

Digital Active Clay Measurement by Spectrophotometric Method in Green Sand Foundries

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ABSTRACT

The measurement of active clay in foundry green sand is an essential component in the control of the metalcasting process. The Methylene Blue (MB) Test is the current AFS standard to measure active clay.

Currently, there are two standard AFS tests for determining MB content. One test uses a boiling method, and the most commonly used test uses an ultrasonic scrubber and tetrasodium pyrophosphate (TSPP). While the ultrasonic test was determined to be safer for the operators, it continues to be time consuming (25-30 minutes per test), qualitative in nature in regard to reading the halo, and dependent on operator judgement and bias effects.

A new spectrophotometric test has been developed that offers a faster, quantitative (digital) measurement for active clay in green sands and does not require extensive training or experience. In this study, this new alternative test is optimized and evaluated at three foundries to determine viability as an alternative measurement of active clay in working foundry green sand systems. The trials were conducted and optimized over two rounds of foundry testing. The variance of the optimized methods has been reviewed relative to the standard MB test using a comparison within each foundry and a gage repeatability and reproducibility test. This analysis confirms that the

new test has similar variability compared to the standard AFS MB test performed by experienced operators. Furthermore, the new test offers a quantitative measurement as an alternative to the standard MB test.

Keywords: digital active clay measurement, spectrophotometric method, green sand foundries

INTRODUCTION

The measurement of active clay is critical to the control of foundry green sand. The amount of active clay present in green sand directly affects the strength, moisture, compactability, and mechanical properties of the mold. By improving the characterization of clay levels, the moisture and compactability could be more accurately controlled. Inadequate compactability control can cause green sand casting defects, and the associated costs of scrap, rework, labor, and energy. A previous study reported that a foundry required an MB clay control within $\pm 0.35\%$ to minimize scrap gray iron castings.¹ These costs warrant investigations into alternative methods of control.

The foundry industry would benefit from a faster, simple, accurate, and low-cost alternative to measure active clay in green sand. The AFS 2210-17-S and AFS 2211-17-S

MB Clay Tests have been used to determine active clay levels in foundry green sands since 1967.² These tests are dependent on an operator making a visual determination which leads to inherent inaccuracies based upon studies and input from numerous AFS Corporate Member foundries.³ Due to this potential bias and other factors, the test reproducibility within and between foundries is currently limited in maintaining ongoing accuracy.

Casting defects are consistently attributed to variations in green sand systems and limitations of the clay control methods for green sand. The standard MB test is dependent on a cation exchange reaction where active binding anionic sites on clay are bound by methylene blue dye, resulting in the sequestration of these dye molecules from solution. The amount of the bound dye molecules is determined by adding the remaining dye solution dropwise to filter paper and reading the resulting “halo”. The reading of this halo requires operators with specialized training and experience. There is often a need to monitor technicians to ensure that there is no drift in calling the halo point. Because of the discretion in calling the halo point, some foundries have reported operator bias factors can affect MB reported test results when the operator calls the halo point to try to be within the control ranges that they are tasked with staying within. This is often evidenced by histogram distributions truncated at the control limit values.

An alternative method to the standard MB test was published in 2013 and 2020.^{4,5} This non-standardized dye absorption and titration methodology offered an accurate and digital measurement of active clay. Moreover, the alternative method provides an avenue to automation much easier than the current AFS standard for active clay measurement.

In this research, the previously developed method from 2013 and 2020 was modified in various procedure aspects to minimize variation, reduce costs, and simplify the method for lower sample processing times and less user error. The proposed modifications included replacing the centrifuge with filtration, as foundries typically do not have a centrifuge with sufficient force for this method. Furthermore, preliminary data suggested that using filtration leads to more reproducible results than using centrifugation in the testing method.

The new spectrophotometric method uses Cu(II) triethylenetetramine, a dye that binds stronger to the active clay binding sites, thereby allowing for lower dye concentrations in the test solution and a dye that can be measured spectrophotometrically. Methylene blue dye needs to be used at a much higher concentration, with a

dye that is opaque and cannot be measured spectrophotometrically unless dramatically diluted.^{4,6}

The goal of these studies was to validate a new standard method for determining active clay content of green sands, with lower variability and a shorter test time than current standard tests. This would also allow for a quicker reaction by the foundry to changing green sand characteristics. In addition, the consumables will be lower cost, safe for use in an industrial environment, and result in easier clean-up compared to the current AFS standard MB Clay test.

In preliminary studies, prior to this funded research project, data was collected in round-robin tests from three different laboratories on over twenty foundry green sand samples. These samples had a wide range of active clay content from 5 to 10% and were measured by this alternative test and compared with the standard MB test. Promising results were obtained as evidenced by lower standard deviation with the new digitized method.

The research was divided into three stages.

- In the *first stage*, the method was optimized in a university laboratory and tested as a standard method for use in foundries.⁷
- In the *second stage*, the optimized method from stage one was tested in 3 working foundries. During stage two, one round of testing was completed at the three foundries. However, due to variability of the test that was conducted at the foundries, the method was further optimized for speed and in response to results from the first round of foundry testing.
- The *third stage* was initially reserved for optimization; however, the method was further optimized and subsequently tested in the second round of foundry testing. After the second round of testing a Gage Repeatability & Reproducibility (GR&R) study was conducted, comparing the new optimized spectrophotometric test to the standard MB test.

