

Investigation into the Impact of Calibration Methods on the Methylene Blue Clay Test Results

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ABSTRACT

In the green sand molding process, the properties required to make molds to achieve the desired casting quality are heavily influenced by the amount of bentonite clay present in the sand. For this reason, one of the most relied upon quality control tests in the foundry is a measure of the useable bentonite in the sand as measured by the methylene blue (MB) clay test.

This study investigates multiple calibration approaches used in the methylene blue clay test to convert the raw results obtained in the procedure to a measure of the amount of usable clay in the sand. The study compares the variation from the titration itself compared to results obtained from calibration using several different approaches discussed in previous publications. This study also outlines an approach to estimate the amount of methylene blue dye required for a calibration standard based on the Cation Exchange Capacity (CEC) of the bentonite.

Keywords: methylene blue clay test, green sand control, calibration

INTRODUCTION

The methylene blue (MB) clay test has been a much debated, but integral part of modern foundry sand control since its introduction in the 1960's.¹ This test is designed to give the foundry operator a guide into how much bentonite is available as a bonding agent in the molding sand, thereby allowing the operator to monitor and adjust this amount to control the sand properties. Controlling the amount of bentonite, the primary bonding agent of the sand, and water content are essential to controlling the performance of the sand.² The amount of bentonite present in the sand will influence a variety of properties of the molding sand from moisture content to compression strength and most, if not all, sand control programs recommend monitoring this property along with compactability, compressive strength and moisture at least daily.³

The fundamental basis for the test uses the inherent property of cation exchange capacity (CEC) of bentonite clays.

Bentonite clay is a naturally occurring ore that is primarily comprised of the mineral montmorillonite.² Montmorillonite is a clay mineral in the smectite family with a layered platelet structure consisting of two tetrahedrally arranged layers of silica atoms on either side of an octahedral arranged layer of aluminum atoms in its unit cell.² While the octahedral layer is primarily composed of aluminum atoms, there are often substitutions of iron and magnesium atoms for some of the aluminum atoms. These substitutions create a localized negative charge imbalance in the platelet, which is counterbalanced by sodium, calcium and to a lesser extent magnesium cations on the surface of the platelet. The surface cations are usually a combination of cations and when sodium cations are dominant on these sites the bentonite is referred to as a "sodium bentonite" and when calcium cations are dominant the bentonite is referred to as a "calcium" bentonite."² The prevalence of either sodium or calcium cations on the surfaces of these tetrahedral layers influence the hydration and bonding properties of the clay. For the purposes of this study only a general introduction into the concept of cation ion exchange capacity is required along with the knowledge that different bentonites can vary in their cation exchange capacity value. While montmorillonite and bentonite are often used interchangeable, technically montmorillonite is a specific mineral in the smectite clay family and bentonite refers to the ore, which is a combination of montmorillonite along with other related accessory minerals commonly found in clay deposits such as quartz and feldspars.

The methylene blue dye test and similar test methods have been employed to determine the CEC of bentonites and clay minerals as early as the 1950's.⁴ A solution of methylthioninium chloride and water, commonly called methylene blue dye was proposed to determine the amount of montmorillonite found in drilling muds and foundry sands.⁴ The methylene blue molecule used in the clay test is an organic compound that is cationic and can be adsorbed onto the cation exchange sites on the surfaces of the clay minerals present in the bentonite.⁴ A solution of methylene dye can be prepared in water, and when

added to a solution of bentonite, the cationic methylene blue dye molecules will displace the sodium, calcium and magnesium cations present on the montmorillonite surfaces.

An important aspect of the test historically has been the relation of the amount of dye absorbed by the bentonite in the foundry sand to a percentage of clay in the foundry sand. Historically this has been accomplished by establishing a calibration factor using prepared samples with known amounts of bentonite present.⁵ It should be noted that the methylene blue dye can be absorbed by other organic additives that can be found in many commercial bentonite-based pre-blends supplied to foundries such as cereal and causticized lignite, however typically these additives make up only a small percentage of the blend (less than 10% total).⁴

Since the introduction and widespread acceptance of this control test in foundries in the 1970's, there has been much debate and research on improving the test.¹ Over the years there has been considerable modification of the methylene blue clay test and many of the modifications relate to improving the ability of the methylene dye to adsorb to the cation exchange sites in the clay. For example, pre-1970 the bentonite was added to an acidified solution prior to addition of the methylene blue dye. Investigators Dietert and Graham noted that sodium and calcium bentonite showed very different adsorption of methylene dye when acidified and they determined that a full exchange of the platelet cation exchange sites to sodium cations was needed prior to addition of the methylene blue dye.⁵ From this study came the recommendation to replace the acidified solution with 2% tetrasodium pyrophosphate solution. These researchers also noted the importance of improved dispersion of bentonite in the solution with the foundry sand to maximize the accessibility of the platelet cation exchange sites to the methylene blue dye. Several authors experimented with boiling of the sample as well as using ultrasonic scrubbing in combination with the 2% tetrasodium pyrophosphate solution and found improved consistency of the results.^{4,5}

The American Foundry Society (AFS) has published numerous research studies specifically aimed at optimizing this test. There have been studies investigating the impact of different concentrations of methylene blue dye and tetrasodium pyrophosphate solution,⁶ investigating the introduction of abrading agents such as fine mesh silicon carbide,⁵ examining the impact of boiling vs. ultrasonic scrubbing,^{7,8} evaluating the impact of various degrees of drying,⁸ and different approaches to calibration of the results to report the amount of clay present in the foundry sand.^{1,7} Despite the positive findings in some of these studies, the conclusions have not always translated into a change in recommended procedure or practice in the foundry. For instance, while there is ample evidence to support the recommendation

for use of the of boiling or (boiling followed by ultrasonic scrubbing) vs. ultrasonic scrubbing alone^{4,7} in 2% tetrasodium pyrophosphate solution, in practice most sand control programs use ultrasonic scrubbing only. Similarly, a study conducted in 1993 that suggested using a much lower concentration of tetrasodium pyrophosphate along with the boiling method for sample preparation produced increased methylene dye absorption and more consistent results compared to ultrasonic agitation and 2% tetrasodium pyrophosphate sample preparation,⁶ however the current procedure still prescribes 2% tetrasodium pyrophosphate. Another similar area of considerable debate in the research relates to the calibration of the analysis or correlation of the methylene blue dye up take to the amount of bentonite present in the sample, which is the subject of the current study.

