TECHBRIEF

How to Determine the Silica Content of Limestone Aggregates at the Quarry in 20 Minutes with No Sample Preparation

FHWA Publication No.: FHWA-HRT-20-034

FHWA Contact: Terence S. Arnold, HRDI-10, ORCID: 0000-0001-5707-6397, (202) 493-3305, Terry.Arnold@dot.gov

Aggregate made from pure limestone, when used in hot-mix asphalt (HMA) pavements, becomes polished as the pavement wears, drastically reducing skid resistance. If the loss of skid resistance is significant, the pavement becomes a major safety hazard. This polishing does not happen if the limestone contains appreciable amounts of silica, typically 40 percent or more. The presence of silica in the surface maintains an acceptable level of skid resistance. States that use limestone aggregates in HMA pavements routinely measure the amount of silica in their limestone aggregates.

The standard test method for determining silica content of limestone aggregates is described in ASTM C25-17 "Insoluble Matter Including Silicon Dioxide."[1] This standard test method comprises three procedures that can be used to determine silica content. Each is complex and involves several steps. In the first procedure, the aggregate is treated with hydrochloric acid, and the limestone is dissolved, leaving behind the insoluble silica. The second procedure uses both nitric and perchloric acids, while the third uses hydrofluoric and sulfuric acids. All these acids are extremely dangerous to use, and they pose a significant waste-disposal problem.

It is possible to measure the amount of silica in limestone aggregates using x ray–fluorescence (XRF) spectroscopy. This measurement can also be taken using a scanning electron microscope (SEM). With this technique, the electron beam in the SEM scans the surface of the aggregate and produces maps. Samples are prepared by casting the aggregate into epoxy resin. When the resin has hardened, it is cut to expose the surface of the aggregate, which is then finely polished before being placed in the SEM. Each map shows the concentration of an element present in the surface as shown in figure 1 and figure 2. The maps show that the distributions of silica (figure 1-A and figure 2-A) and calcium (figure 1-B and figure 2-B) vary widely. (Note that higher concentrations of silica and calcium are indicated by greater color saturation.)

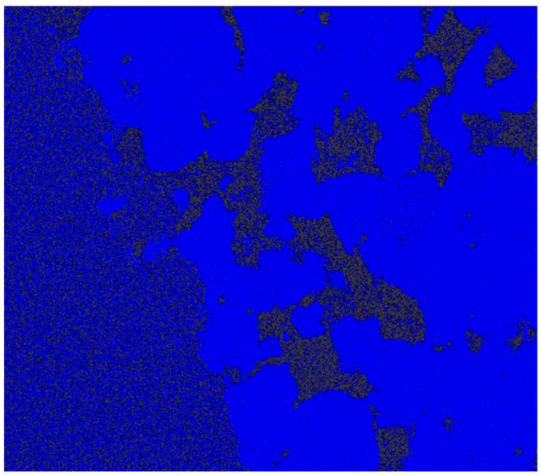
XRF spectroscopy is a technique whereby the chemical elements in a sample can be identified and measured. Handheld devices are available that are very simple to use (figure 3). They are ideal for testing in field environments.

U.S. Department of Transportation
Federal Highway Administration

Research, Development, and Technology
Turner-Fairbank Highway Research Center
6300 Georgetown Pike
McLean, VA 22101-2296

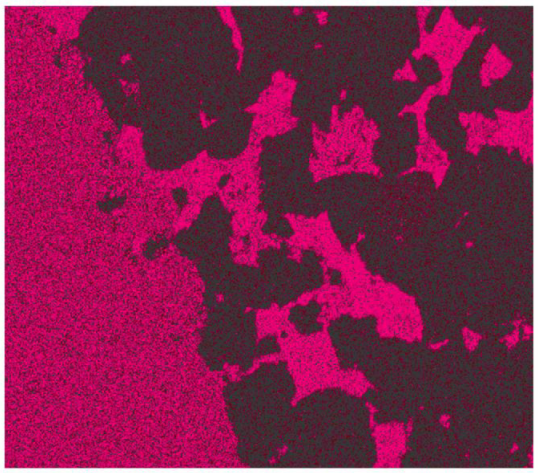
https://highways.dot.gov/research

Figure 1. Photos. Distribution of silica and calcium in sample 18-010.



