scales between 100 nm to 1 μm. This implies an absence of surface features at these length scales which is consistent with the effects of the firing process described above. The jump in the curve at 10^{-6} nm^{-4} may be an artifact associated with the merger of USAXS and SANS data sets at this point. Beyond this point, the curve changes shape, and there is the indication of small amounts of very fine surface structure. Since this brick has been exposed to atmospheric moisture for 100 years, this fine structure may indicate the presence of reconstituted clay minerals decorating the pore walls.

7. Conclusions

The results of these measurements show that SANS/USAXS analysis is feasible on brick and mortar materials. It is also possible to relate features observed in the SANS/USAXS data to physical processes in the development of microstructure, at least on a qualitative basis. Moreover, these results indicate that mathematical models recently developed for quantifying Portland cement paste microstructure from small - angle scattering data can also be applied in the future to brick and mortar samples. [12] In addition, the existence of fractal surfaces at very fine length scales in these materials shows that the assumption of simple cylindrical pores used to interpret mercury intrusion porosimetry may be an oversimplification. This may explain some of the problems with current forms of durability functions based on these pore models. Therefore, the reliability of the durabilìty functions could be improved by using fractal dimension variables. This approach applied to various problems in the field of geology such as the fracturìng of rock has proven very fruitful [13].
Further research will include SANS/USAXS analyses of a greater variety of brick samples, including samples of modern handmade brick from Colonial Williamsburg. Also, supplemental analysis of the microstructure will be made using SEM, X - ray diffractìon etc. For development of durabilìty functions, series of freeze - thaw or salt - cycle tests will be performed.

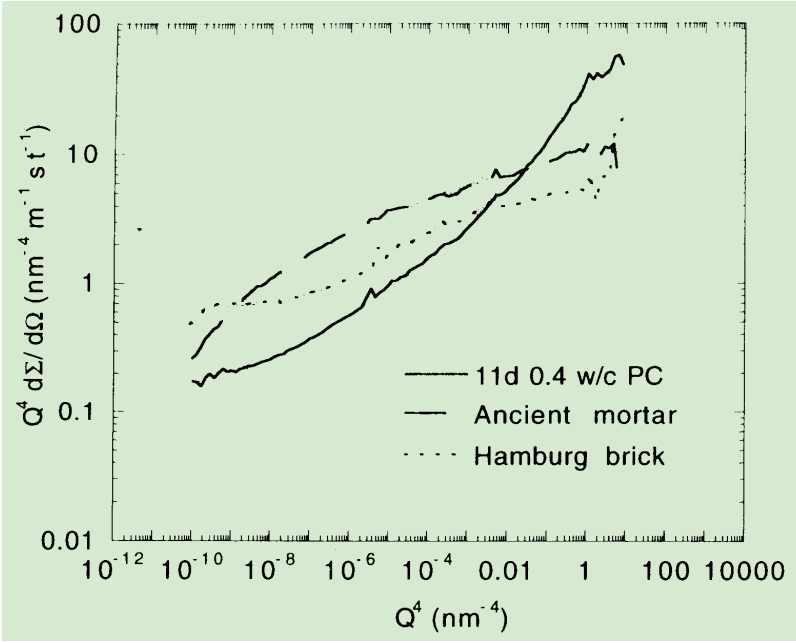

Figure 3. Plot of small-angle scattering data for Hagia Sophia mortar, Hamburg brick and modern Portland cement.

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