As a result of many of the studies, the industry has arrived at two standard methods for determining the amount of bentonite present in foundry molding sands. These can be found in the "AFS Mold and Core Test Handbook" and are referred to as procedures 2210-17-S *Methylene Clay Test, Ultrasonic Method, Molding Sand* and AFS 2211-17-S *Methylene Blue Clay Test, Boiling Method, Molding Sand*.⁹ The key difference in these two test methods is the method of dispersion of clay in the molding sand. As the titles indicate, one uses ultrasonic agitation only while the other uses a boiling method. Both methods use 5.0 grams of dried molding sand, 50 milliliters of 2.0% tetrasodium pyrophosphate solution and both generate a calibration factor to relate the milliliters of methylene dye used to titrate the sample to its endpoint to a percentage of clay present in the molding sand. In both methods, the sample is prepared by agitating and dispersing the clay in the molding sand using the prescribed AFS method followed by an incremental addition of methylene blue dye at a known concentration (0.01 molar or 1 ml= 0.01 meq). Typically, a starting amount of dye (about 80% of the estimated end point⁵) is added to the mixture of molding sand and tetrasodium pyrophosphate solution and allowed to mix using a magnetic stir plate and stir bar for 2 minutes. After the 2-minute mixing time, a glass rod is dipped in the resulting solution and a drop is placed on hardened, ashless filter paper and the dot is examined for the presence of a "halo" or an outside ring of light blue/green surrounding the darker blue dot.⁴ If the halo is not observed, an additional amount of methylene dye is added to the molding sand solution, usually 1-2 milliliters, followed by an additional 2 minutes of mixing time and placement of another drop of solution on the filter paper. This process is repeated until a "halo" is observed and the amount in milliliters of methylene dye required for the halo is recorded. Chemically on the molding sand solution, as the cation exchange sites are replaced with the methylene dye, the platelet exchange sites are saturated with the dye and eventually the dye is present in solution in excess of the number of platelet cation exchange sites. Once the dye is present in solution in excess, the "halo" effect is observed on the filter paper (Figure 1). The

determination of the “halo” can be subjective based on the individual operator, and this is one of the more widely regarded flaws of the current test methods.

The amount of dye uptake in milliliters is correlated to an amount of bentonite by preparing a standard using a known amount of bentonite pre-blended with 5.0 grams of 220 mesh silicon carbide to aid in dispersion of the sample and determining the amount of methylene blue dye required to achieve a halo in the test method. From those results, a calibration factor expressing the volume of methylene dye needed per percent of clay can be determined and is then used to calculate the amount of clay or bentonite in the molding sand. Equations 1 and 2 outline this approach as prescribed in the AFS methods (Eqns. 1, 2).⁹ In the AFS procedure, the calibration standard is prepared by using raw bentonite or pre-blend material added with sand directly in the sample beaker along with 5.0 grams of silicon carbide. In this calibration approach the bentonite is a fine powder that is not well distributed on the sand as is the case with the molding sand sample.

$$\text{Calibration Factor} = \frac{A}{B} \quad \text{Eqn. 1}$$

Equation 1 is the calibration factor determination for the MB Test.

Where:

A = endpoint in mls from calibration procedure and
B = known % of bentonite.

$$\% \text{ Clay in molding sand} = \frac{C}{D} \quad \text{Eqn. 2}$$

Equation 2 is the calculation of percent clay in molding sand.

Where:

C = endpoint in mls required to titrate molding sand and
D = calibration factor (mls/% bentonite).

Along with the subjectivity of determination of the halo, there are other sources of variation in the test method. Sources of variation include the concentration of the methylene blue dye, storage conditions of the methylene blue dye, differences in sample preparation and differences in approaches to establishing a calibration factor. Variations in the method for establishing a calibration factor include the appropriate percentage of bentonite to use, whether to correct for the moisture content of the clay or whether to use a pre-mulled calibration standard. For these reasons it has historically been difficult to compare methylene blue clay results from foundry to foundry and lab to lab.⁸

There are promising new developments for an alternative cation exchange capacity measurement test to determine the amount bentonite in foundry sands. One method under

consideration uses a more selective dye and UV-Visible spectrophotometry to remove the subjectivity of the end point.¹⁰ Despite these potential new developments, the authors of this paper believe that the issue of calibration or correlation of the results to the amount of bentonite will still be applicable in the future.

The goal of this study was to review the AFS prescribed method for generating calibration factors for the methylene blue clay test as well as revisit some previously investigated methods of calibration to assist the foundry operator in understanding the impact of different variables on the calibration factor and in turn, the impact on their process control. A better understanding of the impact of these variables can assist in making an informed decision regarding their calibration and methylene blue monitoring practices as well as better control in the foundry.

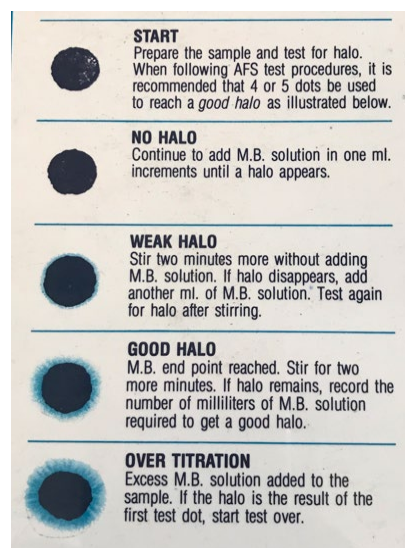


Figure 1. Once the dye is present in solution in excess, the “halo” effect is observed on the filter paper. This artwork shows the varied appearance of the halo. (Artwork courtesy of “Chemical and Physical Factors that influence MB Analysis of Bentonites and System Sands,” Odom, 1992.)⁴

EXPERIMENTAL DESIGN

The author’s employer provides bentonite and bentonite-based pre-blends to the foundry industry and testing on commercial molding sands for customers. For this study, the authors chose commercial molding sands from a Midwestern iron foundry where the formula for the bentonite-based pre-blend was known. This sample was analyzed in triplicate by two different laboratory technicians to determine a baseline for variation on the raw methylene blue dye uptake in the test procedure. As part of the investigation, a lab prepared molding sand using the same bentonite pre-blend was prepared with a known amount of bentonite. These samples were also

measured in triplicate by two laboratory technicians along with 16 different variations of calibration techniques representing different approaches to calibration found throughout the industry and in previous AFS published studies.