Source: FHWA.

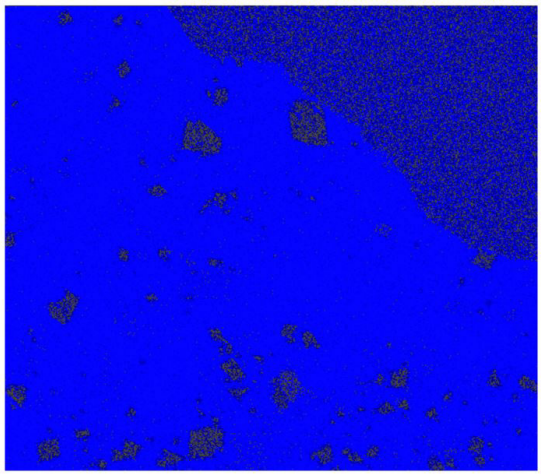
A. X-ray analysis of silica in sample 18-010.



Source: FHWA.

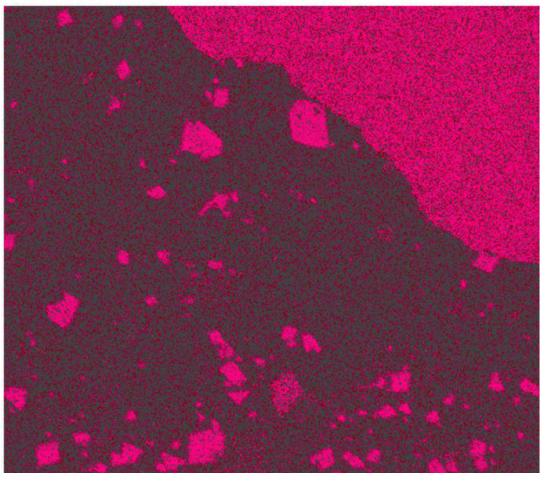
B. X-ray analysis of calcium in sample 18-010.

Figure 2. Photos. Distribution of silica and calcium in sample 18-013.



Source: FHWA.

A. X-ray analysis of silica in sample 18-013.



Source: FHWA.

B. X-ray analysis of calcium in sample 18-013.

Figure 3. Photo. Handheld XRF spectrometer.

Source: FHWA.

