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Quantitative X-ray Diffraction Analysis of Handmolded Brick

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ABSTRACT

The durability of brick is related to its microstructure and mineralogy. It has been proposed that the ratio of cristobalite to quartz would be a reliable predictor of durability. To test this theory, quantitative X-ray diffraction analysis was applied to samples of historic brick from the United States and Europe. The quantitative method was based on finding the reference intensity ratios (RIR) for cristobalite and for quartz relative to an internal standard of corundum (Al_2O_3). Known amounts of corundum were added to the ground brick samples, and replicate X-ray diffraction patterns were taken. The intensities of the cristobalite, quartz, and corundum peaks were calculated after correcting for background. The cristobalite/quartz ratio agreed with the relative durability of bricks from Colonial Williamsburg in the United States. However, cristobalite was not detected in brick samples from Germany. Among other mineralogical differences observed, the German brick contained plagioclase feldspars while the American bricks did not. Also, one set of less durable bricks from Germany had detectable amounts of illite or mica. This suggests that the mineralogy of bricks made in Germany was fundamentally different as a result of either the raw materials used or the firing procedure. Consequently, the cristobalite index may be usable only for bricks with chemical compositions similar to those of Colonial Williamsburg. This study also revealed that corundum may not be the most suitable choice for the internal standard because of overlaps with quartz and feldspar peaks.

INTRODUCTION

The conservation of historic brick buildings requires the ability to predict the durability of the brick itself. The durability of historic brick can vary significantly, depending

both on the material itself and on the local environment. However, even for modern brick, the available methods for predicting durability leave much to be desired (Bortz et al. 1990). These test methods rely on empirical durability functions rather than on a fundamental knowledge of the chemistry and physics of brick manufacture. Consequently, durability relationships developed for one particular type of brick may not apply to others.

A possible materials science approach to the problem of historic brick durability was suggested by an undergraduate researcher, R.E. Lindsley, at the College of William and Mary in Williamsburg, Virginia, who was studying the durability of bricks in the historic Colonial Williamsburg area (Lindsley 1982). She found that the durability of the brick, based on a visual assessment of distress, seemed related to the amount of cristobalite present. Cristobalite is a high-temperature polymorph of quartz. It has been established in experiments on the melting of potassium-rich clay minerals that the amount of cristobalite formed is a function of firing temperature (Brindley and Maroney 1960). As a general rule, bricks fired to a high temperature, around 1000 °C, are more durable than those fired at lower temperatures (Robinson1982).

One explanation for this effect may be found in the melting relationships. Brick-making clay consists of a mixture of clay minerals, either potassium-rich (illite) or sodium and calcium-rich (smectite) and quartz sand (Grim 1974). The composition of the clays in the Williamsburg area is illitic and thus can be displayed in the phase diagram shown in Figure 11.1 (Schairer and Bowen 1947). This phase diagram also applies to porcelain ceramics. This system has a eutectic point at 985°C at the intersection of the potassium feldspar, tridymite, and mullite fields. This suggest that to melt the clay, and thus to form a strong ceramic bond between the quartz grains, it is necessary to achieve at least this temperature.

The equilibrium silica phase at the eutectic is predicted to be tridymite (Schairer and Bowen 1947), but cristobalite is usually seen instead. The amount of cristobalite is associated with the kaolinite content of the clay rather than the amount of quartz that is melted (Brindley and Udagawa 1960).

It is an inconvenient fact that none of the three minerals associated with the eutectic point are usually detected in handmolded brick after firing. Aside from the formation of cristobalite rather than tridymite, crystalline feldspar is not observed, but a glassy phase generally is (Livingston, unpublished). This is consistent with the experimental results of Brindley and Maroney (1960), in which a feldspathic glass rather than feldspar was produced under these conditions. These investigators also found that mullite could not be detected in samples fired at less than 1100°C. This temperature is rarely achieved in brick making, partly for reasons of fuel economy, but also because of the technology of the kiln, which operates under natural draft. In contrast, forced draft kilns, which produce higher temperatures, have been used to make porcelain, which consequently has a large mullite content.

