NIST Special Publication 260-161

Certification of SRM 114q: Part I

Chiara F. Ferraris
William Guthrie
Ana Ivelisse Avilés
Robin Haupt
Bruce S. MacDonald

NIST National Institute of Standards and Technology • Technology Administration • U.S. Department of Commerce

NIST Special Publication 260-161

Certification of SRM 114q: Part I

Chiara F. Ferraris
Materials and Construction Research Division
Building and Fire Research Laboratory

William Guthrie
Ana Ivelisse Avilés
Statistical Engineering Division
Information Technology Laboratory

Robin Haupt
Materials and Construction Research Division
Construction Materials Reference Laboratory

Bruce S. MacDonald
Measurement Services Division
Technology Services

National Institute of Standards and Technology
Gaithersburg, MD 28099

July 2005

U.S. DEPARTMENT OF COMMERCE
Carlos M. Gutierrez, Secretary
TECHNOLOGY ADMINISTRATION
Michelle O'Neill, Acting Under Secretary of Commerce for Technology
NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY
Hratch G. Semerjian, Acting Director

National Institute of Standards and Technology Special Publication 260-161
Natl. Inst. Stand. Technol. Spec. Publ. 260-161, 36 pages (July 2005)
CODEN: NSPUE2

U.S. GOVERNMENT PRINTING OFFICE
WASHINGTON: 2005

For sale by the Superintendent of Documents, U.S. Government Printing Office
Internet: bookstore.gpo.gov — Phone: (202) 512-1800 — Fax: (202) 512-2250
Mail: Stop SSOP, Washington, DC 20402-0001

Abstract

The standard reference material (SRM) for fineness of cement, SRM 114, is an integral part of the calibration material routinely used in the cement industry to qualify cements. Being a powder, the main physical properties of cement, prior to hydration, are its surface area and particle size distribution (PSD). Since 1934, NIST has provided SRM 114 for cement fineness and it will continue to do so as long as the industry requires it. Different lots of SRM 114 are designated by a unique letter suffix to the SRM number, e.g., 114a, 114b, …. ,114q. A certificate that gives the values obtained using ASTM C204 (Blaine), C115 (Wagner) and C430 (45 μm sieve residue) is included with each lot of the material. The supply of SRM 114p, which was released in 1994, was depleted in 2004.

Therefore, a new batch of SRM 114 needed to be developed. This process included selection of the cement, packaging the cement in small vials, and determination of the values for the ASTM tests reported. In this case, the Blaine, Wagner and 45 μm sieve residue were the tests used. Later the particle size distribution (PSD) will be added.

The purpose of this report is to provide a detailed description of the process used to package and certify SRM 114q. All measurements used for the certifications are provided along with descriptions of the statistical analyses.

Acknowledgements

The authors would like to thank all participants of the round-robin (listed below in alphabetical order by institution) for providing time and staff to perform the Blaine, Wagner, and particle size distribution (PSD)[1] tests used for certification of this material.

Also, we would like to thank Stephen Small and the staff of the Cement and Concrete Reference Laboratory (CCRL), who were instrumental in providing the samples to the round-robin participants and making sieve residue measurements.

The authors would also like to thank some NIST key persons without whom this certification could not have being completed: Max Peltz for the PSD measurements; John Winpigler for the homogeneity measurements using loss of ignition; Mark Cronise and Curtis Fales for packaging all the materials; and Vince Hackley of the Materials Science and Engineering Laboratory for the numerous discussions during the planning stage.

Round-Robin Participants (Alphabetical)

American Engineering Testing, Inc., St. Paul, MN: Ken Prom
Armstrong Cement, Cabot, PA: Eugene Szymborski
Ash Grove Cement Co., Chanute, KS: Marc Melton
Ash Grove Cement Co., Louisville, NE: Doug Jaquier
Ash Grove Technical Center, Overland Park, KS: Kristen Freeman
Buzzi Unicem USA Greencastle, IN: John Wachal
Buzzi Unicem USA (formerly Lone Star), Greencastle, IN: W.D. Henry Robinson
Buzzi Unicem USA, Inc. Independence KS Plant, Independence, KS: Jan J Benson
Buzzi Unicem USA, New Orleans Slag Facility, New Orleans, LA: Ronald J. Rajki
California Portland Cement Co., Mojave, CA: Rebecca Lara
Cementa Research AB, Slite: Roger Lehrberg
Cemento De El Salvador S.A., EL Espino Antiguo Cuscatlan: Guillermo Osorio
Cementos Andino-Planta Betania, Bogota, Colombia: Maria M. Penaloza
Cementos Andino-Planta San Gil, Bogota, Colombia: Joost E. Oostra
Cementos del Norte,S.A.,Cortes: Jorge A. De J. Bueso
Cementos Progreso, S.A. Planta San Miguel, La Pedrera Lic.: Luis Velasquez
Cemex Inc. Fairborn, Xenia, OH: Rusty Strader
CEMEX-Central Plans LLC, Dixon, IL: Guido Tenaglia
CEREC-Cementos Progreso, S.A., La Pedrera: Emilio Beltranena
Ciment Quebec Inc., St-Basile (Quebec): Serge Vallerand
Concrete Technology-CECON-INTI, Buenos-Aires: Alejandra Benitez
Connecticut DOT Research & Materials Testing, Rocky Hill, CT: John R. Giannini
Construction Technology Laboratories, Skokie, IL: Ella Shkolnik
Delaware DOT, Dover, DE: Karl Zipf
ESSROC, Logansport, IN: Kevin Jensen

[1] PSD data will be discussed in another report under preparation

ESSROC San Juan, San Juan: Fernando Silvagnoli
ESSROC Bessemer Laboratory, Bessemer, PA: Patricia Dubchak
ESSROC Cement Corporation (Plant 1& Plant 3), Nazareth, PA: Bill Fink
ESSROC Italcementi Group, Picton Ontario: Melissa Eaton
F.L. Smidth A/S, Laboratory Copenhagen: Bjarne Osbaeck
GCC Dacotah, Rapid City, SD: Larry Paulsen
Glens Falls Lehigh Cement, Glens Falls, NY: Donna Malone
Hanson Permanante Cement, Cupertino, CA: John Lacy
Hawaii DOT Materials Testing and Research Branch, Honolulu, HI: Jonathan Yee
Hawaiian Cement-Cement Division, Kapolei, HI: Len B. Lagunoy
Hellenic Cement Research Center (EKET) Attikis: Vassilis Kaloidas
Hercules Cement Company, Stockertown, PA: Charles R. Ogle
Holcim Group Support Ltd., Holderbank: Werner Flueckiger
Holcim US Inc. Theodore Plant, Theodore, AL: Alissa Collins
Kansas DOT Central Laboratory, Topeka, KS: Rodney Montney
Lafarge - St. Constant, St. Constant, Quebec: Julie Arsenault
Lafarge North America, Ravena, NY: Randy Bitely
Lafarge North America, Calera, AL: Liz Higgins
Lafarge North America Alpena Plant, Alpena, MI: William Ulrich
Lafarge North America Exshaw Plant, Exshaw, Alberta: Carol Zaleski
Lafarge North America Joppa Plant, Grand Chain, IL: Eric Bowman
Lafarge North America Paulding Plant, Paulding, OH Tim Rawlsky
Lafarge North America Sugar Creek Plant, Sugar Creek, MO: Nick Ewing
Lehigh Cement Company, Leeds, AL: Michael Reylander
Lehigh Cement Company, Waco, TX: J.W.Davis
Lehigh Cement Company Union Bridge, Union Bridge, MD: Jeff Hook
Lehigh Southwest Cement Co., Tehachapi, CA: Garry Bell
Lone Star Industries- Buzzi Unicem USA, Pryor, OK: Mike Trimble
Master Builders, Inc., Cleveland, OH: Brad Hulvey
MD State Hwy Administration, Lutherville, MD: Vicki R. Stewart
Minnesota DOT, Maplewood, MN: Rod Patrin
Mississippi DOT, Jackson, MS: Richard Sheffield
Mitsubishi Cement Corp., Lucerne Valley, CA: Tom Gepford
Montana DOT.-Mat.Bureau ,Helena, MO: R. Scott Barnes
National Cement Co., Ragland, AL: Frank Holcomb
ND DOT, Bismarck, ND: Dennis Blasl
Nebraska Dept. of Roads-Mat.& Res. Div., Lincoln, NE: George Woolstrum
NORCEM AS, Brevik Brevik: David Verdu
Ohio DOT, Office of Materials Mgmt. Columbus, OH: Bryan Struble
Penn DOT Materials & Testing Lab, Harrisburg, PA: Roy Trout
RMC Pacific Materials Inc., Davenport, CA: Chow Yip
St. Lawrence Cement, Inc., Mississauga, Ontario: John Falletta
St. Marys Cement, Detroit, MI: Linda Harris
St. Marys Cement, St.Marys : Walter Pearce
Texas Lehigh Cement Co., Buda, TX: Jim Jarl
Texas Midlothian Cement Plant, Midlothian, TX: Jeff Wendel