This analysis suggests that the new spectrophotometric test has variability that is comparable to the standard AFS MB test. This research has refined the spectrophotometric method, making it user-friendly with minimal training, accelerating the testing process.

This test has been submitted to be approved as an AFS standard test for active clay in green sands and included in the “AFS Mold & Core Test Handbook.”²

EXPERIMENTAL PROCEDURE AND MATERIALS

The new spectrophotometric procedure is comprised of four main steps: 1) weighing and mixing of the green sand with the copper triethylenetetramine solution, 2) equilibrium settling, 3) filtration of the sand from the dye, and 4) spectrophotometric reading of the dye absorbance at a specific wavelength of 578 nm. Much like the standard MB test, the active clay in this procedure effectively sequesters the dye from the solution, resulting in a less concentrated dye solution that can be measured. This dye more specifically binds active clay sites, and thus a lower concentration of dye can be used. Therefore, it is more translucent to light and thus can be measured spectrophotometrically, which allows for a digital quantitative reading.

The equipment/consumables, specifications and the specific models and item numbers that are used in this project are listed in Table 1.

Table 1: Serial dilution for Cu(II)-Triethylenetetramine dye calibration		
Equipment/Consumable	Specifications	Specific model/ part used in these studies
Triethylenetetramine	Liquid, 97% or higher purity	Sigma Aldrich 90460
Cu-sulfate standard solution	0.1 mol/L	Millipore Cat. HC91079184
Spectrophotometer or absorbance meter	Capable of measuring absorbance at 578 nm	Unico model 1205 UV-Vis spectrophotometer
Vortex mixer	Able to vortex up to 2000 or more rpm	Fisher Vortex Genie 2 Cat. No. 12-812
Analytical balance	0.001g sensitivity	Mettler Toledo 30029075
Bottletop volumetric dispenser	Able to draw up volume to +0.1 mL up to 15 mL	Fisherbrand Cat. 13681527
Centrifuge test tube with cap	15mL, preferably polystyrene or polypropylene	Fisherbrand Cat. 05-539-5
Clear polystyrene disposable cuvette	4.5 mL square bottom	Fisherbrand Cat. 14955129
Disposable syringe	3 mL	BHSupplies Part BH3LS
Syringe filter	PES, 13mm, 0.45 micron	Steritech 1470354
Glass funnel	50 or 75mm diameter	Fisherbrand Cat. 03-865
Small measuring scoop	1/16 to 1/8 teaspoon	New Star Foodservice 42924
Test tube holder (2)	Holds 15mL tubes	SP Bel Art 187960000
Disposable optical wipe	Preferably dust free	Kimwipes
Magnetic stir plate	5x7" surface, stirring up to 100 rpm	Corning PC-420
Magnetic stir bar	1-2 inches	Corning 400430
Glass amber bottle	2 L	Kitchentoolz Boston Round 2L Amber bottles
Glass volumetric flask	2000 mL	Pyrex 44422L
Glass beaker	100 mL	Fisherbrand FB102100

DYE SOLUTION PREPARATION

A dye solution of 3.33 mmol/L of Cu(II)-triethylenetetramine (Cu-T) solution was prepared. 1.005 g of liquid triethylenetetramine was weighed and dissolved with 50 mL deionized (DI) water in a beaker. 66.67 mL of 0.1 mol/L of copper sulfate solution was measured using a measuring cylinder and an adjustable 1-10 mL pipette. Both solutions were transferred to a 2L volumetric flask, and the flask was then filled to 2L with DI water. A magnetic stir bar was used to gently stir the solution overnight while covered to allow for sufficient

formation of dye complexes. The Cu-T solution was then transferred to a large amber container and stored in a cool and dark place. Due to the hygroscopic nature of triethylenetetramine, rapid handling and proper storage of the solution is required.

SAMPLE WEIGHT AND DOSING

To optimize the dye usage, a study was completed on multiple foundry laboratory scales to determine the level of scale accuracy. Various tests were performed to determine the lowest dye and sand sample sizes that could be used while maintaining an acceptable variance. A green sand sample size of 0.5 g (± 0.1 g) along with 10 mL (± 0.1 mL) of Cu-T dye was used in the optimized procedure. In the first-round testing, the amount was set to use exactly or close to 0.500 g of green sand sample with weighing paper and 10 mL of dye with a bottle top dispenser with recirculation valve into a 15 mL centrifuge tube.

In the second-round testing, a 15 mL centrifuge tube was weighed, recorded, and tared, and 10 mL (± 0.1 mL) was pipetted using a bottle top dispenser with recirculation valve into the centrifuge tube. The dye was then weighed, recorded, and tared again. Using a glass funnel, and a 1/16 or 1/8 teaspoon measure, green sand samples were scooped and transferred into the centrifuge tube. Density and properties of the foundry sands may necessitate the use of the different measuring spoon capacity. The green sand sample was weighed and recorded.

