Analytical Results for MOX Colemanite Concrete Samples

Received on November 21, 2013

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REVIEWS AND APPROVALS

AUTHORS:

M. M. Reigel, Engineering Process Development Date

TECHNICAL REVIEW:

A. D. Cozzi, Engineering Process Development, Reviewed per E7 2.60 Date

APPROVAL:

E. N. Hoffman, Manager Date
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Environmental & Chemical Process Technology Research Programs

LIST OF REVISIONS		
Revision Number	**Summary of Changes**	**Date**
0	**Initial Issue**	**12/19/13**
1	**Corrected administrative errors and typos**	**5/20/14**

EXECUTIVE SUMMARY

The Mixed Oxide Fuel Fabrication Facility (MFFF) will use colemanite bearing concrete neutron absorber panels credited with attenuating neutron flux in the criticality design analyses and shielding operators from radiation. The Savannah River National Laboratory (SRNL) is tasked with measuring the total density, partial hydrogen density, and partial boron density of the colemanite concrete.

SRNL received two samples of colemanite concrete for analysis on November 21, 2013. The average total density of each of the samples measured by the ASTM method C 642, the average partial hydrogen density was measured using method ASTM E 1131, and the average partial boron density of each sample was measured according to ASTM C 1301. The lower limits and measured values for the total density, hydrogen partial density, and boron partial density are presented in the following table. For all the samples tested, the total density and the boron partial density met or exceeded the specified limit. None of the samples met the lower limit for hydrogen partial density.

Sample ID	Total Density Lower Bound [g/cm^3]		Hydrogen Partial Density Lower Bound [g/cm^3]		Boron Partial Density Lower Bound [g/cm^3]	
	Limit	Measured	Limit	Measured	Limit	Measured
Sample 4	1.88	2.08	6.04E-02	4.25E-02	1.65E-01	1.98E-01
Sample 5		2.07		4.37E-02		1.99E-01

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LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
DSC	Differential Scanning Calorimetry
ICP	Inductively Coupled Plasma
MFFF	Mixed Oxide Fuel Fabrication Facility
OES	Optical Emission Spectrometer
PSAL	Process Science Analytical Laboratory
SRNL	Savannah River National Laboratory
TGA	Thermal Gravimetric Analysis

1.0 Introduction

The Mixed Oxide Fuel Fabrication Facility (MFFF) will use colemanite bearing concrete neutron absorber panels credited with attenuating neutron flux in the criticality design analyses and shielding the operator from radiation.[1] The properties listed in Table 1-1 are from Table 2.1.2.3 in Reference 1. Savannah River National Laboratory (SRNL) is tasked with measuring the properties of colemanite concrete identified in Table 1-1.[2]

Table 1-1. Acceptable Material Neutron Absorber Characteristics

Material Type	Total Density Lower Bound (g/cm^3)	Hydrogen Partial Density Lower Bound (g/cm^3)	Boron Partial Density Lower Bound (g/cm^3)
Borated Concrete (Colemanite)	1.88	6.04E-02	1.65E-01

2.0 Experimental Results

Two samples of colemanite concrete poured on October 14, 2013 were delivered to SRNL on November 21, 2013. All samples arrived in plastic containers and weighed approximately 2000 grams. The samples were delivered in individual plastic bags without a source of moisture and appeared to be dry (Figure 2-1).

