

# **An Investigation of the Methylene Blue Titration Method for Clay Activity of Oil Sands Samples**

R. Currie, S. Bansal, I. Khan and H. Mian

NAIT Applied Research Centre for Oil Sands Sustainability (NARCOSS)

December 2014



## Oil Sands Research and Information Network

The Oil Sands Research and Information Network (OSRIN) is a university-based, independent organization that compiles, interprets and analyses available knowledge about managing the environmental impacts to landscapes and water affected by oil sands mining and gets that knowledge into the hands of those who can use it to drive breakthrough improvements in regulations and practices. OSRIN is a project of the University of Alberta's School of Energy and the Environment (SEE). OSRIN was launched with a start-up grant of \$4.5 million from Alberta Environment and a \$250,000 grant from the Canada School of Energy and Environment Ltd.

OSRIN provides:

- **Governments** with the independent, objective, and credible information and analysis required to put appropriate regulatory and policy frameworks in place
- **Media, opinion leaders and the general public** with the facts about oil sands development, its environmental and social impacts, and landscape/water reclamation activities – so that public dialogue and policy is informed by solid evidence
- **Industry** with ready access to an integrated view of research that will help them make and execute environmental management plans – a view that crosses disciplines and organizational boundaries

OSRIN recognizes that much research has been done in these areas by a variety of players over 40 years of oil sands development. OSRIN synthesizes this collective knowledge and presents it in a form that allows others to use it to solve pressing problems.

### Citation

This report may be cited as:

Currie, R., S. Bansal, I. Khan and H. Mian, 2014. An Investigation of the Methylene Blue Titration Method for Clay Activity of Oil Sands Samples. Oil Sands Research and Information Network, University of Alberta, School of Energy and the Environment, Edmonton, Alberta. OSRIN Report No. TR-60. 50 pp.

Copies of this report may be obtained from OSRIN at [osrin@ualberta.ca](mailto:osrin@ualberta.ca) or through the OSRIN website at <http://www.osrin.ualberta.ca/en/OSRINPublications.aspx> or directly from the University of Alberta's Education & Research Archive at <http://hdl.handle.net/10402/era.17507>.

## Table of Contents

LIST OF TABLES .....	iv
LIST OF FIGURES .....	iv
REPORT SUMMARY .....	vi
ACKNOWLEDGEMENTS .....	viii
1 INTRODUCTION .....	1
1.1 Methylene Blue Index (MBI).....	2
1.2 Factors Affecting MBI Determinations .....	3
1.2.1 Dispersion.....	3
1.2.2 Endpoint Detection.....	4
1.2.3 Clay to Water Ratio.....	4
1.3 Design Of Experiment Investigation Of Main Factors .....	4
1.4 Objectives .....	5
2 TWELVE-FACTOR PLACKETT-BURMAN DESIGN OF EXPERIMENT.....	6
2.1 Preliminary Procedural Considerations .....	6
2.1.1 Source of MFT Samples.....	6
2.1.2 Titration Procedure Using the Halo for Endpoint Detection.....	6
2.1.3 A Non-visual more Objective Halo Detection Procedure.....	8
2.1.4 Spectrophotometric Endpoint Detection .....	9
2.1.5 DOE Experimental Procedure.....	13
2.2 Twelve-Factor DOE Results .....	14
3 SEVEN-FACTOR PLACKETT-BURMAN DOE.....	20
4 SEVEN-FACTOR FOLDED PLACKETT-BURMAN DOE .....	22
5 OVERVIEW OF PLACKETT-BURMAN DOE EXPERIMENTS .....	27
5.1 Basic pH.....	28
5.2 Sonication .....	28
5.3 Objective MBI Endpoint Detection .....	29
5.4 Peroxide .....	29
5.5 Stirring and Temperature .....	30
5.6 Bicarbonate .....	30

5.7	Sample Cleaning .....	30
5.8	Soaking .....	31
6	DISPERSION USING VARIATIONS AT HIGH PH .....	31
7	TITRATION USING FIBRE OPTICS AND VISIBLE SPECTROSCOPY .....	33
8	NUCLEAR MAGNETIC RESONANCE STUDIES ON METHYLENE BLUE .....	36
9	CONCLUSION AND FUTURE STUDIES .....	37
10	REFERENCES .....	39
11	GLOSSARY .....	41
11.1	Terms .....	41
11.2	Acronyms .....	43
11.3	Chemicals.....	44
	LIST OF OSRIN REPORTS .....	45

## LIST OF TABLES

Table 1.	Composition of MFT samples analyzed. ....	6
Table 2.	Slope values within the expected halo region during the titration. ....	9
Table 3.	Band position ( $\lambda$ ) and molar absorptivity ( $\epsilon$ ) of methylene blue. ....	10
Table 4.	Twelve-factor Plackett-Burman design of experiment. ....	15
Table 5.	Experimental results for 12-factor Plackett-Burman DOE. ....	16
Table 6.	Analysis of variance for 12-factor Plackett-Burman DOE. ....	16
Table 7.	Least Squares Means for 12-factor Plackett-Burman DOE. ....	18
Table 8.	Seven-factor Plackett-Burman DOE with experimental results. ....	21
Table 9.	Analysis of variance results for 7-factor Plackett-Burman DOE. ....	22
Table 10.	Least squares means for Plackett-Burman 7-factor DOE. ....	23
Table 11.	Seven-factor folded Plackett-Burman DOE. ....	24
Table 12.	Experimental results for seven-factor folded Plackett-Burman DOE. ....	25
Table 13.	Analysis of variance results for 7-factor “folded” Plackett-Burman DOE. ....	26
Table 14.	Least squares means for 7-factor folded Plackett-Burman DOE. ....	27

## LIST OF FIGURES

Figure 1.	Octahedral and tetrahedral isomorphic substitution sites (from Johnston 2011). ...	1
Figure 2.	Filter paper grid to organize the recording of titration data. ....	7
Figure 3.	Magnification (38 x) of methylene blue spot at different stages of titration. ....	7
Figure 4.	Intensity changes within halo region. ....	8
Figure 5.	Aqueous methylene blue absorbance spectra during the titration. ....	11
Figure 6.	Changes in the monomer to dimer absorbance ratio during the titration. ....	12
Figure 7.	Spectroscopic endpoint detection methods. ....	13
Figure 8.	Half normal plot for 12-factor Plackett-Burman DOE. ....	17
Figure 9.	Comparison of average differences in least squares means for DOE factors. ....	28
Figure 10.	Probe sonication times to disperse cleaned MFT. ....	32
Figure 11.	Effect of pH of dispersing solution on MBI values. ....	33
Figure 12.	Turbidity effects on absorbance with change in solid content. ....	34

Figure 13.	Spectral changes during a methylene blue titration. ....	35
Figure 14.	Stack plot of methylene blue $^1\text{H}$ NMR spectra at various concentrations. ....	36
Figure 15.	Methylene blue saturated montmorillonite. ....	38

## REPORT SUMMARY

The purpose of this report is to use a design of experiment (DOE) approach to examine the main factors affecting the determination of methylene blue index (MBI) values for oil sands samples. The methylene blue titration of clays has become a principle tool to assess extraction efficiency of oil sand ores and as a tool to assess the properties of the various tailings streams.

The report uses a Plackett-Burman (PB) DOE approach which is designed to screen a method for the principle factors affecting the test result. It does not reveal interaction between factors that could affect the significance of a main effect in the study. The purpose of the PB DOE screen is to help identify the main effects so that a more complete full factorial DOE can be implemented. A full factorial DOE allows more than two procedures/conditions or levels for each of the main effects identified by a screening DOE. This enables the conditions and procedures for specific factors in a test method to be adjusted simultaneously as other factors are varied. Thus interactions that could affect test results are accounted for which ensures that the final test method exhibits ruggedness and is capable of generating reliable data with good precision.

This report is the initial phase in the development of a rugged and robust method for methylene blue (MB) determinations. A principle requirement of the method is the dispersion of the clay samples to ensure methylene blue is capable of complete cation exchange with the clay. A 12-factor PB DOE investigated two mature fine tailings (MFT) samples for the effects of bicarbonate, basic pH adjustment, peroxide treatment, sonication, stirring, soaking, heating and Dean and Stark sample cleaning on dispersion procedures. If the number of procedures needed to disperse the clays can be minimized, without affecting the reliability of the MBI results, the method is easier to perform in a timely manner. Included in the 12-factor PB DOE was an assessment of the effects of acidic pH adjustment, preceding the titration, and variations in filter paper porosity and optional endpoint detection procedures during the titration.

A 7-factor PB DOE, using both normal and folded designs, was conducted to confirm features of the 12-factor PB DOE. The main effects studied were peroxide treatment, bicarbonate, basic pH adjustment, stirring at both room temperature and heating at 60°C, sonication and variation in endpoint detection procedures. The folded design was to help minimize the effects of confounding or aliasing of the data where main effects can be influenced by interactions between main effect components. When this occurs a main effect may be viewed as significant when in fact it is not.

The study emphasizes the importance of basic pH and sonication to enhance dispersion. Peroxide treatment was shown in the PB DOE to have beneficial effects when the sample is exposed to lower sonication energies, as in a bath sonicator. However, in a mini-study using a probe sonicator, where the energy generated is greater, peroxide was not found to be essential in aiding dispersion as evident by consistent MBI values even when peroxide was omitted. The importance of acidifying the dispersed sample before titration is also emphasized from the PB DOE studies.

The goal of this work is to ultimately develop an automated procedure for MBI determinations. A major challenge is to provide a more objective means of identifying the endpoint of the

MB titration. The report proposes a more objective non-visual endpoint based on the current halo procedure. To this end the effect of varying filter paper porosity as well as a comparison of subjective and objective endpoint detection procedures were included in the DOE. Alternative endpoint detection procedures focused on the use of spectroscopy. A spectroscopy procedure which measured changes in the aqueous forms of MB during the titration was included in the 12-factor PB DOE.

The report also discusses an innovative use of fibre optic visible spectroscopy to monitor the spectra of clay-MB interactions during the MB titration. The ability to assess whether the MB is interacting on the external or interlamellar surface of clays can enhance the information about the properties of clays in different sample types. This approach is very attractive since much more detail can be mined from the titration data than simply MBI values. This may dramatically improve the characterization of ores and tailings streams and improve process decisions regarding suitable ores for extraction and optional tailings treatments.

Finally an attempt to use NMR as a tool to monitor the titration and provide additional insight into the properties of the oil sands samples being titrated with MB is reported. Although NMR is capable of observing methylene blue in an aqueous media, and could be used similar to the spectroscopy method in the 12-factor PB DOE, it is incapable of detecting MB when the clays were also present.



## **ACKNOWLEDGEMENTS**

The Oil Sands Research and Information Network (OSRIN), School of Energy and the Environment (SEE), University of Alberta provided funding for this project.

The authors wish to thank Dr. Michael Slaney, instructor in the Chemical Technology program at NAIT, for conducting the NMR study on methylene blue.

We wish to also thank unnamed operators for providing MFT samples used in this study.

## **DISCLAIMER**

The mention of names of individual instruments and/or methodologies is not to be taken as an endorsement of the instrument or technology by OSRIN, the University of Alberta, the Northern Alberta Institute of Technology, or Alberta Environment and Sustainable Resource Development.

# 1 INTRODUCTION

Clays are classified by size (less than 2 micron), and structure. The clay minerals are phyllosilicates, meaning silicates with a planar structure, and are chemically hydrated aluminosilicates. The crystalline structure is based on the organization of the coordinated tetrahedrons (T) of silicon atoms with oxygen atoms at the four vertices of the tetrahedron and the coordinated octahedrons (O) of aluminum or magnesium atoms with oxygen atoms and OH groups at the six vertices of the octahedron. The organization of the T-O sheets is used to classify the different clay minerals. Isomorphous substitution shown in Figure 1, involves the substitution of  $\text{Si}^{4+}$  by  $\text{Al}^{3+}$  or  $\text{Fe}^{3+}$  for the T sites and substitution of  $\text{Al}^{3+}$  by  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  for O sites, can alter the electronic charges on the surface of the structural units. The electronic charge on the basal, or outer surface, is negative whereas the edges of the structural units are positive. Depending on the solution media, available external cations and anions exchange with these sites to compensate for the charges on the structural units of the clay (Chiappone et al. 2004).

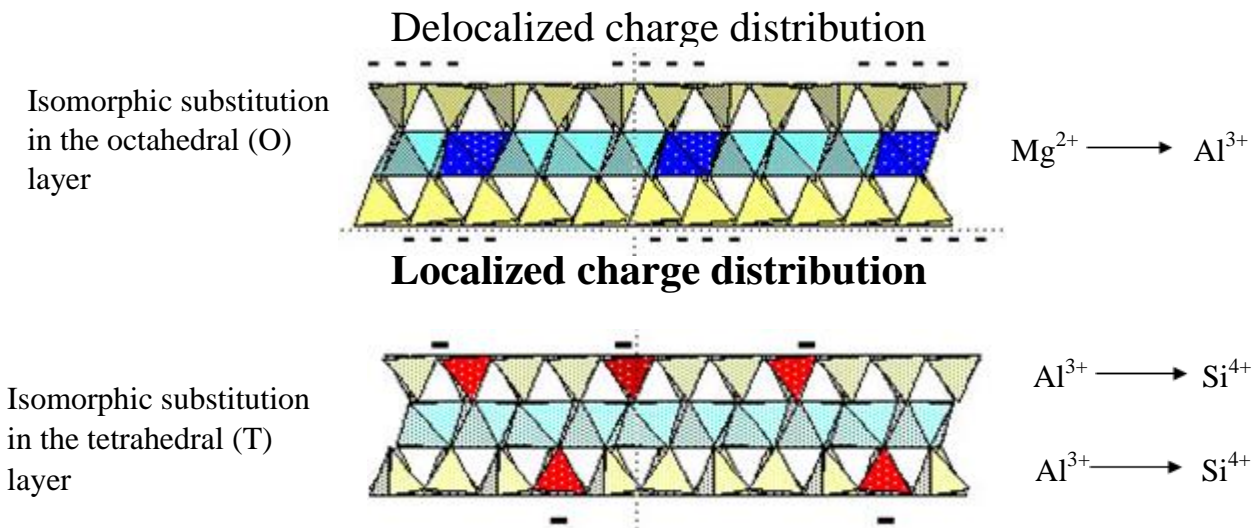


Figure 1. Octahedral and tetrahedral isomorphous substitution sites (from Johnston 2011).

Clays are very influential in virtually all aspects of oil sands operations. One of the factors related to clay content is bitumen extraction efficiency. Xu et al. (2013) showed how bitumen loss during extraction was less than 18% when the fines content was below 6 wt% but increased to over 60% when the fines content was greater than 18 wt%. A corresponding chart indicated that the dominant component of the fines were clays. This observation emphasizes the value of having a method which can assess clay content and thus enable the selection of good processing ores.

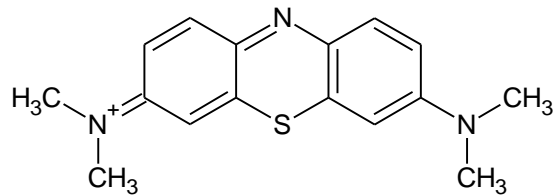
Boxill (2011) suggested that an alternative method to Atterberg limits for characterizing clay behaviour in geotechnical applications was needed for oil sands. Boxill emphasized the benefits

of assessing the cation exchange capacity of clays to predict the properties of various clay minerals in the management of tailings waste streams. Management of tailings ponds and their reclamation is a critical factor in expanding oil sand operations.

Efforts to meet Directive 074 (Energy Resources Conservation Board 2009) required by the Alberta Energy Regulator has meant that methods of reliably assessing clay content is needed for various consolidation strategies. For example, the clay water ratio is a major factor in determining polymer dosage levels and the clay content is measured using methylene blue titration data.