Finally, cristobalite theoretically ought not to be found in the bricks after cooling to room temperature, but its persistence can be explained by the fact that aluminum is

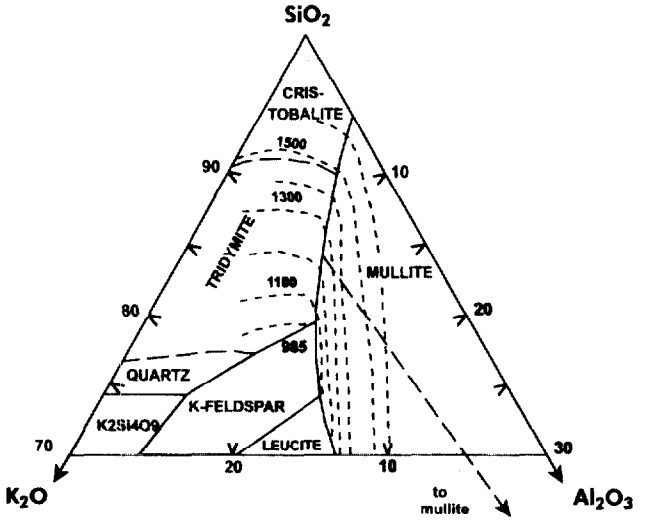

Figure 11.1 Part of the phase diagram of system K_2O-Al_2O_3-SiO_2 (after Schairer and Bowen 1947).

known to enter into the cristobalite crystal structure, thereby stabilizing it (Perotta et al. 1989).

The results of Lindsley led to the concept of a cristobalite index that could be used as the basis for durability prediction. The cristobalite index, η, is defined as:

$$\eta = \frac{X_{Cr}}{X_{Qz} + X_{Cr}}, \tag{11.1}$$

where X_{Cr} and X_{Qz} are the weight percentages of cristobalite and quartz, respectively. This ratio was chosen as a measure rather than the absolute amount of cristobalite in order to compensate for the variability of the constituents among bricks.

To determine the cristobalite index of a brick specimen, it is necessary to analyze the minerals present. The most practical method is X-ray diffraction (XRD). While the peak intensities in an XRD pattern should be proportional to the abundance of a phase in a mixture, this is in reality only a semi-quantitative measurement because the peak intensity-concentration relationship is not exactly linear. The departures from linearity arise from differential absorption of X-rays by the mineral phases in the sample itself. However, Klug and Alexander (1974) show that an absorption correction can be made by the use of an internal standard and associated calibration procedures. The internal standard is a mineral phase, absent in the original sample, that is added to the mixture in a known proportion. Given a known amount of internal standard, the concentration of the unknown phase can then be found from the peak intensity ratio of

the unknown and internal standard. This approach to quantitative XRD has been successfully applied at the National Institute of Standards and Technology to determine the mineralogical composition of Portland cement clinker reference materials (Stutzman 1992).

An initial trial of the cristobalite index was undertaken as part of the NATO-CCMS Pilot Study on the Conservation of Historic Brick. As outlined in Appendix I (this volume), this was an international program for cooperation in research in the deterioration and conservation of historic brick. The pilot study provided a convenient means to obtain samples of historic bricks from different geographical regions, as well facilitating the cooperative analyses.

QUANTITATIVE XRD USING THE REFERENCE INTENSITY RATIO (RIR) METHOD

The reference intensity ratio (RIR) method is a specific application of the internal standard method for quantitative XRD. The RIR is a constant relating the X-ray scattering power of a phase to that of the internal standard (Klug and Alexander 1974; Stutzman 1992). The RIR is defined as the ratio of the strongest peak of the unknown phase to that of an internal standard in a one-to-one mixture (Chung 1974; Hubbard and Snyder 1988).