The Euclid Chemical Co., Cleveland, OH: Bob Bucheral
TPI Polene Standard Laboratory, Saraburi: Zaw Zaw Hlaing
Texas DOT, Austin, TX: Lisa Lukefahr
TXI Hunter Cement,New Braunfels, TX: Herman Borchers
TXI Riverside Cement Co., Riverside, CA: Syed A. Rasheed
TXI Riverside Cement Co., Oro Grande Plant , Oro Grande, CA: Bob Sylvia

Table of Contents

1 Introduction 1
2 Description of methods used 2
2.1 Blaine ASTM C 204 2
2.2 Wagner ASTM C 115 2
2.3 Sieve Residue ASTM C 430 3
3 Materials 4
3.1 Characteristics of the cement 4
3.2 Packaging 5
3.3 Homogeneity determination 5
4 Experiment Design and Data Analysis 7
4.1 Blaine ASTM C 204 7
4.2 Wagner ASTM C 115 8
4.3 Sieve Residue ASTM C 430 9
4.3.1 Cross check of the residue 14
5 Summary of Certified Values 15
6 Process Improvement 16
6.1 Packaging 16
6.2 Testing 16
7 Acknowledgments 16
8 References 17
9 Appendices 18
10 Certificate of SRM 114q 23

List of Tables

Table 1: Chemical composition 4
Table 2: Cement compounds according to ASTM C150 5
Table 3: Results from the LOI tests 6
Table 4: ANOVA Output from the Fit of a Nested, Random-Effects Model with Factors Box, Lab, and Vial to the Blaine Data 7
Table 5: Summary of the Specific Surface Area Results for SRM 114q using the Blaine Procedure 8
Table 6: ANOVA Output from the Fit of a Nested, Random-Effects Model with Factors Box, Lab, and Vial to the Wagner Data 9
Table 7: Summary of the Specific Surface Area Results for SRM 114q: Wagner Procedure 9
Table 8: ANOVA Output from the Fit of a Nested, Random-Effects Model with Factors Box and Vial to the Sieve Residue Data for the 38 μm Sieve 11
Table 9: ANOVA Output from the Fit of a Nested, Random-Effects Model with Factors Box and Vial to the Sieve Residue Data for the 47 μm Sieve 11
Table 10: ANOVA Output from the Fit of a Nested, Random-Effects Model with Factors Box and Vial to the Sieve Residue Data for the 56 μm Sieve 12
Table 11: Residue Verification Using SRM's 114p and 114q 15

List of Figures

Figure 1: Plot of sieve residue data showing two outliers (square plotting symbols) from a vial that had been noted as containing cement of a different color than the other vials. 10
Figure 2: Plot of sieve residue data for the 47 μm sieve (with the outlier omitted) that shows evidence of day-to-day variation in the measurement process. 10
Figure 3: A Brooks-Gelman-Rubin plot [12] showing the ratio (upper trace) of the variation between and within (lower pair of traces) four parallel Markov chains that were simulated for this model. The fact that the ratio approaches 1 and the variation within and between chains levels off by 50 000th iteration indicates convergence. 13
Figure 4: The posterior probability distribution of the sieve residue for a 45 μm sieve. 14

1 Introduction

A standard reference material (SRM) is a material that has been well characterized with regard to its chemical composition, physical properties, or both. National Institute of Standards and Technology (NIST) provides over 1300 different SRMs to industry and academia. These materials are used in quality assurance programs, for calibration, and to verify the accuracy of experimental procedures. Every NIST SRM is provided with a certificate of analysis that gives the official characterization of the material's properties. In addition, supplementary documentation, such as this report, that describes the development, analysis and use of SRMs is also often published by NIST to provide the context necessary for effective use of these materials.

There are several SRMs related to cement (http://ts.nist.gov/ts/htdocs/230/232/232.htm). SRM 114 is related to the fineness of cement, as measured by various indirect methods giving its surface area and by passing the material through a fine sieve. This SRM is an integral part of the calibration material routinely used in the cement industry to qualify a cement. Being a powder, the main physical properties of cement are its surface area and particle size distribution (PSD). Since 1934, NIST has provided SRM 114 for cement fineness and it will continue to do so as long as the industry requires it. Different lots of SRM 114 are designated by a unique letter suffix to the SRM number. A certificate that gives the values obtained using ASTM C 204 (Blaine) [1], C 115 (Wagner) [2] and C 430 (45-μm residue) [3] is included with each lot of the material.

In 1934, only the Wagner test and the 45 μm residue were listed. In 1944, the Blaine measurement was added to the certificate of the SRM 114. In 2003, the PSD measured by laser diffraction was added as an information value, i.e., not certified. The PSD was obtained under the sponsorship of ASTM Task Group C01.25.01 [4, 5, 6].

The supply of SRM 114p, which was released in 1994, was depleted in 2004. Therefore, a new batch of SRM 114 needed to be developed. The development process included the selection of a cement, packaging of the cement in small vials, and determination of the values for the ASTM tests reported. In this case, the Blaine, Wagner and 45 μm sieve residue were the tests used. Later the particle size distribution (PSD) will be added.

The values given in this report were obtained through a round-robin inter-laboratory study by volunteer participants from companies participating in the CCRL certification program. The particle size distribution by laser diffraction was also collected in the same round-robin study but will be discussed in a separate report.

The purpose of this report is to provide the description of the development of SRM 114q. It includes a detailed description of the process used to package and certify the cement. Also a brief description of the ASTM tests in the certificate is given. All measurements used for the certifications are provided along with the statistical analysis.

2 Description of methods used

2.1 Blaine ASTM C 204

The Blaine measurement described in ASTM C 204 was adopted by ASTM in 1946. R.L. Blaine published the test in 1943 [7]. The principle of operation is that the permeability of a bed of fine particles is proportional to the fineness of the particles. Therefore, the test is a measurement of the flow rate of air through a bed of cement particles. From the beginning, it was stated that this is a relative test as it depends on the shape of the particles, and the compaction level or porosity of the bed. For this reason, ASTM C 204 section 4.1 states that the calibration of the instrument needs to be done by using a reference material, such as SRM 114 [8].

In brief, the test is carried out by packing the cement to be measured in a cell of known volume and placing it on top of a U-tube manometer that contains a non-hygroscopic liquid of low viscosity and density, e.g., dibutyl phthalate or a light grade of mineral oil. The cell is placed on the U-tube in such a way that a tight seal is created and a vacuum is created under the cement cell so that the liquid in the manometer is higher toward the cell. Then, the air is allowed to flow back only through the cement sample. The time for the liquid in the manometer to descend a set distance is measured. This time is used to calculate the fineness quantified by the surface area S of the cement defined using the following formula:

$$S = \frac{S_s \sqrt{T}}{\sqrt{T_s}} \quad \textbf{(1)}$$

where S_s is the surface area of the reference material, i.e., SRM 114
T_s is the time of flow using the reference material, i.e., SRM 114
T is the time of flow of the material under test
S is the surface area of the material under test

Therefore, the surface area of the material tested can be calculated from the reference material.

The results requested from the participants in the round-robin study to determine the value of SRM 114q were calculated using SRM 114p as the reference material. All participants were requested to measure the SRM 114p material immediately before measuring the SRM 114q material and to report both results.

2.2 Wagner ASTM C 115

The Wagner test method described in ASTM C115 was adopted by ASTM in 1934 after a paper published by L.A. Wagner in 1933 [9]. This test is also referred as the turbidimeter fineness test because it measures the turbidity of a cement suspension in kerosene.

A source of light shines through the cement suspension and is detected by a photoelectric cell. The intensity of the current generated by the cell is recorded. The calibration is done by calculation of a calibration factor, K, which depends on the cell used. To determine this factor a reference material, such as SRM 114, must be used.

Using a reference with known surface area, this test can be used to obtain the surface area of materials similar to the reference, (i.e. Portland cements), by comparing the two relative levels of turbidity. This method could also determine the particle size distribution, but is limited to particles larger than 7.5 μm. Due to this bound on particle size and various other sources of error, it is rarely used for PSD determinations.

The results requested from the participants in the round-robin study for SRM 114q used SRM 114p as the calibrant.

2.3 Sieve Residue ASTM C 430

The principle of this test is to measure the residue or retained amount of cement on a calibrated sieve. The sieve was selected as having a 45 μm opening (No. 325[2]). Since a direct certification of sieve openings is impractical and expensive for production-scale work, sieves are calibrated by using a reference material, such as SRM 114. A sieve correction factor is calculated by measuring SRM 114 on the selected sieve and correcting the result with the certified value of the SRM 114.

To avoid the need to propagate the SRM 114p uncertainty in the certification of the sieve residue for the SRM 114q material, however, three sieves with nominal openings of 38 μm, 47 μm, and 56 μm were directly calibrated for use in reference material certification. Interpolation was then used to obtain the value at 45 μm.