### 1.1 Methylene Blue Index (MBI)

Young and Sethi (1981) patented a procedure for measuring clay content by using methylene blue<sup>1</sup> to effect cation exchange with clays. Figure 1 shows the structure of methylene blue (MB) as indicated in the Cenens and Schoonheydt (1988) paper:



Following dispersion of the clays, the clay suspension is acidified to ensure that the amorphous form of  $Fe_2O_3$  is positively charged and not capable of adsorbing MB. This ensures that MB interacts with the clays on the basis of cation exchange and thus reflects the properties of the clays primarily on the basis of isomorphous substitution.

The current MB procedure proposed by the COSIA Clay Focus Group has identified the following equations to calculate various methods of assessing clay properties following the MB titration. The methylene blue index (MBI) calculates the milliequivalents of MB/100 g of solids titrated:

$$MBI \left( \frac{meq}{100g} \right) = \frac{mLs \text{ MB} \times Normality \text{ of MB}}{mass \text{ of dried sample (g)}} \times 100$$

Another calculation often requested by oil sands operators, but not treated as a direct output of the methylene blue test, is the calculation of weight percent clay using the empirical equation proposed by Yong and Sethi (1981):

$$Wt\% \text{ Clay} = \frac{mLs \text{ MB} \times 0.006 \text{ N} + 0.04}{14} \times 100$$

*It should be noted that the Wt% Clay calculated with this equation can be greater than 100% based on the properties of the clays and solids being titrated.*

---

<sup>1</sup> See [http://en.wikipedia.org/wiki/Methylene\\_blue](http://en.wikipedia.org/wiki/Methylene_blue)

Hang and Brindley (1970) proposed the following equation to calculate the active surface area of clays, is based on the dimensions of the MB molecule:

$$Surface\ Area\ \left(\frac{m^2}{g}\right) = MBI \times 130 \times 0.06022$$

The methylene blue number (MB#) reported by some operators and stated by the COSIA Clay Focus Group is:

$$MB\# \left(\frac{mLs\ 0.006\ N\ MB}{100\ g\ dried\ sample}\right) = \frac{mLs\ 0.006\ N\ MB}{mass\ of\ sample\ (g)} \times 100$$

The clay water ratio (CWR) is important in determining the effects of clays on many oil sands processes. It is calculated using the Wt% Clay equation described above and the water content from Dean and Stark analysis of oil sands sample or tailings. The CWR equation is:

$$CWR = \frac{Wt\% \text{ clay in sample}}{Wt\% \text{ water in sample}}$$

## 1.2 Factors Affecting MBI Determinations

Wallace (2011), when discussing the influence of clay and water chemistries on extraction performance, suggested that although MBI is the strongest single predictor of poor to average quality of oil sands, an improvement in the repeatability of the MBI measurement would improve predictions. The relative error in the measurement was reported to be 30% to 40%. Factors affecting determination of MBI are considered in the following section. Although sampling and subsampling errors usually dominate any analytical procedure this issue is not the major focus of this paper.

### 1.2.1 Dispersion

Dispersion of agglomerated clays is necessary to ensure MB can adsorb to the clays. Numerous methods are used to enhance dispersion of the clays, including: soaking, heating, stirring and sonication. One of the most important factors in promoting dispersion of the clays is pH. Vietti (2011), in discussing slurry colloidal mechanisms, showed that below pH 8, edge-face interactions cause clay particles to associate. However, in the range of pH 8 to 11 the negative charge on the clays is promoted causing particle repulsion and thus colloidal stability due to the dispersed state of the clay particles. However, at pH 11.5 and higher the basic pH no longer promoted dispersion and led to particle aggregation.

Vietti (2011) also showed that the exchangeable sodium ion improved dispersion compared to calcium showing that ionic composition is an important factor in effecting clay dispersion. However, even with hydrated sodium ions, when the ionic concentration becomes too high the attractive forces dominate hindering dispersion. This is believed to be due to the size of the

cation cloud about the clay particle being reduced allowing for clay interaction and thus minimizing dispersion.

Another factor that is considered to influence dispersion of clays is the presence of organic matter. Robertson et al. (1984) discussed how humic and fulvic acid components and polysaccharide gums can stabilize clay aggregates making dispersion difficult. In their study, successive additions of 10% hydrogen peroxide were found to effectively remove organics and promote dispersion. Di Stefano et al. (2010) also showed that treatment with hydrogen peroxide shifted the particle size distribution toward finer particles. This was considered to be due to the removal of organics reducing the aggregation of clay particles.

Studies on the MBI of clays that have been cleaned show that Dean and Stark (D&S) removal of bitumen, followed by drying the solids using heating, results in an extremely aggregated solid. A disaggregation step involving mortar and pestle or hammer mill is often required before dispersion is initiated. Omotoso (2011) showed that a prolonged dispersion time of at least 20 minutes using both stirring and sonication is required to disperse the clays when D&S extracted. A preference for conducting the MBI test using a slurry without cleaning was proposed. This suggests that although certain organics can affect MBI; bitumen does not seem to have the same adverse effects on MBI values.

### **1.2.2 Endpoint Detection**

The determination of MBI in the Yong and Sethi (1981) patent involved detection of the endpoint by the presence of a permanent halo of non-adsorbed MB diffusing from a central application spot on filter paper. This type of endpoint detection has proven to be very subjective and can contribute to variation in the endpoint volume for different operators. Ideally a more objective, unambiguous method of detecting the endpoint would be preferred.

### **1.2.3 Clay to Water Ratio**

Mikula (2011) emphasized the importance of clays in understanding oil sands operations at all stages. A particularly important factor was not the solids content but the clay to water ratio (CWR) within oil sands samples. Since this factor is so important to understanding the effect of clays on operations, it emphasizes the need to have a reliable test method for MB titrations.

## **1.3 Design Of Experiment Investigation Of Main Factors**

The Plackett-Burman (PB)<sup>2</sup> design of experiment (DOE) is an excellent approach to screen a method for the main factors affecting a test method result (ASTM 2014<sup>3</sup>). The advantage of this approach is that all factors are simultaneously varied between two levels/conditions/procedures and confirms whether these changes are affecting the test method result. The Plackett-Burman DOE has an advantage over a full factorial DOE in that the number of experiments needed to

---

<sup>2</sup> See [http://en.wikipedia.org/wiki/Plackett%E2%80%93Burman\\_design](http://en.wikipedia.org/wiki/Plackett%E2%80%93Burman_design)

<sup>3</sup> See <http://www.astm.org/Standards/E1169.htm>

screen the method is reduced. Unfortunately, it is incapable of assessing whether some of the significant main effects are due to interactions of other factors. Confounding or aliasing of main effect data occurs when interactions contribute to a main effect response; possibly making it significant when it is not. An option to minimize confounding or aliasing is to conduct a “foldover” design<sup>4</sup> where the experiments are repeated but with the two procedures for a given factor being reversed. Minitab allows individual or all factors to be assessed using the foldover design. In this study the 7-factor “folded” DOE was conducted using Minitab to generate a foldover for all factors.

Although the foldover approach is helpful, these DOE procedures should only be viewed as a screening tool to define the main effects. Once the main effects have been defined a full factorial DOE should be conducted. This allows for more than two procedures, conditions or levels for each of the main effects to be tested. This enables the conditions and procedures for specific factors in a test method to be adjusted simultaneously as other factors are varied. Thus interactions that could affect test results are accounted for and the method ensures that the final test method exhibits ruggedness and is capable of generating reliable data with good precision.

Least squares means values that are generated from the DOE analysis are helpful in comparing differences in the levels (procedures) for a main effect. It must be understood that the means are influenced by all other factors and cannot be viewed as an absolute MBI value for that factor alone. However, the orthogonal or balanced design of the DOE permits a comparison of the individual levels (procedures) being examined; each of the procedures are being affected in the same manner by other factors which allows the comparison to be made.

#### **1.4 Objectives**

The purpose of this report is to identify the main factors affecting the MBI determination using a DOE approach. Additionally, the need to automate MBI determinations requires the identification of the key features of the procedure that must be included and those that could be omitted. More steps in a procedure not only create further uncertainty but also lengthen the time needed to conduct the method and make online applications of methylene blue data less likely. Another requirement is to allow for a more objective endpoint detection procedure. Currently the endpoint determined by the appearance of a halo of methylene blue is very subjective. A more objective procedure will ultimately permit automation but should also improve the precision so essential to making meaningful decisions based on MBI values.

Since a full factorial DOE could not be conducted due to time limitations, this report can only be viewed as the initial phase of developing a rugged and robust method involving methylene blue titrations.

---

<sup>4</sup> See <http://support.minitab.com/en-us/minitab/17/topic-library/modeling-statistics/doe/basics/what-is-folding/>

## 2 TWELVE-FACTOR PLACKETT-BURMAN DESIGN OF EXPERIMENT

### 2.1 Preliminary Procedural Considerations

#### 2.1.1 Source of MFT Samples

MFT from the same tailings pond, but sampled at different sites, was the source of the two MFT samples studied. Table 2 indicates the features of the MFT samples used in this study. Although the CWR is different for the samples the major factor affecting the MBI value is reflected in the different mass of solids and particularly the clay to solids ratio (CSR). MFT-1 has a higher CSR which is based on the clay content determined using MB titration data. Inclusion of different MFT samples in the DOE provides a check that variation in the levels (procedures) for each of the main effects will still generate significant differences for MFT samples that differ in clay content. The data used to construct Table 1 were provided by a 3<sup>rd</sup> party lab based on their determination of MBI and D&S analysis of the MFT samples. The pH of MFT-1 and MFT-2 were 6.5 and 7.5, respectively. During the MBI determinations the bitumen would form a froth which was not removed during the titration.

Table 1. Composition of MFT samples analyzed.

<b>MFT reference</b>	<b>MFT-1</b>	<b>MFT-2</b>
Mass of MFT (g)	5.00	5.00
Mass of clay (g)	0.87	1.34
Mass of water (g)	3.99	2.88
Mass of solids (g)	0.98	2.06
Mass of bitumen (g)	0.03	0.07
Clay to water ratio	0.22	0.46
Clay to solids ratio	0.89	0.65

#### 2.1.2 Titration Procedure Using the Halo for Endpoint Detection

From previous applications of the MB titration at NARCOSS, it was found that delivery of 0.006 N MB with a micropipette was preferred to using a burette. The volumes of MB added could be added in a controlled and consistent manner which allowed precise timing when spotting the filter paper following MB addition. The volumes added were usually in 1 mL intervals until a halo was observed 20 s after spotting on the filter paper; but the halo would disappear when another sample was taken 40 s after the last MB addition. This indicated the endpoint was near, requiring the MB delivery to be reduced to 0.5 mL. Reducing the titration volume near the endpoint improves the precision of the endpoint recorded volume. The MB addition continued until a permanent halo was observed on the filter paper when spotting at 20, 40 and 60 s after the MB delivery. This was viewed as the endpoint of the titration. MB addition beyond the endpoint was continued to help confirm that the endpoint had been identified.

The mass of MFT chosen is such that at least a 10 mL volume of 0.006 N MB is required to reach the endpoint so as to minimize the titration error. A fifteen microlitre aliquot of the slurry being titrated was removed for spotting on the filter paper. This helped ensure a consistent spot

size for viewing. A grid pattern was generated within Excel and was used to print the grids on the filter paper to help ensure the volumes were properly recorded and that spotting of the filter was easy to assess (Figure 2). Figure 3 shows, in a magnification of the spot, that the endpoint was more easily viewed when the paper was wet than when dry.

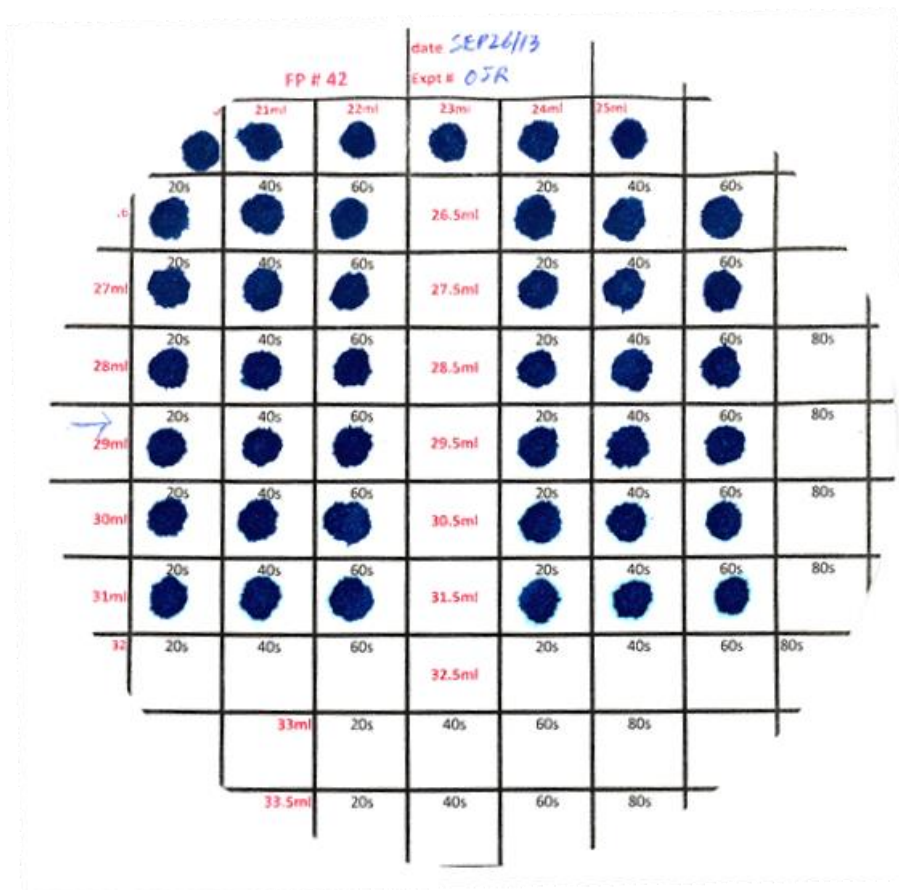


Figure 2. Filter paper grid to organize the recording of titration data.



A. Before endpoint (-1.5 mL)

B. At endpoint

C. After endpoint (+ 2 mL)

Figure 3. Magnification (38 x) of methylene blue spot at different stages of titration.



### 2.1.3 A Non-visual more Objective Halo Detection Procedure

In an effort to avoid the more subjective visual assessment of the endpoint, NARCOSS decided to investigate alternative approaches to determine the endpoint of the titration. Figure 2 shows a 38 x magnification of the methylene blue spot at various stages of the MB titration. A Dino-Lite AM413T digital microscope was used to capture the images of the slurry deposit during the titration. The appropriate image was then opened using National Instrument Vision Assist software to capture a digital density image of a line drawn horizontally through the centre of the spot, using the software.

Figure 4 reveals the intensity change for a selected pixel range that encompasses the dense central spot on the filter paper. The sharp changes in intensity at the boundaries of the spot are easily seen. Most importantly, the pixel intensity near these spot boundaries is found to change depending on the state of the titration. Before the endpoint, the transition between the boundary and the spot is reasonably sharp. However, at the endpoint the halo region is evident by a slope change near the boundary. After the endpoint, a very extensive pixel region of slope change is evident.