The RIR values are calculated from a standard composite sample, consisting of a mixture of the pure phase and the internal standard phase, as follows:

$$RIR_{i\alpha} = \frac{I_{i\alpha}}{I_{jCo}} \times \frac{X_{Co}}{X_{\alpha}}, \tag{11.2}$$

where: $RIR_{i\alpha}$ = RIR for peak i of mineral phase α,
$I_{i\alpha}$ = intensity of peak i of mineral phase α,
I_{jCo} = intensity of peak j of the internal standard, i.e., corundum,
X_{Co} = concentration of internal standard in the standard composite sample,
X_{α} = concentration of mineral phase α in the standard composite sample.

Then Y'_{α}, the concentration of mineral phase α in an unknown composite sample is:

$$Y'_{\alpha} = \frac{I_{i\alpha}}{I_{jCo}} \times \frac{Y_{Co}}{RIR_{i,\alpha}}. \tag{11.3}$$

Finally, the concentration of the mineral phase in the original sample is obtained by correcting for the dilution caused by the addition of the reference phase:

$$Y_{\alpha} = \frac{Y'_{\alpha}}{1 - Y_{Co}}. \tag{11.4}$$

The precision of this technique can be affected by the heterogeneity of the composite sample and by preferred orientation. The sample heterogeneity is dealt with by grinding the sample to a very fine size, < 10 μm, and thorough homogenization. The effect of particle orientation is minimized by making replicate scans of each sample, rehomogenizing and repacking the sample in the sample holder between each scan.

SAMPLE COLLECTION

German Historic Brick

Nine samples of historic brick were obtained from several buildings in the North German cities of Lübeck and Hamburg, and some historic churches on the sea coast along the North Sea, as described in Chapter 4 (this volume). The dates of the buildings ranged from the 14^{th} to 19^{th} centuries. Individual bricks were removed by cutting out the mortar joints with an electric chisel. This method of sampling was chosen instead of drilling out cores in order to make the replacement less obtrusive. However, only very small quantities, on the order of 1 gram, were required for XRD. The bulk of each brick was used for other types of tests.

Colonial Williamsburg Modern Handmolded Brick

Although brick samples are available from historic buildings in Colonial Williamsburg, it was decided instead to perform the XRD on some contemporary samples from the brick-making exhibition area. The brickmakers use a clay and sand mixture that is consistent from one batch to another. However, a particular batch was not fired at sufficiently high temperatures, producing poor quality bricks that failed the standard durability tests. Therefore, a sample of these failed bricks was obtained along with a sound brick from another properly fired batch. This was intended to provide a rough test of the ability of the cristobalite index to discriminate between good and poor quality brick.

PROCEDURE

X-Ray Equipment

An automated Philips X-ray powder diffractometer with sample changer was used for data collection. The system operates at 45 kV and 35 mA using copper Kα radiation, a variable divergence slit, 0.02° receiving slit, diffracted beam monochromater, and a scintillation detector. The diffraction patterns are recorded in the form of electronic digital data files rather than on paper strip charts. This makes it possible to process them on a personal computer for phase identification, peak profile fitting, and quantitative analysis.

Cristobalite and Quartz RIRs

A pair of RIRs for cristobalite and for quartz were prepared for the diffractometer using standards of pure cristobalite (NIST SRM 1879) and quartz from clean quartz crys-

tal fragments selected under a stereomicroscope. The ideal internal standard should not produce diffraction peaks that interfere with peaks from phases being measured in the sample. It should be an easily obtainable, stable, pure material with a fine (1 μm-10 μm) particle size, and low susceptibility to orientation (Klug and Alexander 1974). This study used corundum (α-alumina) as the internal standard, specifically the standard reference material provided by the United States National Institute for Standards & Technology, NIST SRM 674a. Mixtures of 50% corundum and 50% cristobalite or quartz were prepared. Each composite sample was then wetted with ethanol to make a slurry and blended with the assistance of a high-power ultrasonic probe. It should be noted that standard RIR mixtures need not be restricted to equally proportioned binary mixtures. Chung (1974) demonstrated that multi-phase mixtures of known phase abundance composition can be used. Snyder and Bish (1989) found that multiple standard mixtures using different phase-to-standard ratios provided more accurate RIRs, while the use of multiple peaks for each phase minimized effects of preferred orientation.