Although direct sieve calibration was also used for previous generations of this material, The procedure used for the 114q material was different in several respects from the certification of the two preceding lots of SRM 114:

- For SRM 114n sieves with openings of 42 μm to 43.9 μm were used. The average results were plotted against the average sieve opening. The certified value was calculated by extrapolation to 45 μm.
- For SRM 114p sieves with openings of 42 μm to 46 μm were used and all data points (rather than the averages) were plotted against the minimum sieve opening. The certified value was calculated by interpolation to 45 μm.

[2] Sieve number follow the USA definition given in ASTM E11

3 Materials

3.1 Characteristics of the cement

Based on the properties of past lots of SRM 114, CCRL and NIST identified a plant with a suitable cement for SRM 114q from Lehigh Cement Company[3], Union Bridge, Maryland, who donated 1300 kg of the cement for this SRM. The material selected was Type I according to the ASTM C 150 Standard Classification, and had a mass fraction of less than 8 % tricalcium aluminate (C_3A) as defined by ASTM C 150. This requirement was the same as for SRM 114p. Material was collected for shipment to NIST directly from the finish mill process stream into bags.

The approximate chemical composition has been determined by ASTM Standard Test Method C 114-02 to provide additional information on this cement. The analyses of this cement (CCRL Portland Cement Proficiency Sample No. 150) were performed by 70 to 170 laboratories. The composition, which is not certified but is provided for information only, is shown on Table 1.

Calculation of cement compounds from this chemistry, according to ASTM C 150-02, are shown in Table 2, again for information only.

The density of the cement was also measured using a modified ASTM C 188 method. The modification was to use isopropanol (IPA) as the medium instead of kerosene, otherwise a calibrated Le Chatelier flask was used as described in the ASTM test. Two measurements were done: 3.255 g/cm^3 and 3.248 g/cm^3. This leads to an average of 3.25 g/cm^3 $\pm$ 0.005 g/cm^3.

Table 1: Chemical composition

	CaO	SiO_2	$A1_2O_3$	Fe_2O_3	SO_3	K_2O	TiO_2	P_2O_5	Na_2O	MgO	loss on ignition
Percent by mass fraction	64	20.7	4.7	3.2	2.4	0.7	0.3	0.12	0.07	2.2	1.67

[3] Commercial equipment, instruments, and materials mentioned in this report are identified to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology (NIST), nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Table 2: Cement compounds according to ASTM C150

Compound	Percent by mass fraction
C_3S (tricalcium silicate)	60
C_2S (dicalcium silicate)	14
C_3A (tricalcium aluminate)	7
C_4AF (tetracalcium alumino-ferrite)	10

3.2 Packaging

Upon its arrival at NIST, the cement was blended in a V-blender (1.7 m^3 or 60 ft^3) and then transferred to 0.2 m^3 (55 gal) drums lined with 0.15 mm (6 mil) polyethylene liners to minimize hydration of the cement in storage prior to preparation and packaging. Over the next two days, the cement from each drum was sealed in foil bags, each containing about 16 kg of cement. The foil bags were stored, and subsequently packaged as described below into vials, in a climate-controlled area.

Each foil bag was packaged into vials and capped and boxed. Each box contained approximately 500 sealed vials and the boxes were sequentially labeled from 1 to 118. Usually about five boxes were filled per day. The more than 60 000 glass vials produced, each containing approximately 5 g of cement, were subsequently sealed into smaller individual foil bags. The vials were randomly selected (see section 4) and shipped to the participating laboratories for measurements. After the analysis of the results was completed the vials were packaged in boxes containing 20 vials each.

3.3 Homogeneity determination

After the material was packaged, it was necessary to determine whether the material in different vials was the same. A special concern was any absorption of moisture during packaging from original delivery to placement in the vials. Therefore, the first test that was performed was loss of ignition (LOI). Cement taken from random vials was submitted to the following procedure:

- The content of each sampled vial was divided among 3 crucibles (about 2 g of cement per crucible) and the mass was recorded
- The crucible was placed in an oven at 105 °C for 12 h, and then allowed to cool down in a dessicator containing a desiccant.
- The mass was recorded, and the crucible was placed in a furnace at 950 °C for 3 h.
- The sample was allowed to cool down in a dessicator and the mass was recorded.
- The LOI was calculated as the water loss during the residence in the furnace per mass of the sample (after the oven drying).

The LOI value is an indication of the amount of water loss during the drying procedure. A high value would be an indication of improper handling of the cement.

The LOI values are shown in Table 3. The Box # identifies a randomly sampled vial from that box. The LOI averages are very small (less than 0.15 %). Therefore, we conclude that there was no significant intake of moisture during packaging.

Nevertheless, further checks were performed during the analysis of the round-robin data by determining whether a box-to-box or vial-to-vial variation was detected (see Section 4).

Table 3: Results from the LOI tests

Box #	LOI [%]	Average [%]	St. Dev [%]
9	0.224	0.11	0.10
	0.045		
	0.050		
27	0.097	0.15	0.07
	0.224		
	0.137		
35	0.100	0.13	0.10
	0.243		
	0.048		
47	0.047	0.08	0.09
	0.179		
	0.000		
53	0.000	0.02	0.03
	0.000		
	0.046		
56	0.049	0.11	0.16
	0.000		
	0.290		
72	0.048	0.11	0.05
	0.135		
	0.141		
76	0.139	0.13	0.07
	0.189		
	0.049		
98	0.091	0.03	0.05
	0.000		
	0.000		
118	0.089	0.08	0.03
	0.046		
	0.100		

4 Experiment Design and Data Analysis

4.1 Blaine ASTM C 204

The data for the Blaine test, ASTM C 204, were collected using a nested experiment design with three factors, laboratory, box, and vial. In this design, two randomly selected laboratories who use the Blaine test were each supplied two randomly drawn vials of cement from a randomly assigned box of vials. The laboratory was then asked to measure duplicate samples from each vial. Use of this design allows assessment of lab-to-lab variability, box-to-box heterogeneity of the cement, and vial-to-vial heterogeneity of the cement.

For the analysis of the Blaine data, the first step was to screen the data for non-statistical problems. Based on this screening, results from three labs, 209, 247, and 932, were eliminated from the data set. In each case, the data from these laboratories were omitted from the analysis because Blaine measurements were made on one vial from the box designated for the Blaine measurements and one vial from the box designated for the Wagner measurements. Due to the nature of the experiment design, including these results would have made it more difficult to distinguish between the different potential sources of variation.

Next, a nested, random-effects, analysis of variance (ANOVA) model [10] was fit to the remaining data to check for box-to-box, lab-to-lab, and vial-to-vial variability. Residual plots to verify that the model fit the data showed that two labs each had two extreme outlying measurements. Since there were a large number of labs (66) for this analysis and only two had unusual data, the data from these two labs (123 and 886) was also omitted from the analysis. After refitting the model, residual plots indicate that the model fits the data well. The output from the analysis of variance is shown in Table 4. The low p values (<0.05) corresponding to the F tests for the significance of lab-to-lab and vial-to-vial variability provide strong evidence that there is significant lab-to-lab variation and vial-to-vial heterogeneity. The high p value for the F test for box-to-box variability (0.365) indicates that there is not strong evidence of significant box-to-box heterogeneity in this data.

Table 4: ANOVA Output from the Fit of a Nested, Random-Effects Model with Factors Box, Lab, and Vial to the Blaine Data

Source	Degrees of Freedom	Sums of Squares	Mean Squares	F Statistic	p value
Box-to-Box	37	18703.91	505.511	1.143	0.365
Lab-to-Lab (in Box)	26	11494.21	442.085	29.328	0.000
Vial-to-Vial (in Box/Lab)	64	964.72	15.074	2.960	0.000
Residuals	128	651.83	5.092		

Because there is significant vial-to-vial heterogeneity, a prediction interval should be used for certification. Based on the ANOVA results above, a summary of the material's properties as measured with the Blaine procedure is given in Table 5.

Table 5: Summary of the Specific Surface Area Results for SRM 114q using the Blaine Procedure

Mean Blaine Result:	381.81	m^2/kg
Standard Uncertainty of Mean:	1.31	m^2/kg
Effective Degrees of Freedom:	26.00	
Standard Uncertainty of Heterogeneity:	2.23	m^2/kg
Effective Degrees of Freedom:	26.55	
Standard Uncertainty of 114p	2.93	m^2/kg
Effective Degrees of Freedom:	60.00	
Combined Standard Uncertainty:	3.91	m^2/kg
Effective Degrees of Freedom:	102.66	
Coverage Factor (95 % coverage):	1.98	
Expanded Uncertainty:	7.76	m^2/kg

4.2 Wagner ASTM C 115

The experiment design and analysis used for the Wagner [2] data are analogous to the design and analysis used for the Blaine data. As the first step in the analysis, the Wagner data were also screened for non-statistical problems. Based on this screening, data from one lab, 247, were eliminated from the data set because Wagner measurements were made on one vial from the box designated for the Wagner measurements and one vial from the box designated for the Blaine measurements.