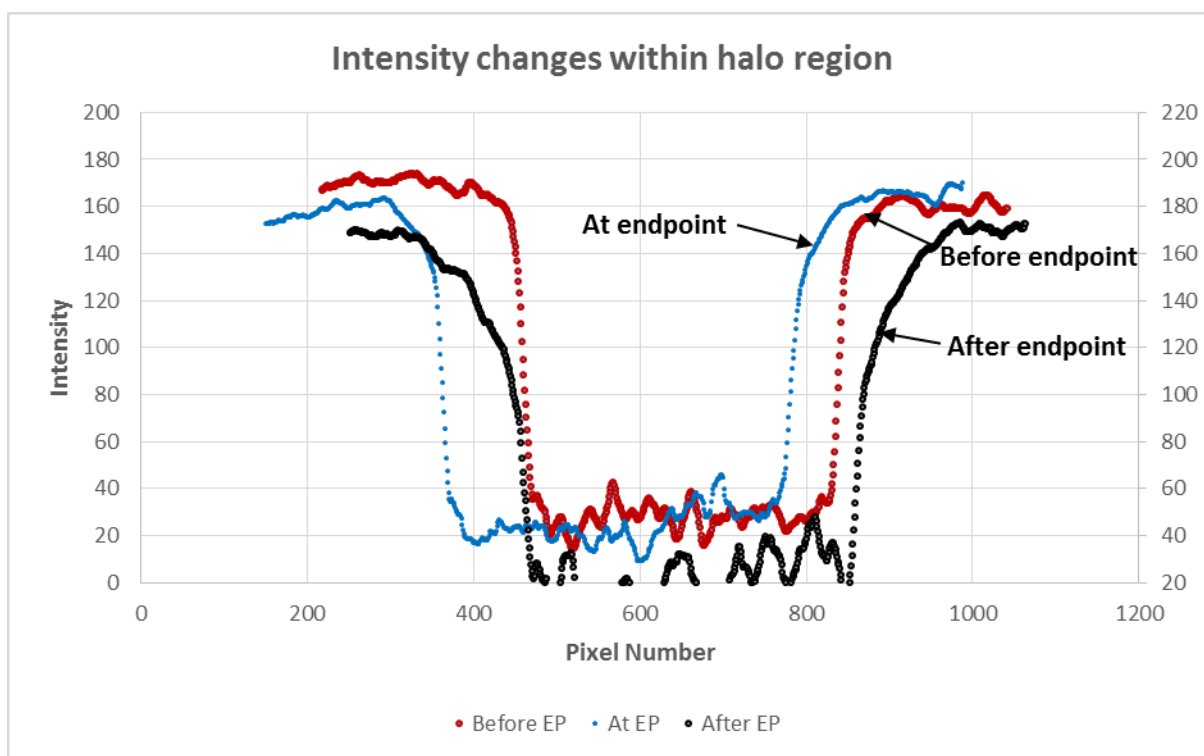


Figure 4. Intensity changes within halo region.

An Excel macro was developed by NARCOSS to calculate the 1st derivative identifying the pixel position of the boundary and based on this position an adjacent pixel range was used to calculate a slope value. When an appropriate slope change was first observed this was chosen as the endpoint of the titration. Table 2 shows the typical slope changes at various volumes before the visual halo endpoint was identified. A slope value greater than 0.45 intensity change/pixel

was found to be the most appropriate value to use in identifying the endpoint of the titration. These choices were based on the MB titration procedures discussed earlier and the captured images depicted in Figure 3. In this example, the endpoint would have been detected 0.5 mL before the conventional halo endpoint method. The coefficient of determination,  $R^2$ , from the regression analysis is a measure of how well the regression line represents the data. This value was found to be closer to 1 when the slope was determined near the endpoint of the titration.

Table 2. Slope values within the expected halo region during the titration.

Volume Before End Point (mL)	Slope (intensity/pixel)	$R^2$
5.0	-0.02	0.03
4.5	0.22	0.98
4.0	-0.18	0.68
3.5	0.01	0.00
3.0	-0.02	0.20
2.5	0.16	0.50
2.0	0.27	0.71
1.5	0.23	0.77
1.0	0.28	0.96
<b>0.5</b>	<b>0.51</b>	<b>0.92</b>
<b>0.0</b>	<b>0.47</b>	<b>0.97</b>

A lower slope value indicates a region where no halo exists; the plateau region for the “before the endpoint” plot in Figure 4. This simply reflects the intensity changes in the wet filter paper. Although at times the  $R^2$  may be relatively high showing good agreement in how the regression line represents the data, it is not the factor which is used to identify the presence of the MB halo.

The DOE experiments always included the visual halo endpoint detection procedure. However, the data in Table 2 suggests that using slope detection, as a more objective endpoint detection tool, a smaller MBI value than the conventional visual detection method would be expected.

A comparison of the visual and slope detection endpoint detection methods were included in both 7-factor PB DOE experiments.

#### 2.1.4 Spectrophotometric Endpoint Detection

Cenens and Schoonheydt (1988) used visible spectroscopy to study MB adsorption in both aqueous solution and when adsorbed to various surfaces of clays. Table 3 shows the species band position ( $\lambda$ , nm) and molar absorptivity ( $\epsilon$ , L/mol.cm) for different types of solution and clay interactions involving MB. The species in aqueous solution can be detected by differences in the lambda ( $\lambda$ ) maximum as shown in the shaded are of the table. The monomer,  $MB^{1+}$ , absorbs at 664 nm; the dimer,  $(MB^{1+})_2$ , absorbs at 605 nm; and the trimer,  $(MB^{1+})_3$ , absorbs at 580 nm. The acid form ( $MBH^{2+}$ ) which has a pKa of 0.5 would only exist under very acidic

conditions. Within the 12-factor DOE the presence of the aqueous monomer and dimer MB species were monitored throughout the titration when using a spectrophotometric MBI endpoint detection procedure.

Table 3. Band position ( $\lambda$ ) and molar absorptivity ( $\epsilon$ ) of methylene blue.

Species	In aqueous solution		Adsorbed on clays		Comments on adsorption
	$\lambda$ (nm)	$\epsilon$ (L/mol.cm)	$\lambda$ (nm)	$\epsilon$ (L/mol.cm)	
$\text{MB}^{1+}$	664	95,000	653	100,000	Blue shift, less aromatic, interlamellar surface
			673	116,000	Red shift, more aromatic, external surface
$\text{MBH}^{2+}$	741	76,000	763	86,000	Very acidic conditions, $\text{pK}_a = 0.5$
$(\text{MB}^{1+})_2$	605	132,000	596	80,000	Interlamellar surface, less aromatic
	697	22,000	718	30,000	External surface, more aromatic
$(\text{MB}^{1+})_3$	580	110,000	570	114,000	Only external surface

The spectrophotometric endpoint procedure used in this study involved taking 4 samples at 2 mL intervals before the endpoint and another 4 samples at 1 mL intervals after the endpoint. At the appropriate sampling interval a 150  $\mu\text{L}$  sample was diluted to 5 mL, centrifuged at 40,000 rpm for 10 minutes using a Beckman TL-100 ultracentrifuge, and the supernatant scanned between 400 and 800 nm with a Genesis 10UV spectrophotometer.

Figure 5 shows the spectral changes observed during the titration with sampling at the volumes stated in the legend. As indicated in the figure, 665 nm was used to represent the monomer,  $\text{MB}^{1+}$ , and the shoulder at 615 nm to represent mainly the dimer,  $(\text{MB}^{1+})_2$ .

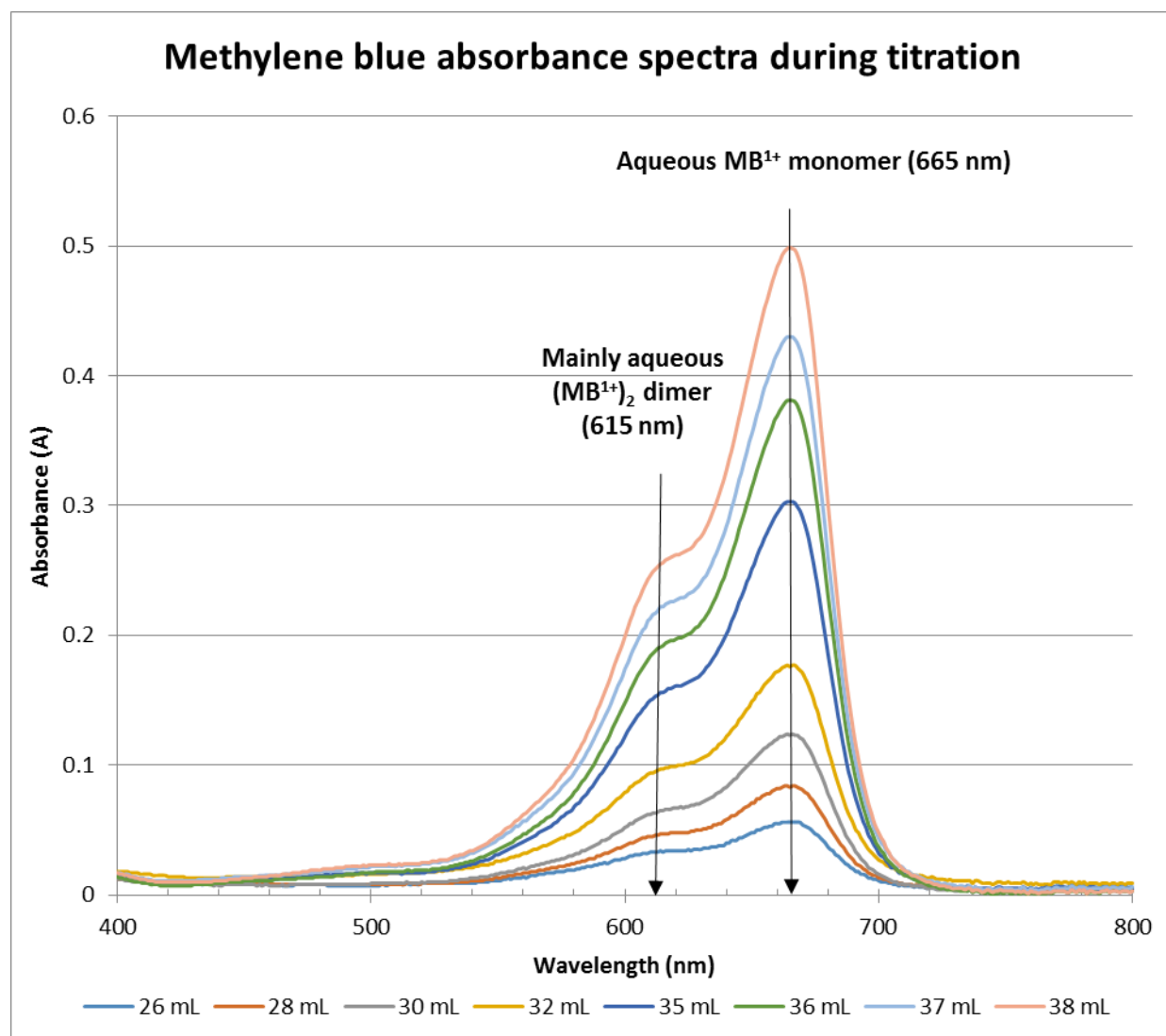


Figure 5. Aqueous methylene blue absorbance spectra during the titration.

During the titration an interesting finding was the change in the ratio of the monomer to dimer absorbance ratios ( $A_{665} / A_{615} \text{ nm}$ ) of the supernatant. Figure 6 shows that this ratio was smaller before the endpoint than the ratio following the titration. This implies that the dimer was preferentially adsorbing to the clays during the titration compared to the monomer.

Two methods of determining the endpoint by spectroscopy are revealed in Figure 7. We have observed that some authors have chosen the endpoint volume for the titration by extrapolating the absorbance values post-endpoint to report the intersect volume on the methylene blue axis. Although the volume discrepancy between extrapolation of the monomer and dimer absorbance values is negligible ( $\sim 30.2 \text{ mL}$ ) it has been found that this underestimates the true endpoint. The virtually identical values obtained by extrapolation are likely due to the consistency in the absorbance ratio post-endpoint (EP).

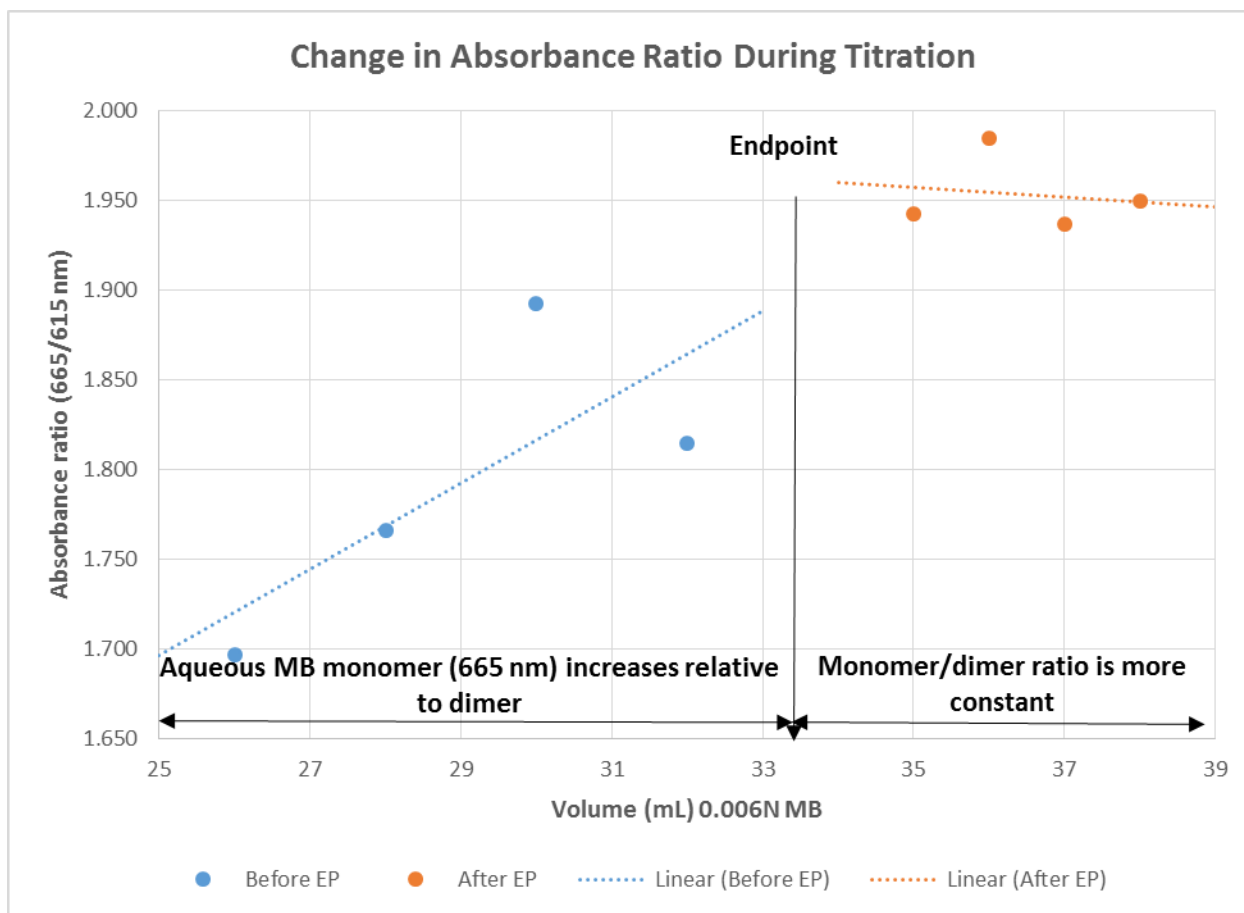


Figure 6. Changes in the monomer to dimer absorbance ratio during the titration.

The alternative spectrophotometric approach (Figure 6) generates endpoint volumes closer to the visual halo endpoint determination. The endpoint volume is calculated using the pre- and post-endpoint (EP) slope and intercept values following regression analysis. The equation used is:

$$\text{End point volume (mL)} = \frac{\text{Intercept (Post - EP)} - \text{Intercept (Pre - EP)}}{\text{Slope (Pre - EP)} - \text{Slope (Post - EP)}}$$

The volume differences, 33.2 and 33.5 mL although small, are likely due to the changes in the monomer and dimer ratios pre-endpoint observed in Figure 6. For the 12-factor PB DOE the monomer absorbance, 665 nm, was chosen for regression analysis and the endpoint calculation.