The calibration standards were grouped into four areas of investigation:

1. Investigating the impact of compensating for the moisture in the bentonite clay in the calibration standard;
2. Investigating different clays and combinations of clays with organic foundry additives (also known as a “pre-blend”);
3. Comparing the “at the cup” method of calibration standard preparation vs. pre-mulling the bentonite with sand and water and then drying before testing; and
4. Evaluation of the use of silicon carbide (SiC) addition to the “at the cup” method of standard preparation.

The standard deviations observed for milliliters of dye uptake for each sample and each calibration standard is presented along with the related calibration factors, and these results are compared to the known composition of the lab prepared sample. The results and impact of the calibration factor are discussed in the conclusion and summary sections.

While there are several methods for determining the cation exchange capacity of bentonite clay alone, the determination of this property using methylene blue dye is still a common approach for many laboratories. For bentonite analysis, a method utilizing both boiling and ultrasonic agitation was used to obtain maximum dispersion of the bentonite in the solution before titration with methylene blue dye. A 0.5-gram sample of each clay was used and based on the concentration of the methylene blue dye (0.01 meq/ 1 ml) the cation exchange capacity can be expressed in meq per 100 grams (meq/100g). Cation exchange capacity results for the two bentonite samples used in the study are presented and the estimated milliliters of methylene blue dye required for various amounts of bentonite are presented using the concentration of methylene blue dye and the starting cation exchange capacity of the bentonite (Table 1 and Eqn. 3). These estimates are used as a reference to make observations about the relative effectiveness of each calibration method to fully disperse the bentonite and make the cation exchange capacity sites available for the methylene dye. Arguments can be made regarding the appropriate or preferred method for cation exchange capacity measurements of bentonite, but since we are using similar concentrations of dye (0.01 meq/ 1ml dye)

we can compare the relative uptake of the dye for a given amount bentonite in the standard vs the estimated uptake based on the cation exchange capacity. For reference and comparison, the observed calibration factors determined from the various calibration standards are compared to the expected calibration factors derived using the initial cation exchange capacity of the bentonites.

The main variables investigated in this study are the correction of moisture in the bentonite used for calibration, evaluating the impact of using bentonites with different cation exchange capacities, the impact of pre-mulling of bentonite with sand prior to analysis, and use of silicon carbide (SiC) as a dispersion/abrading agent.

Variables not investigated in this study are concentration of methylene blue dye (dye was prepared at recommended 0.01 M or 0.01 meq/ ml concentration), concentration of tetrasodium pyrophosphate (recommended 2% solution was used), ultrasonic agitation time (7 minutes was used in a ultrasonic bath capable of 50-55 khz output), drying time and temperature (splits of 50 grams of molding sands were pre-dried in 105C (221F) oven for 1 hour prior to testing, (the bentonite clay was not pre-dried but corrected for moisture by increasing the weight of the sample to ensure weight on dry basis).

The pre-mulled calibration standards were prepared on a 3,000-gram batch basis. The moisture of the clay was corrected for by adding 6 or 10% of bentonite on a dry basis to the batch and adding sufficient water to achieve a 40-45% compactability during an 8-minute mulling cycle on a Simpson lab muller (wheel style muller). A split of the pre-mulled calibration standard sand (approximately 50 grams) was placed in a 105C (221F) oven for 1 hour and then allowed to cool to room temperature before methylene blue testing. The lab prepared molding sand was prepared in the same manner with 8% bentonite on an as received moisture (7.2% bentonite on a dry basis). The pre-blend formula used was identical to the formula supplied to the commercial iron foundry and consisted of 77% total clay (ratio of 74/26 Bentonite A and Bentonite B) along with a balance comprised of bituminous seacoal, causticized lignite, cereal, and soda ash. The total pre-blend percentage in the lab prepared molding sand was 10.4%.

The laboratory technicians were provided an estimate of 80% of the total methylene blue dye requirements to use as starting point but if halo was observed initially the test was repeated with a lower starting point. Technicians determined their own sample halo (endpoint), and these were visually compared on the filter papers to ensure they were similar between technicians.

EXPERIMENTAL RESULTS

Table 1. Cation Exchange Capacities of Bentonite used in Present Study- As Received Moisture

Bentonite / Blend	Initial Moisture of Bentonite or Blend (Dried at 105C/221F 1 hr)	mls of dye required for 0.5-gram sample of bentonite (as received)	Cation Exchange Capacity (meq / 100 grams) *As Received Moisture	Expected mls of uptake of 0.01 meq/ 1 ml Methylene Blue Solution for 10% bentonite	Expected mls of uptake of 0.01 meq/ 1 ml Methylene Blue Solution for 6% bentonite	Anticipated Calibration Factor (mls/ % bentonite present)
Bentonite A- Sodium Bentonite	8.95	54	108	54	32	5.4
Bentonite B- Calcium Bentonite	13.10	44	88	44	26	4.4
Pre-blend (Ratio of 74% Bentonite A/ 26% Bentonite B)	9.03	51	102	51	31	5.1

Equation 3 shows the CEC calculation for bentonite and Eqn. 4 shows the calculation for a 10% standard.

$$CEC \left(\frac{meq}{100grams} \right) = mls \text{ of dye required for } 0.5 \text{ grams bentonite} \times 0.01 \frac{meq}{1 ml} \times 2 = \frac{meq}{1 gram} \times 100 = \frac{meq}{100 grams} \quad \text{Eqn. 3}$$

$$Expected \text{ mls for } 10\% \text{ Bentonite Standard} = 108 \frac{meq}{100 grams} \times 1 \frac{milliliter}{0.01 meq} = 10,800 \frac{ml}{100 grams} \times \frac{1}{200} = 54 \frac{mls}{0.5 grams}$$

Eqn. 4

Table 2. Cation Exchange Capacities of Bentonite used in present study-Corrected for Moisture Content