Next we fit a nested, random effects, analysis of variance model to the remaining data to check for box-to-box, lab-to-lab, and vial-to-vial variability. Residual plots indicate that the model fits the data well, although there is only one degree of freedom for estimating the lab-to-lab variability. The analysis of variance results are shown in Table 6. The high p values for the tests for significant box-to-box and vial-to-vial variability do not provide strong evidence that the material is heterogeneous as measured by the Wagner method. Even with one degree of freedom, however, significant lab-to-lab variation is evident as indicated by the low p value for the F test for the significance of lab-to-lab variability.

Table 6: ANOVA Output from the Fit of a Nested, Random-Effects Model with Factors Box, Lab, and Vial to the Wagner Data

Source	Degrees of Freedom	Sums of Squares	Mean Squares	F Statistic	p value
Box-to-Box	4	250579.600	62644.900	0.335	0.841
Lab-to-Lab (in Box)	1	186966.100	186966.100	295.696	0.000
Vial-to-Vial (in Box/Lab)	6	3793.800	632.300	0.907	0.522
Residuals	12	8367.500	697.300		

Since there is no evidence of vial-to-vial or box-to-box variability, it was decided to base the certified value and uncertainty for the Wagner method on the mean and standard deviation of the laboratory means. Based on this decision, a summary of the certification results is given in Table 7. The final uncertainty is large because so few labs are using the Wagner method and could provide results using this method in the inter-laboratory study.

Table 7: Summary of the Specific Surface Area Results for SRM 114q: Wagner Procedure

Mean Wagner Result:	218.33	m^2/kg
Standard Uncertainty of Mean:	6.04	m^2/kg
Effective Degrees of Freedom:	5.00	
Standard Uncertainty of 114p:	2.35	m^2/kg
Effective Degrees of Freedom:	60.00	
Combined Standard Uncertainty:	6.48	m^2/kg
Effective Degrees of Freedom:	6.62	
Coverage Factor (95 % coverage):	2.44	
Expanded Uncertainty:	15.86	m^2/kg

4.3 Sieve Residue ASTM C 430

A nested design with three factors, day, box and vial was used to collect the sieve residue data. The same design values were used to make measurements on each of the three sieves with one measurement per sieve made from each vial tested. This design allows for the estimation of day-to-day, box-to-box, and vial-to-vial variation. In addition, since the three sieves are each of different sizes spanning the sieve value of interest, 45 μm, the data from this experiment can also be used to fit a model relating sieve residue to the sieve opening size.

For the analysis of the sieve residue data, the data were first plotted to graphically identify potential factor effects and to look for any unusual observations. The plot in Figure 1 identifies two outliers, from measurements on a vial that had been noted to contain a different color of cement than the others. Since these points were obtained from a suspect sample and were very different from all of the other data, they were eliminated from the analysis. Measurements of other samples from this vial, which did not appear to

have unusual values, were still used, however. After removal of the outliers, some evidence of day-to-day variation between the samples is also evident in Figure 2.

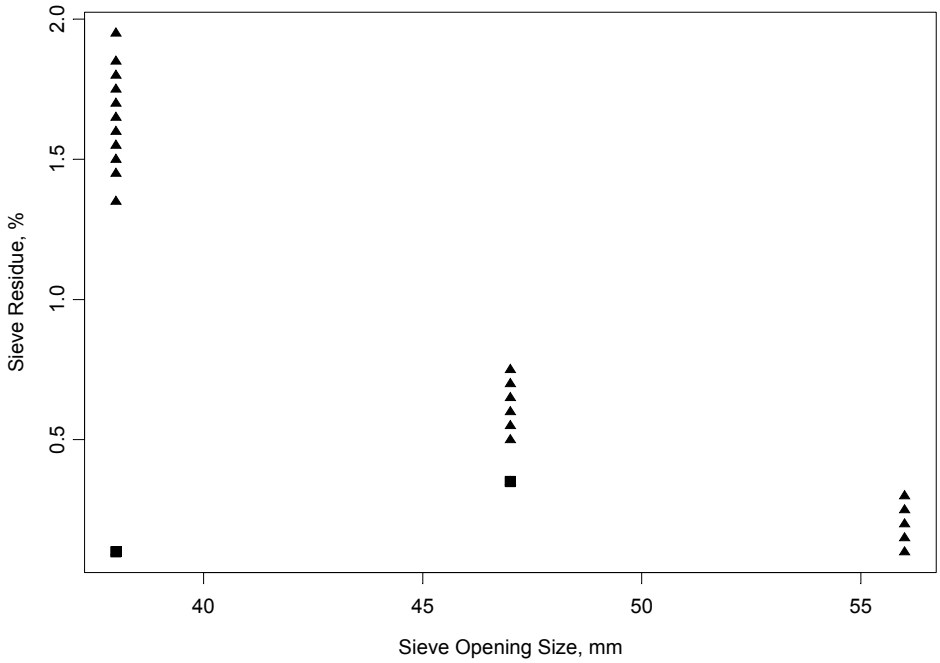

Figure 1: Plot of sieve residue data showing two outliers (square plotting symbols) from a vial that had been noted as containing cement of a different color than the other vials.

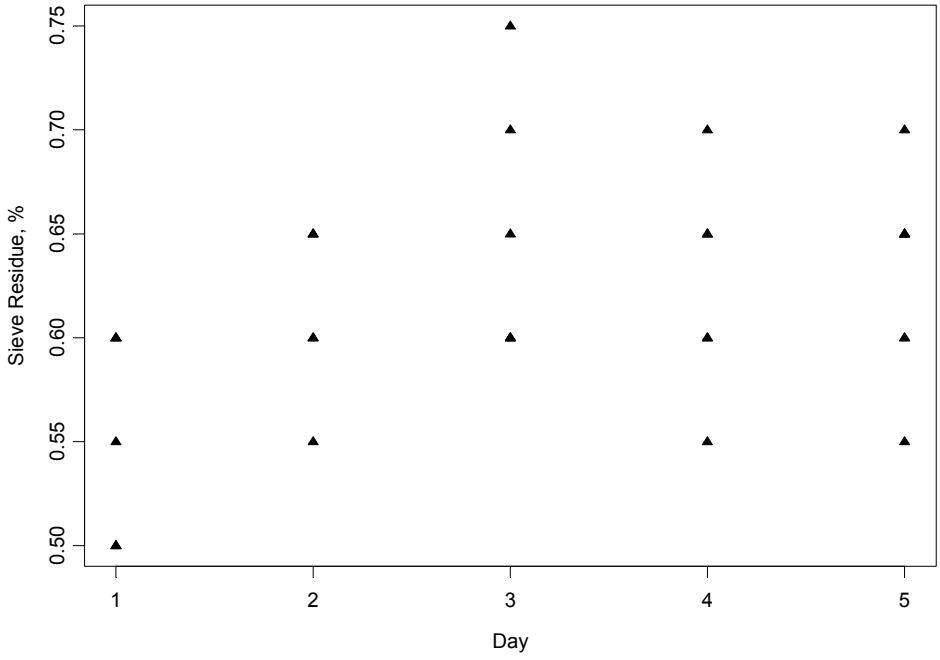

Figure 2: Plot of sieve residue data for the 47 μm sieve (with the outlier omitted) that shows evidence of day-to-day variation in the measurement process.

Next, a nested, random effects analysis of variance model was fit to the data from each sieve to check for day-to-day, box-to-box, and vial-to-vial variability. To maintain the balance of the design for the two sieves for which 1 of the 40 measurements was omitted, the means of the remaining data from the same box as the omitted vial were substituted for the missing data points. Residual plots from each fit verify that the models fit the data from each sieve reasonably well. The ANOVA results, showing the output from the fit of the model to the data from each sieve, are given in Table 8 to Table 10. The relatively high p values in Table 8 ($p > 0.05$) indicate that there is not strong evidence for day-to-day, box-to-box, or vial-to-vial in these data collected using the 38 μm sieve. The low p value for the F test for significant day-to-day variation (0.025) does indicate that there is significant day-to-day variation in the data collected using the 47 μm sieve. There is no evidence of significant variability from the other two factors, however. Finally, the high p values for day-to-day and box-to-box variability for the 56 μm sieve indicate that those factors are not significant, but the low p value for the F test for vial-to-vial variability indicates that there is significant vial-to-vial variation in the measurements made with the 56 μm sieve

Table 8: ANOVA Output from the Fit of a Nested, Random-Effects Model with Factors Box and Vial to the Sieve Residue Data for the 38 μm Sieve

Source	Degrees of Freedom	Sums of Squares	Mean Squares	F Statistic	p value
Day-to-Day	4	0.124	0.031	1.126	0.439
Box-to-Box (in Day)	5	0.138	0.028	2.085	0.095
Vial-to-Vial (in Day/Box)	10	0.178	0.018	1.614	0.174
Residuals	20	0.220	0.011		

Table 9: ANOVA Output from the Fit of a Nested, Random-Effects Model with Factors Box and Vial to the Sieve Residue Data for the 47 μm Sieve

Source	Degrees of Freedom	Sums of Squares	Mean Squares	F Statistic	p value
Day-to-Day	4	0.047	0.012	7.406	0.025
Box-to-Box (in Day)	5	0.008	0.002	0.722	0.612
Vial-to-Vial (in Day/Box)	10	0.017	0.002	0.679	0.731
Residuals	20	0.049	0.002		