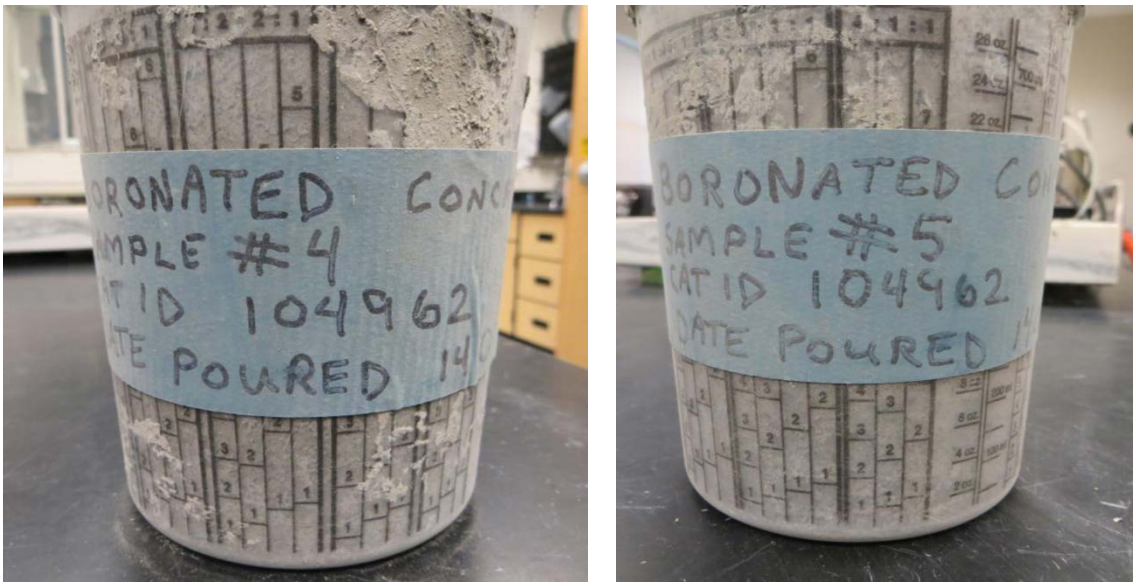

Figure 2-1. Colemanite concrete samples as-received at SRNL on November 21, 2013.

2.1 Total Density

The total density of each sample was determined according to ASTM standard C 642-06 for determining the density of hardened concrete.[3] The ASTM method was followed with the exception of sample size. Section 4.1 of the ASTM procedure specifies a sample size of approximately 800 grams. It was difficult to retrieve an intact sample of 800 grams, a reduced sample size was used. Triplicate samples for total density were obtained by cleaving pieces from

the as-received sample. Mass measurements were taken after each treatment (Table 2-1) as outlined in the ASTM standard with the masses designated as A through D, where:

A = mass of oven-dried sample in air between 100 to 110 °C, g
B = mass of surface-dry sample in air after immersion, g
C = mass of surface-dry sample in air after immersion and boiling, g
D = apparent mass of sample in water after immersion and boiling, g

Using the calculations in the ASTM method, the following properties were calculated (Table 2-2):

Absorption after immersion, $\% = \frac{B-A}{A} \times 100$, (1)

Absorption after immersion and boiling, $\% = \frac{C-A}{A} \times 100$, (2)

Bulk density, dry = $\frac{A}{C-D} \times \rho$, (3)

Bulk density after immersion = $\frac{B}{C-D} \times \rho$, (4)

Bulk density after immersion and boiling = $\frac{C}{C-D} \times \rho$, (5)

Apparent density = $\frac{A}{A-D} \times \rho$, (6)

Volume of permeable pore space = $\frac{C-A}{C-D} \times 100$ (7)

Table 2-1. Mass measurements after each treatment per ASTM C 642-06.

Sample ID	Run #	Dry (A) [g]	Saturated (B) [g]	Boiled (C) [g]	Suspended (D) [g]
Date		*11/26/13*	*12/3/13*	*12/5/13*	*12/5/13*
Sample 4	A	32.012	36.109	36.512	19.280
	B	51.787	59.021	59.671	31.360
	C	43.499	49.189	50.100	26.291
Sample 5	A	27.538	31.349	31.593	16.501
	B	34.263	38.952	39.288	20.579
	C	54.329	62.227	62.898	32.749

The density, ρ, used in these calculations is that of water, (1 g/cm^3). The results of the calculations performed with Equations 1-7 are tabulated and averaged in (Table 2-2).

Table 2-2. Calculated results using equations 1 – 7 for samples received November 21, 2013.

Sample ID	Run #	Eq. 1 [%]	Eq. 2 [%]	Eq. 3 [g/cm^3]	Eq. 4 [g/cm^3]	Eq. 5 [g/cm^3]	Eq. 6 [g/cm^3]	Eq. 7 [%]	Average (Eq. 4) [g/cm^3]
Sample 4	A	12.798	14.057	1.858	2.095	2.119	2.514	26.114	2.08
	B	13.969	15.224	1.829	2.085	2.108	2.535	27.848	
	C	13.081	15.175	1.827	2.066	2.104	2.528	27.724	
Sample 5	A	13.839	14.725	1.825	2.077	2.093	2.495	26.869	2.07
	B	13.685	14.666	1.831	2.082	2.100	2.504	26.858	
	C	14.537	15.772	1.802	2.064	2.086	2.518	28.422	