Bentonite / Blend	Initial Moisture of Bentonite or Blend (Dried at 105C/221F 1 hr)	Cation Exchange Capacity (meq / 100 grams) *Corrected for moisture content	Expected mls of uptake of 0.01 meq/ 1 ml (Methylene Blue Solution for 10% bentonite	Expected mls of uptake of 0.01 meq/ 1 ml Methylene Blue Solution for 6% bentonite	Anticipated Calibration Factor (mls/ % bentonite present)
Bentonite A Sodium Bentonite	8.95	119	60	36	6.0
Bentonite B Calcium Bentonite	13.10	101	50	30	5.1
Pre-blend (Ratio of 74% Bentonite A/ 26% Bentonite B)	9.03	112	56	34	5.7

Equation 5 is the moisture correction calculation and Equation 6 is the example calculation.

$$CEC \text{ Moisture Corrected} = CEC \times \frac{1}{(1 - (\frac{\% \text{ Moisture}}{100}))} \quad \text{Eqn. 5}$$

$$Expected \text{ mls for } 10\% \text{ Bentonite Standard} = 118 \frac{meq}{100 grams} \times 1 \frac{milliliter}{0.01 meq} = 11,800 \frac{ml}{100 grams} \times \frac{1}{200} = 59 \frac{mls}{0.5 grams}$$

Eqn. 6

Table 3. Results of Methylene Blue Dye Uptake on Commercial Green Sand and Lab Prepared Sand

Technician	Sample (5.0-gram dried sample)	mls	mls	mls	Avg (mls)	STDEV	Overall Average (mls)	Overall STDEV (mls)
1	Commercial Green Sand	44	45	45	44.7	0.58	44.7	0.52
2	Commercial Green Sand	45	45	44	44.7	0.58		
1	Lab Prepared Green Sand at 7.3% Clay (Dry basis)	42	44	43	43.0	1.00	42.8	0.75
2	Lab Prepared Green Sand at 7.3% Clay (Dry basis)	43	43	42	42.7	0.58		

Table 4. Calculated Calibration Factors with Bentonite A

Technician	Sample	% Bentonite in Standard	Avg (mls)	STDEV	Overall Average (mls)	Overall STDEV (mls)
1	0.5 grams Bentonite A	10%	48.7	0.58	48.5	0.55
2	0.5 grams Bentonite A	10%	48.3	0.58		
1	0.5 grams Bentonite A Moisture corrected	10%	53.0	1.00	52.7	1.63
2	0.5 grams Bentonite A Moisture corrected	10%	52.3	2.31		

Table 5. Comparison of Observed and Calculated Calibration Factors with Bentonite A

Technician	Sample	% Bentonite in Standard	Average Calibration Factor (mls/ % Bentonite)	STDEV Calibration Factor (mls/% Bentonite)	Expected Calibration Factor based on CEC	% Difference
1	0.5 grams Bentonite A	10%	4.9	0.06	5.4	-10.7%
2	0.5 grams Bentonite A	10%				
1	0.5 grams Bentonite A Moisture corrected	10%	5.3	0.16	6.0	-13.0%
2	0.5 grams Bentonite A Moisture corrected	10%				

Equation 7 is the % difference calculation.

$$\% \text{ Difference} = \frac{\text{observed} - \text{expected}}{\text{Average of (observed + expected)}} \times 100 \quad \text{Eqn. 7}$$

Table 6. Calculated Calibration Factors with Bentonite B

Technician	Sample	% Bentonite in Standard	Avg (mls)	STDEV	Overall Average (mls)	Overall STDEV (mls)
1	0.5 grams Bentonite B	10%	41.3	2.08	40.2	1.94
2	0.5 grams Bentonite B	10%	39.0	1.00		
1	0.5 grams Bentonite B Moisture corrected	10%	50.0	1.00	48.0	2.53
2	0.5 grams Bentonite B Moisture corrected	10%	46.0	1.73		

Table 7. Comparison of Observed and Calculated Calibration Factors with Bentonite B

Technician	Sample	% Bentonite in Standard	Average Calibration Factor (mls/ % Bentonite)	STDEV Calibration Factor (mls/% Bentonite)	Expected Calibration Factor based on CEC	% Difference
1	0.5 grams Bentonite B	10%	4.0	0.19	4.4	-9.1%
2	0.5 grams Bentonite B	10%				
1	0.5 grams Bentonite B Moisture corrected	10%	4.8	0.25	5.1	-6.1%
2	0.5 grams Bentonite B Moisture corrected	10%				

Table 8. Calculated Calibration Factors with Pre-blend

Technician	Sample	% Bentonite in Standard	Avg (mls)	STDEV	Overall Average (mls)	Overall STDEV (mls)
1	0.5 grams pre-blend corrected for clay weight	10%	48.0	1.00	47.5	0.84
2	0.5 grams pre-blend corrected for clay weight	10%	47.0	0.00		
1	0.5 grams pre-blend corrected for clay weight and moisture	10%	52.3	0.58	52.0	1.55
2	0.5 grams pre-blend corrected for clay weight and moisture	10%	51.7	2.31		

Table 9. Comparison of Observed and Calculated Calibration Factors with Pre-blend

Technician	Sample	% Bentonite in Standard	Average Calibration Factor (mls/ % Bentonite)	STDEV Calibration Factor (mls/% Bentonite)	Expected Calibration Factor based on CEC	% Difference
1	0.5 grams pre-blend corrected for clay weight	10%	4.8	0.08	5.1	-7.1%
2	0.5 grams pre-blend corrected for clay weight	10%				
1	0.5 grams pre-blend corrected for clay weight and moisture	10%	5.2	0.16	5.7	-9.2%
2	0.5 grams pre-blend corrected for clay weight and moisture	10%				

Table 10. Calculated Calibration Factors with Pre-mulled Bentonite

Technician	Sample	% Bentonite in Standard	Avg (mls)	STDEV	Overall Average (mls)	Overall STDEV (mls)
1	Bentonite A pre-mulled Moisture corrected	6%	35.7	0.58	35.0	0.89
2	Bentonite A pre-mulled Moisture corrected	6%	34.3	0.58		
1	Bentonite A pre-mulled Moisture corrected	10%	56.0	1.00	56.7	1.03
2	Bentonite A pre-mulled Moisture corrected	10%	57.3	0.58		

Table 11. Comparison of Observed and Calculated Calibration Factors with Pre-mulled Bentonite A