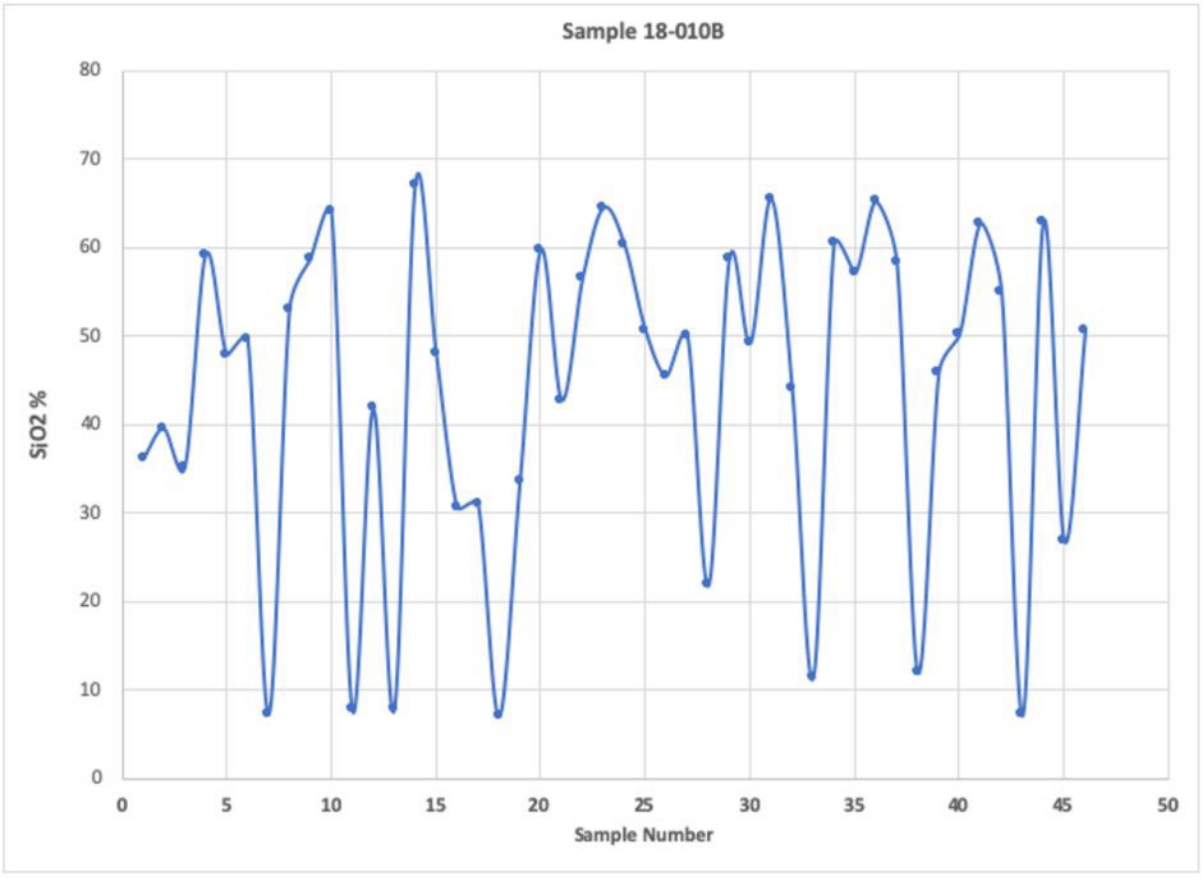
X-rays penetrate only a few microns into the sample being tested, so XRF spectroscopy only measures the composition of the exposed surface of the aggregate. It is to be expected that surface analyses of crushed aggregate would give widely varying levels of silica. The XRF-spectroscopy results for silica from 11 random pieces of aggregate taken from each of 10 crushed limestone samples are shown in table 1. Although there is wide variation, quite a few of the analyses have similar results, which raises the possiblity of averaging. The question is: How many pieces need to be tested to have a reasonable analysis for the batch?

Approximately 50 pieces of aggregate picked at random from each of the 10 samples showed wide

Table 1. Silica content of 11 pieces from each sample of crushed limestone aggregate.