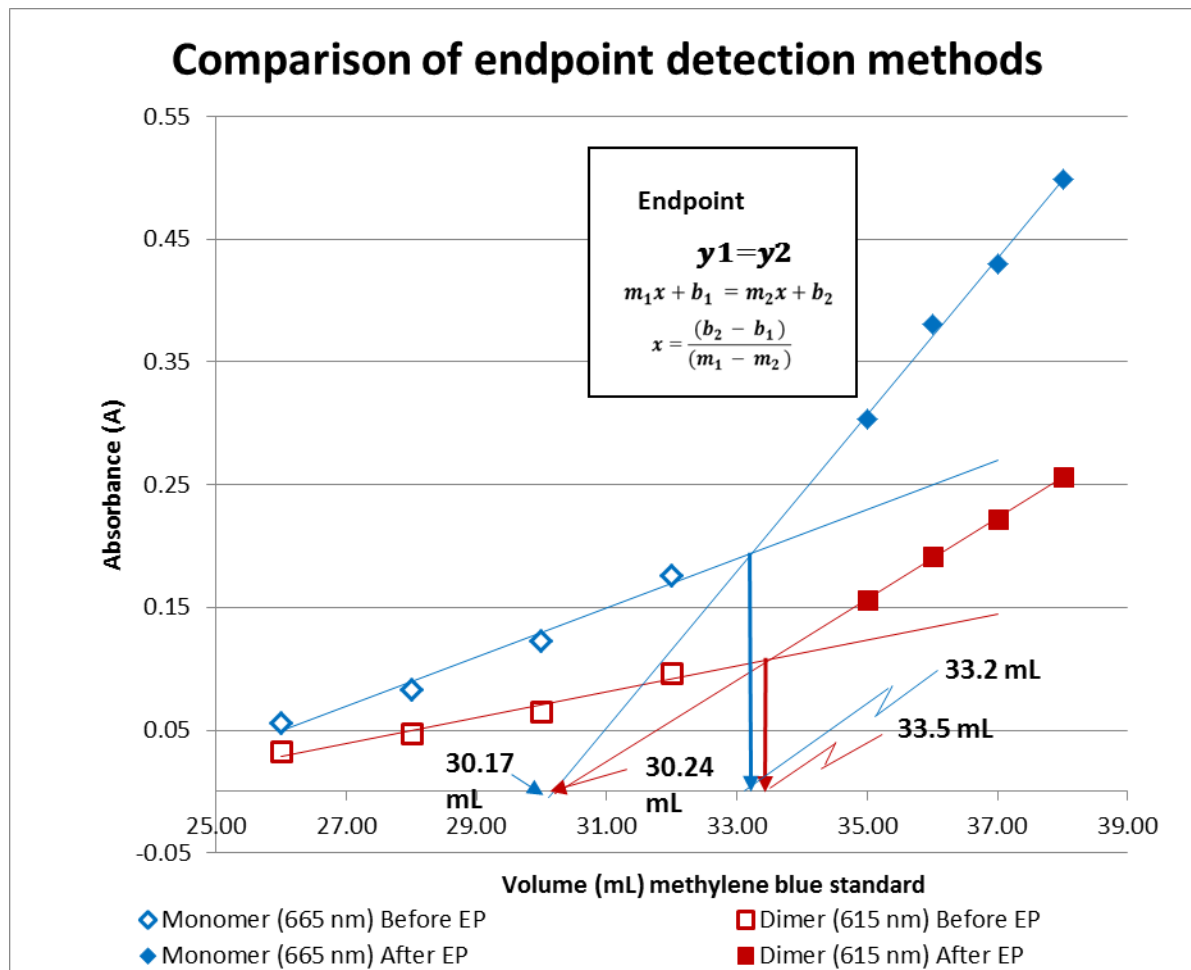


Figure 7. Spectroscopic endpoint detection methods.

### 2.1.5 DOE Experimental Procedure

A 1 L volume of the appropriate MFT type was mixed with a Gang mixer at 300 rpm for 5 minutes before slurry subsampling. Five grams of MFT was removed from the slurry and diluted with either 50 mL of deionized water or 5% hydrogen peroxide. The slurry was then mixed using a magnetic stirrer for 5 minutes at 500 rpm. Conditions specified in the DOE were achieved in the following manner:

- When  $\text{NaHCO}_3$  was specified in the DOE a 1 M  $\text{NaHCO}_3$  solution was added to the slurry to achieve a 0.015 M concentration and was stirred for 2 minutes at 500 rpm
- A basic pH adjustment was achieved by adding 10 wt% NaOH until the pH was in the range of 9.5 to 10.5 and was stirred during the pH adjustment
- Soaking involved leaving the slurry suspension in the appropriate dispersing media overnight for at least 18 h

- Stirring meant that the treated slurry was stirred at 250 rpm for 20 minutes either at room temperature or 60°C
- Sonication used a 130 watt bath sonicator for 20 minutes; the sample heated to about 70 °C without any external heat source thus increasing the heating time when sonication is specified in the DOE
- Acidic pH adjustment of the slurry was accomplished by adding 10 wt% sulphuric acid to obtain a pH between 2.5 and 3.8 with stirring during the pH adjustment.

The titration with MB and the determination of the endpoint was performed as discussed in the previous sections. Whatman #42 is a finer pore paper than is Whatman #41.

## 2.2 Twelve-Factor DOE Results

In this screening study the Plackett-Burman (PB) DOE used a “with” and “without” approach for the majority of the procedures studied. Table 4 shows the experimental design. The horizontal rows identify the conditions for each of the 20 experiments within 1 block. Replicates were performed thus 2 blocks or a total of 40 experiments were conducted under the prescribed conditions. The organization of the table was obtained using Minitab software following the input of the main factors and procedures.

The orthogonal design is evident – each factor has 10 experiments at one level and 10 using the other level or procedure within each block. As mentioned previously, this is important when comparing the least squares of the means.

Table 5 displays the average of the replicate data for each of the 20 experiments; showing how the combination of treatments affected the measured MBI values.

The MBI data for each experiment entered into Minitab were the average of the spectroscopy endpoint and the visible halo endpoint values. Table 6 shows the results of the ANOVA DOE analysis. The large P value (0.797) for blocks shows good agreement between the replicate data. The identical values for the sequential sum of squares (Seq SS) and the adjusted sum of squares (Adj SS) confirm the balanced design of the DOE.

All of the main effects showed significance, P values less than 0.05, with the exception of bicarbonate addition (P value = 0.487). This suggests that bicarbonate alone cannot elevate the pH sufficiently to effect dispersion; the pH with bicarbonate alone would be expected to be within 7 and 8. Although basic pH adjustment was sufficient to statistically effect dispersion (P value = 0.000), the presence of bicarbonate is desirable since it would generate a stable bicarbonate/carbonate buffer pair following the addition of sodium hydroxide; a desired feature for pH control.

Table 4. Twelve-factor Plackett-Burman design of experiment.

Exp.# and MFT type	Endpoint detection method	Filter paper #	Additional main factor treatments								
			5% Peroxide	Soaking (18 h)	Stirring (20 min)	Heating (60°C, 20 min)	Sonication (20 min)	Dean and Stark (D&S)	0.015 M NaHCO <sub>3</sub>	Basic pH (9.5 to 10.5) adjustment	Acidic pH (2.5 to 3.8) adjustment
Exp1 MFT-2	Visual halo	41	With	Without	Without	Without	Without	With	With	With	With
Exp2 MFT-2	Visual halo	42	With	Without	With	With	Without	Without	Without	Without	With
Exp3 MFT-1	Spectroscopy	42	Without	With	Without	With	Without	With	With	Without	Without
Exp4 MFT-1	Spectroscopy	42	Without	Without	With	Without	With	Without	With	With	Without
Exp5 MFT-2	Spectroscopy	41	With	Without	Without	With	With	Without	With	Without	Without
Exp6 MFT-2	Spectroscopy	42	Without	Without	Without	Without	With	Without	Without	With	With
Exp7 MFT-2	Visual halo	41	Without	With	With	Without	Without	Without	With	With	Without
Exp8 MFT-2	Spectroscopy	41	Without	Without	With	With	Without	With	Without	Without	Without
Exp9 MFT-1	Spectroscopy	41	With	With	With	With	Without	Without	With	With	With
Exp10 MFT-2	Visual halo	42	Without	With	With	With	With	Without	With	Without	With
Exp11 MFT-1	Spectroscopy	41	With	Without	With	Without	With	With	With	Without	With
Exp12 MFT-2	Spectroscopy	41	Without	With	Without	With	With	With	Without	With	With
Exp13 MFT-1	Visual halo	42	Without	Without	Without	With	Without	With	With	With	With
Exp14 MFT-2	Visual halo	42	With	With	Without	Without	With	With	With	Without	Without
Exp15 MFT-1	Visual halo	41	Without	With	With	Without	With	With	Without	Without	With
Exp16 MFT-1	Spectroscopy	42	With	With	Without	Without	Without	Without	Without	Without	With
Exp17 MFT-1	Visual halo	41	Without	Without	Without	Without	Without	Without	Without	Without	Without
Exp18 MFT-1	Visual halo	42	With	Without	With	With	With	With	Without	With	Without
Exp19 MFT-2	Spectroscopy	42	With	With	With	Without	Without	With	Without	With	Without
Exp20 MFT-1	Visual halo	41	With	With	Without	With	With	Without	Without	With	Without



Table 5. Experimental results for 12-factor Plackett-Burman DOE.

Exp #	Average MBI values between replicates	Exp #	Average MBI values between replicates	Exp #	Average MBI values between replicates	Exp#	Average MBI values between replicates
1	7.77	6	8.37	11	11.85	16	11.69
2	8.83	7	11.92	12	7.60	17	12.15
3	13.01	8	6.89	13	11.65	18	18.86
4	15.36	9	12.22	14	10.06	19	10.11
5	9.88	10	9.72	15	12.31	20	18.41

Table 6. Analysis of variance for 12-factor Plackett-Burman DOE.

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Blocks	1	0.044	0.044	0.044	0.07	0.797
Main Effects	12	383.181	383.181	31.932	49.31	0.000
MFT type	1	214.74	214.74	214.74	331.6	<b>0.000</b>
Peroxide	1	11.385	11.385	11.385	17.58	<b>0.000</b>
Soaking	1	2.948	2.948	2.948	4.55	<b>0.042</b>
Stirring	1	5.595	5.595	5.595	8.64	<b>0.007</b>
Heating	1	2.998	2.998	2.998	4.63	<b>0.041</b>
Sonication	1	26.115	26.115	26.115	40.33	<b>0.000</b>
Dean and Stark	1	7.106	7.106	7.106	10.97	<b>0.003</b>
Endpoint detection	1	21.565	21.565	21.565	33.3	<b>0.000</b>
Bicarbonate (NaHCO <sub>3</sub> )	1	0.322	0.322	0.322	0.5	0.487
Filter paper porosity	1	4.429	4.429	4.429	6.84	<b>0.015</b>
Basic pH adjustment	1	25.265	25.265	25.265	39.01	<b>0.000</b>
Acidic pH adjustment	1	60.713	60.713	60.713	93.75	<b>0.000</b>
Residual Error	26	16.837	16.837	0.648		
Total	39	400.062				

The actual P value is not recorded in Table 6 for the most significant main effects, P value = 0.000. However, the larger the F value the more significant the main factor. Thus, as expected, the F value for MFT type is very large (331.6).

The comparison of the effects is more easily seen in Figure 8 with the half normal plot and the least squares means found in Table 7. The further to the right a factor is in the half normal plot (Figure 8) the more significant is its effect on the MBI. Thus MFT type, as expected, is the

furthest to the right. The least squares means for MFT type (Table 7) show a considerable difference between MFT-1 and MFT-2, 13.75 and 9.12 respectively, confirming the sensitivity of MBI to the clay activity of different sample sources.

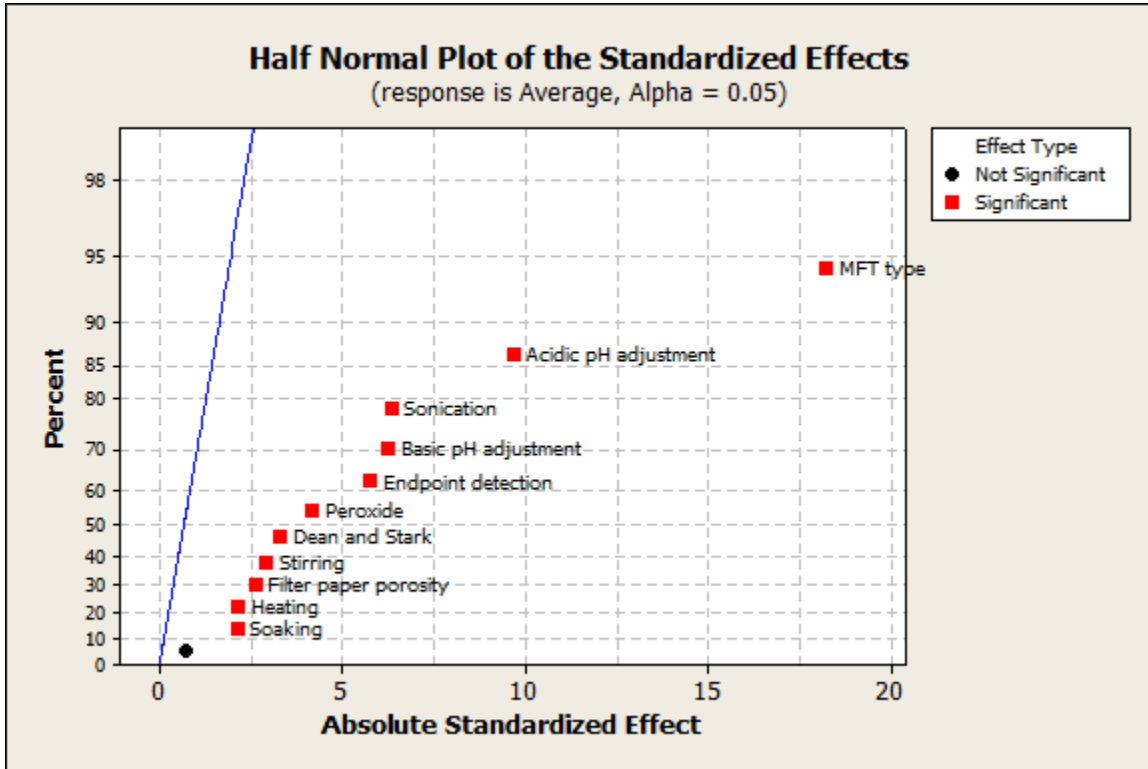


Figure 8. Half normal plot for 12-factor Plackett-Burman DOE.

Acidic pH is the second most significant factor affecting MBI. As expected the least squares means values are higher without acid adjustment, 12.7 compared to 10.2. The data suggest that to observe true clay activity, sites for cation exchange that are not due to isomorphous substitution must be minimized. The MB-clay interaction must relate to the type of clay and not due to components such as  $Fe_2O_3$  that may be present.

Sonication was found to be a very important procedure for the dispersion of the clays. The least squares means are 10.6 without sonication but increase to 12.2 with sonication. During the course of 20 minute bath sonication, heating to temperatures above 70 °C were common. Although heating as a factor was shown to be significant, the least squares means of 11.2 without and 11.7 with heating is not as effective as sonication in dispersing the clays.

Table 7. Least Squares Means for 12-factor Plackett-Burman DOE.