Technician	Sample	% Bentonite in Standard	Average Calibration Factor (mls/ % Bentonite)	STDEV Calibration Factor (mls/% Bentonite)	Expected Calibration Factor based on CEC	% Difference
1	Bentonite A pre-mulled Moisture corrected	6%	5.8	0.15	6.0	-2.8%
2	Bentonite A pre-mulled Moisture corrected	6%				
1	Bentonite A pre-mulled Moisture corrected	10%	5.7	0.10	6.0	-5.7%
2	Bentonite A pre-mulled Moisture corrected	10%				

Table 12. Calculated Calibration Factors with Pre-mulled Bentonite B and Pre-blend

Technician	Sample	% Bentonite in Standard	Avg (mls)	STDEV	Overall Average (mls)	Overall STDEV (mls)
1	Bentonite B pre-mulled Moisture corrected	10%	53.3	0.58	52.0	1.55
2	Bentonite B pre-mulled Moisture corrected	10%	50.7	0.58		
1	Pre-blend pre-mulled Moisture corrected	10%	59.0	2.65	58.8	1.84
2	Pre-blend pre-mulled Moisture corrected	10%	58.7	1.16		

Table 13. Comparison of Observed and Calculated Calibration Factors with Pre-mulled Bentonite B and Pre-blend

Technician	Sample	% Bentonite in Standard	Average Calibration Factor (mls/ % Bentonite)	STDEV Calibration Factor (mls/% Bentonite)	Expected Calibration Factor based on CEC	% Difference
1	Bentonite B pre-mulled Moisture corrected	10%	5.2	0.16	5.1	1.9%
2	Bentonite B pre-mulled Moisture corrected	10%				
1	Pre-blend pre-mulled Moisture corrected	10%	5.9	0.18	5.7	3.2%
2	Pre-blend pre-mulled Moisture corrected	10%				

Table 14. Calculated Calibration Factors with Bentonite A with Silicon Carbide (SiC)

Technician	Sample	% Bentonite in Standard	Avg (mls)	STDEV	Overall Average (mls)	Overall STDEV (mls)
1	Bentonite A with SiC	10%	49.0	0.00	49.3	0.52
2	Bentonite A with SiC	10%	49.7	0.58		
1	Bentonite A with SiC (Moisture corrected)	10%	53.3	1.16	52.5	2.51
2	Bentonite A with SiC (Moisture corrected)	10%	51.7	3.51		

Table 15. Comparison of Observed and Calculated Calibration factors with Bentonite A with Silicon Carbide (SiC)

Technician	Sample	% Bentonite in Standard	Average Calibration Factor (mls/ % Bentonite)	STDEV Calibration Factor (mls/% Bentonite)	Expected Calibration Factor based on CEC	% Difference
1	Bentonite A with SiC	10%	4.9	0.05	5.4	-9.0%
2	Bentonite A with SiC	10%				
1	Bentonite A with SiC (Moisture corrected)	10%	5.3	0.25	6.0	-13.3%
2	Bentonite A with SiC (Moisture corrected)	10%				

Table 16. Calculated Calibration Factors with Bentonite B with Silicon Carbide (SiC)

Technician	Sample	% Bentonite in Standard	Avg (mls)	STDEV	Overall Average (mls)	Overall STDEV (mls)
1	Bentonite B with SiC	10%	41.7	1.53	40.5	1.64
2	Bentonite B with SiC	10%	39.3	0.58		
1	Bentonite B with SiC (Moisture corrected)	10%	48.7	0.58	47.3	1.63
2	Bentonite B with SiC (Moisture corrected)	10%	46.0	1.00		

Table 17. Comparison of Observed and Calculated Calibration Factors with Bentonite B with Silicon Carbide (SiC)

Technician	Sample	% Bentonite in Standard	Average Calibration Factor (mls/ % Bentonite)	STDEV Calibration Factor (mls/% Bentonite)	Expected Calibration Factor based on CEC	% Difference
1	Bentonite B with SiC	10%	4.1	0.16	4.4	-8.3%
2	Bentonite B with SiC	10%				
1	Bentonite B with SiC (Moisture corrected)	10%	4.7	0.16	5.1	-7.5%
2	Bentonite B with SiC (Moisture corrected)	10%				

Table 18. Calculated Calibration Factors with Pre-blend with Silicon Carbide (SiC)

Technician	Sample	% Bentonite in Standard	Avg (mls)	STDEV	Overall Average (mls)	Overall STDEV (mls)
1	Pre-Blend with SiC	10%	47.0	0.00	47.2	0.41
2	Pre-Blend with SiC	10%	47.3	0.58		
1	Pre-blend with SiC (Moisture corrected)	10%	52.3	2.08	52.0	2.61
2	Pre-blend with SiC (Moisture corrected)	10%	51.7	3.51		

Table 19. Comparison of Observed and Calculated Calibration Factors with Pre-blend with Silicon Carbide

Technician	Sample	% Bentonite in Standard	Average Calibration Factor (mls/ % Bentonite)	STDEV Calibration Factor (mls/% Bentonite)	Expected Calibration Factor based on CEC	% Difference
1	Pre-Blend with SiC	10%	4.7	0.04	5.1	-7.8%
2	Pre-Blend with SiC	10%				
1	Pre-blend with SiC and moisture corrected	10%	5.2	0.26	5.7	-9.2%
2	Pre-blend with SiC and moisture corrected	10%				