To note, total volume should not exceed 10.5 mL to provide sufficient space for proper mixing in the tube. The use of weighing paper for measurement of sand that was used in the first-round testing was removed due to the electrostatic forces acting on the green sand which may cause interference in the transference of green sand into the centrifuge tube. The glass funnel technique eliminates the electrostatic forces and saving time. With a 1/16 or a pinch scoop, the green sand can be easily measured to 0.5 g (± 0.1 g) and need not be the exact amount as the weight of the sand sample and dye can be adjusted in the CEC calculation. Additionally, removing the step of using a weighing paper also minimized user error that may occur if sand accidentally is deposited underneath the weighing paper during measurement.

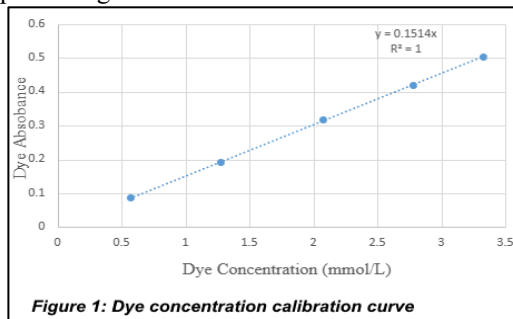


Figure 1: Dye concentration calibration curve

MIXING/ AGITATION

The prepared samples were first mixed by vigorously shaking by hand for 5 seconds and then mixed by vortex mixer at speed setting of approximately 2000 rpm for 10 seconds. The samples are then allowed to sit for at least 2 minutes to allow sufficient settling and equilibration of the green sand. Most foundry green sand sample settles to the bottom quickly, but in some cases if it does not, please allocate extra time for settling. Then the samples are vortexed and allowed to settle a second time for 2 minutes. This second mixing and settling step, as well as use of the vortex instead of an orbital shaker were modified in the optimized procedure from the first set of foundry trials.

SEPARATION BY SYRINGE FILTRATION

Using a 3 mL disposable syringe 3 mL of the supernatant dye was pipetted and filtered through a 25mm 0.45 µm PTFE or 13mm 0.45 µm polyethersulfone (PES) syringe filter into a 4.5 mL clear polystyrene disposable cuvette. The 13mm 0.45 µm syringe filter was preferred by the operators as it was easier to expel the liquid into the full cuvette volume. Square bottom cuvettes were necessary to minimize variance in our tests and trials. Cuvettes that have a tapered bottom proved to be problematic in the spectrophotometer when measuring absorbance in the next step, as these did not sit in a consistent position in the spectrophotometer.

UV-VIS SPECTROPHOTOMETRY

The UV-VIS spectrophotometer is first tared with a cuvette that is filled with deionized (DI) water. The outer walls of the sample cuvette as prepared above were wiped with disposable wipes and inserted into the spectrophotometer. Absorbance was measured at the peak wavelength of the Cu-T solution of 578 nm.

CONFIRMATION OF ABSORBANCE LINEARITY OF CU-T DYE SOLUTION

To verify the linearity of the exchange solution, the absorbance of the Cu-T dye at various concentration levels was plotted (Figure 1). The R² value of the calibration curve should not drop below 0.997. Based on testing, it was shown that the dye remained stable for at least 6 months and this linearity was maintained during this period.

Because of this linearity, we can determine the absorbance for each new batch of dye. That value is used to calculate the slope without needing to run additional diluted samples.

For the test study, the spectrophotometers used at WMU and supplied to industry partners were all calibrated using standard filters.

Details regarding dye mixing/ verification instructions and recommendations for maintaining calibration consistency of absorbance-measuring equipment will be available in the AFS procedure that is forthcoming.

CEC (CATION EXCHANGE CAPACITY) DETERMINATION

CEC was determined by the difference in the concentration of Cu-T of the sample to a referenced standard, considering the volume of exchange solution and valance of the copper cation, and adjusting for the weight and the moisture content of the sample. Since there is an equivalent exchange of sample and solution, the valance of the Cu-T is the charge of the dye, which is 2. The sample concentration of Cu-T was calculated by dividing the sample absorbance obtained from the spectrophotometer by the absorbance of the straight Cu-T dye batch sample and this ratio is multiplied by the calculated batch concentration of the straight Cu-T dye. This straight Cu-T dye concentration should typically be very close to the 3.33 mmol/L that is prepared as described above. Moisture content was determined by weighing sand sample before and after drying in an oven at 107C (224.6F). Moisture content was adjusted in the CEC calculation only and not during other methodology. CEC was calculated using the equation below.

$$CEC = \frac{\left(X_o - \left(\frac{A_s}{A_o} \right) \cdot X_o \right) \cdot \left(\frac{D}{1000} \right) \cdot 100 \cdot z}{M_{\text{sample}} \cdot \left(1 - \left(\frac{W_{107}}{100} \right) \right)}$$

CEC = cation exchange capacity, expressed in cmolc/kg

X_o=concentration of Cu(II) [mmol/l]

A_o = UV Vis Spectrophotometer Absorbance of straight dye

A_s = UV Vis Spectrophotometer Absorbance Value of Sand Sample

D = dye volume [mL]

z = valency of index cation

M_{sample} = sample weight [mg]

W_{107°} = sample moisture measured at 107C (224.6F)

RESULTS

The objective of this research was to optimize the new spectrophotometric method for integration into foundries as an alternative method for measuring the active clay in green sands. Trials were conducted as described at three foundries, EJ, John Deere (JD) and Metal Technologies Inc (MTI). The active clay content was measured for several green sand samples in a series of two rounds of testing. In the first round of testing the method was tested using modifications from previous spectrophotometric-based measurements. The spectrophotometric method was then optimized to reduce variability of the test, and then

the optimized method was used in a second round of testing.