2.2 Partial Hydrogen Density

The hydrogen partial density of the colemanite concrete was determined using the ASTM method for determining volatile content using thermogravimetric analysis.[4] The ASTM E 1131-08 defines highly volatile matter as components that will volatilize < 200°C and medium volatile matter as components that will degrade or volatilize in the range 200 - 750 °C. In an evaluation of the thermal decomposition of colemanite, Waclawska et al, determined that the release of water from colemanite was complete at 600 °C and that melting and crystallization of a calcium borate phase occurred above 650 °C.[5] A Netzsch STA 409 Luxx, which couples Differential Scanning Calorimetry (DSC) with Thermal Gravimetric Analysis (TGA) was used for determining the partial hydrogen density of the colemanite concrete samples. After loading the sample, the chamber was purged with nitrogen at 60 ml/min prior to heating. Triplicate samples were heated at 5 °C/min up to 650 °C in a flowing nitrogen atmosphere of 60 ml/min. The results for each sample received November 21, 2013 are shown in Table 2-3. The initial mass loss is associated with the free water from the mix. The second mass loss beginning at approximately 300 °C is due to the thermal decomposition of the colemanite. summarizes the mass change and hydrogen partial density for the two samples. The mass loss graphs for the two samples are shown in Figure 2-2 and Figure 2-3.

In order to calculate the hydrogen partial density, it is assumed the average total mass loss for each sample in Table 2-3 is due to water, both free and from the decomposition of colemanite. The hydrogen partial density is calculated from the average mass loss (Table 2-3) and density of the sample (Table 2-2) as shown in equations 8 – 12. The average of triplicate runs from sample 4 is used as the example calculation.

$$Moles\ H_2O\ in\ 100\ g\ concrete = \frac{mass\ fraction\ H_2O}{MW\ H_2O} = \frac{18.25\ \frac{g\ H_2O}{g\ concrete}}{18.015\ g\ mol\ H_2O} = 1.01\ mol H_2O, \quad (8)$$

$$\frac{g\ H}{Mole\ H_2O} = 2.016\ g\ H, \quad (9)$$

$$g\ H\ in\ 100\ g\ concrete = 1.01\ mol\ H_2O \times 2.016\ g\ H = 2.04\ g\ H, \quad (10)$$

$$Volume\ concrete = \frac{mass\ concrete}{density\ concrete} = \frac{100\ g\ concrete}{2.08\frac{g}{cm^3}} = 48.03\ cm^3\ concrete, \quad (11)$$

$$H\ density\ \frac{g}{ml} = \frac{mass\ H}{volume\ concrete} = \frac{2.04\ g\ H}{48.03\ ml\ concrete} = 4.25E-02\ \frac{g\ H}{ml\ Concrete} \quad (12)$$

Table 2-3. Mass loss from 25 to 650 °C for samples received November 21, 2013.

Sample ID	Run #	Mass Loss [%] 25 - 175 °C	Mass Loss [%] 300 - 600 °C	Total Mass Loss [%]	Average Total Mass Loss [%]	Total Hydrogen Partial Density [g/cm^3]
Sample 4	A	6.78	8.19	15.69	18.25	4.25E-02
	B	6.02	12.00	18.50		
	C	7.50	12.37	20.57		
Sample 5	A	8.11	8.86	17.56	18.81	4.37E-02
	B	7.68	10.89	19.32		
	C	8.72	9.85	19.54		