Table 10: ANOVA Output from the Fit of a Nested, Random-Effects Model with Factors Box and Vial to the Sieve Residue Data for the 56 μm Sieve

Source	Degrees of Freedom	Sums of Squares	Mean Squares	F Statistic	p value
Day-to-Day	4	0.010	0.003	0.965	0.500
Box-to-Box (in Day)	5	0.013	0.003	1.066	0.399
Vial-to-Vial (in Day/Box)	10	0.4690	0.005	3.261	0.012
Residuals	20	0.029	0.001		

For the certification analysis, a Bayesian model relating the sieve residue of the 114q material from each sieve to the measured sieve size was developed. A Bayesian model was used in order to be able to account for the uncertainty in both the sieve calibrations and the measurements of the reference material made using those sieves. Because of the apparent day-to-day and vial-to-vial variation, and to allow for the fact that those effects were not consistently visible for all sieves, the Bayesian model accounts for all four possible sources of random variation that were included in the design, day-to-day, box-to-box, vial-to-vial, and measurement uncertainty. Although it might not be necessary to treat all of the sieves in the same way, since only one exhibited significant apparent day-to-day variability and one exhibited significant apparent vial-to-vial variability, it was decided to treat them consistently in case those effects (or box-to-box effects) were simply not detected for the other two sieves.

In order to specify inter-relationships among the data, the model specifies the hypothesized relationships between the unknown true values underlying the data (called parameters in statistical jargon), which are to be estimated. In this case, the model specifies a quadratic relationship between the true sieve residues and true sieve sizes. The data gives us the quantitative information needed to estimate the parameter values. Then the model is used to interpolate the result that would be obtained from a sieve with openings of exactly 45 μm.

In order to use the Bayesian model, initial assessments of the values of each parameter in the model must be provided. The initial assessment for each parameter is specified as a probability distribution for the parameter's unknown value. Because these probability distributions are specified independently of the data (i.e. before the data are observed or used), these distributions are commonly called prior distributions. For this analysis, non-informative prior distributions were used. These distributions are essentially very flat and have very large variances so that they will not provide any quantitative information about the values of the parameters as part of the model.

A probability distribution for each measurement, given with respect to the parameters in the model, is also specified. This distribution is called the likelihood of the data. For this analysis, based on typical assumptions for the statistical analysis of metrological data, normal distributions with means specified by the quadratic relationship between residue and sieve size and standard deviations based on sieve size were used for the likelihood. Then, based on the hypothesized relationships between the parameters, the likelihood, and the observed data, the prior distributions for each parameter are updated using Bayes'

Theorem to obtain new distributions for each parameter given the information in the data. Finally, these new distributions, called posterior distributions, are used to obtain uncertainty intervals about each quantity of interest.

The Bayesian model was fit using Markov Chain Monte Carlo simulation [11]. Figure 3 shows a plot comparing the within and between chain variation [12] that indicates that the Markov Chains had converged by the 50 000th iteration of the simulation. Then 10 000 additional iterations were run for each of 4 parallel Markov chains to estimate the parameter values. Based on these results, the posterior probability distribution describing the sieve residue for a 45 μm sieve is shown in Figure 4. A 95 % probability interval for the value of the sieve residue obtained from this posterior distribution is 0.79 % ± 0.19 %.

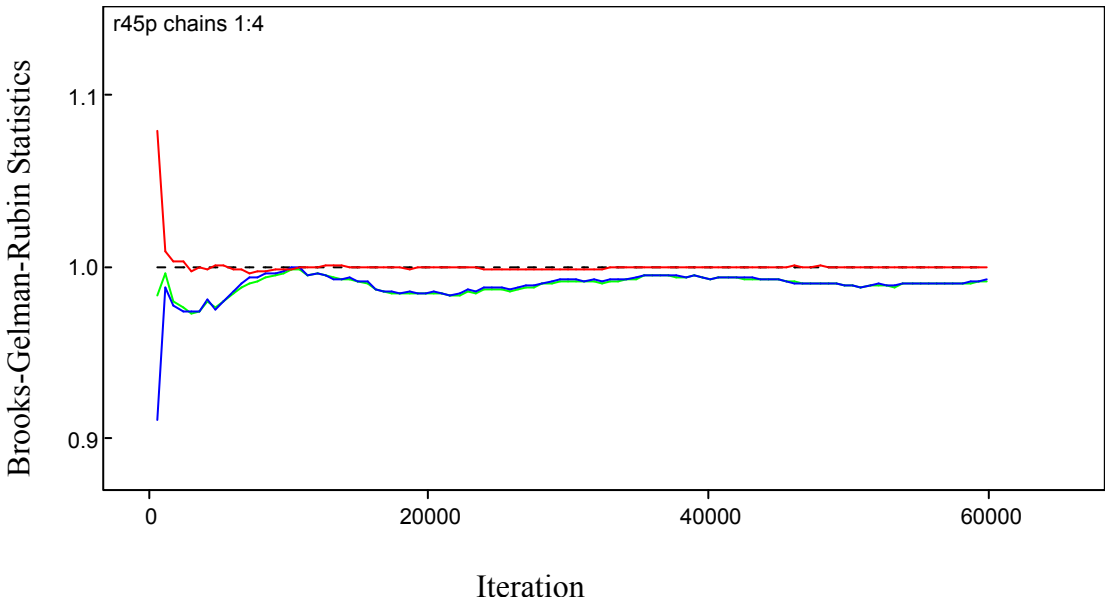

Figure 3: A Brooks-Gelman-Rubin plot [12] showing the ratio (upper trace) of the variation between and within (lower pair of traces) four parallel Markov chains that were simulated for this model. The fact that the ratio approaches 1 and the variation within and between chains levels off by 50 000th iteration indicates convergence.

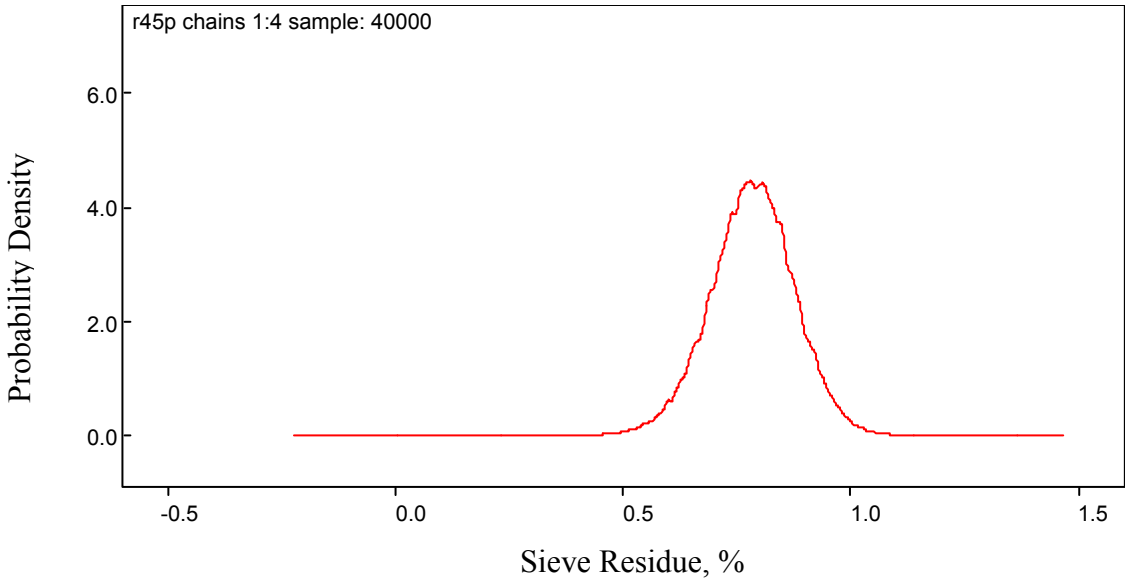

Figure 4: The posterior probability distribution of the sieve residue for a 45 μm sieve.

4.3.1 Cross check of the residue

Because the 114q material has such a different residue than previous generations of this material, it is important to verify that the correct results will be obtained when the certified value is used to calibrate a sieve as described in ASTM C430. The standard implies that the SRM 114q is sieved using a sieve with an unknown opening (although it should nominally be about 45 μm). The result is used with the certified value to calibrate the sieve and correct results of unknown cements.

To verify the performance of the 114q material, we did a double verification as shown in Table 11. The verification consisted of calculating the correction factor using one of the SRMs and testing the other SRM using this correction factor. For example in column 1 (Table 11) SRM 114p is used to calculate the correction factor that is then used to correct a measurement of SRM 114q. If everything it working as expected, the residue found for SRM 114q should match the value found in the certificate, which it does. Similarly, the results obtained for SRM 114p, when 114q is used to calibrate the sieve, do not disagree with the value from the 114p certificate, although the uncertainty in the corrected result for 114p is rather large.