During this testing, the three foundries conducted tests on several individual samples that were taken during their own operations in their respective facilities. These samples are labeled as MTI, EJ, or JD samples to indicate their origin in the data tables. The three foundries each used Cu-T dye from the same batch as prepared by Western Michigan University (WMU).

FIRST ROUND OF TESTING IN FOUNDRIES

In the first round of testing, the use of a centrifuge for green sand and dye mixture separation was substituted with syringe filtration as noted above. In this first round of testing, 10 mL \pm 0.1 mL of Cu-T dye was added to a centrifuge tube. Then 0.50 \pm 0.01 g of green sand foundry sample was measured as precisely as possible on weighing paper and transferred into a 15 mL centrifuge tube with the dye. The green sand dye mixture was shaken by hand for 5 seconds and transferred to an orbital shaker and mixed for 2 minutes at 300-500 RPM. It was allowed to sit for at least 2 minutes for sediment of the green sand particles and using a 3 mL syringe, 3 mL of supernatant dye was picked up and filtered through a 25 mm 0.45 μ m PTFE syringe filter. CECs and standard deviations (SDs) were calculated and averaged across three repetitions per sample ID. All the absorbance results were measured using the same model equipment at the three foundries. The averaged CEC and the standard deviation of CEC results from MTI, EJ and JD are shown in Table 2.

Table 2: First round testing with syringe filtration								
MTI			EJ			JD		
Sample ID	CEC (cmol/kg)	SD CEC (cmol/kg)	Sample ID	CEC (cmol/kg)	SD CEC (cmol/kg)	Sample ID	CEC (cmol/kg)	SD CEC (cmol/kg)
MTI-1	8.47	0.07	EJ-1	6.58	0.16	JD-1	6.87	0.29
MTI-2	8.41	0.24	EJ-2	6.53	0.09	JD-2	7.85	0.78
MTI-3	8.66	0.17	EJ-3	6.50	0.06	JD-3	7.48	0.15
MTI-4	8.88	0.15	EJ-4	6.30	0.14	JD-4	7.54	0.31
MTI-5	9.28	0.13	EJ-5	6.47	0.26	JD-5	7.37	0.21
MTI-6	8.51	0.15	EJ-6	6.57	0.31	JD-6	7.79	0.06
MTI-7	8.56	0.24	EJ-7	6.49	0.03	JD-7	7.86	0.20
MTI-8	8.42	0.10	EJ-8	6.49	0.33	JD-8	7.77	0.04
MTI-9	8.44	0.03	EJ-9	6.41	0.14	JD-9	7.36	0.09
MTI-10	8.49	0.24	EJ-10	6.60	0.26	JD-10	7.81	0.24
MTI-11	8.31	0.03	EJ-11	6.30	0.06	JD-11	7.66	0.17
MTI-12	8.17	0.10	EJ-12	6.38	0.32	JD-12	7.25	0.16
MTI-13	8.20	0.04	EJ-13	6.29	0.14	JD-13	7.98	0.95
MTI-14	9.03	0.06	EJ-14	6.84	0.10	JD-14	7.16	0.14
MTI-15	9.36	0.14	EJ-15	6.40	0.03	JD-15	7.43	0.07
MTI-16	8.57	0.06	EJ-16	6.38	0.21	JD-16	7.15	0.15
MTI-17	8.78	0.36	EJ-17	6.38	0.12	JD-17	7.85	1.05
MTI-18	7.92	0.04				JD-18	7.35	0.16
MTI-19	8.07	0.13				JD-19	8.33	1.07
MTI-20	8.30	0.10				JD-20	8.00	0.37
Average		0.13	Average		0.16	Average		0.33

First round testing results from the three foundries show good reproducible data with low SD values for most of

the samples. The average SD value for each foundry were reported to be 0.13 (MTI), 0.16 (EJ) and 0.33 (JD). A few outliers, marked with an asterisk, were left out of this calculation due to tubes falling off the shaker and other procedural issues. These results have some samples with higher variation. This was potentially due to issues with the test or equipment, with some variance potentially due to operator error. These samples were sent to the laboratory at WMU and tested independently as shown in Table 3.

The WMU laboratory analyzed all the same individual foundry green sand samples as tested at each foundry to compare and to confirm reproducibility of data. According to the data, it was shown that the new alternative technique does work with low SD value in the WMU lab. The average SD value obtained from WMU for each foundry was 0.17 (MTI), 0.16 (EJ) and 0.19 (JD). These results showed slightly lower variance and low standard deviation for sample CEC measurements.