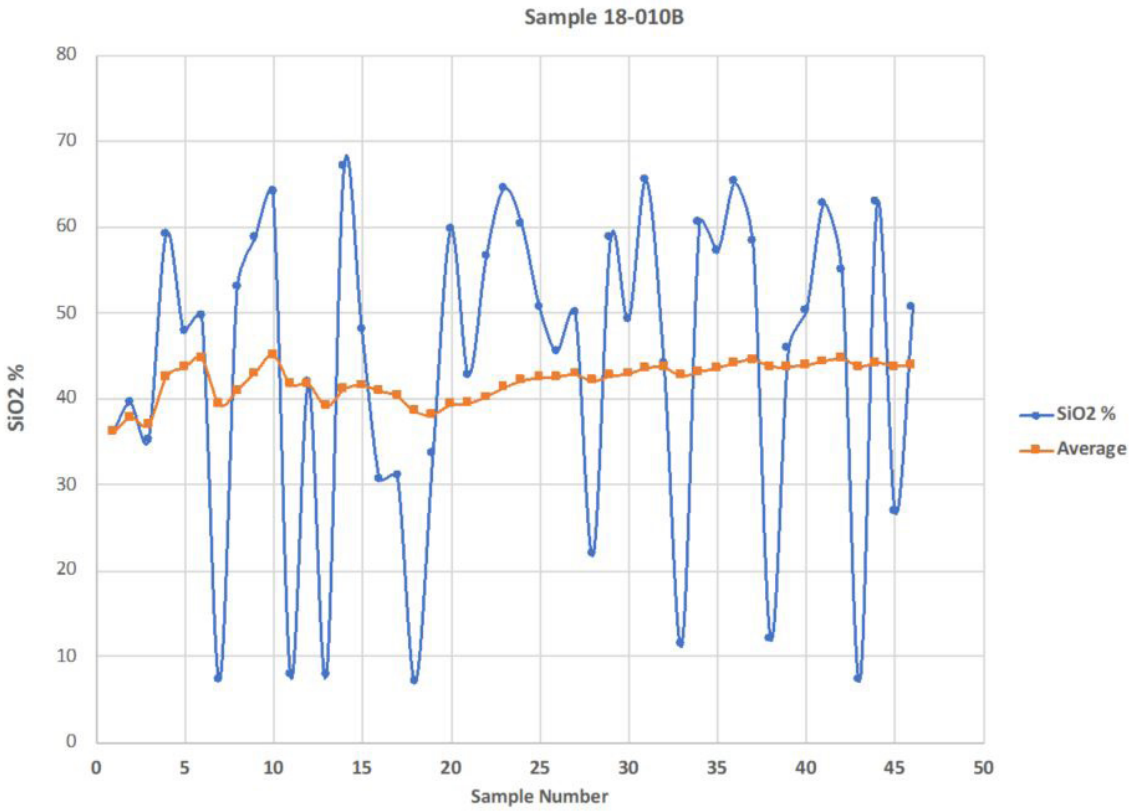
18-009A (%)	18-009B (%)	18-010A (%)	18-010B (%)	18-011A (%)	18-011B (%)	18-012A (%)	18-012B (%)	18-013A (%)	18-013B (%)
45.3	46.5	7.6	21.9	38.0	38.2	19.0	10.7	37.9	29.4
46.3	48.5	31.9	23.4	41.2	38.7	21.0	13.4	42.7	29.4
47.3	48.2	45.4	32.5	44.5	38.8	36.9	26.3	43.1	31.2
47.6	49.3	50.4	33.2	46.6	40.0	39.5	40.5	44.2	43.5
48.3	50.0	56.3	35.9	48.5	43.0	41.9	46.1	46.5	44.3
48.9	50.6	57.9	38.8	49.7	45.5	45.4	48.8	46.9	47.6
49.1	52.1	61.3	41.5	52.3	45.9	46.6	49.3	47.8	57.2
52.7	53.1	62.3	47.1	53.2	46.0	47.5	58.5	50.0	58.1
54.7	53.5	63.6	53.1	54.5	46.9	49.8	60.2	51.0	65.1
68.2	56.0	64.9	54.1	54.6	47.5	52.4	90.0	51.6	76.4
50.8	50.9	50.2	38.1	48.3	43.1	40.0	44.4	46.2	48.2

Figure 4. Graph. Silica content of limestone aggregate sample 18-010B.