Table 20. Calculated Clay Contents for Commercial and Lab Prepared Molding Sands

Calibration Standard (% Clay in Standard and Preparation Notes)	Avg Calibration Factor (mls/% Clay)	Expected Calibration Factor based on CEC of Bentonites (mls/ % Clay)	Average % Clay Calculated Commercial Green Sand	Standard Deviation	Average % Clay Calculated Lab sand prepared	Standard Deviation
10% Bentonite A as received moisture	4.9	5.4	9.2	0.08	8.8	0.11
10% Bentonite A moisture Corrected	5.3	6.0	8.5	0.31	8.1	0.29
10% Bentonite A as received with SiC	4.9	5.4	9.1	0.16	8.7	0.20
10% Bentonite A moisture corrected with SiC	5.3	6.0	8.5	0.46	8.2	0.43
6% Bentonite A pre-mulled, moisture corrected	5.8	6.0	7.7	0.21	7.3	0.19
10% Bentonite A pre-mulled, moisture corrected	5.7	6.0	7.9	0.16	7.6	0.17
10% Bentonite B as received moisture	4.0	4.4	11.1	0.45	10.7	0.39
10% Bentonite B moisture corrected	4.8	5.1	9.3	0.53	8.9	0.48
10% Bentonite B as received moisture with SiC	4.1	4.4	11.0	0.48	10.6	0.49
10% Bentonite B moisture corrected with SiC	4.7	5.1	9.4	0.36	9.1	0.33
10% Bentonite B pre-mulled moisture corrected	5.2	5.1	8.6	0.28	8.2	0.24
10% Clay (premix) as received moisture	4.8	5.1	9.4	0.15	9.0	0.16
10% Clay (premix) moisture corrected	5.2	5.7	8.6	0.47	8.2	0.29
10% Clay (premix) as received moisture with SiC	4.7	5.1	9.5	0.17	9.1	0.21
10% Clay (premix) moisture corrected with SiC	5.2	5.7	8.6	0.47	8.3	0.49
10% Clay (premix) pre-mulled, moisture corrected	5.9	5.7	7.6	0.28	7.3	0.32
Min			7.6	0.08	7.3	0.11
Max			11.1	0.53	10.7	0.49

- Lab Sand Prepared at 8.0% Clay on as received basis or 7.2% on Dry Basis

Table 21. Comparison of Calculated Methylene Blue Clay Content Results vs. Estimated Clay Content for Lab Prepared Molding Sand

Calibration Standard (% Clay in Standard and Preparation Notes)	Average % Clay Calculated Lab sand prepared at 7.2% Clay on dry basis	Standard Deviation	Estimated Methylene Blue Clay Content	% Difference observed vs. estimated
10% Bentonite A as received moisture	8.8	0.11	8.0	10%
10% Bentonite A moisture corrected	8.1	0.29	7.2	13%
10% Bentonite A as received with SiC	8.7	0.20	8.0	9%
10% Bentonite A moisture corrected with SiC	8.2	0.43	7.2	14%
6% Bentonite A pre-mulled, moisture corrected	7.3	0.19	7.2	2%
10% Bentonite A pre-mulled, moisture corrected	7.6	0.17	7.2	5%
10% Bentonite B as received moisture	10.7	0.39	8.0	33%
10% Bentonite B moisture corrected	8.9	0.48	7.2	24%
10% Bentonite B as received moisture with SiC	10.6	0.49	8.0	32%
10% Bentonite B moisture corrected with SiC	9.1	0.33	7.2	26%
10% Bentonite B pre-mulled moisture corrected	8.2	0.24	7.2	14%
10% Clay (premix) as received moisture	9.0	0.16	8.0	13%
10% Clay (premix) moisture corrected	8.2	0.29	7.2	14%
10% Clay (premix) as received moisture with SiC	9.1	0.21	8.0	14%
10% Clay (premix) moisture corrected with SiC	8.3	0.49	7.2	15%
10% Clay (premix) pre-mulled, moisture corrected	7.3	0.32	7.2	1%
Min	7.3	0.11		
Max	10.7	0.49		

- **Lab Sand Prepared at 8.0% Clay on as received basis or 7.2% on Dry Basis**

CONCLUSIONS

The results of the methylene blue clay analysis of the commercial foundry sand and the lab prepared molding sand can be found in Table 3. The results of the raw milliliters of dye uptake show variation of less than 1 ml between the two technicians. This variation of approximately 1 ml is estimated to result in a range of 0.2 -0.3% in the methylene blue clay percentage when using any of the individual calibration factors presented in Table 20.

In Table 20 the left column of the table presents the various calibration standards used with the amount of clay used for the calibration standard and a description of the preparation of the standard (i.e., as received or moisture corrected) followed by average calibration factor calculated from that standard compared to the expected calibration factor based on the initial cation exchange capacity of the clay used for the standard. Table 20 also shows the average calculated methylene blue clay content for the commercial green sand and lab prepared green

sand using the calibration factor established from each standard along with the standard deviation from those measurements. In Table 21 again the left column provides the calibration standard used with the amount of clay used for the standard as well as a description of treatment of the standard along with the calculated methylene blue clay content for the lab prepared molding sand. In Table 21 since the sample was prepared with a known amount of clay the estimated methylene blue clay content can be estimated from the cation exchange capacity of the clay used, this estimate along with the percent difference between measured and expected is presented.

In Table 20 and 21, it can be noted that depending on the calibration factor used the resulting methylene blue content can vary by as much as 3.4-3.5%. This shows the potential for variation in results when comparing results from two potential foundries who measure the same milliliter uptake of dye on a sample but use different calibration approaches.

Table 22. Comparison of Samples Prepared with Increasing Amounts of Bentonite A Analyzed using Both Ultrasonic and Boiling Methods for Methylene Blue Clay Test

Sample prepared	mls MB Dye uptake via Ultrasonic Method	mls MB Dye uptake via Boiling Method	Expected mls based on CEC of Bentonite used
4% Bentonite A as received moisture	23	23	22
4% Bentonite A moisture Corrected	23	24	24
6% Bentonite A as received moisture	32	33	32
6% Bentonite A moisture Corrected	35	36	36
10% Bentonite A as received moisture	49	54	54
10% Bentonite A moisture Corrected	53	60	60
6% Bentonite A pre-mulled moisture corrected	35	36	36
10% Bentonite A pre-mulled moisture corrected	59	60	60
Commerical Green Sand	45	46	NA
Lab Prepared Sand at 7.2% Clay (dry basis)	43	44	41

INVESTIGATION INTO CORRECTION FOR MOISTURE CONTENT OF BENTONITE IN CALIBRATION STANDARD

When reviewing previously published research on calibration of the methylene blue clay content method, several general themes were noted. One discussion point was that the method calls for drying of the molding sand to a constant weight before testing to reduce variation due to moisture content, however it has been recommended by several authors that the calibration standards be prepared on an “as received” moisture basis.⁸ Several authors have pointed out that they believe the drying of the bentonite was influencing the amount of methylene blue dye absorbed by the calibration standard.^{4,8} One way to eliminate the impact of moisture is to dry the sample. The other way would be to measure the moisture content and correct the weight of the sample used to account for that moisture. One series of calibration factors examined the difference in methylene blue dye uptake between “as received” moisture prepared calibration standards and those prepared with a “moisture corrected” amount of sample. These results appear in Tables 4-9. While the increase in sample weight to compensate for the moisture did increase the amount of methylene absorbed, the standard deviation observed in the technician results increased in almost every case (Tables 4-9). It should be noted that while the results from the moisture corrected samples when prepared with raw clay showed greater difference between observed and expected values as seen in Tables 5,7,9,15,17 and 19 the calibration factor did increase resulting in a higher overall uptake of methylene dye per percent of clay. This may be attributed to the

increased weight of the calibration standard which adds more clay to a solution that was not well dispersed at the lower weight (0.5 grams).