Table 3: WMU trial on foundries green sand sample for comparison								
MTI			EJ			JD		
Sample ID	CEC (cmol/kg)	SD CEC (cmol/kg)	Sample ID	CEC (cmol/kg)	SD CEC (cmol/kg)	Sample ID	CEC (cmol/kg)	SD CEC (cmol/kg)
MTI-1	8.53	0.18	EJ-1	6.68	0.22	JD-1	7.56	0.16
MTI-2	8.19	0.22	EJ-2	6.35	0.05	JD-2	7.70	0.11
MTI-3	8.82	0.06	EJ-3	6.35	0.32	JD-3	7.54	0.23
MTI-4	8.80	0.30	EJ-4	6.39	0.25	JD-4	7.54	0.39
MTI-5	9.01	0.07	EJ-5	6.60	0.22	JD-5	7.75	0.13
MTI-6	8.40	0.36	EJ-6	6.54	0.22	JD-6	7.59	0.11
MTI-7	8.62	0.08	EJ-7	6.52	0.14	JD-7	7.77	0.14
MTI-8	8.63	0.14	EJ-8	6.60	0.09	JD-8	7.83	0.27
MTI-9	8.73	0.23	EJ-9	6.40	0.13	JD-9	7.79	0.12
MTI-10	8.49	0.27	EJ-10	6.25	0.18	JD-10	7.72	0.17
MTI-11	8.45	0.20	EJ-11	6.27	0.08	JD-11	7.76	0.10
MTI-12	8.14	0.16	EJ-12	6.45	0.11	JD-12	7.72	0.03
MTI-13	8.42	0.21	EJ-13	6.34	0.16	JD-13	7.49	0.32
MTI-14	8.80	0.13	EJ-14	6.25	0.04	JD-14	7.15	0.49
MTI-15	9.23	0.03	EJ-15	6.41	0.13	JD-15	7.72	0.04
MTI-16	8.72	0.04	EJ-16	6.52	0.17	JD-16	7.55	0.46
MTI-17	8.87	0.20	EJ-17	6.45	0.14	JD-17	8.15	0.04
MTI-18	8.23	0.23				JD-18	7.91	0.04
MTI-19	8.25	0.07				JD-19	8.09	0.01
MTI-20	8.38	0.16				JD-20	7.99	0.49
Average		0.17	Average		0.16	Average		0.19

METHOD OPTIMIZATION BETWEEN FIRST AND SECOND ROUNDS OF FOUNDRY TESTING

Although most of the samples showed low variance in CEC values between samples, our research group strove to improve the test and further reduce variability of the test. During these efforts, 12 green sand samples that had a higher SD value (between 0.49 to 0.23) were tested with a new method that is the optimized final method as described in the *Experimental Procedures & Materials* section. In the modifications to further reduce variability of the test, the dye was transferred into the centrifuge tube and weighed first before the sand sample. Instead of using weighing paper to measure the weight of the green sand

sample, a glass funnel and a 1/16 teaspoon measuring scoop was used to weigh out the sand directly in the centrifuge tube. Furthermore, a weight of $0.5\text{g} \pm 0.1\text{ g}$ was used instead of $0.50\text{g} \pm 0.01$ as the sample weight can be directly incorporated into the CEC equation and an exact sample weight of 0.50 g is not necessary for a successful measurement. Finally, instead of orbital shaking, a vortex mixer at speed setting 7 for 10 seconds was used to mix the green sand dye mixture. User feedback indicated that sometimes the samples flew off the orbital shaker, and vortex mixing uses a lower cost instrument (~\$300 instead of ~\$2500) and avoids this issue that may contribute to increased variance of the test.

The variance of the test was greatly reduced for these 12 samples when using the modified method. Using this modified method, the highest SD value of the samples tested at WMU reduced from 0.49 to 0.14 (JD-20 sample) and from 0.49 to 0.07 (JD-14 sample).

User feedback from the first round of testing also indicated that filters had significant backpressure, sometimes resulting in leakage of the syringe filter, thereby causing a poor user experience and potential increase in variability of the test. In the second round of testing, the material was changed to 13 mm PES instead of 25 mm PVDF membranes (both with $0.45\mu\text{m}$ pore size), resulting in less backpressure without affecting filtration performance (tests were performed to confirm performance but not included in this report).

Testing at the EJ foundry indicated that some samples had not yet fully equilibrated after one cycle of vortex and settling for 2 minutes. As such, after one cycle in which the samples are vortexed and equilibrated for at least 2 minutes, the samples were vortexed again for another 10 seconds and left to rest for a second time for at least another 2 minutes. This allowed for the samples to equilibrate enough to further reduce variability of the test. Finally, with lower active clay content, the sample weight could be increased to reduce variability of the test as indicated in the submitted protocol. Since the active clay content of green sand samples at the EJ foundry are generally lower than the other foundries in the study, the remaining dye left is higher after mixing, resulting in higher absorbance values in the test. As such, the sample size of green sand tested at the EJ foundry was increased from 0.5 g to $0.75\text{ g} \pm 0.1\text{ g}$ in the second round of testing to use more of the available dye and improve test accuracy. In a separate note, absorbance values below 0.12 are generally below the range for the most reliable test results and results below this range should be avoided by adjusting sand sample size.

SECOND ROUND OF TESTING IN FOUNDRIES

The further optimized procedure was disseminated to be used in all foundries, and a second round of testing was then conducted at each foundry. The results for the second round of foundry testing are shown in Table 4. The average SD value for each foundry were reported to be 0.21 (MTI), 0.12 (EJ) and 0.22 (JD).