The composite standard samples for RIR development were then packed into standard 16 mm × 20 mm cavity mount sample holders. To ensure that the scanned surface was a smooth as possible, the powders were backloaded against a glass plate. Data scans encompassed a 2 range to include all peaks of interest at a scan rate of 2 seconds per 0.02° (2) step. Peak intensity ratios from four replicate scans, with the sample repacked for each scan, were averaged to establish the RIR.

Sample Preparation and Analysis

Each sample was first crushed by hand in a mortar and pestle. It was then reduced to final size by grinding in a orbital grinding mill with corundum cylinders to a particle size <10 μm. The next step consisted of adding 10% corundum internal standard. The composite sample was then homogenized by mixing the powder with ethanol and sonicating the resulting slurry with an ultrasonic probe. Each sample was scanned three times, with repacking of the powder between each scan. Diffraction scans were made from 10 to 54° (2) with a two second count time per 0.02° (2) step.

Data Reduction

The quantitative XRD method uses the integrated intensity, i.e., the total number of counts under each peak, rather the intensity of the peak channel alone. The calculation of the integrated intensity requires fitting the raw data to a specified profile shape, eliminating the contribution of overlapping peaks, and subtracting background. In this study, this was done using the commercially available software SHADOW[1]. The pseudo-Voight function provided the best fit as the profile shape to the diffraction

1 Materials Data, Inc., Livermore

The revised fig. Sent in April is corrupted -- need new file.

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Figure 11.2 X-ray diffraction pattern for Colonial Williamsburg good brick.

peaks. The ability to run SHADOW in batch mode facilitated rapid and reproducible peak area measurements.

RESULTS

Quartz was found in all samples. However, cristobalite was detected only in the brick samples for Colonial Williamsburg (Figure 11.2). The quartz and cristobalite mass percentages and the cristobalite indices for these two samples are summarized in Table 11.1. The uncertainties were computed solely from the counting statistics. It can be seen that the cristobalite index for the sound brick is significantly higher than for the failed brick. The comparison of the data among the replicates show very good repeatability, indicating that the procedure is not very sensitive to the procedure for packing individual powder samples for XRD. However, the sum of quartz and cristobalite typically falls in the 70%-80% range. This is somewhat higher than the total SiO_2 content of these bricks, roughly 65% ± 1.3%, as measured by X-ray fluorescence. Conversely, the quartz content measured in the German historic bricks falls in the range of 20%-50%, Table 11.2, which is lower than would be expected. This suggests that the measurements may have a bias.

Regarding some qualitative results of the XRD patterns, the German bricks all contained plagioclase feldspar. The sound brick from Colonial Williamsburg also showed traces of feldspar, but of a more potassium-rich type (Figure 11.1). However, no feld-

Table 11.1 Quartz and cristobalite mass percentages in Colonial Williamsburg brick.

SOUND WILLIAMSBURG BRICK				
Scan #	**Quartz**	**Cristobalite**	**Quartz + Cristobalite**	**Cristobalite Index**
1	67.3% ± 12.1%	15.8% ± 3.0%	83.1% ± 12.5%	0.19 ± 0.046
2	53.2% ± 8.8%	13.3% ± 2.3%	66.5% ± 9.1%	0.20 ± 0.044
3	51.4% ± 8.4%	15.8% ± 2.2%	67.2% ± 8.7%	0.24 ± 0.045
Mean	57.3% ± 9.9%	15.0% ± 2.5%	72.3% ± 10.2%	0.24% ± 0.045%
FAILED WILLIAMSBURG BRICK				
Scan #	**Quartz**	**Cristobalite**	**Quartz + Cristobalite**	**Cristobalite Index**
1	71.5% ± 10.8%	5.57% ± 0.95%	77.1% ± 10.8%	0.07 ± 0.016
2	74.2% ± 11.3%	5.75% ± 0.99%	80.0% ± 11.4%	0.07 ± 0.016
3	73.2% ± 11.2%	5.69% ± 0.99%	78.9% ± 11.3%	0.07 ± 0.016
Mean	73.0% ± 11.0%	5.67% ± 0.98%	78.7% ± 11.2%	0.07 ± 0.016