When the samples weights were adjusted for moisture, it was also noted that agreement between the expected calibration factor based on cation exchange capacity and the observed calibration factor did not improve. In fact, for Bentonite A and the pre-blend calibration standards we saw the difference between these factors increase by 2% when correcting for moisture. This could be attributed to the increased volume of bentonite being more difficult to disperse in the solution.

In Table 20, the calculated clay contents are presented for the commercial grey iron foundry sand and the lab prepared molding sand (prepared at 8.0% clay by weight, 7.2% dry clay weight). In Table 21, a comparison of the calculated results vs. the estimated known clay content in the laboratory batch is presented. With Bentonite A and the pre-blend material we can see that the calculated results show a higher difference between the observed and expected clay contents when moisture corrected, and they are 10-15% higher than expected. This difference is attributed to the full cation exchange capacity of the calibration standards not being achieved due to incomplete dispersion of the bentonite in the tetrasodium pyrophosphate solution. We can also see the more limited dispersion and uptake of methylene dye when comparing the calibration standards for bentonite A prepared “at the cup” vs the milliliters adsorbed in Table 1 using the boiling and ultrasonic method (average of 49 mls for 0.5

grams of bentonite when prepared using ultrasonic agitation alone vs. 54 mls for the same 0.5 grams of bentonite when boiled followed by ultrasonic agitation). This data is in line with previous observations that the boiling method generates higher methylene blue dye absorption due to better dispersion of the bentonite.⁴

To investigate further the if the dispersion is playing a role in the differences observed with the 10% “at the cup” calibration standard a small follow up experiment was performed. The calibration standards were prepared with Bentonite A (sodium bentonite) at increasing amounts and tested with sample weights including the as received moisture as well as with the increased sample weight to compensate for the moisture. The calibration standards were tested using both the ultrasonic and boiling methods. Results appear in Table 22. Table 22 shows that samples prepared with 4 or 6% bentonite A show small difference between the milliliters of methylene blue uptake using the ultrasonic method vs the boiling method while at 10% the differences between methods increases. Table 22 also shows that the differences between samples that have been mulled, including the commercial green sand and lab prepared sand show small differences between the two methods, this suggests that the mulling of the 10% calibration standard is improving dispersion and allowing for more uptake of dye in the ultrasonic test vs. adding the same amount of powder clay into the sample cup for analysis.

It is also noteworthy that there have been several papers published that relate clay content and other variables to mechanical molding sand properties such as such as works by Green, Heine, Shih and others that have used a calibration factor of 6 mls per percent clay when using the boiling method for methylene blue content.^{11,12} In those studies working the calibration factor of 6 mls back out to the CEC of the clay would equate to a cation exchange capacity of 120 meq/100 grams which is in line with results for this study and with literature estimating the cation exchange capacity of montmorillonite clay based on theoretical calculations from the layer charge of the mineral structure.^{13,14} While not definitive this suggests that those previous authors may have been using a calibration factor that was based on the dry amount of bentonite clay.

INVESTIGATION INTO DIFFERENCES IN BENTONITES USED FOR CALIBRATION

As mentioned previously, different bentonites can have different cation exchange capacities and these differences can influence the amount of methylene blue dye adsorbed by the calibration standard. One series of calibration standards used two different bentonites with different initial cation exchange capacities while another series of calibration standards used a combination of both bentonite sources as well as additional organic foundry additives commonly found in commercial pre-blend

formulas. In Tables 4-9 we can see a distinct difference in the calibration factors obtained from Bentonite A (a higher CEC sodium bentonite) vs. Bentonite B (a lower CEC calcium bentonite). In Table 20 it is observed that the percent methylene blue clay values when calculated using Bentonite B as the calibration standard are the highest in the series. In Table 21 the difference between the calculated methylene blue clay content and the expected methylene blue clay content are the largest, generally at least 2x higher than when compared to an analogous calibration standard prepared with Bentonite A or the pre-blend. This difference is attributed to the lower CEC of the calibration clay versus the dominant clay in the lab prepared molding sand (ratio of Bentonite A to Bentonite B in prepared sand is 74/26). When the preblend calibration standard is used, which represents the same ratio of Bentonite A to Bentonite B as the lab prepared molding sand, the % difference between observed and expected reduces to similar levels as when calibrated with 10% standards prepared “at the cup” with Bentonite A.

INVESTIGATION INTO PRE-MULLING CALIBRATION STANDARD

Another approach to calibration that is used extensively in practice in the foundry industry and has not been recommended by previous studies is the use of a moisture corrected “pre-mulled” calibration standard. Some writers believe that preparing a pre-mulled calibration standard with a known percentage of bentonite clay on a dry basis is a reliable approach to obtaining a consistent calibration factor to relate milliliters of methylene dye absorbed to the present bentonite in the molding sand. In this method, the calibration standard and the molding sand to be evaluated would be treated and prepared in the same manner prior to testing. It is hypothesized that the mulling of the clay and sand in a laboratory sand muller would aid in the dispersion of the bentonite in the calibration standard and the correction for moisture would provide a more direct comparison to the amount and condition of clay in the molding sand that is being evaluated. One series of calibration standards was prepared by mixing a known amount of bentonite (corrected for dry weight) with sand and water to a compactability between 40-45% in a laboratory muller and then dried before testing in the same manner as the commercial molding sand (or any other molding sands to be evaluated).