Table 4: Second round testing of foundry green sand								
MTI			EJ			JD		
Sample ID	CEC (cmol/kg)	SD CEC (cmol/kg)	Sample ID	CEC (cmol/kg)	SD CEC (cmol/kg)	Sample ID	CEC (cmol/kg)	SD CEC (cmol/kg)
MTI-1	8.38	0.14	EJ-1	5.82	0.17	JD-1	9.17	0.33
MTI-2	8.01	0.35	EJ-2	5.60	0.38	JD-2	8.68	0.28
MTI-3	8.55	0.15	EJ-3	5.70	0.22	JD-3	6.63	0.29
MTI-4	8.53	0.18	EJ-4	5.90	0.07	JD-4	9.00	0.22
MTI-5	8.57	0.08	EJ-5	6.12	0.20	JD-5	9.45	0.69
MTI-6	7.95	0.24	EJ-6	5.92	0.11	JD-6	9.48	0.11
MTI-7	8.38	0.23	EJ-7	5.74	0.00	JD-7	9.26	0.16
MTI-8	7.76	0.62	EJ-8	5.69	0.15	JD-8	8.73*	0.72*
MTI-9	8.57	0.20	EJ-9	5.97	0.20	JD-9	8.75*	0.73*
MTI-10	8.58	0.11	EJ-10	6.08	0.15	JD-10	9.25	0.13
MTI-11	8.71	0.26	EJ-11	6.00	0.14	JD-11	8.69	0.10
MTI-12	8.46	0.35	EJ-12	5.85*	0.00*	JD-12	8.75	0.13
MTI-13	8.11	0.22	EJ-13	5.59	0.19	JD-13	8.51	0.09
MTI-14	8.41	0.13	EJ-14	5.66	0.07	JD-14	8.67	0.33
MTI-15	8.34	0.24	EJ-15	5.86	0.10	JD-15	8.69*	0.70*
MTI-16	7.78	0.06	EJ-16	5.84	0.27	JD-16	8.53	0.39
MTI-17	7.92	0.10	EJ-17	5.96	0.03	JD-17	8.88	0.34
MTI-18	8.51	0.15	EJ-18	5.79	0.13	JD-18	8.49	0.31
MTI-19	8.40	0.15	EJ-19	5.62	0.02	JD-19	8.67	0.36
MTI-20	8.69	0.26	EJ-20	5.78	0.19	JD-20	9.23	0.31
MTI-21	8.33	0.14	EJ-21	6.05	0.07	JD-21	8.30	0.19
MTI-22	8.79	0.23				JD-22	8.50	0.30
MTI-23	8.08	0.12				JD-23	8.99	0.22
MTI-24	8.29	0.17				JD-24	9.11	0.02
MTI-25	7.66	0.17						
Average		0.21	Average		0.12	Average		0.22

With the exception of the MTI results, the test variability was reduced during the second-round testing. At MTI there was a dedicated operator for the first round of trials, and a new operator needed to be trained in order to complete the second round of trials. This turnover in operators and less familiarity with the test procedure likely accounts with the slight increase in variability of the test in the second round of trials at MTI.

CONVERSION BETWEEN CATIONIC EXCHANGE CAPACITY (CEC) AND STANDARD METHYLENE BLUE (MB) ACTIVE CLAY MEASUREMENTS

Active clay has traditionally been measured as a percentage, with this percentage measured as compared to active bentonite. This bentonite is assumed as “100%” active.

However, this standard bentonite can vary in activity, dependent on the source of the standard, with most standard being 80-90% active. Studies have shown the samples are consistent based on type of bentonite (sodium or calcium).¹ The CEC measurement is a direct measure of cation exchange activity and allows for direct comparison between foundries regardless of clay blend used.

CEC can be converted over to active clay to compare the new spectrophotometric active clay test to the traditional methylene blue active clay measurement. The method to convert to a MB equivalent is similar to that used in the current standard MB tests. A known standard of clay at a known concentration is tested using the new test technique and an MB conversion factor is calculated and applied to the subsequent CEC results from each sand test.

The active clay measurements from the second round of testing conducted on daily foundry sand samples are shown in Figure 2; these measurements are converted to traditional active clay % (in orange/dashed lines) and compared to traditional MB test results (in gray/solid lines). As shown here, the measurements generally have good agreement for the JD and EJ foundries, while there is an offset between the measurements for the MTI foundry.

After some additional analysis, it was determined that this is likely due to a normalization issue with a change in active clay standard and should be able to be corrected with appropriate normalization to the standard bentonite clay. These types of issues can be avoided using the CEC measurement, which is a direct measurement of cationic activity of clay and not dependent on bentonite standards.

COMPARISON OF THE NEW DIGITAL ACTIVE CLAY MEASUREMENT IN GREEN SANDS WITH THE TRADITIONAL MB ACTIVE CLAY MEASUREMENT

As previously noted, Figure 2 shows a comparison from the results of the new method testing from second round testing and the traditional MB test for all three foundries, MTI, EJ, and JD all presented in percent active clay. The results for JD and EJ foundries have consistent active clay content using either test. MTI results show the noted discrepancy, but the overall data show a consistent trend in active clay.