Note: The error terms are one standard deviation in mass percentage, calculated from X-ray counting statistics.

spar was observed in the failed brick. Some phyllosilicate minerals, illites, and micas appeared in the diffraction patterns for the bricks from Garding, Germany. These bricks had displayed a tendency toward sanding or granular disintegration. The presence of the illite and mica indicates either that these bricks were not fired at high enough temperatures, or that over time the glassy phase in the bricks had reacted with water. Finally, bassanite, $CaSO_4 \cdot \frac{1}{2}H_2O$, was detected in a sample from Hamburg. This is associated with gypsum, $CaSO_4 \cdot 2H_2O$ created in the brick by reaction with sulfur dioxide air pollution. It occurs in the less hydrated form of bassanite because the bricks samples were heated for other analyses prior to the XRD studies.

DISCUSSION

Sources of Bias

There seems to be a bias in concentrations found for the individual mineral phases. This bias is less of a problem for the cristobalite index since it is a ratio rather than an absolute value, and the individual biases may cancel each other out to a certain extent.

Nevertheless, before proceeding further, it is extremely desirable to identify the source of the bias so that it can be eliminated. Inspection of Equation 11.3 suggests three possible sources of bias. One possibility is the RIR, which is derived from a simple binary mixture of quartz and corundum, rather than a multicomponent mixture that more closely reflects the composition of bricks.

Table 11.1 Quartz contents of German historic brick.

Sample ID#	Sample Name	Mean	Std. Dev.
RL1	Dankwart	22.26%	1.52%
RL2	Marles	38.60%	3.53%
RL3	Hiobs luh	38.80%	9.78%
RL4	Garding 4	43.70%	3.79%
RL5	Garding 3H	31.20%	6.89%
RL6	Garding 3V	156.10%	38.33%
RL7	Hiobs 4uv	51.50%	5.09%
RL8	Hiobs 14g	33.10%	1.84%
RL9	Hiobs 14h	26.70%	0.49%

Another possibility lies in the measured corundum intensity, I_{jCo}. As can be seen in Figure 11.1, this is calculated from a small peak at 25.6° that lies on the shoulder of the major quartz peak at 26.7°. It also overlaps with a feldspar peak at 25.5-25.8°. Moreover, the feldspathic glass phase normally found in bricks produces a broad diffuse background in the region of roughly 25°-35°. All these factors complicate the determination of the background in the vicinity of the corundum peak and so could all affect the computation of the the corundum intensity.

All of this suggests that corundum may not be the most suitable internal standard for quantitative XRD of bricks. Other internal reference minerals should be evaluated, using a control sample consisting of specified amounts of quartz, cristobalite, and an appropriate feldspathic glass.

Quantitative Durability Functions Based on the Cristobalite Index

The ranking of the Colonial Williamsburg brick by the cristobalite index corresponds to their durabilities. This is at least consistent with Lindsley's earlier results, and suggests that it would be worthwhile to investigate this concept further. To develop a statistically significant correlation between durability and the cristobalite index would require a much larger number of samples. It may be difficult to obtain a sufficient number of samples from a standing historic structure.

A more fundamental problem concerns an appropriate quantitative durability measurement for correlation with the cristobalite index. The method used here was essentially a visual assessment of distress, which involves a subjective judgement. The standard quantitative measurements of durability involve cycling by freezing and thawing; however, this method is not always reliable (Ritchie 1982). Other methods

of quantifying durability using sulfate tests, sonic modulus measurements, or SEM image analysis have been suggested, but these have not yet been standardized (Bortz et al. 1990). Nevertheless, some quantitative measurement of durability must be made consistently on the brick samples in order to have data to correlate with the cristobalite content.