Main Effect	Mean	SE Mean	Main Effect	Mean	SE Mean
<b>MFT type</b>			<b>Dean and Stark</b>		
MFT-1	13.8	0.180	Without	11.8	0.180
MFT-2	9.1	0.180	With	11.0	0.180
<b>Peroxide</b>			<b>Endpoint detection</b>		
Without	10.9	0.180	Halo	12.2	0.180
With	12.0	0.180	Spectroscopy	10.7	0.180
<b>Soaking</b>			<b>Sodium bicarbonate (NaHCO<sub>3</sub>)</b>		
Without	11.2	0.180	Without	11.5	0.180
With	11.7	0.180	With	11.3	0.180
<b>Stirring</b>			<b>Filter paper porosity</b>		
Without	11.1	0.180	41	11.1	0.180
With	11.8	0.180	42	11.8	0.180
<b>Heating</b>			<b>Basic pH adjustment</b>		
Without	11.2	0.180	Without	10.6	0.180
With	11.7	0.180	With	12.2	0.180
<b>Sonication</b>			<b>Acidic pH adjustment</b>		
Without	10.6	0.180	Without	12.7	0.180
With	12.2	0.180	With	10.2	0.180

Basic pH adjustment is very important to the dispersion of the clays. The least squares means are 10.6 without and 12.2 with basic pH adjustment. The enhanced negative charge on the clays imparted by high pH improves dispersion of the clays and thus an increase in the measured MBI value. Since MFT type and acidic pH adjustment were expected to be major factors influencing MBI differences, the data suggest basic pH adjustment is the most critical factor in dispersing clays and ensuring reliable MBI values for clay activity.

The visual halo and spectroscopy methods for endpoints show significant differences. The least squares means of 12.2 with the visual halo compared to 10.7 for spectroscopy suggests that the more objective method of assessing the endpoint, spectroscopy, detects the presence of non-adsorbed MB earlier than the visual halo procedure and thus a smaller volume delivered at the endpoint. It is interesting that the more objective halo endpoint detection depicted in [Table 2](#), also showed that an earlier endpoint would be expected than with visual halo detection. This supports the suggestion that a more objective method of endpoint detection is more sensitive to

the detection of MB not being adsorbed to the clays. This should remove operator bias in making MBI measurements but may require the development of an empirical factor to enable a comparison of previous subjective MBI values with the more objective values. The advantage of having a more objective endpoint detection procedure should be an improvement in MBI precision; an important factor in decisions related to MBI data.

Peroxide addition was found to increase MBI values suggesting an improvement in dispersion even for the short treatment times and relatively low peroxide concentrations used in this study. As previously discussed, peroxide treatment is added to remove organics that have been found to interfere with clay dispersion. The relatively low concentrations and temperatures used in this study would mean that this treatment would not completely oxidize the organics to carbon dioxide and water but would degrade the structures sufficiently to reduce the tendencies of the clays to agglomerate. During sonication and heating a significant bubbling action was observed due to the decomposition of hydrogen peroxide and it is not known if this too helped improve dispersion.

When hydrogen peroxide was added to the dispersing solution it was found that considerably more NaOH was needed to accomplish the basic pH adjustment. The pKa of hydrogen peroxide is 11.6 and so behaves as a very weak acid. Calculations would suggest that only an additional 0.65 mL of 10 wt% NaOH would be needed to adjust the pH to 10 to account for the presence of peroxide. However, considerably more base than this was added and could be explained by the variety of buffering mechanisms present in the slurry. However, it would be interesting to speculate and eventually investigate whether some of the additional base needed is to neutralize organic acids being released from the clays by peroxide treatment.

D&S-cleaned MFT solids were found in the DOE to be statistically different from the slurry MFT. The slurry MFT generated higher least squares means values, 11.8 compared to 11.0 for D&S-cleaned solids. The issue may have been related to the sonication times in the bath sonicator. The energy imparted to the sample with a bath sonicator is less than that achieved with a probe sonicator. [Figure 10](#), from the mini-study on the effects of pH on dispersion, reveals that even with the higher energy probe sonicator, about 45 minutes is needed to achieve consistent MBI values for a D&S cleaned MFT sample. The bath sonicator may have to be run for even longer periods of time to effectively disperse the samples and provide equivalent data for D&S treated compared to slurry MFT samples.

Although stirring, filter paper porosity, heating and soaking factors were shown to be statistically different, the least squares means for these parameters are likely not practically different. It should be noted that stirring, heating and soaking all showed increases in MBI values but with the exception of soaking and filter porosity these steps would be a component of any analytical procedure where the most practical dispersion techniques would be used.

Whatman #42 filter paper, with finer pores than Whatman #41, showed an increase in the least squares means MBI value. This is likely due to a reduced diffusion of MB away from the central spot making the intensity of the halo easier to observe.

In summary, the 12-factor DOE has emphasized the importance of basic pH, sonication and peroxide treatment as the most critical factors affecting dispersion of the clays. Additionally, the method of endpoint detection can significantly affect the MBI value. It is considered beneficial to use a more objective method of endpoint detection since this will be expected to improve the precision of the MBI determination. Two endpoint detection procedures were tested during this study. The first uses the conventional halo on filter paper where the fine pore filter paper, Whatman #42, was preferred since the halo region was tighter and less diffuse. The second was the more objective spectroscopy procedure using the calculated MB titration volume based on before and after endpoint absorbance data for the aqueous monomer form of MB. However, details regarding the nature of the clay-MB interaction are lacking when simply using spectroscopy to measure the aqueous supernatant during the titration; it is simply an alternative endpoint detection option.

### **3 SEVEN-FACTOR PLACKETT-BURMAN DOE**

A 7-factor PB DOE was used to focus on an assessment of the three key factors found in the 12-factor DOE: basic pH adjustment, peroxide treatment and sonication. Bicarbonate, stirring at both room temperature and heating (60°C) were included to assess once again their contribution to the dispersion of clays. The 7-factor PB DOE design and the response for each experiment is indicated in Table 8.

In an effort to automate MBI determinations it is beneficial to have fewer procedures since it would reduce the complexity of the system design and thus make it easier to implement. For example, minimal heating requirements would reduce delays in initiating the titration and also reduce the power requirements. Fewer reagents would also simplify the operation.

Automation of MBI determinations would also require an objective, non-operator endpoint detection system. Thus the effect of the more subjective visual halo detection compared to the more objective slope detection procedure discussed in section 2.1.3 was included in the design. The filter paper chosen was Whatman #42 since the tighter porosity of this paper had been found in the 12-factor PB DOE study to improve the visual endpoint detection. Whatman #42 was also found during the development of the objective slope halo detection procedure to generate a more reproducible slope response.

Only one MFT type was studied and since acidifying the slurry before titration was proven to be essential these aspects were not reassessed. Replicates were not performed in this study.

Table 8. Seven-factor Plackett-Burman DOE with experimental results.

Exp #	Endpoint Detection	Additional main factor treatments						MBI value
		5% peroxide	0.015 M NaHCO <sub>3</sub>	Basic pH (9.5 - 10.5) adjustment	Stirring @ RT (20 min)	Stirring @ 60°C (20 min)	Sonication (20 min)	
1	Slope	Without	Without	Without	Without	With	Without	8.35
2	Slope	With	With	With	Without	Without	With	8.70
3	Visual	Without	With	With	Without	With	With	8.83
4	Visual	With	With	Without	Without	With	With	8.34
5	Slope	Without	Without	With	Without	With	Without	8.25
6	Visual	Without	Without	Without	With	Without	With	8.35
7	Slope	With	Without	With	Without	With	With	9.14
8	Slope	With	With	Without	Without	Without	Without	8.26
9	Slope	With	Without	Without	With	With	Without	8.16
10	Slope	Without	Without	With	With	Without	With	8.78
11	Slope	Without	With	Without	With	With	With	8.56
12	Visual	Without	Without	Without	Without	Without	Without	8.47
13	Slope	With	With	With	With	Without	Without	8.69
14	Visual	With	Without	With	With	With	With	8.86
15	Visual	With	With	Without	With	With	Without	8.53
16	Slope	Without	With	Without	With	Without	With	8.52
17	Visual	Without	With	With	With	With	Without	8.55
18	Visual	With	Without	Without	Without	Without	With	8.54
19	Visual	Without	With	With	Without	Without	Without	8.75
20	Visual	With	Without	With	With	Without	Without	8.52

Table 9 contains the ANOVA results for the DOE. The most significant factors affecting the results were basic pH adjustment (P value = 0.004) and sonication (P value = 0.029).

Table 9. Analysis of variance results for 7-factor Plackett-Burman DOE.

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	7	0.6886	0.688602	0.098372	2.7	0.063
Peroxide	1	0.00465	0.004651	0.004651	0.13	0.727
Bicarbonate	1	0.00471	0.004712	0.004712	0.13	0.725
Basic pH adjustment	1	0.4503	0.4503	0.4503	12.36	<b>0.004</b>
Room Temperature	1	0.00066	0.000661	0.000661	0.02	0.895
Heating (60°C)	1	0	0	0	0	0.999
Sonication (20 min)	1	0.22239	0.222394	0.222394	6.1	<b>0.029</b>
Endpoint Detection	1	0.00588	0.005882	0.005882	0.16	0.695
Residual Error	12	0.43721	0.437215	0.036435		
Total	19	1.12582				

Although it was expected that differences in the visual and slope halo detection procedures may exist, based on [Table 2](#) data, this was not observed in this short study. Stirring at either room temperature or at 60°C did not have significant effects on the MBI values reported. A major discrepancy with the 12-factor DOE results is the lack of significant peroxide effects.

Although the ANOVA data did not show significant differences between some of these factors it is interesting to observe the trends in the least squares means for each of the main effects as shown in Table 10. Although not significantly different, peroxide treatment still elevated the mean from 8.54 to 8.57. Also the visual halo detection procedure did provide a larger MBI value than the more objective slope detection procedure which may be expected from the [Table 2](#) observation. In attempt to clarify the data a 7-factor “folded” PB DOE was conducted.

#### 4 SEVEN-FACTOR FOLDED PLACKETT-BURMAN DOE

Unfortunately, when using the Plackett-Burman DOE, interactions between factors which can ultimately affect the statistic for the main factors, cannot be determined. ASTM E1169-07 (ASTM 2014), in discussing standard practice for conducting ruggedness tests, suggests “foldover” to reduce this problem. The design of the 7 factor “folded” DOE is shown in Table 11. To illustrate the “foldover” it can be seen that Experiment #1 has factor treatments that are opposite those in Experiment #21. The purpose of this design is to separate main effects from factor interactions that can alias or make a main effect statistically unreliable.

Table 10. Least squares means for Plackett-Burman 7-factor DOE.

<b>Treatment</b>	<b>Mean</b>	<b>SE Mean</b>
<b>Peroxide</b>		
Without	8.54	0.0604
With	8.57	0.0604
<b>Bicarbonate</b>		
Without	8.54	0.0604
With	8.57	0.0604
<b>Basic pH adjustment</b>		
Without	8.41	0.0604
With	8.71	0.0604
<b>Room Temperature</b>		
Without	8.56	0.0604
With	8.55	0.0604
<b>Heating (60C)</b>		
Without	8.56	0.0604
With	8.56	0.0604
<b>Sonication (20 min)</b>		
Without	8.45	0.0604
With	8.66	0.0604
<b>Endpoint Detection</b>		
Visual	8.57	0.0604
Slope	8.54	0.0604



Table 11. Seven-factor folded Plackett-Burman DOE.

Exp #	Endpoint Detection	Additional main factor treatments					
		5% peroxide	0.015 M NaHCO <sub>3</sub>	Basic pH (9.5 - 10.5) adjustment	Stirring @ RT @ RT (20 min)	Stirring @ 60°C (20 min)	Sonication (20 min)
1	Visual	With	Without	With	With	Without	Without
2	Visual	With	With	Without	With	With	Without
3	Visual	Without	With	With	Without	With	With
4	Slope	Without	Without	With	With	Without	With
5	Slope	With	Without	Without	With	With	Without
6	Visual	With	With	Without	Without	With	With
7	Slope	With	With	With	Without	Without	With
8	Slope	With	With	With	With	Without	Without
9	Visual	Without	With	With	With	With	Without
10	Visual	With	Without	With	With	With	With
11	Slope	Without	With	Without	With	With	With
12	Slope	With	Without	With	Without	With	With
13	Slope	Without	With	Without	With	Without	With
14	Slope	Without	Without	With	Without	With	Without
15	Visual	Without	Without	Without	With	Without	With
16	Slope	Without	Without	Without	Without	With	Without
17	Visual	With	Without	Without	Without	Without	With
18	Slope	With	With	Without	Without	Without	Without
19	Visual	Without	With	With	Without	Without	Without
20	Visual	Without	Without	Without	Without	Without	Without
21	Slope	Without	With	Without	Without	With	With
22	Slope	Without	Without	With	Without	Without	With
23	Slope	With	Without	Without	With	Without	Without
24	Visual	With	With	Without	Without	With	Without
25	Visual	Without	With	With	Without	Without	With
26	Slope	Without	Without	With	With	Without	Without
27	Visual	Without	Without	Without	With	With	Without
28	Visual	Without	Without	Without	Without	With	With
29	Slope	With	Without	Without	Without	Without	With
30	Slope	Without	With	Without	Without	Without	Without
31	Visual	With	Without	With	Without	Without	Without
32	Visual	Without	With	Without	With	Without	Without
33	Visual	With	Without	With	Without	With	Without
34	Visual	With	With	Without	With	Without	With
35	Slope	With	With	With	Without	With	Without
36	Visual	With	With	With	With	Without	With
37	Slope	Without	With	With	With	With	Without
38	Visual	Without	Without	With	With	With	With
39	Slope	With	Without	Without	With	With	With
40	Slope	With	With	With	With	With	With

Although 12 experiments would have been adequate to meet the Plackett-Burman design, the decision to conduct 20 experiments for each block was because Minitab allowed a greater number of experiments to ensure a more reliable standard error determination.

The main factors chosen were a repetition of the key factors found in the both the 12- and 7-factor DOE: basic pH adjustment, peroxide treatment and sonication. Bicarbonate, stirring at room temperature and at 60°C were included to assess once again their contribution to the dispersion of clays. The subjective and objective methods of visual and slope halo detection procedures, respectively, were also included in the design of experiment.

Table 12 contains the experimental results for each of the 40 experiments which were entered into Minitab to generate the statistical data.

Table 12. Experimental results for seven-factor folded Plackett-Burman DOE.

<b>Exp #</b>	<b>MBI value</b>	<b>Exp #</b>	<b>MBI value</b>	<b>Exp#</b>	<b>MBI value</b>	<b>Exp #</b>	<b>MBI value</b>	<b>Exp#</b>	<b>MBI value</b>
1	8.62	9	8.72	17	8.42	25	9.11	33	8.74
2	8.82	10	9.12	18	8.91	26	8.45	34	8.93
3	8.75	11	8.52	19	8.71	27	8.53	35	8.62
4	8.39	12	9.12	20	8.46	28	8.48	36	8.58
5	8.43	13	8.55	21	8.62	29	8.56	37	8.76
6	9.05	14	8.29	22	8.91	30	7.41	38	8.85
7	9.00	15	8.57	23	8.43	31	8.67	39	8.27
8	9.18	16	8.01	24	8.84	32	8.76	40	8.33

Table 13 provides the ANOVA results for this DOE. The blocks (P value = 0.328) are non-significant showing good agreement between replicates. Basic pH adjustment (P value = 0.023), endpoint detection (P value = 0.039) and peroxide addition (P value = 0.045) showed significant effects on the MBI. It was surprising that sonication was not found to have a significant effect on dispersion even at  $\alpha = 0.10$ .

Table 13. Analysis of variance results for 7-factor “folded” Plackett-Burman DOE.