A GR&R study was performed to determine if the optimized spectrophotometric test had similar or better variability when different operators performed the test as compared to variability of the methylene blue test. After the GR&R tests were performed, it was concluded that the new test had similar or better variability when compared to the traditional methylene blue historical study results conducted independently by three foundries. (Table 5).

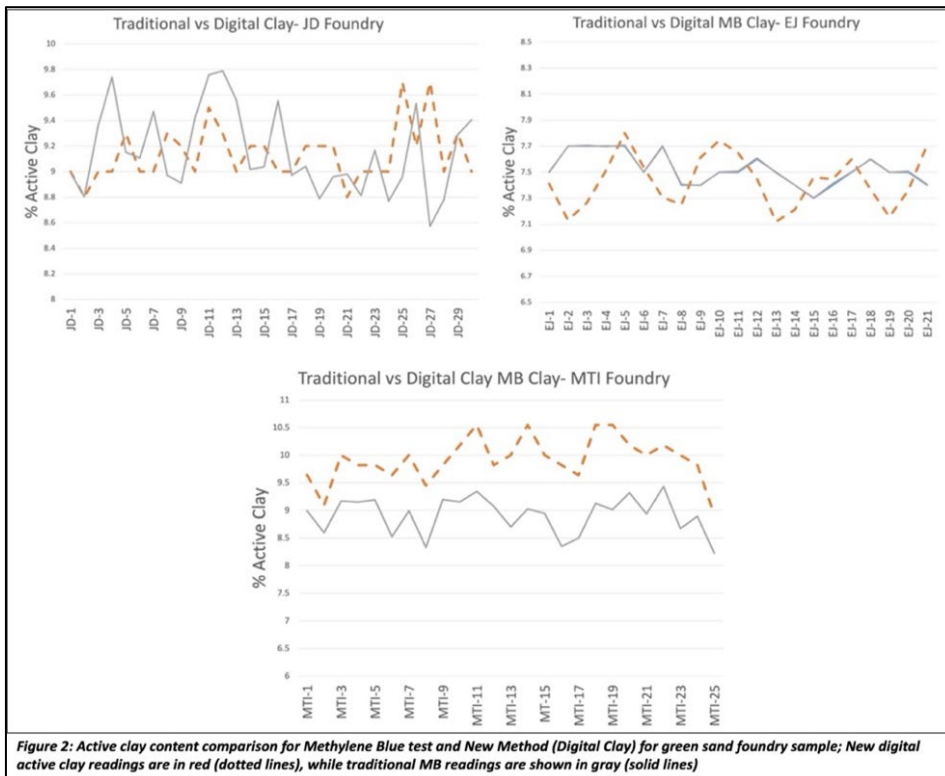
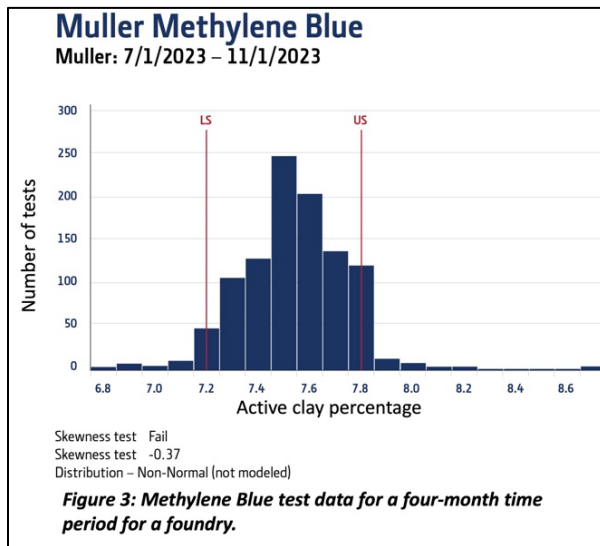


Table 5: Gage R&R results for MB and Digital Active Clay tests					
GR&R Comparison Equalized to Same Tolerance Range (1.2%) for All Tests - Xbar/Range Method					
MB Clay Test – Ultrasonic GR&R Results from Various Foundries					
Test By:	Repeatability (EV) % Of Tolerance	Reproducibility (AV) % Of Tolerance	Total R&R % of Tolerance	Standard Deviation	Method
Foundry 1	64%	0%	64%	0.127	10 Samples, 3 tests per sample, 3 operators.
Foundry 2	59%	24%	64%	0.128	10 Samples, 3 tests per sample, 2 operators.
Foundry 3	33%	33%	58%	0.116	2 Samples, 10 tests per sample, 2 operators.
Digital Active Clay Test					
Test By:	Repeatability (EV) % Of Tolerance	Reproducibility (AV) % Of Tolerance	Total R&R % of Tolerance	Standard Deviation	Method
WMU and EJ	64%	0%	64%	0.128	10 Samples, 3 tests per sample, 3 operators.

A concern with the traditional MB test is the influence that the operator can have biasing results to meet internal specifications. The qualitative aspect in calling the halo point allows wide latitude to the operator. Figure 3 shows the MB test data for a foundry during a four-month period. This foundry has an internal specification range with a lower limit of 7.2 and an upper limit of 7.8 percent active clay. As shown, the data is skewed to the upper specification limit, suggesting that the operators are biasing the results to meet the upper specification limits.