Such a correlation would be an improvement over the existing state of knowledge. Nevertheless, it would still be a statistical relationship, rather than one based directly on materials science.

Ultimately it will be necessary to determine the role that cristobalite plays in the brick's durability. Does it in itself contribute to the durability? Or is it merely a surrogate for other phenomena that occur during the firing of the brick?

The Absence of Cristobalite in German Bricks

Since cristobalite was not detected in the samples from Germany, it is obviously impossible to apply the cristobalite index to these bricks. The absence of cristobalite could be due to several causes: low firing temperatures, different clay chemistry, or reversion of cristobalite to quartz over long time periods. Given the abundance of aluminum to stabilize the cristobalite, it is unlikely that reversion to quartz has occurred. Low firing temperatures are a possibility, but it is difficult to determine this. Thus, the most likely possibility is different clay chemistry.

The chemical compositions of the German and Colonial Williamsburg samples are tabulated in Table 11.3. For ease of comparison, only the major fluxes (Na_2O, K_2O, CaO, and Fe_2O_3) are presented. These are the elements that affect the melting process of the clays in the brick. These have also been normalized by dividing each concentration by the sum of the fluxes in each sample. The German bricks were analyzed by X-ray fluorescence and the Colonial Williamsburg bricks by prompt-gamma neutron activation.

It can be seen that the Fe_2O_3 content of the fluxes is roughly comparable among the samples. The major difference lies in the amounts of K_2O and Na_2O relative to CaO. The CaO proportion of the German bricks is roughly six times greater than that of Colonial Williamsburg bricks, while the K_2O content is only about one-half. It is known that such significant variations will affect the type of feldspar that is formed, and also the melting temperatures (Deer et al. 1966). In a study of bricks made with calcium-rich Canadian clay, Grattan-Bellew and Litvan (1978) found a linear relationship between the firing temperature and the amount of laboradorite, a plagioclase feldspar, in the fired brick. As noted above, firing temperature appears to be a good predictor of durability. Franke and Schumann (Chapter 3) present a method for measuring temperature using hematite crystallinity. This is based on the same set of samples used in this study.

Consequently, the chemistry of the brick must be known to apply the cristobalite index successfully. Alternatively, a durability function based on feldspar formation may be applicable to bricks like those from Germany.

Table 11.3 Flux constituents in brick samples.

Sample ID#	Sample Name	Oxide as Percent of Total Fluxes				Total Fluxes (mass %)
		Na_2O	K_2O	CaO	Fe_2O_3	
Germany						
RL1	Dankwart	5.2	20.1	30.7	44.0	18.9
RL2	Marles	16.0	18.5	35.7	29.8	23.8
RL3	Hiobs 1uh	2.1	18.3	37.2	42.4	15.3
RL4	Garding 4	6.8	22.5	18.6	52.0	12.9
RL5	Garding 3H	10.2	16.1	38.0	35.6	20.5
RL6	Garding 3V	10.2	16.1	38.0	35.6	20.5
RL7	Hiobs 4uv	2.1	18.3	37.2	42.4	15.3
RL8	Hiobs 14g	2.6	16.0	40.3	41.0	14.4
RL9	Hiobs 14h	2.6	16.0	40.3	41.0	14.4
Colonial Williamburg						
CWGB	Sound brick	13.1	35.3	5.8	45.8	17.3
CWBB	Failed brick	16.0	34.7	4.9	44.3	16.8

CONCLUSIONS

This study has shown that quantitative XRD can be applied to measure cristobalite and quartz in historic bricks. However, corundum may not be the best internal standard for this application. The cristobalite index seems to be useful as a predictor of durability for Colonial Williamsburg-type bricks, i.e., those with a high K/Ca ratio. However, it is universally not applicable, as shown by the German bricks. Perhaps a two-dimensional index that also takes into account the formation of feldspar would cover a wider variety of brick types.

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