Source	DF	Seq SS	Adj SS	Adj MS	F	P
<b>Blocks</b>	1	0.08245	0.08245	0.082446	0.99	0.328
<b>Main Effects</b>	7	1.61847	1.61847	0.23121	2.77	0.023
<b>Peroxide</b>	1	0.36443	0.36443	0.364428	4.37	<b>0.045</b>
<b>Bicarbonate (NaHCO<sub>3</sub>)</b>	1	0.19768	0.19768	0.197684	2.37	0.134
<b>Basic pH</b>	1	0.4783	0.4783	0.478297	5.74	<b>0.023</b>
<b>Room temperature (20 min)</b>	1	0.00048	0.00048	0.000476	0.01	0.940
<b>Heating (60°C, 20 min)</b>	1	0.00125	0.00125	0.001254	0.02	0.903
<b>Sonication (20 min)</b>	1	0.18824	0.18824	0.188238	2.26	0.143
<b>Endpoint Detection</b>	1	0.38809	0.38809	0.38809	4.65	<b>0.039</b>
<b>Residual Error</b>	31	2.58487	2.58487	0.083383		
<b>Total</b>	39	4.28579				

However, Table 14 does show that the least squares means with sonication (8.71) is greater than without sonication (8.57). It is not believed that the significant effects of sonication in the previous DOE studies was simply due to interaction effects which is expected to be reduced in the “foldover” design.

A possible explanation for the variation in the statistics between the different PB DOE studies in this report is differences in the Block P values. The 12-factor DOE and the 7-factor folded DOE Block P values are 0.797 and 0.328, respectively. In the 12-factor DOE significant differences between main effects were observed when it was thought unlikely. In contrast, the 7-factor folded DOE did not show significant differences where expected. For example, sonication did not reveal significant differences using ANOVA whereas the least squares means were very different for the “with” and “without” sonication options. The data suggest that the greater the precision in the experimental values the more likely significant differences will be observed. However, what may be statistically significant may not be practically significant.

Table 14 Least squares means for 7-factor folded Plackett-Burman DOE.

	Mean	SE Mean
<b>Peroxide</b>		
Without	8.54	0.0646
With	8.73	0.0646
<b>Bicarbonate (NaHCO<sub>3</sub>)</b>		
Without	8.57	0.0646
With	8.71	0.0646
<b>Basic pH adjustment</b>		
Without	8.53	0.0646
With	8.75	0.0646
<b>Stirring @ room</b>		
Without	8.63	0.0646
With	8.64	0.0646
<b>Stirring @ 60°C</b>		
Without	8.63	0.0646
With	8.64	0.0646
<b>Sonication (20 min)</b>		
Without	8.57	0.0646
With	8.71	0.0646
<b>Endpoint Detection</b>		
Visual	8.74	0.0646
Slope	8.54	0.0646

## 5 OVERVIEW OF PLACKETT-BURMAN DOE EXPERIMENTS

Figure 9 summarizes the average differences in the least squares means for the procedures associated with each of the main factors that were common to all three DOE studies conducted. It must be emphasized this does not reflect the true differences in MBI values that would be expected because the least squares means are influenced by all other factors in the experiment and so cannot be viewed as an absolute MBI value for that factor alone. However, the orthogonal or balanced design of the DOE permits a comparison of the effects of different procedures for a given factor. Thus the “with” factor, perhaps basic pH adjustment, is measured under the same combination of procedures as the “without” factor, i.e., without basic pH adjustment in this example. The values charted in Figure 8 are least squares means of the “with” procedure subtracted from the least squares means of the “without” procedure.

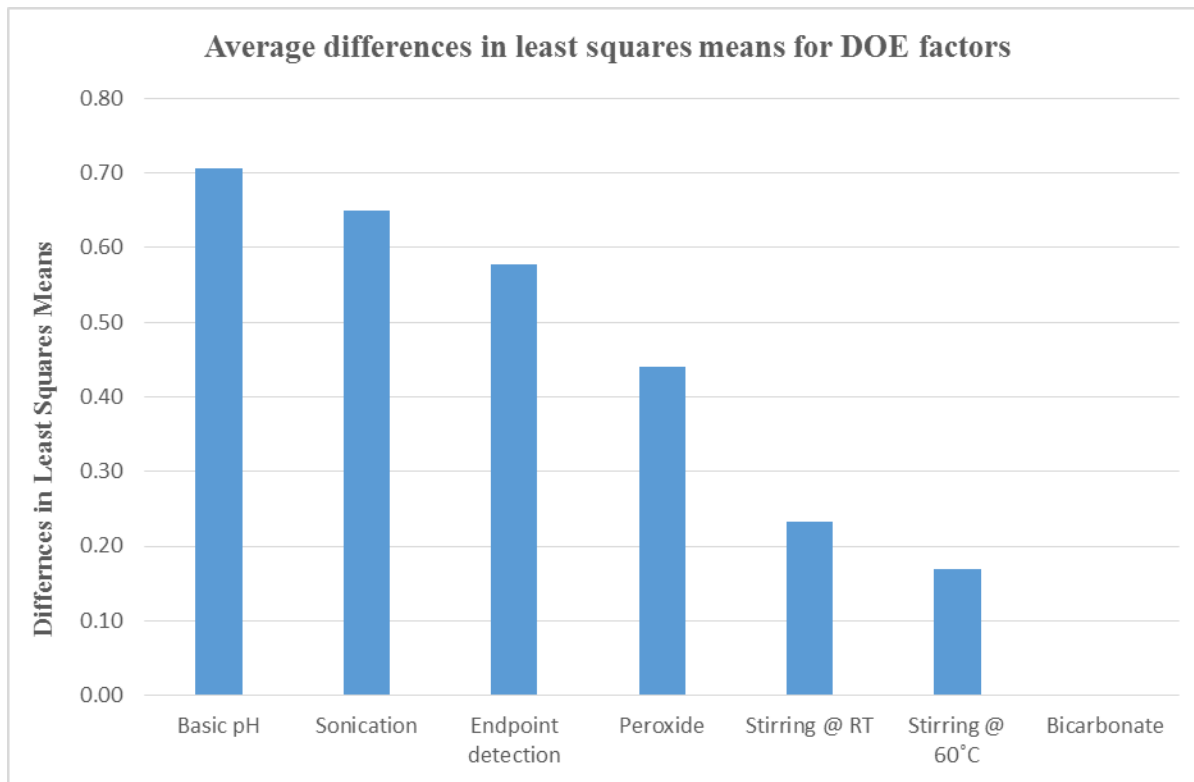


Figure 9. Comparison of average differences in least squares means for DOE factors.

### 5.1 Basic pH

A dominant requirement for clay dispersion is a basic pH (9.5 to 10.5 in this study) – this is needed to enhance the negative charge on the clays, making them repulsive and preventing agglomeration. When the clays are well dispersed it permits cation exchange of MB with the clays. In the development of an automated MBI method this would be a critical factor. Figure 9 shows that basic pH has the greatest difference in least squares means.

### 5.2 Sonication

Sonication is achieved by the rapid vibration of a tip, for a sonication probe, or the pan for a bath sonicator. This motion causes cavitation leading to the formation and implosive collapse of microscopic bubbles. The release of energy as a result of this phenomena impacts objects and surfaces which in the case of clays promotes dispersion. Figure 9 shows that sonication provided the second greatest difference in least squares means between “with” sonication and “without” sonication. In the development of an automated MBI method this would be a critical factor to incorporate into the analytical system. In the PB DOE studies only a bath sonicator was used where the energy used to effect dispersion would be smaller than that achieved with a probe sonicator.

### 5.3 Objective MBI Endpoint Detection

In an automated system for MBI it is imperative that an objective endpoint detection method be implemented. Two approaches to an objective determination of the endpoint were investigated. The spectroscopy method used in the 12-factor PB DOE provided some insight into the form of MB interacting with the clays. Experimental data suggested that the MB dimer is adsorbed to the clays since concentration of the aqueous MB dimer decreased in comparison to the MB monomer. However, the manner in which the MB dimer associated with the clay could not be ascertained. Additionally, this spectrophotometric method would require modification if it were to be implemented into an online system. Perhaps a filtration procedure rather than centrifugation would remove solids and permit the spectrophotometric determination of the MBI concentration in the filtrate.

The second application investigated was the detection of the halo using slope detection of a pixel density image. A method of spotting, capture of a digital image and an algorithm used for slope detection in the halo region may be feasible.

The least square means using the visual halo method was found to be greater than the more objective methods studied; whether it be spectrophotometric or the slope detection procedure for halo detection on filter paper. The objective methods were also found to be more sensitive to the presence of aqueous MB not associated with the clays contributing to an earlier endpoint than the visual method of detection.

### 5.4 Peroxide

Relatively low peroxide concentrations and residence times provided the next most significant effect on the difference in least square means. The source of the improved dispersion is thought to be mainly due to the removal of organics associated with the clays. However, the turbulence due to bubbling action associated with oxygen release from the decomposition of excess hydrogen peroxide may also have played a role in promoting dispersion. The evidence furnished in this study would suggest that peroxide addition should be a component of an automated MBI system under the conditions used.

To assess the importance of peroxide, a mini-study was developed to assess the effect of increasing the sonication energy using a sonication probe rather than a bath. A bicarbonate/carbonate buffer at pH 9.6 was used but included variable peroxide concentrations at 0, 5, 10 and 15 wt% for the analysis of uncleaned MFT-2 in the slurry form. After 5 minutes of stirring, the sonication probe (QSONICA Model Q700 with a 3/4" diameter probe tip, frequency 20 kHz) was operated for 15 minutes. An average total energy delivered to the samples was 69,000 Joules and was accompanied by the temperature of the dispersing media increasing to about 88°C. The amplitude was adjusted to 90% and the power decreased during operation from 90 to 50 watts as the viscosity of the sample decreased.

Regression analysis showed a P value = 0.590 suggesting no slope change with peroxide concentration. When the study was repeated with D&S-cleaned MFT-2 sample dispersed using the probe sonicator for 45 minutes there was also no statistical differences with and without

5% peroxide treatment. This suggests that the addition of peroxide may not be necessary if the energy associated with the sonication step is increased. It is difficult to assess the efficiency of energy in a bath sonicator but using the ratio of the area of the beaker to the pan, for a 130 watt sonication bath, it was calculated the maximum energy applied to the sample would be 13,000 Joule.

Another factor, to be discussed in the conclusions and future work section is the concomitant production of peroxide during sonication (Nascentes et al. 2001). The level of peroxide formation during the sonication procedure may also play a role in promoting dispersion. This would be desirable since any reduction in the number of reagents required for the MBI determination make automation simpler to implement.

### **5.5 Stirring and Temperature**

“With” and “without” stirring at 250 rpm for 20 minutes under either room temperature or 60°C showed some improvement in the difference in least squares means, but if compared to the circulation promoted during sonication it cannot be viewed as a major factor. An encouraging observation is that heating was not a prerequisite to achieving dispersion. Room temperature was just as effective in promoting dispersion. If heating is not a requirement this may have a simplifying aspect to the development of an automated system.

Heating is associated with sonication operations and although not investigated in this study, it should be incorporated into future full factorial DOE studies to see whether temperature increase during sonication should be controlled when implementing an automated system.

### **5.6 Bicarbonate**

The presence of 0.015 M NaHCO<sub>3</sub> did not show differences in least square means from experiments when it was omitted. Although sodium bicarbonate is a basic salt it is incapable of elevating the pH into the dispersion promoting range. However, it is viewed as an important component of the bicarbonate/carbonate buffer pair that would be generated with the addition of sodium hydroxide. For this reason it is considered an essential component of any automated system for MBI determinations.

### **5.7 Sample Cleaning**

The use of D&S to clean the sample resulted in a least squares means of 11.0 compared to using MFT slurry, 11.8. Thus the removal of bitumen does not appear to be essential to obtaining useful MBI values. The data suggest that D&S cleaning followed by dispersion, using the conditions in this study, may actually result in lower MBI values. The problem likely lies in the difficulty of dispersing the enhanced aggregation of the solids imparted by cleaning and heating during the drying of the solids. D&S cleaning would be very impractical in an automated analytical system for MBI determinations. Alternative methods of sample cleaning, such as a cold wash extraction of the bitumen in toluene followed by centrifugation or filtration, would be undesirable but may be necessary if some automated options are to be implemented where bitumen fouling could interfere. The information inferred from the 12-factor DOE would

suggest that reliable data can be obtained even in the presence of bitumen. Bitumen may not interfere with dispersion as severely as the presence of organic acids or other organic species associated with the clays. These concerns would require additional studies to confirm whether these conclusions are supported.

### **5.8 Soaking**

Soaking did not appear to increase the least squares means sufficiently to be viewed as an essential feature of an MBI determination. This too is desired since 18 h soaking would be impractical in implementing procedures dependent on retrieving MBI data in an expedient manner and would be undesirable in an on-line automated MBI system.

## **6 DISPERSION USING VARIATIONS AT HIGH PH**

Although a full factorial DOE where multiple pH levels along with the other principle factors would have been ideal, it was considered expedient to conduct a mini-study on the effects of pH on dispersion. Rather than working with slurry samples, MFT-2 was cleaned by D&S and then dispersed at different basic pH levels using a probe sonicator. The cleaned MFT was disaggregated by mortar and pestle to pass an 850 micron sieve and then rotary riffled to a uniform mass before beginning dispersion procedures. These steps were taken to reduce subsampling errors. Following the addition of a 0.015 M NaHCO<sub>3</sub> solution to the cleaned MFT solids, the pH was adjusted to specific pH values within the range of 9.1 and 11.6 and dispersion was assessed on the basis of MBI values.

Cleaned MFT is more difficult to disperse and so the time required to operate the probe sonicator (QSONICA Q700 with a 3/4" diameter probe tip) was determined by measuring the MBI following different sonication times. The operating conditions were the same as those discussed in section 5.4. Figure 10 shows the sonication time and the associated energies needed to disperse cleaned MFT-2. The dispersion is seen to be complete at 45 minutes when the MBI values were at a plateau.

The temperature of the dispersing solution increased to 88°C within 10 minutes and then remained at that temperature during sonication. The temperature profile was obtained using a Pasco PASPort Chemistry Sensor PS-2100A and DataStudio software. Evaporation losses were overcome by adding water to maintain the volume of the dispersing solution.



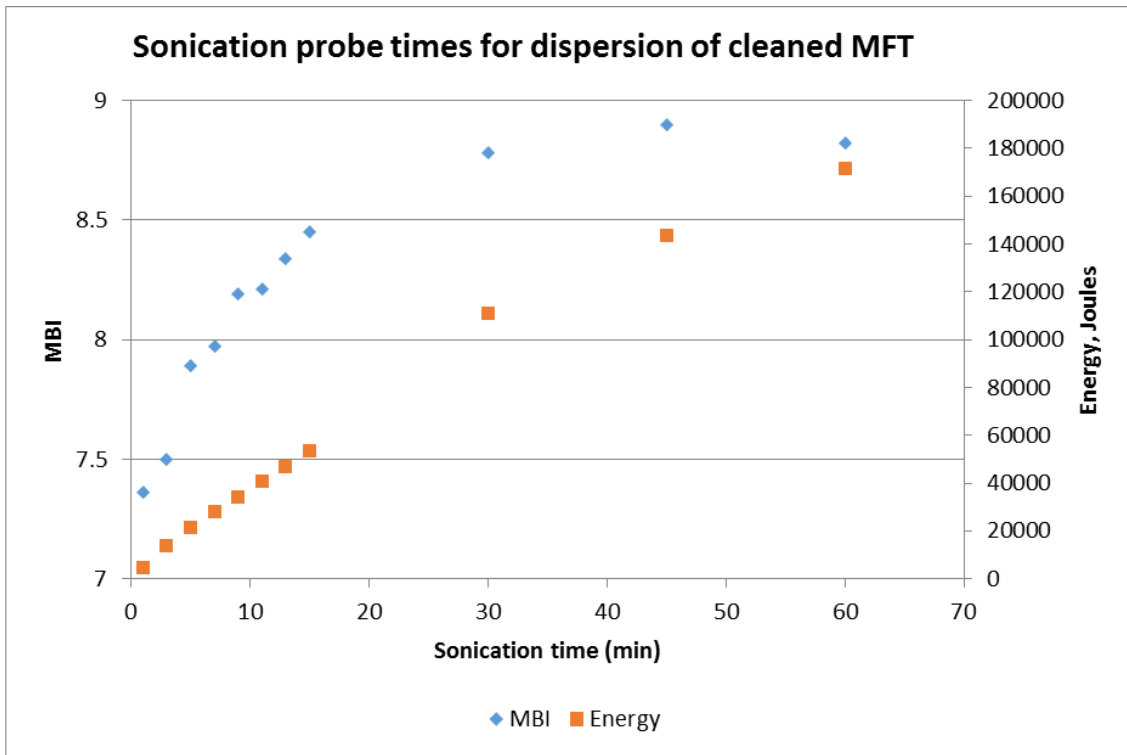


Figure 10. Probe sonication times to disperse cleaned MFT.