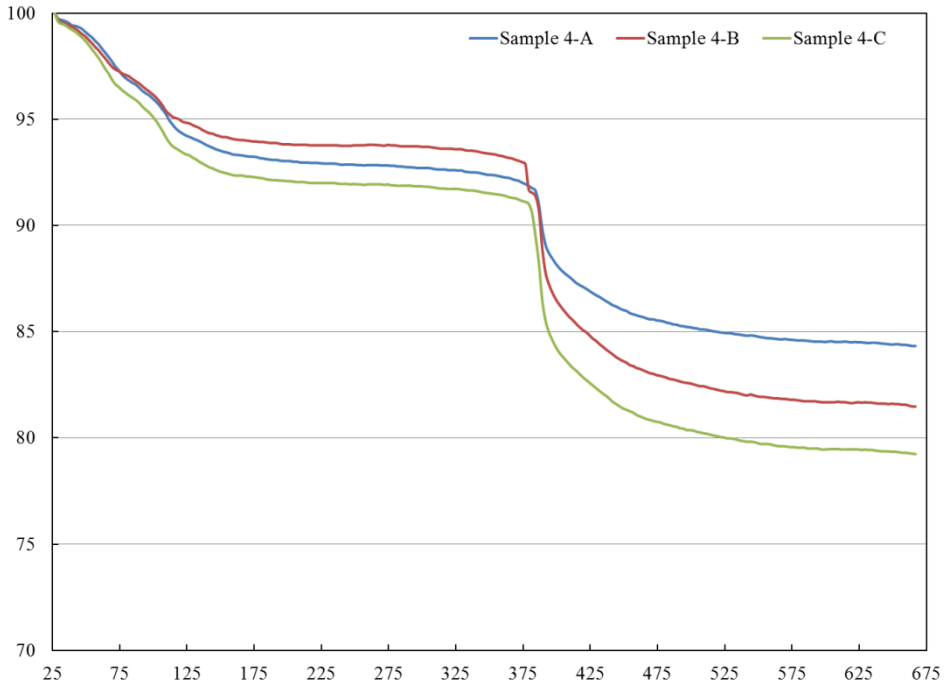

Figure 2-2. TGA curve showing mass loss for sample 4.

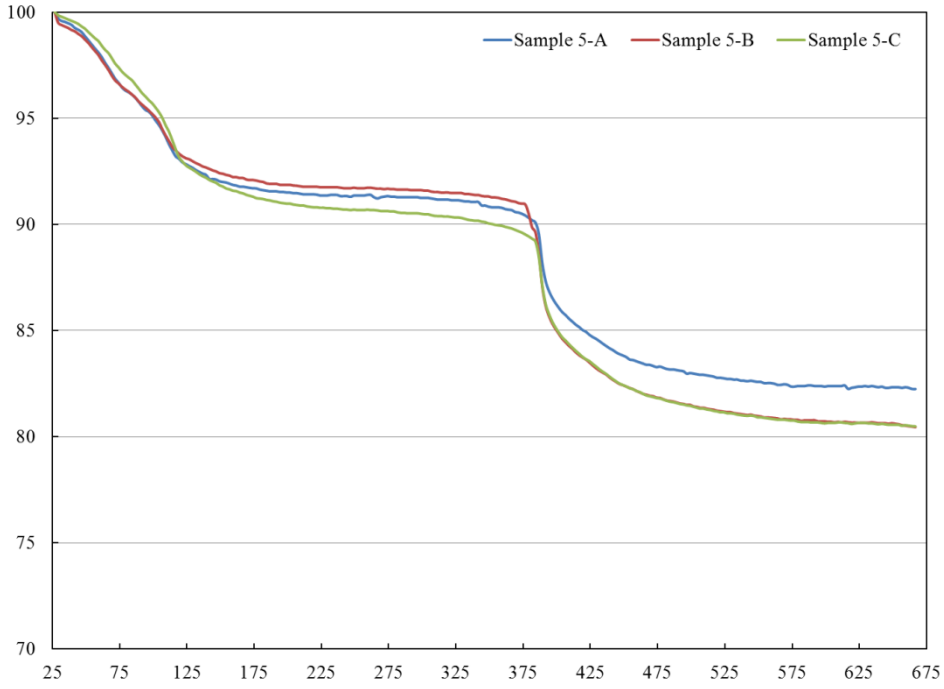

Figure 2-3. TGA curve showing mass loss for sample 5.

2.3 Boron Partial Density

Subsamples of the samples received on November 21, 2013 were crushed, dried in an oven to remove moisture, and digested in triplicate using the ASTM method for trace metals analysis in limestone.[6] Aliquots of each sample were weighed in separate beakers and then 10 ml of HCl and 4 ml of HNO_3 were added. The acid mixture was heated at 85 °C for 60 minutes on a hotplate, with the sample covered with a watch glass. After heating was complete, the sample cooled for an additional 60 minutes to ensure complete boron dissolution. The sample was then diluted up to a final volume of 100 ml with deionized water. The samples were analyzed on the Agilent 730 Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES). Boron was calibrated using a High Purity NIST traceable standard (Lot 1235253), Appendix A: Boron Certificate of Analysis. An internal standard (Yttrium) was used to compensate for matrix effects. The dissolution method prescribed in the ASTM method resulted in complete dissolution of the samples. Table 2-4 is the analytical results of the dissolution of colemanite concrete using the prescribed ASTM method.