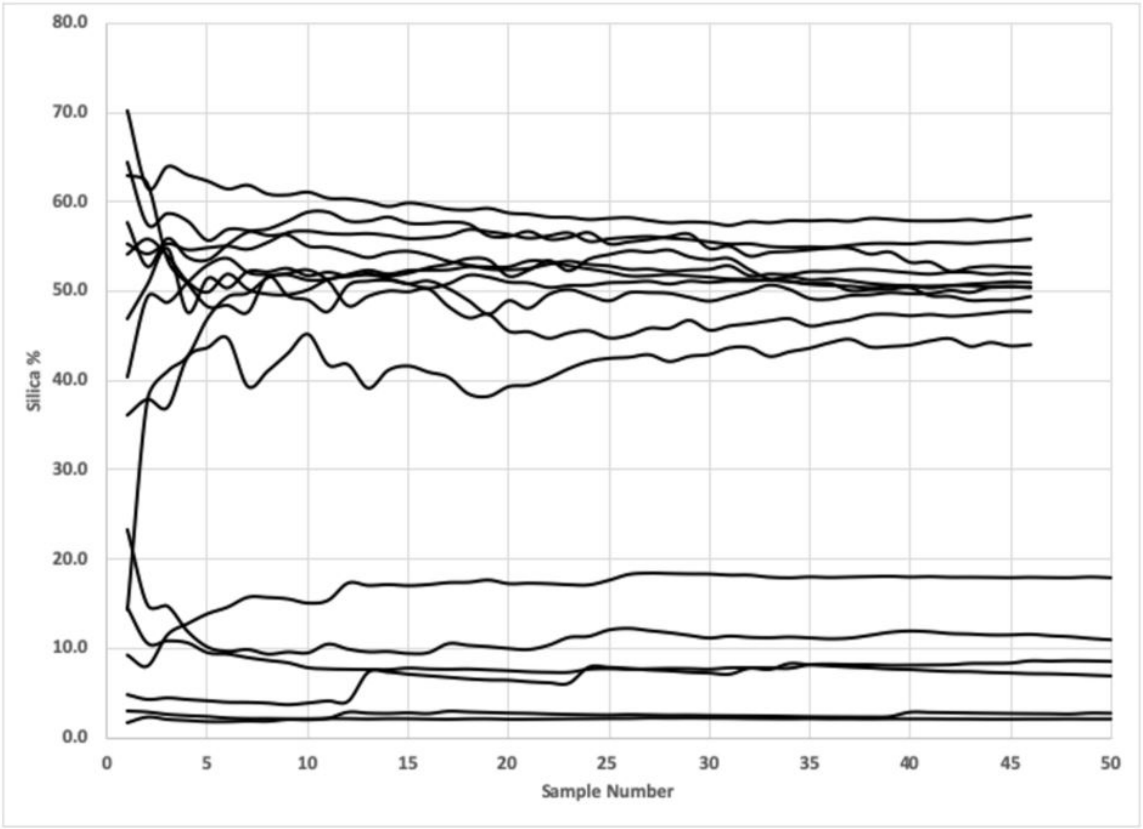
Source: FHWA.

Figure 5. Graph. Silica content of limestone aggregate sample 18-010B with the running average shown.



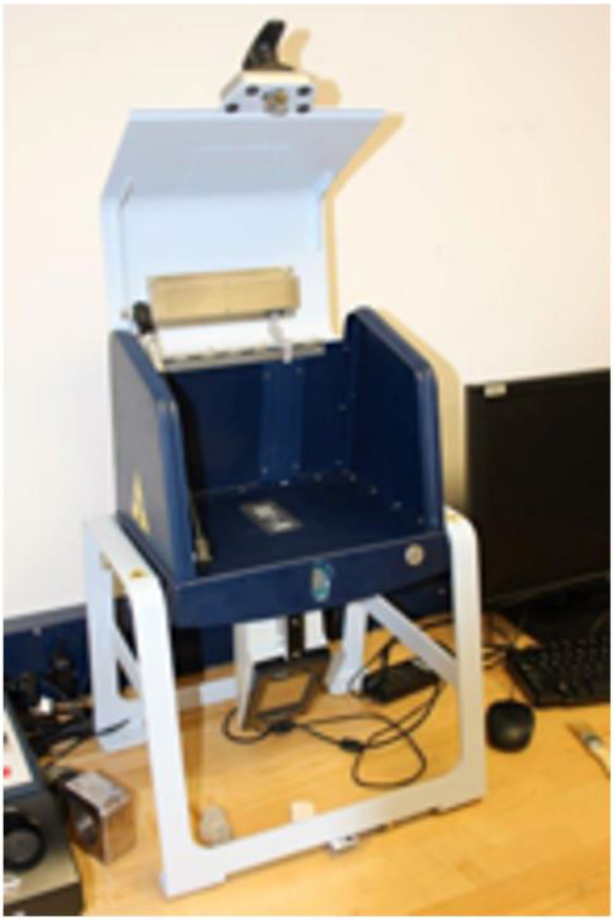
Source: FHWA.