Figure 11 shows the effect of pH of the dispersing solution on MBI values. The data suggest that pH of the dispersing solution should be carefully controlled rather than accepting a large pH range window. Regression analysis shows that MBI values change at a rate of 0.16 MBI/pH unit and so carefully controlling the pH should help to improve the precision of MBI values. A pH in the range of 9.6 to 9.8 may be appropriate since it is approximately midway between a low pH (8.0) where dispersion is not promoted and a high pH (11.5) where coagulation is often observed (Vietti 2013). Although the data suggest a greater level of dispersion is achieved at higher pH there are benefits in keeping the pH within a narrow range to improve MBI precision and yet avoid the pH boundaries where clay dispersion can be adversely affected.

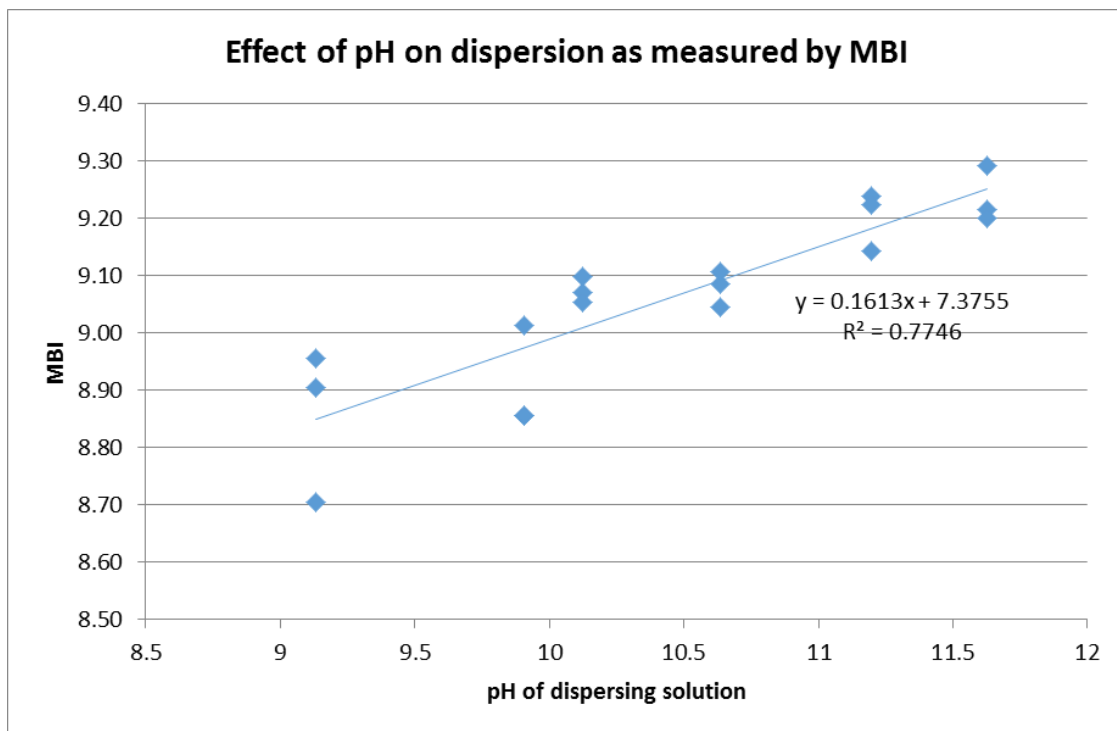


Figure 11. Effect of pH of dispersing solution on MBI values.

## 7 TITRATION USING FIBRE OPTICS AND VISIBLE SPECTROSCOPY

Cenens and Schoonhedt (1988) and Johnston (2011) have discussed the unique visible wavelength spectra obtained for different types of clays. [Table 3](#) reveals wavelengths of interest when observing MB, in its various forms, adsorbed on the external and interlamellar surfaces of clays. The nature of the interaction with adsorbed clay is evident by the effect on the lambda maximum. Interlamellar surface interactions cause a loss of aromaticity in the MB structure leading to a blue shift for MB<sup>1+</sup> (653 nm) compared to MB<sup>1+</sup> when in an aqueous solution (664 nm). An external surface interaction enhances the planar nature of the MB molecule causing it to have more of an aromatic structural character which results in a red shift (673 nm). As previously discussed in section 2.1.4; the monomer, dimer and trimer forms of MB in aqueous solutions also show unique wavelengths.

Absorbance at wavelengths corresponding to these forms provides unique information about the clays which is lost when only MBI is reported. Thus the ability to gain additional information about clays during the MB titration would be very beneficial and was the reason that a novel approach to acquiring this information was investigated.

NARCOSS approached Perkin Elmer in September 2013 to configure a spectrophotometer to allow fibre optics to be used in a double beam mode. This instrument was received in October 2014 and although experimental conditions have not been optimized the results of a trial titration have been included in this report.

A Perkin Elmer model Lambda 45 double beam spectrophotometer was chosen. It was configured with two fibre optic dipping probes, one for the reference and the other for the sample beam. Each of the probes had a 2 mm path length for the current study. The data were collected by scanning between 500 and 800 nm at 60 nm/min, with a slit width of 1 nm. The spectra were processed using UV WinLab V6.0 software.

During the titration, the reference probe is placed in a dispersed clay sample which is kept suspended using a magnetic stirrer. An equal volume of water is added to this reference beaker for each aliquot of 0.006 N MB added to the sample beaker to help maintain consistent solids turbidity between the two beakers. Using both a sample probe and a reference probe in a double beam spectrophotometer, the spectra recorded is due to spectral changes in MB alone since the reference beam is subtracted from the sample beam.

To choose an appropriate solids loading for the titration, different masses of clean and dry MFT solids following D&S were dispersed in 53 mL of a bicarbonate buffer at pH 9.8 and dispersed using probe sonication. Figure 12 shows the change in absorbance at various solid loadings at the wavelengths scanned. The results validate the use of a reference beam during the titration since the absorbance of the clays themselves is changing. This observation is similar to that reported by Chen et al. (1979). A loading of approximately 0.025 g of dispersed MFT solids was considered appropriate for the trial titration. The background absorbance from the sample solids would be relatively low compared to the MB absorbance within this spectral range with reduced light scattering. At the same time there were sufficient solids available to adsorb MB and reveal the spectral wavelengths of interest.

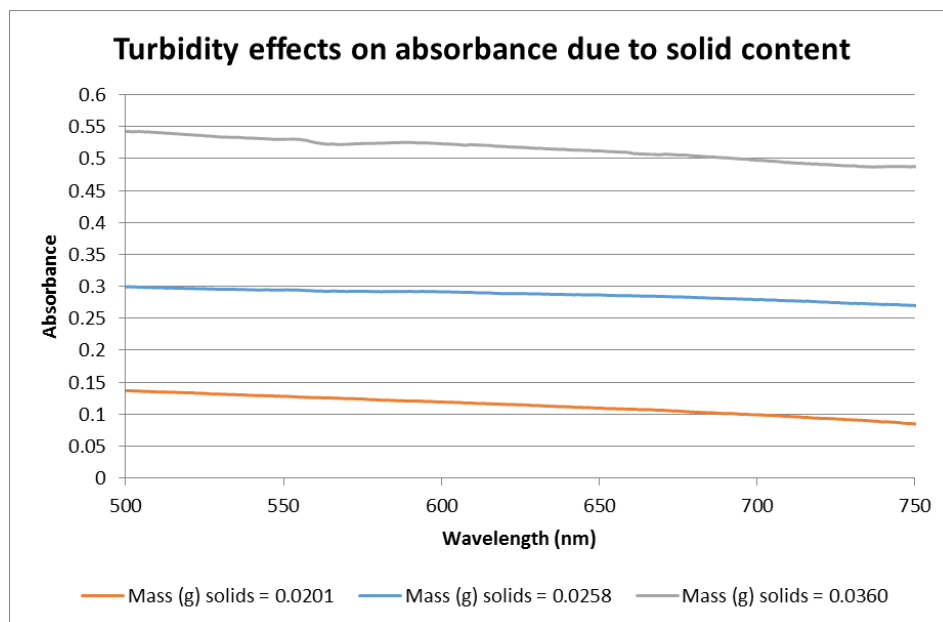


Figure 12. Turbidity effects on absorbance with change in solid content.

Figure 13 reveals the changes in the spectra during the titration of a dispersed MFT sample at the volumes of 0.006 M MB listed in the legend. A conventional visual halo detection procedure was also used to identify the endpoint which was observed at 600  $\mu\text{L}$ . The spectra at this point in the titration shows that the aqueous  $\text{MB}^{1+}$  monomer is clearly evident by the peak at 664 nm.

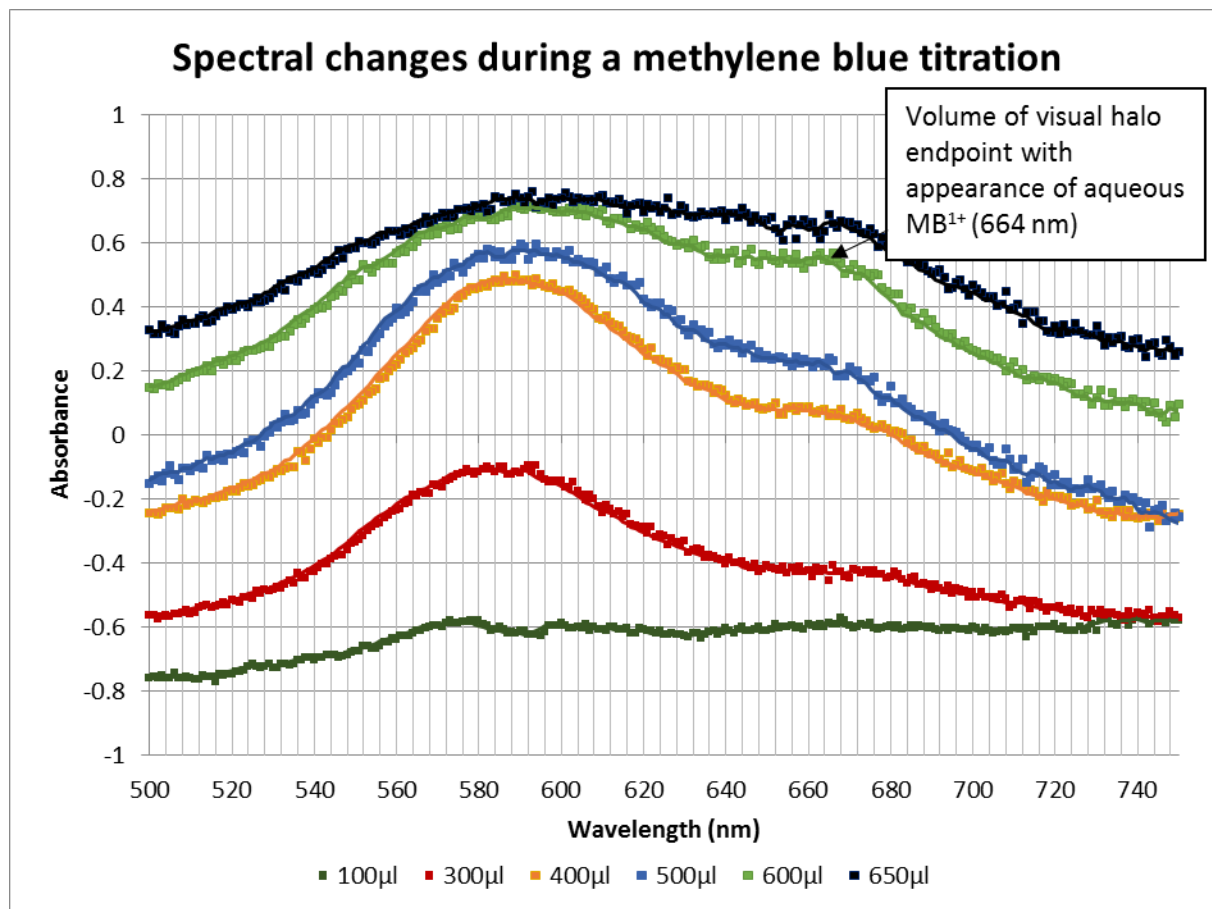


Figure 13. Spectral changes during a methylene blue titration.

As the MB is added it is noted that predominantly the dimer  $(\text{MB}^{1+})_2$  is being adsorbed on the interlamellar surface of the clays as seen by the blue shift in the absorbance. The peak in the region of 588 to 596 nm dominates the absorbance spectra as the amount of MB increases from 300 to 600  $\mu\text{L}$ . Hang and Brindley (1970) show conditions where a double layer of MB molecules is to be expected at certain loading levels on the surface of clays and may account for the preference for dimer loading. The negative values in the absorbance spectra are due to slightly more solids in the reference beaker than in the sample beaker being titrated. The absorbance measured is the difference between the absorbance of the sample and absorbance of the reference beams when using the double beam spectrophotometer.

As stated, this is a preliminary study where conditions have not been optimized in terms of scan rate, slit width, clay loading and fibre optic path length; these features need to be studied to improve the signal to noise ratio and optimize the acquired spectra. However, it demonstrates the potential for this form of spectroscopy to be used for MB titrations and the potential to determine not only MBI but also the nature of the clays being titrated. The MFT titrated here show spectra similar to the high charge smectite discussed by Johnston (2011).

## 8 NUCLEAR MAGNETIC RESONANCE STUDIES ON METHYLENE BLUE

Nuclear magnetic resonance (NMR) spectroscopy was also examined as a means of studying MB adsorption to clays. Proton NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer, with all data being analyzed using Bruker's TopSpin 3.2 software.

Figure 14 shows how the NMR spectra changes with concentration of aqueous MB in water in the range of  $2.00 \times 10^{-5}$  M to  $2.00 \times 10^{-2}$  M, reflecting how the signal from the aromatic protons within the structure changes with concentration. At  $2.00 \times 10^{-5}$  M spectral detail is virtually absent due to the very small signal to noise ratio. The actual quantity of MB in the NMR vial for each of the determinations ranged between 0.005 and 5 mg for the lowest and highest concentrations respectively. The different proton assignments within the NMR spectra for MB are found in in Table 11.