Table 11: Residue Verification Using SRM's 114p and 114q

Sieve Correction Factor Calculation	SRM 114p	SRM 114q
Certified residue on 45 μm sieve [%]	8.24 ± 0.37	0.79 ± 0.19
Residue for 1 g sample [g]	0.0824 ± 0.0037	0.0079 ± 0.0019
Residue on sieve being calibrated [g]	0.0683 ± 0.0068	0.0060 ± 0.0006
Difference [g]	0.0141 ± 0.0077	0.0019 ± 0.0020
Correction factor [%]	20.6442 ± 13.22	31.6667 ± 34.2949

Cement Tested	SRM 114q	SRM 114p
Residue from sample being tested [g]	0.0060 ± 0.0006	0.0683 ± 0.0068
Corrected residue [%]	0.7239 ± 0.1074	8.9928 ± 2.5090
Certified residue on 45 μm sieve [%]	0.79 ± 0.19	8.24 ± 0.37

Note: Uncertainties shown for each value are expanded uncertainties at the 95 % confidence level. A coverage factor of $k = 2$ was used in all cases.

5 Summary of Certified Values

The certified values for the SRM 114q certificate are:

Measurement and ASTM Method	Result
Specific Surface Area C 204-96a (Blaine)	3818 cm^2/g ± 78 cm^2/g (381.8 m^2/kg ± 7.8 m^2/kg)
Specific Surface Area C 115-96a (Wagner)	2183 cm^2/g ± 160 cm^2/g (218 m^2/kg ± 16 m^2/kg)
Sieve Residue C 430-96 (45 μm sieve)	0.79 % ± 0.19 %

6 Process Improvement

6.1 Packaging

As stated above, the cement received from the manufacturer was sealed in foil bags after being blended. It was the original intention that each foil bag would be open, divided in the vials and any left over would be discarded. This would ensure that the cements left in the foil bags overnight (or longer due to scheduling) would not hydrate in between vial filling. If hydration occurs the cement properties will change. As a further quality assurance, the temperature, relative humidity should be recorded. If a log is kept of the temperature, relative humidity, vials filled, it would results in a better correlation between homogeneity problems and specific vials.

During the filling of this batch of 600 000 vials, the procedure outlined above was followed but no log was kept of the temperature and relative humidity. Therefore, when it was discovered that vials, checked for homogeneity using other methods such as PSD, were found not satisfactory [13], it was not possible to rule out that the packaging conditions were one of the effects.

This situation did not affect the data presented here probably because none of the tests used are sensitive to complete dispersion, as it is the case for PSD measurements.

6.2 Testing

As shown in Table 3, one vial per box was used for the LOI testing. With this design, box-to-box and vial-to-vial differences in the LOI results cannot be differentiated. One minor improvement to the design for LOI testing in the future would be to sample two vials per box so that potential vial-to-vial variability could be separated from box-to-box variability in the LOI results. If necessary, half as many boxes could be sampled in order to keep the total number of measurements the same. Reducing the number of boxes sampled would reduce our ability to identify box-to-box differences, since some of the degrees of freedom would be used to check for vial-to-vial variability, but the added ability to separate vial-to-vial variability from box-to-box variability would give us the potential for additional insight into the process that would offset that loss.

Because of the small sieve residue for this cement, some digitization was evident in the sieve residue data. For future sieve residue assessments on cements with residues in this low range, use of a balance with a finer resolution would be advantageous.

7 Acknowledgments

The authors would like to thank Max Peltz for helping with the sample preparations, and Romayne Hines for helping in distribution of the samples for the round-robin. Special thanks are extended also to Vince Hackley for his numerous suggestions and fruitful

discussions, and Edward Garboczi (NIST), Kenneth Snyder (NIST) and Charles Hagwood (NIST) for their valuable comments.

8 References

1. "Standard Test Method for Fineness of Hydraulic Cement by Air Permeability Apparatus", ASTM C204-00 Volume: 04.01
2. "Standard Test Method for Fineness of Portland Cement by the Turbidimeter", ASTM C115-96a (2003) Volume: 04.01
3. "Standard Test Method for Fineness of Hydraulic Cement by the 45-μm (No. 325) Sieve", ASTM C430-96 (2003) Volume: 04.01
4. Ferraris, C.F, Hackley V.A., Aviles A.I., Buchanan C.E., "Analysis of the ASTM Round-Robin Test on Particle Size Distribution of Portland Cement: Phase I" NISTIR 6883, May 2002 (http://ciks.cbt.nist.gov/~garbocz/nist6883/nistir6883.htm)
5. Ferraris, C.F, Hackley V.A., Aviles A.I., Buchanan C.E., "Analysis of the ASTM Round-Robin Test on Particle Size Distribution of Portland Cement: Phase II" NISTIR 6931, December 2002
6. Ferraris C.F., Hackley V.A., Avilés A.I., "Measurement of Particle Size Distribution in Portland Cement Powder: Analysis of ASTM Round-Robin Studies", Cement, Concrete and Aggregate Journal, Dec. 2004, vol. 26 #2, pp 71-81
7. Blaine R.L., "A Simplified Air Permeability Fineness Apparatus" , ASTM Bulletin, No.123, 1943, pp 51-55
8. Bean L. B., Dise J.R., "Causes of Variation in Chemical Analyses and Physical Tests of Portland Cement", NBS, Building Series #17, 1969
9. Wagner, L. A., "A Rapid Method for the Determination of the Specific Surface of Portland Cement," *Proceedings*, ASTM, ASTEA, Vol 33, Part II, 1933, p. 553
10. Montgomery, Douglas C., *Design and Analysis of Experiments*, 2nd Edition, John Wiley and Sons, New York, 1984
11. Gelman, A., Carlin, J.B., Stern, H.S., Rubin, D.B., *Bayesian Data Analysis*, Chapman and Hall, London, 1995
12. Brooks S.P. and Gelman A. "Alternative methods for monitoring convergence of iterative simulations," *Journal of Computational and Graphical Statistics*, 7, 1998, pp 434-455
13. Ferraris, C.,F. Avilés A.I., Guthrie W., Haupt, R., MacDonald, B. S., Peltz, M. "Certification of SRM 114q: Part II", to be published in 2005

9 Appendices

Appendix A: Data received from the round robin for Blaine

CCRL Lab Code	Raw data as received: Grey [m^2/ kg]; white [s]								Calculated Blaine (SRM 114p & data provided)					
	SRM 114p		Vial #1			Vial #2			Vial #1			Vial #2		
	Meas#1	Meas.#2	Box #	Meas#1	Meas.#2	Box #	Meas#1	Meas.#2	Box #	Meas#1	Meas.#2	Box #	Meas#1	Meas.#2
6	85.1		19	89.9	89.46	19	89.01	88.35	19	3878	3869	19	3859	3845
10	104		45	90.7	89.8	45	88.56	89.3	45	3525	3507	45	3483	3497
11	74		89	80	78	89	79	79	89	3924	3875	89	3899	3899
18	85	87.5	30	71	66.5	30	64.5	67.5	30	3424	3314	30	3264	3339
19	118		70	129.2	129.4	70	129.6	128.8	70	3949	3952	70	3955	3943
20	85.3		114	91.6	90.01	114	91.29	92.6	114	3912	3877	114	3905	3933
27	152	149	107	157	157	107	158	157	107	3855	3855	107	3867	3855
28	3800		81	3910	3910	81	3880	3900	81	3910	3910	81	3880	3900
40	109.6	108.7	109	121.1	119.9	109	115.5	117.9	109	3975	3956	109	3882	3922
41	75.7		9	76.9	76.7	9	75.9	76	9	3804	3799	9	3779	3781
43	91.4		55	95.2	95.1	55	95.7	95.8	55	3852	3850	55	3862	3864
54	3772	3770	89	3814	3748	89	3878	3882	89	3814	3748	89	3878	3882
56	3820	3840	50	3810	3770	50	3810	3790	50	3810	3770	50	3810	3790
60	114	114	80	121	120	80	119	120	80	3888	3872	80	3856	3872
69	77.4	76.8	40	78.8	79.1	40	78.6	78.2	40	3815	3823	40	3811	3801
73	80		58	83	82	58	80	81	58	3844	3821	58	3774	3798
75	3810	3800	77	3695	3715	77	3697	3708	77	3695	3715	77	3697	3708
84	115.4		120	116.555	115.7	120	122.1	121.4	120	3793	3779	120	3881	3870
92	68.8	66.56	118	71.35	68.0	118	70.17	69.5	118	3876	3784	118	3844	3827
95	77.5	77	80	85.5	85	80	85	85.5	80	3970	3959	80	3959	3970
105	85.4	85.9	11	86.7	86.9	11	85.7	86	11	3797	3801	11	3775	3782
121	81.4		47	83.20	84.6	47	84.3	84.1	47	3816	3847	47	3840	3836
123	84		88	105	80	88	83	83.5	88	4219	3683	88	3751	3763