Table 2-4. Boron results for samples received November 21, 2013.

Sample ID	Average Boron Content [wt %]	Average Partial Boron Density [g/cm^3]
Sample 4	9.51	1.98E-01
Sample 5	9.62	1.99E-01

The average partial boron density for each sample is calculated using the calculated colemanite concrete density for each sample in Table 2-2. An example calculation for the partial density of sample 4 is shown in equations 13 – 15:

$$Mass\ boron\ in\ 100\ g\ concrete\ from\ \text{Table 2-4} = 9.51\ g \quad (13)$$

$$Volume\ concrete = \frac{mass\ concrete}{density\ concrete} = \frac{100\ g\ concrete}{2.08\ \frac{g}{cm^3}} = 48.03\ cm^3\ concrete \quad (14)$$

$$Boron\ density\ \frac{g}{ml} = \frac{mass\ B}{volume\ concrete} = \frac{9.51\ g\ B}{48.03\ cm^3} = 1.98E-01\ \frac{g\ boron}{cm^3\ Concrete} \quad (15)$$

Comparing the results in Table 2-4 to the acceptability limits in Table 1-1, the two samples are above the limit (1.65E-01 g/cm^3) for the average partial boron density.

2.4 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.

3.0 Conclusions

The lower limits and measured values for the total density, hydrogen partial density, and boron partial density are presented in the following table. For all the samples tested, the total density and the boron partial density met or exceeded the lower bounds specified in Reference 1. None of the samples passed the hydrogen partial density lower limit.

Sample ID	Total Density Lower Bound [g/cm^3]		Hydrogen Partial Density Lower Bound [g/cm^3]		Boron Partial Density Lower Bound [g/cm^3]	
	Limit	Measured	Limit	Measured	Limit	Measured
Sample 4	1.88	2.08	6.04E-02	4.25E-02	1.65E-01	1.98E-01
Sample 5		2.07		4.37E-02		1.99E-01

4.0 References

1. Wead, R., "Radiation Shielding and Fixed Neutron Absorber Panel Material and Inspection Requirements," DCS01-ZMJ-DS-SPE-M-19109-2, Revision 2, 2007.

2. "Equipment Calibration Services / Material Testing," WTA-040-11, Section 9 (f), October 10, 2012.

3. "Standard Test Method for Density, Absorption, and Voids in Hardened Concrete," ASTM International, ASTM C 642-06.

4. "Standard Test Method for Compositional Analysis by Thermogravimetry," ASTM International, ASTM E 1131-08.

5. Waclawska, I., Stoch, L., Paulik, J., and Pauliik, F., "Thermal Decomposition of Colemanite," *Thermochimica Acta,* **126**, 307-18 (1988).

6. "Major and Trace Elements in Limestone and Lime by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP) and Atomic Absorption (AA)," ASTM International, ASTM C 1301-95 (reapproved 2009).

Appendix A. Boron Certificate of Analsyis

HIGH-PURITY STANDARDS
www.highpuritystandards.com
P.O. Box 41727
Phone (843) 767-7900
Fax (843) 767-1306

Certificate of Analysis 11569-1

Product Description:

Name:	Boron	Source Material:	Boric Acid
Part Number:	**10007-4**	Material Purity:	99.999%
Lot Number:	**1235253**	Matrix:	H_2O

Certified Value: 1000 µg/mL ± 3 µg/mL

The Certified value is based on gravimetric and volumetric preparation, and confirmed against SRM 3107 (lot number 070514) by inductively coupled plasma optical emission spectrometry (ICP-OES) using an internal laboratory-developed method. The uncertainty in the certified value is calculated for a 95% confidence interval and coverage factor *k* is about 2.

Density: 1.000 g/mL ± 0.002 g/mL @ 22.5°C

Uncertified Values:

Titration Value: 1019.16 µg/mL

Trace Metal Impurity Scan: The data reported are based upon a scan of this specific lot at 1000 µg/mL via ICP analysis. The values are reported in µg/L.