WASTE DISPOSAL CONSIDERATIONS AND COST OF STARTUP OF NEW TEST IN FOUNDRIES

It was also important to determine the safety and environmental characteristics of the waste components and solution. The dye and the spent dye from the new spectrophotometric test were analyzed using several different environmental tests that are typical in waste disposal in a foundry. The toxicity characteristic leaching procedure (TCLP) was performed to determine metal levels, organic levels (including volatile organics and semi-volatile organics), and pesticides to test for potential

environmental concerns. Additionally, the Safety Data Sheets (SDSs) of the components and concentrations were also analyzed by environmental personnel in addition to these test results. It was determined that the waste solution and waste consumables are generally nonhazardous and solution disposal would likely be similar to traditional methylene blue dye disposal, depending on local regulations.

The cost of the new optimized procedure was also analyzed. The equipment requirements for the new procedure for most foundries include a UV-VIS spectrophotometer (~\$1,500), a vortex mixer (~\$300-\$500), a glass funnel and scoop (~\$20) for a total equipment cost approximately of \$2,000. There may be an opportunity to reduce overall startup costs using a less expensive specialized spectrophotometer.

The consumable costs per the Digital Active Clay Test are shown in Table 6. These numbers are conservative and potentially the centrifuge tubes, the cuvettes, and the syringes may be able to be cleaned and reused multiple times. Additionally, less expensive tubes can be used, although initial tests indicate that screw cap centrifuge tubes prevent leakage of the samples. A comparison of the costs for the standard MB test is shown in the same table. Labor costs are not considered in this analysis, and it should be noted that the time to run the Digital Active Clay Test is less than the time to run the standard MB tests.

Table 6: Estimated cost comparison for MB and Digital Active Clay tests	
Cost Breakdowns	
Digital Clay Test	Cost Per Test
Cu(II) triethylenetetramine Dye	\$0.08
Centrifuge Tube	\$0.25
Syringe	\$0.12
Syringe Filter	\$0.20
Cuvette	\$0.25
Total Per Test	\$0.90
MB Clay Test	Cost Per Test
Sodium Pyrophosphate	\$0.15 - \$0.65
MB Solution	\$0.79 - \$0.84
Filter Paper	\$0.49 - \$1.18
Total Per Test	\$1.44 - \$2.66

CONCLUSIONS

In this study we have demonstrated that a new spectrophotometric method for measuring active clay in green sands works well with low variability over the entire range of clay levels used in most foundries. This method has been simplified by using filtration for separation of sand from the dye as opposed to centrifugation that was used in previous work. Not only does this simplify the process to work well in foundries and lower sample measurement time, but this also

eliminates the need to use a high-speed centrifuge, which is a costly piece of equipment with required periodic maintenance.

In the first round of trials, variability was relatively low, but variability was further reduced in all three foundries by optimizing the method further. In this optimized method, variability was further reduced by defining cuvettes that provide the least testing variation, as well as determining mixing times to lower variability. The PES syringe filters also lowered necessary pressure to use by the operator of the test, lowering the chance for error the test, damage to the filter, and injury from pressing the syringe.

Measurements from the new test are taken as a CEC measurement, which can be correlated to the standard MB test measurement for comparison. We recommend eventual conversion by foundries to the new CEC measurement instead of the standard MB measurement that is dependent on purchased bentonite standards that can vary by supplier. However, the new CEC measurements compared well with converted measurements to the standard MB test. We suggest that during the transition to the new spectrophotometric test, foundries take standard MB measurements and the new measurements side-by-side for comparison until they are comfortable with a full transition to the new test.

The standard MB test method is prone to subjectivity and takes a great deal of training and experience for success. Additionally, it was observed that several operators run the test, keeping a known target in mind, potentially biasing readings. We tested the alternative active clay test, comparing it with the standard MB test in a GR&R study. In this study we demonstrate that the alternative test has similar variance as the standard MB test when operators measured a series of random test samples without knowledge of the estimated active clay percentage going into the test (as in a GR&R study).

Overall, we demonstrate in this research study that the spectrophotometric measurement active clay test offers an enhanced alternative option to the standard MB test. This new test is relatively simple to perform, without extensive training or experience required, as is necessary for the standard MB test. The digital test also has low startup and operation costs, and the test can be conducted in 10 minutes or less time. This test is also conducive to automated operation, which may be explored in subsequent research studies.

ACKNOWLEDGMENTS AND INDUSTRY PARTNERS

- We are thankful for the generous support of AFS through contract 21-22#05.
- The primary WMU research team includes James Springstead, Sam Ramrattan, and Piao Jian Tan. Our research team greatly appreciates the important contributions of our steering committee and industry partners:
 - Brian Rachwitz, Quality and Technical Services Manager, EJ
 - Michelle Ring, Technical Director, Ductile Iron Society and Technical Manager, Norican Group
 - Steve Neltner, Technical Service Engineer, REFCOTEC, Inc.
 - Thomas Arenholz, Sr. Applications Engineer, Simpson
 - Scott Outman, Manager, Quality, Metal Technologies, Inc.
 - Jay Morrison, Carpenter Brothers, Inc.
 - Liam Miller, Mineral Technologies Inc.
- We are also thankful for the important direction of Andreas Decher of Andreas Decher Mineral Services in Wenden, Germany and for his early contributions in the development of this method

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