CCRL Lab Code	Raw data as received: Grey [m^2/ kg]; white [s]								Calculated Blaine (SRM 114p & data provided)					
	SRM 114p		Vial #1			Vial #2			Vial #1			Vial #2		
	Meas#1	Meas.#2	Box #	Meas#1	Meas.#2	Box #	Meas#1	Meas.#2	Box #	Meas#1	Meas.#2	Box #	Meas#1	Meas.#2
124	70	70.5	13	75	75.5	13	75.5	75.5	13	3900	3912	13	3912	3912
125	3752		11	3861	3861	11	3796	3752	11	3861	3861	11	3796	3752
148	83.9	82.8	75	81.0	79.3	75	82.8	82.2	75	3720	3680	75	3761	3748
151	89.1	86.6	116	87.3	86.0	116	90.8	88.7	116	3762	3734	116	3837	3793
157	93		58	95	94	58	94	93	58	3814	3794	58	3794	3774
162	3745	3756	14	3796	3806	14	3777	3788	14	3796	3806	14	3777	3788
166	81	81	86	90	90	86	90	90	86	3978	3978	86	3978	3978
167	3750	3730	98	3800	3800	98	3860	3850	98	3800	3800	98	3860	3850
175	106	110	30	110	111	30	109	111	30	3809	3827	30	3792	3827
178	77.5	77.4	3	67.4	69.5	3	73.6	70.3	3	3521	3575	3	3679	3596
205	90	89.8	50	91.9	90.9	50	90.9	91.5	50	3816	3795	50	3795	3807
209	85.3	84	66	90.7	89.9	113	88.4	91.0	66	3907	3889	113	3857	3913
222	87.7		28	87.8	86.5	28	87.6	87.3	28	3776	3748	28	3772	3765
225	105	106	40	110	111	40	109	110	40	3854	3871	40	3836	3854
245	80		19	73	72.5	19	73	74	19	3605	3593	19	3605	3630
246	71.5		21	81	80.3	21	79.8	79.1	21	4017	4000	21	3987	3970
247	88		43	93		109	92		43	3880	0	109	3859	
254	3765	3788	97	3854	3846	97	3807	3815	97	3854	3846	97	3807	3815
255	3730		77	3800	3720	77	3800	3839	77	3800	3720	77	3800	3839
284	97.0	97.5	86	104.0	104.0	86	104.0	103.5	86	3903	3903	86	3903	3893
303	92.9	92.2	32	94.5	93.9	32	95.5	92.4	32	3814	3801	32	3834	3771
309	88	88	116	90	90	116	90	90	116	3817	3817	116	3817	3817
354	77.7	76.5	31	80.95	80.65	31	79.82	78.75	31	3867	3860	31	3840	3814
360	100	100	3	100	98	3	99	97	3	3774	3736	3	3755	3717
413	Too variable to report													
441	3760	3760	114	3740	3650	114	3710	3690	114	3740	3650	114	3710	3690
493	83	84	32	87	90	32	90	88	32	3852	3918	32	3918	3874
494	97	98	66	100	100	66	98	98	66	3822	3822	66	3784	3784

CCRL Lab Code	Raw data as received: Grey [m^2/ kg]; white [s]								Calculated Blaine (SRM 114p & data provided)					
	SRM 114p		Vial #1			Vial #2			Vial #1			Vial #2		
	Meas#1	Meas.#2	Box #	Meas#1	Meas.#2	Box #	Meas#1	Meas.#2	Box #	Meas#1	Meas.#2	Box #	Meas#1	Meas.#2
551	3751	3769	112	3892	3887	112	3926	3930	112	3892	3887	112	3926	3930
557	100	100	18	101	100	18	100	101	18	3793	3774	18	3774	3793
605	3816		28	3879	3879	28	3859	3816	28	3879	3879	28	3859	3816
690	3774		88	3801	3801	88	3828	3828	88	3801	3801	88	3828	3828
736	99.6	97.8	71	108.2	105.3	71	107.6	106.5	71	3951	3898	71	3939	3920
886	3705	3735	119	3832	3784	119	3624	3851	119	3832	3784	119	3624	3851
932	115.4		19	121.4	122.9	75	123.2	123.8	19	3871	3895	75	3899	3909
1042	111.6	111.1	21	114.4	114.3	21	110.9	112.6	21	3824	3823	21	3766	3795
1054	83	85	14	93	93	14	90	90	14	3971	3971	14	3907	3907
1251	3765	3757	107	3891	3874	107	3883	3883	107	3891	3874	107	3883	3883
1715	72.9	72.3	13	74.8	75.1	13	75.6	75.5	13	3829	3837	13	3850	3848
1773	101.1	101.4	47	91.3	91.6	47	90.4	90.7	47	3584	3590	47	3566	3572
1819	82.59	83.00	9	86.4	87.1	9	86.1	86.5	9	3855	3870	9	3850	3858
1916	88.9	88.7	31	94.1	95.2	31	95.6	94.2	31	3884	3908	31	3916	3887
1940	3716	3753	18	3870	3901	18	3825	3922	18	3870	3901	18	3825	3922
2116	47.5	48.0	118	50.5	50.0	118	50.5	49.5	118	3881	3862	118	3881	3843
2190	85.3	86.0	111	86.3	85.8	111	87.5	86.3	111	3789	3778	111	3815	3788
2191	75.4	74.3	111	73.6	77.4	111	79.7	81.4	111	3744	3837	111	3896	3937
NA	65.2	64.8	70	66.7	67.0	70	66.5	66.5	70	3824	3832	70	3816	3818

Appendix B: Data received from the round robin for Wagner

CCRL code	114p		Box A			Box B		
	Meas. #1	Meas. #2	Box #	Meas. #1	Meas. #2	Box #	Meas. #1	Meas. #2
73	2049		9	1984	1986	9	1997	2040
125	2130		9	2330	2290	9	2310	2300
205	2070		119	2380	2380	119	2380	2350
247			43	2280	2240	109	2260	2280
254	2060	2085	43	2046	2020	43	2117	2043
494	2088	2078	66	2113	2126	66	2135	2079
551	2045	2067	113	2227	2262	113	2272	2232

Appendix C: Data obtained for Residue

Day	Box	Vial	Residue		
			Sieve 1	Sieve 2	Sieve 3
1	118	1	0.0010 g	0.0035 g	0.0015 g
1	35	1	0.0150 g	0.0060 g	0.0030 g
1	118	1	0.0160 g	0.0050 g	0.0010 g
1	35	2	0.0160 g	0.0050 g	0.0020 g
1	35	2	0.0155 g	0.0060 g	0.0010 g
1	35	1	0.0150 g	0.0055 g	0.0030 g
1	118	2	0.0170 g	0.0050 g	0.0025 g
1	118	2	0.0150 g	0.0060 g	0.0025 g
2	47	2	0.0160 g	0.0060 g	0.0025 g
2	27	1	0.0180 g	0.0065 g	0.0010 g
2	27	1	0.0180 g	0.0060 g	0.0020 g
2	47	2	0.0160 g	0.0060 g	0.0025 g
2	27	2	0.0185 g	0.0060 g	0.0020 g
2	47	1	0.0175 g	0.0060 g	0.0030 g
2	27	2	0.0160 g	0.0055 g	0.0025 g
2	47	1	0.0170 g	0.0065 g	0.0020 g
3	53	2	0.0150 g	0.0060 g	0.0020 g
3	98	1	0.0165 g	0.0065 g	0.0025 g
3	53	2	0.0160 g	0.0065 g	0.0025 g
3	98	2	0.0170 g	0.0075 g	0.0025 g
3	98	2	0.0155 g	0.0060 g	0.0020 g
3	98	1	0.0150 g	0.0060 g	0.0025 g
3	53	1	0.0170 g	0.0070 g	0.0025 g
3	53	1	0.0150 g	0.0060 g	0.0015 g
4	76	2	0.0135 g	0.0055 g	0.0025 g
4	72	2	0.0165 g	0.0060 g	0.0025 g
4	76	1	0.0170 g	0.0065 g	0.0025 g
4	76	2	0.0150 g	0.0065 g	0.0025 g
4	76	1	0.0135 g	0.0060 g	0.0020 g
4	72	1	0.0195 g	0.0070 g	0.0025 g
4	72	1	0.0175 g	0.0065 g	0.0025 g
4	72	2	0.0145 g	0.0065 g	0.0025 g
5	56	2	0.0160 g	0.0055 g	0.0025 g
5	56	2	0.0160 g	0.0060 g	0.0020 g
5	9	1	0.0180 g	0.0065 g	0.0030 g
5	56	1	0.0170 g	0.0070 g	0.0025 g
5	9	2	0.0155 g	0.0065 g	0.0025 g
5	56	1	0.0165 g	0.0060 g	0.0025 g
5	9	1	0.0180 g	0.0065 g	0.0025 g
5	9	2	0.0165 g	0.0065 g	0.0025 g

Note: Box 118 vial 1 - slightly different color than that of box 118 vial 2 and both vials 1 and 2 from box 35

10 Certificate of SRM 114q

Below the certificate of SRM 114q is provided for information only. As, the certificate will be updated later in 2005 to add the particle size distribution of the cement [13], the official version is the available online at: https://srmors.nist.gov/certificates/view_cert2gif.cfm?certificate=114q

Or by selecting “Standard Reference Materials” from the website www.NIST.GOV and typing in 114q

National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 114q

Portland Cement Fineness Standard

This Standard Reference Material (SRM) is intended for use in calibrating fineness testing equipment according to ASTM Standard Methods. The SRM unit consists of 20 glass vials with plastic caps containing powdered cement (each vial is contained in a sealed foil bag). Each vial contains approximately 5 g of cement.