Ag	<	0.02	Cu	<	0.1	Li	<	0.02	Rb	<	0.02	Th	<	0.02
Al	<	0.1	Dy	<	0.02	Lu	<	0.02	Re	<	0.02	Ti	<	0.02
As	<	0.05	Er	<	0.02	Mg	<	0.5	Rh	<	0.02	Tl	<	0.02
Au	<	0.02	Eu	<	0.02	Mn	<	0.1	Ru	<	0.02	Tm	<	0.02
B		M	Fe	<	1	Mo	<	0.02	Sb	<	0.02	U	<	0.1
Ba	<	0.02	Ga	<	0.02	Na	<	3	Sc	<	0.02	V	<	0.05
Be	<	0.02	Gd	<	0.02	Nb	<	0.02	Se	<	0.1	W	<	0.02
Bi	<	0.02	Ge	<	0.02	Nd	<	0.02	Si	<	10	Y	<	0.02
Ca	<	1	Hf	<	0.02	Ni	<	0.1	Sm	<	0.02	Yb	<	0.02
Cd	<	0.02	Ho	<	0.02	Os	<	0.02	Sn	<	1	Zn	<	0.5
Ce	<	0.02	In	<	0.02	Pb	<	0.05	Sr	<	0.02	Zr	<	0.02
Co	<	0.05	Ir	<	0.02	Pd	<	0.02	Ta	<	0.02			
Cr	<	0.1	K	<	1	Pr	<	0.02	Tb	<	0.02			
Cs	<	0.02	La	<	0.02	Pt	<	0.02	Te	<	0.02			

Preparation Information:

The standard solution is prepared using high purity materials and assayed by analytical methods for conformity prior to use. This standard was prepared using the methods developed at NIST for SRM Spectrometric Standard Solutions under appropriate laboratory conditions. The matrix is 18 megaohm deionized water.
Stability of this product is based upon rigorous short term and long term testing of the solution for the certified value. This testing includes, but is not limited to, the effect of temperature and packaging on the product.

Lot No.: **1235253**
Rev. No.: 5.1.0
Page 1 of 2

High-Purity Standards is certified to ISO 9001:2008 and accredited to ISO/IEC 17025:2005 and ISO Guide 34:2009.

Intended Use:

This Certified Reference Material (CRM) is intended for use as a calibration standard for the quantitative determination of boron, calibration of instruments such as ICPOES, ICPMS, AAS and XRF, and validation of analytical methods. It also can be used in EPA, ASTM and other methods.

Traceability Information:

The traceability of this standard is maintained through an unbroken chain of comparisons to appropriate standards with suitable procedure and measurement uncertainties. The maintenance of the base and derived units of International System of Units (SI) with traceability of measurement results (contemporary metrology) to SI ensures their comparability over time as follows.

a. **Standard Weight and Analytical Balance**
The standard weights (NBS weights Inventory No 20231A) are calibrated every two years by South Carolina Metrology Laboratory that is a participant in "NIST Weights and Measures Measurement Assurance Program" with a certificate of measurement traceability to NIST primary standards.
The balances are calibrated yearly by the ISO 17025 accredited metrology service, and are verified weekly by an in-house method using standard weights.

b. **Volumetric Device**
The calibration of volumetric vessels is checked annually using the NBS 602 method.

c. **Thermometer**
The standard thermometers are calibrated every year by the ISO 17025 accredited metrology service. The thermometers used in-house are verified against the standard thermometers yearly.

d. **Calibration Standards:**
The Calibration Standard is directly traceable to SRM 3100 Series Spectrometric Standard Solutions.

Packaging and Storage Conditions:

The standard is packaged in a pre-cleaned polyethylene bottle. To maintain the integrity of this product, the solution should be kept tightly capped and stored under normal laboratory conditions.

Refer to Material Safety Datasheet (MSDS) for hazardous information.

Expiration Information:

The expiry date is guaranteed to be valid for eighteen months from the shipping date provided. For this reason, standards from the same lot may have different expiration dates.

Preparation Date:	**December 17, 2012**
Shipped Date:	**August 12, 2013**
Expiration Date:	**February 12, 2015**
Certificate Issue Date:	**January 11, 2013**

Quality Information:

ISO/IEC 17025:2005 Accreditation
Certificate Number AT-1529

Vanny T. Yib,
Inorganic Laboratory Manager

ISO Guide 34:2009 (RMP) Accreditation
Certificate Number AR-1436

Angel Sellers
Quality Manager

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Page 2 of 2

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