In Tables 10-13 the data for the pre-mulled calibration standards are presented. A 6% by dry weight pre-mulled sample of Bentonite A was prepared (as this is the traditional calibration standard used in the author’s laboratory) along with a 10% by dry weight pre-mulled sample of Bentonite B and the preblended mixture of bentonite A, B and organic foundry additives (the amount of preblend was adjusted to compensate for both moisture and non-bentonite additives in the blend). It was noted that for bentonite A the standard deviation observed for the pre-mulled samples was in line with the standard

deviation observed when evaluating the commercial foundry sand and lab prepared molding sand (approximately 1 ml standard deviation). In Table 11, it is observed that the 6% and 10% pre-mulled sample of Bentonite A were in close agreement with the expected calibration factor estimated from the initial CEC of bentonite A (1.1% and 0.6% lower than expected). Similarly, in Table 13 the 10% pre-mulled sample of the preblend material shows slightly larger deviation from the expected calibration factor based on CEC but is only 3% higher than expected. The 10% sample of pre-mulled bentonite B was 5.9% higher than expected. In Table 21, it is observed that the calculated methylene blue clay content with the pre-mulled bentonite A samples are between 3-6% higher than the estimated methylene blue clay content of the lab prepared batch, using the 10% pre-mulled preblend calibration standard the calculated methylene blue clay content is only 3% higher than the expected amount. The difference between the expected uptake of methylene dye and the observed are much less for the pre-mulled calibration standards vs. the calibration standards prepared at the cup, this is believed to be related to the increased dispersion of the bentonite prior to testing. These results obtained using the calibration factors for pre-mulled bentonite A and the preblend are in much closer agreement to the expected value of 7.2% clay on dry basis than any of the “at the cup” calibration standards that were prepared.

Previous studies such as investigations by Graham and Praski (1978) have advised against using pre-mulled calibration standards and they cite reasons such as influences of mixing time and changes of methylene blue requirements of the standard over time. In that investigation, the authors were using a paddle style kitchen mixer and cited uncertainty in determining the initial moisture of the bentonites, and the influence of drying procedure.⁸ While these concerns were not directly investigated the preparation of the standards in this study used a lab scale foundry type mixer with a mixing time that typically yields at least 85% of the typical green compression strength in the lab as observed in the foundry. While there are key differences between commercial sands and laboratory prepared sands, such as the presence of fines and thermally degraded clay, differences in sand type etc., this approach does provide confidence that the bentonite is dispersed across the sand grains and developed in a comparable manner as in a commercial foundry. The impact of drying was not investigated but was constrained by drying the calibration standards and the molding sands at the same temperature and for the same approximate time. This paper’s authors believe that Graham and Praski’s comments regarding consistency of the calibration standard can be attributed to the drying and segregation of the pre-mulled calibration standard over time, and as with any calibration standard if a notable change in methylene blue dye uptake is noted it should be investigated and potentially replaced with a new standard.

While the Graham and Praski calibration approach may still have its limitations, as it is not feasible to prepare a pre-mulled standard for every commercial pre-blend, the approach of using a pre-mulled calibration standard of the predominant bentonite in the commercial pre-blend does appear promising and can improve correlation of results between labs if the same standard is used. As noted previously it is recommended to use the predominant bentonite in the commercial pre-blend for calibration as there may be differences in cation exchange capacities between bentonites from different suppliers. For most ferrous foundry operations, Bentonite A, or a similar sodium bentonite would be the predominant bentonite in the blend.

INVESTIGATION INTO THE USE OF FINE MESH SILICON CARBIDE

The AFS procedure recommends the addition of 5.0 grams of 220 grit silicon carbide to the calibration standard as an abrading agent to aid in the dispersion of the clay added to the sample beaker. This step can be found as a recommendation as early as 1970 in the work by Dietert and Graham,⁵ however in practice this paper authors have observed many foundries omitting this step when using the AFS method of calibration. A series of calibration standards were prepared with and without the silicon carbide to evaluate the impact of this material on the dispersion of the clay in the calibration standard.

In Tables 14-19, the results of calibration standards prepared with and without fine mesh silicon carbide are presented. In general, when comparing results in Tables 4-9 and 14-19, the addition of the silicon carbide to the “at the cup” prepared calibration standards does not appear to significantly increase the amount of methylene dye absorbed by the standard. It was noted that in each case the standard deviation of the measurements increased with the addition of the silicon carbide. The intent of the silicon carbide is to further disperse the clay in the solution, however the technicians performing the test commented that the addition of silicon carbide appeared to “trap” the sample at the bottom of the cup creating a noticeable “clump” of material that could be felt with the glass rod during testing. This observed lack of difference between addition and no addition of the silicon carbide may be reason that it is absent from many calibration methods used at foundries today.

SUMMARY

The methylene blue clay test is dependent on the cation exchange capacity of the bentonites used as bonding agents in the sand. It was shown in this study that clays with different initial cation exchange capacities can generate very different calibration factors for the methylene blue clay content test. Previous research has shown that measuring the cation exchange capacity of

bentonites and the methylene blue clay content of molding sands is heavily influenced by the ability to disperse the bentonite into the solution prior to titration with methylene blue dye. The AFS procedure for methylene blue clay content prescribes the drying of the molding sand before testing but not the clay to prepare the calibration standard, and investigation into whether compensating for the moisture in the bentonite used in the calibration standard showed that when using the “at the cup” preparation of calibration standards the compensation for moisture did not appear to have a positive impact. The present study showed that using an “at the cup” calibration method combined with ultrasonic agitation only shows a tendency to over-estimate the amount of bentonite in the molding sand by 10-15%, most likely due to inadequate dispersion of the clay in the solution. However, compensating for the moisture and pre-mulling the bentonite with sand and water showed promising results and appears to correlate better with estimates of actual bentonite present in the molding sand. This is believed to be due to the additional dispersion of the bentonite onto the sand particles during mulling, making the calibration standard very similar in nature to the molding sands being evaluated.

This study does not suggest that using a pre-mulled bentonite standards will reduce all potential sources of variation in the methylene blue clay test, but does suggest that foundries and labs may achieve improved correlation of results if they take steps to ensure that they are calibrating their test results with a known consistent bentonite that is the same as in their molding sand and take steps to ensure that the bentonite is well dispersed prior to testing. This study also presents an approach to compare the methylene dye uptake of their calibration standard with estimated results obtained by the cation exchange capacity of the bentonite they are using.

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