Certified Values and Uncertainties: A NIST certified value is a value for which NIST has the highest confidence in its accuracy and that all known or suspected sources of bias have been investigated or accounted for by NIST. The certified values for specific surface area and sieve residue are given in Table 1. The certified values for the surface area are the mean of results from analyses performed by cooperating laboratories. The certified value for sieve residue was calculated from a quadratic fit of NIST data using three sieves having openings ranging from 38 μm to 56 μm.

The expanded uncertainties of the certified values for specific surface area were calculated according to the NIST uncertainty policy described in the NIST Technical Note 1297 [1], and are at the 95 % confidence level. The uncertainties include measurement variability within and between laboratories. The surface area uncertainties also include material variability and the uncertainty of the surface area values for the superseded SRM 114p *Portland Cement Fineness Standard*, which was used as the calibrant for this material. The expanded uncertainty for the sieve residue was computed using a Bayesian analysis and is also at the 95 % probability level. The expanded uncertainty accounts for the variability of random measurement effects, sieve calibrations, and material inhomogeneity.

Table 1. Certified Values

Measurand	ASTM Method	Certified Value and Expanded Uncertainty
Specific Surface Area (Blaine)	C 204-96a[(a)]	3818 cm^2/g ± 78 cm^2/g (381.8 m^2/kg ± 7.8 m^2/kg)
Specific Surface Area (Wagner)	C 115-96a[(b)]	2183 cm^2/g ± 160 cm^2/g (218 m^2/kg ± 16 m^2/kg)
Sieve Residue (45 μm residue)	C 430-96[(c)]	0.79 % ± 0.19 %

(a) Standard Test Method for Fineness of Portland Cement by Air Permeability Apparatus [Blaine].

(b) Standard Test Method for Fineness of Portland Cement by the Turbidimeter [Wagner].

(c) Standard Test Method for Fineness of Hydraulic Cement by the 45 μm (No. 325) Sieve.

Expiration of Certification: The certification of SRM 114q is valid, within the measurement uncertainties specified, until **31 December 2016,** provided the SRM is handled in accordance with the instructions given in this certificate (see "Instructions for Use"). This certification is nullified if the SRM is contaminated or otherwise modified.

Maintenance of Certification: NIST will monitor representative samples from this SRM lot over the period of its certification. If substantive changes occur that affect the certification before the expiration date, NIST will notify the purchaser. Registration (see attached sheet) will facilitate notification.

James St. Pierre, Chief
Materials and Construction Research Division

Gaithersburg, MD 20899
Certificate Issue Date: 24 March 2005

Robert L. Watters, Jr., Chief
Measurement Services Division

See Certificate Revision History on Last Page

The preparation of the material and the coordination of the technical measurements leading to certification were performed by C. Ferraris of the NIST Materials and Construction Research Division.

Statistical consultation on measurement design and analysis of the certification data was performed by W.F. Guthrie and A.I. Avilés of the NIST Statistical Engineering Division.

The support aspects involved in the issuance of this SRM were coordinated through the NIST Standard Reference Materials Program by B.S. MacDonald of the NIST Measurement Services Division.

INSTRUCTIONS FOR USE

Stability and Use: This material is considered to be extremely hygroscopic. Based on measurements in 1993 of several earlier renewals of SRM 114, the properties certified are stable as long as the foil bag remains sealed. The specific surface area of cement changes on exposure to the moisture in air. Therefore, this cement should be used immediately after opening the outer foil bag.

Allow the sealed foil bag to equilibrate to testing temperature before opening. To open the pouch, cut off the end with scissors. Fluff the cement in accordance with ASTM Standard C204, Section 3.4, allow the cement to settle for 2 minutes, and then perform the measurement.

Material Selection and Packaging: The desired properties were determined to be generally the same as those selected for the previous issues of SRM 114; however, in order to better represent current cements, the material selected for SRM 114q consists of a finer particle size distribution than previously issued. The Cement and Concrete Reference Laboratory (CCRL) and NIST identified a plant with suitable cement: Lehigh Cement Company (Union Bridge, Maryland)[4] donated 1300 kg of appropriate cement for this SRM. The material selected was Type I according to the ASTM C 150 Standard Classification and had a mass fraction of less than 8 % tricalcium aluminate (C_3A). The material was collected for shipment to NIST directly from the finish mill process stream into bags. Upon arrival at NIST, the cement was blended in a V-blender (1.68 m^3) and then transferred to 208 L (55 gallon) drums lined with 0.015 cm (6 mil) polyethylene liners to minimize hydration of the cement in storage prior to preparation and packaging. Over the next two days, the cement from each drum was sealed in foil bags, each containing about 16 kg of cement. The foil bags were stored in a climate-controlled area. The contents of each bag were subsequently packaged into vials. The vials were then capped and packaged in boxes of about 500 vials per box. The boxes were sequentially labeled from 1 to 118. About 5 boxes were filled per day. Nearly 59 000 glass vials, each containing approximately 5 g of cement, were produced. Each vial was then individually sealed in a foil bag. Vials were selected from the lot by stratified random sampling [2] for both homogeneity and certification analyses. Selected vials were shipped to the participating laboratories for measurements. The remaining vials were packaged into SRM unit boxes of 20 vials each.

Homogeneity Assessment and Certification Analyses: Homogeneity testing of the material was performed on 48 random-selected samples. Measurements of the loss of ignition (LoI) showed no reversible moisture take-up by the cement during packaging. The data received from the round-robin participants were also checked for laboratory-to-laboratory (or day-to-day in the case of sieve residue) variability, box-to-box variability, and vial-to-vial variability. No significant box-to-box or vial-to-vial variability was detected except for the Wagner or sieve residue tests, and therefore it was determined that the samples were homogeneous for the ASTM measurements. Significant vial-to-vial variability was observed using the Blaine test and the certified values reflect this source of uncertainty.

Certification analyses for specific surface areas using ASTM Standard Test Methods C 115-96a and C 204-00 were performed on two samples at each of the participating laboratories. SRM 114p *Portland Cement Fineness Standard* was used for calibration. Raw data were submitted by each laboratory to NIST for tabulation and calculation of surface areas, which for the Blaine test, assumed a density of 3.15 g/cm^3. The density was measured twice at NIST: the results were 3.255 g/cm^3 and 3.248 g/cm^3.

Certification analyses according to ASTM Standard Test Method C 430-96 for the 45 μm sieve residue were performed at NIST on 40 samples from 20 vials of cement.

Laboratories performing certification analyses are members of the CCRL (http://www.ccrl.us) proficiency program. The full list is provided in the report describing the details of the certification process [2].

[4]Certain commercial equipment, instruments, or materials are identified in this certificate in order to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Information Values: NIST information values are considered to be of interest to the SRM user, but are not certified because insufficient information is available to assess adequately the uncertainty associated with the values or only a limited number of analyses were performed. Information values for SRM 114q are given in Tables 2 and 3. Table 2 provides the approximate chemical composition determined by ASTM Standard Test Method C114-02. The analysis of this cement (CCRL Portland Cement Proficiency Sample No. 150) was performed by 70 to 170 laboratories; the number of participating laboratories depends on the value measured.

Table 2. Information Values for Chemical Composition

Compound	Mass Fraction (%)	Compound	Mass Fraction (%)
CaO	64.0	K_2O	0.70
SiO_2	20.7	TiO_2	0.30
Al_2O_3	4.7	P_2O_5	0.12
Fe_2O_3	3.2	Na_2O	0.07
SO_3	2.4	MgO	2.2
Loss on Ignition	1.67		

Table 3 provides the calculation of cement compounds according to ASTM C 150-02.

Table 3. Information Values for Cement Compounds (Calculation from Table 2)

Compound		Mass Fraction (%)
C_3S	(tricalcium silicate)	60
C_2S	(dicalcium silicate)	14
C_3A	(tricalcium aluminate)	7
C_4AF	(tetracalcium alumino-ferrite)	10

REFERENCES

[1] Taylor, B.N.; Kuyatt, C.E.; NIST Technical Note 1297, *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results* (1993).

[2] Ferraris, C.F.; Avilés A.J.; Guthrie W.; Haupt, R.; *Certification of SRM 114q, Phase I*, NIST SP260-161 (2005).

Certificate Revision History: 24 March 2005 (This technical revision corrects the certified values and expanded uncertainties for the measurand); 23 March 2005 (Original certificate date).

Users of this SRM should ensure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at: telephone (301) 975-6776; fax (301) 926-4751; e-mail srminfo@nist.gov; or via the Internet http://www.nist.gov/srm.