Figure 6. Graph. Running average of silica content for 15 limestone aggregate samples.



Source: FHWA.

Figure 7. Photo. Handheld XRF spectrometer mounted under a bench stand.



Source: FHWA.

variation. Figure 4 is a plot of the XRF-spectroscopy results for sample 18-010B. The 44 individual aggregate pieces are shown on the x-axis, and the measured percentage of silica in each piece is on the y-axis.

The silica contents of the pieces from limestone aggregate sample 18-100B vary from about 7 to 67 percent (figure 4). Figure 5 depicts the average silica content of limestone aggregate sample 18-100B; the trend shows that it only takes 10 to 15 pieces to give a good estimation of the average silica content of the aggregate batch.

Analyzing random pieces of aggregate from 15 samples of washed limestone aggregate produced widely varying results (similar to the example in figure 4). Figure 6 shows the running averages for the 15 samples of limestone aggregate. For each sample, the running average quickly reached a steady level. Even in the worst cases, it took fewer than 20 aggregate pieces to determine the silica content of the sample. As the analysis for each piece takes only 30 seconds or so, handheld XRF spectroscopy can provide a field analysis at a quarry in less than 20 minutes with no sample preparation needed.

Handheld XRF spectrometers from different manufacturers are produced with different degrees of sophistication. Some are preprogrammed for different applications, while others can be programmed by the user. All need to be calibrated by setting up an analytical procedure using standard samples of known composition. Instrument suppliers provide calibration procedures.

The x-ray energy of handheld XRF spectrometers is very low. They are safe to use, but some care needs to be taken. Review the safety instructions that were supplied with the spectrometer. To avoid unnecessary exposure to radiation, do not hold the pieces while taking a reading. Instead, place the pieces on a flat surface and then take the reading. In the Turner-Fairbank Highway Research Center chemistry lab, a bench stand allows samples to be analyzed safely (figure 7). It is a steel box that acts as a shield from the x-rays.

REFERENCES

1. ASTM International. (2017). ASTM C25-17: *Standard Test Methods for Chemical Analysis of Limestone, Quicklime, and Hydrated Lime*, ASTM, West Conshohocken, PA.

Researchers—This study was performed by Terence S. Arnold (HRDI-10) in the Turner-Fairbank Highway Research Center chemistry lab.

Distribution—This TechBrief is being distributed according to a standard distribution.

Availability—This TechBrief may be obtained online at https://highways.dot.gov/research.

Key Words—Silica, limestone, skid resistance, handheld XRF spectrometer.

Notice—This document is disseminated under the sponsorship of the U.S. Department of Transportation (USDOT) in the interest of information exchange. The U.S. Government assumes no liability for the use of the information contained in this document. The U.S. Government does not endorse products or manufacturers. Trademarks or manufacturers' names appear in this TechBrief only because they are considered essential to the objective of the document.

Quality Assurance Statement—The Federal Highway Administration (FHWA) provides high-quality information to serve Government, industry, and the public in a manner that promotes public understanding. Standards and policies are used to ensure and maximize the quality, objectivity, utility, and integrity of its information. FHWA periodically reviews quality issues and adjusts its programs and processes to ensure continuous quality improvement.

APRIL 2020

FHWA-HRT-20-034
HRDI-10/04-20(WEB)E