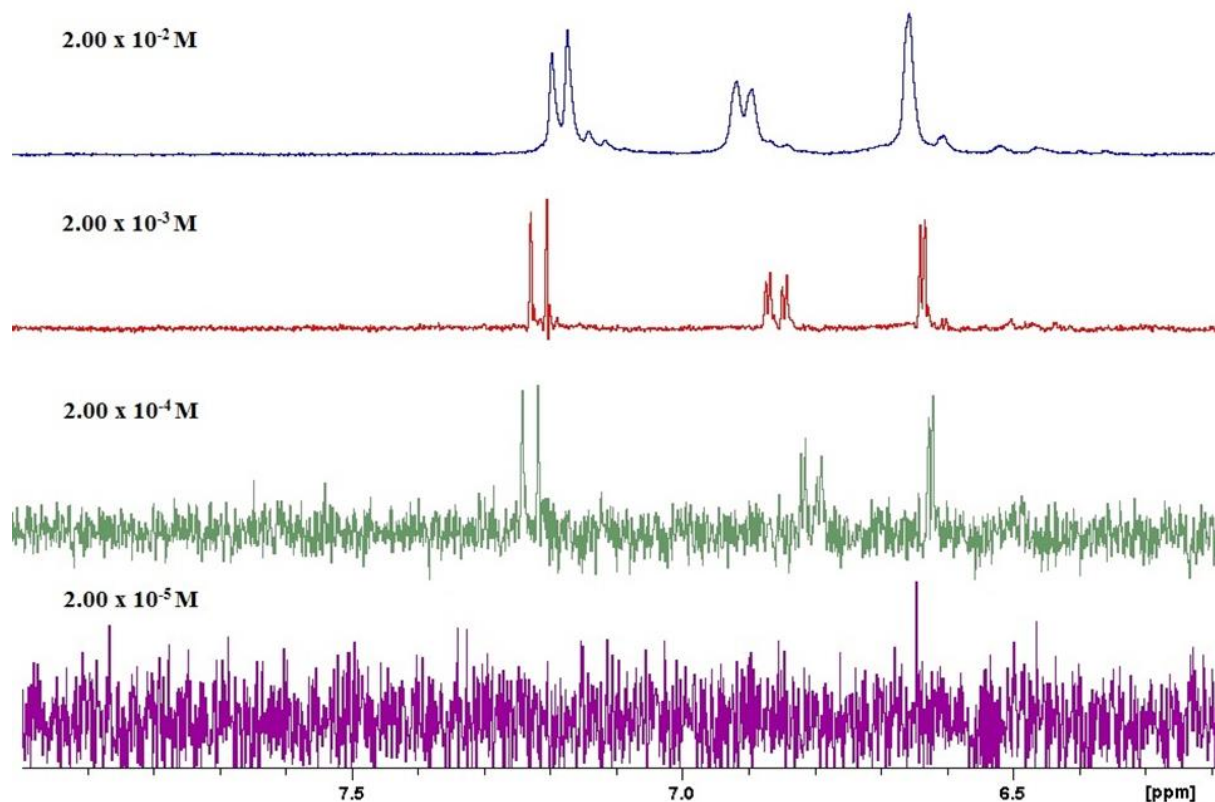
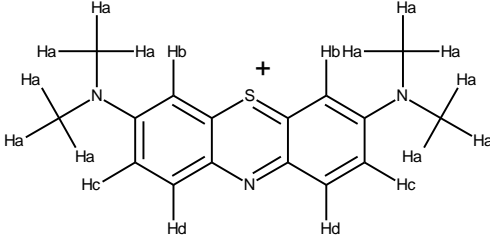


Figure 14. Stack plot of methylene blue <sup>1</sup>H NMR spectra at various concentrations.

Table 11. NMR assignments for aqueous methylene blue.

	Chemical Shift (ppm)	Assignment
		7.11 (doublet)
	6.89 (doublet of doublets)	H <sub>b</sub>
	6.62 (doublet)	H <sub>c</sub>
	3.02 (singlet)	H <sub>a</sub>

To test the possibility of using NMR to detect MB interacting with clays, 0.5431 g of montmorillonite clay<sup>5</sup> was dispersed in 50 mL of 0.015 M bicarbonate/carbonate buffer use a bath sonicator for 20 minutes. To this slurry a solution of 0.006 M MB was added until the amount of MB was equivalent to 150 meq MB/100 g clay ensuring that the clay had undergone complete cation exchange. This mixture was filtered and the clay-MB filter cake was placed in the NMR tube and analyzed. Previous work on this montmorillonite clay from Source Clays Repository at Purdue University found the cation exchange capacity to be 100 meq MB/100 g clay. This would indicate that about 174 mg of MB should be associated with the clays which is about 35 times the mass needed to observe MBI peaks when in aqueous media alone.

However, the spectra in Figure 15 shows no signs of any of the MB assignments identified in Table 11. This suggests that alternative NMR methods of analyzing MB-clay interactions, such as solid state NMR, would have to be investigated as a possible means for assessing MB interactions with clays.

## 9 CONCLUSION AND FUTURE STUDIES

The goal of this project was to identify the essential components of an MBI method and also investigate innovative endpoint detection procedures that would allow for automation of the MB titration. In addition to basic pH adjustment, sonication is considered to be an important component of the analytical procedure to achieve dispersion of the clays. The mini-study using the probe sonicator for just 15 minutes suggests that dispersion can be achieved without the use of reagents other than the bicarbonate/carbonate buffer system when working with slurry forms of MFT samples. Peroxide was found to promote dispersion when in the lower energy bath sonicator.

<sup>5</sup> See <http://en.wikipedia.org/wiki/Montmorillonite>

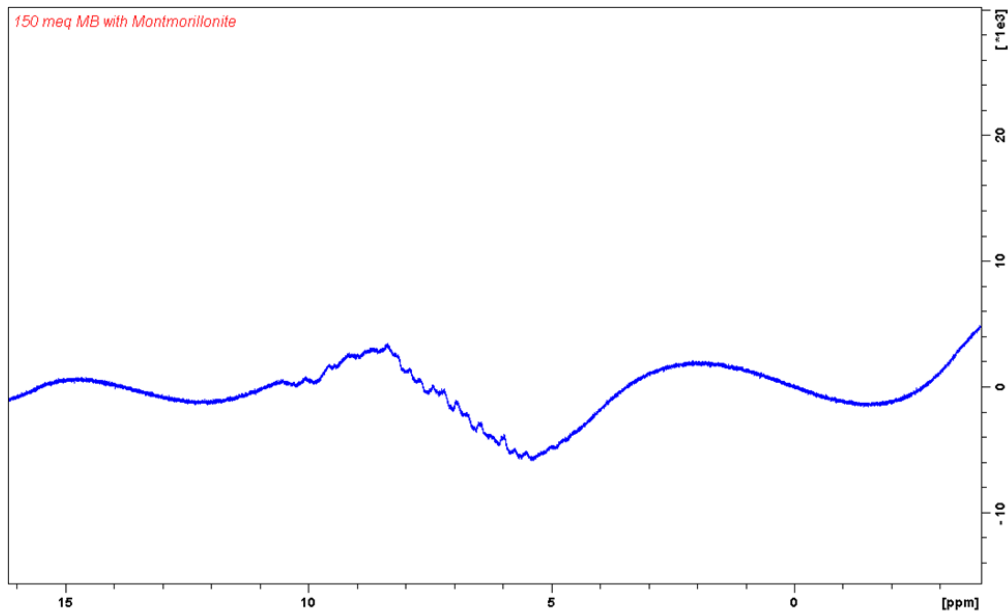


Figure 15. Methylene blue saturated montmorillonite.

A future investigation that may help to better understand the steps needed to ensure probe and bath sonication procedures are equivalent is to optimize conditions based on the work of Nascentes et al. (2001). Using their procedure, parameters such as water volume, tube position, temperature, and sonication time, to name a few variables, can be assessed spectrophotometrically. This is accomplished by measuring the amount of  $I_2$  formed from a solution containing KI and ammonium molybdate and is related to the energy imparted to the sample by the sonication type and conditions.

Interestingly, the paper also provides a procedure to measure the level of peroxide formed from water during sonication. The test is based on the catalytic effect of cobalt on the oxidation of Tiron by peroxide. Thus the level of peroxide formed during sonication could be determined to establish whether this plays a role in the results obtained using the probe sonicator.

Optimization of the novel double beam fibre optic visible spectroscopy conditions in terms of scan speed, sample loading, path length, slit width and subsampling procedures using a full factorial DOE approach should be performed to enable this more objective endpoint detection system to be implemented. Another factor to address when optimizing fibre optic spectrophotometry is the handling of slurry samples that have not been cleaned as fouling of the fibre optic probe is anticipated. However, the use of fibre optics during MB titration is very attractive since much more detail can be mined from the titration data than simply MBI values. This may dramatically improve the characterization of ores and tailings streams, and improve process decisions related to MB titrations of oil sands samples.

Once sonication performance and fibre optic spectroscopy is developed, a full factorial DOE should be conducted. It has the advantage over all other factorial designs in that more than two

levels or procedures can be assessed along with the identification of significant interactions that may be influencing main effect results. Based on these findings and least squares means, conditions clearly affecting the test method can be fully understood. This would help ensure that the final test method exhibits ruggedness and is capable of generating reliable data with good precision and accuracy.

A full factorial design involving pH of the dispersing solution, variable sonication times of probe and bath sonication, assessment of various dispersion temperatures when using sonication, effects of variation in the ionic strength of the dispersing solution, and a comparison of visual halo with fibre optic visible spectroscopy endpoints could be some of the features studied and eventually optimized. The key findings may help to reduce the analysis times so essential to allow MBI values to be used to control process operations.

Ideally once these conditions have been optimized, titrations of various oil sand and tailings samples should be conducted using fibre optic visible spectroscopy to determine how various oil sands and tailings samples respond to MB titrations. The unique properties of the various samples based on clay type would be expected to be revealed by the manner in which MB interacts with different clay types. Fully understanding these profiles may help select the most appropriate ores for bitumen extraction purposes but could also influence the best options for tailings streams treatment to promote dewatering and consolidation of tailings. Included in such a study should be an assessment of the effects of solids on changes in the clay to water ratio for various oil sands as measured during the MB titration.

A study involving the use of atomic force microscopy with Raman may help to understand better the process of MB interacting with various clay types and also assess the potential of Raman as another spectrophotometric detection procedure. The advantage of Raman is that both organic and inorganic structure can be investigated. Coupling these findings with x-ray diffraction and small angle x-ray scattering should help reveal the mechanism of MB interaction with clays from various oil sand and tailings sources. This information may be critical to determine the stacking of MB when interacting with clays and allow a better assessment of the surface area of clays based on MB titrations.

## **10 REFERENCES**

ASTM, 2014. E1169-07 Standard Practice for Conducting Ruggedness Tests. ASTM International, West Conshohocken, Pennsylvania.

Boxill, L., 2011. Potential for use of methylene blue index testing to enhance geotechnical characterization of oil sands ores and tailings. IN: Proceedings Tailings and Mine Waste, 2011, Vancouver, British Columbia, November 6 to 9, 2011. 15 pp.

<http://www.infomine.com/library/publications/docs/boxill2011.pdf> [Last accessed December 1, 2014].

Cenens, J. and R.A. Schoonheydt, 1988. Visible spectroscopy of methylene blue on hectorite, laponite B and barasym in aqueous suspension. *Clays and Clay Minerals* 36: 214-224.



- Chen, Y., D. Shaked and A. Banin, 1979. The role of structural iron (III) in the UV absorption by smectites. *Clay Minerals* 14: 93-102.
- Chiappone, A., S. Marengo, C. Scavia and M. Setti, 2004. Clay mineral characterization through the methylene blue test: comparison with other experimental techniques and applications of the method. *Canadian Geotechnical Journal* 41: 1168-1178.
- Di Stefano, C., V. Ferro and S. Mirabile, 2010. Comparison between grain-size analyses using laser diffraction and sedimentation methods. *Biosystems Engineering* 106: 205-215.
- Energy Resources Conservation Board, 2009. Directive 074: Tailings performance criteria and requirements for oil sands mining schemes. Energy Resources Conservation Board, Calgary, Alberta. 14 pp. <http://www.aer.ca/documents/directives/Directive074.pdf> [Last accessed November 17, 2014].
- Hang, P.H. and G.W. Brindley, 1970. Methylene blue absorption by clay minerals. Determination of surface areas and cation exchange capacities (clay-organic studies XVIII). *Clays and Clay Minerals* 18: 203-212.
- Johnston, C.T., 2011. Influence of clay mineralogy on clay-bitumen interactions. IN: CONRAD Clay Workshop, March 9-10, 2011, Edmonton, Alberta.
- Mikula, R.J., 2011. Understanding clays in oil sands processes. IN: CONRAD Clay Workshop, March 9-10, 2011, Edmonton, Alberta.
- Nascentes, C., M. Korn, C. Sousa and M. Arruda, 2001. Use of ultrasonic baths for analytical applications: A new approach for optimisation conditions. *Journal of the Brazilian Chemical Society* 12: 57-63.
- Omotoso, D., 2011. Clay characterization in the oil sand industry. IN: CONRAD Clay Workshop, March 9-10, 2011, Edmonton, Alberta.
- Robertson, J., C.J. Thomas, B. Caddy and A.J.M. Lewis, 1984. Particle size analysis of soils – a comparison of dry and wet sieving techniques. *Forensic Science International* 24: 209-217.
- Vietti, D., 2011. Clay mineralogy and water chemistry on tailings settling and rheology. IN: CONRAD Clay Workshop, March 9-10, 2011, Edmonton, Alberta.
- Wallace, D., 2011. The influence of clay and water chemistry on extraction performance. IN: CONRAD Clay Workshop, March 9-10, 2011, Edmonton, Alberta.
- Xu, Z., L. Yan, L. Alagha and J. Masliyah, 2013. Probing anisotropic surface characteristics of clay minerals by atomic force microscope. IN: CONRAD Oilsands Clay Conference, February 20-21, 2013, Edmonton, Alberta.
- Yong, R.N. and A. Sethi, 1981. Method for determining clay content in tailings and sludge. Patent# 44529000.

## 11 GLOSSARY

### 11.1 Terms

#### **Aliasing (confounding)**

Effects that cannot be estimated separately from each other are said to be confounded. Confounding occurs when you use a fractional factorial design, because you do not run all factor level combinations. For example, if factor A is confounded with the 3-way interaction BCD, then the estimated effect for A is the sum of the effect of A and the effect of BCD. You cannot determine whether a significant effect is because of A or because of the BCD interaction. Usually, you assume that the effect is because of the simpler term. These effects are also said to be aliased. The alias structure describes the confounding that occurs in the design.

<http://support.minitab.com/en-us/minitab/17/topic-library/modeling-statistics/doe/basics/what-are-confounding-and-alias-structure/>

#### **Absorbance**

In spectroscopy, the absorbance (also called optical density) of a material is a logarithmic ratio of the amount of radiation falling upon a material to the amount of radiation transmitted through the material. <http://en.wikipedia.org/wiki/Absorbance>

#### **Adjusted Mean Squares (AdjMS)**

Adjusted mean squares are calculated by dividing the adjusted sum of squares by the degrees of freedom. <http://support.minitab.com/en-us/minitab/17/topic-library/modeling-statistics/anova/anova-statistics/understanding-mean-squares/>

#### **Adjusted Sum of Squares (AdjSS)**

Adjusted sums of squares does not depend on the order the factors are entered into the model. It is the unique portion of SS Regression explained by a factor, given all other factors in the model, regardless of the order they were entered into the model.

For example, if you have a model with three factors, X1, X2, and X3, the adjusted sum of squares for X2 shows how much of the remaining variation X2 explains, given that X1 and X3 are also in the model. <http://support.minitab.com/en-us/minitab/17/topic-library/modeling-statistics/anova/anova-statistics/understanding-sums-of-squares/>

#### **Adsorption (adsorb)**

Adsorption is the adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid to a surface. This process creates a film of the adsorbate on the surface of the adsorbent.

#### **Analysis of Variance**

The name "analysis of variance" is based on the approach in which the procedure uses variances to determine whether the means are different. The procedure works by comparing the variance between group means versus the variance within groups as a way of determining whether the groups are all part of one larger population or separate populations with different characteristics.

<http://support.minitab.com/en-us/minitab/17/topic-library/modeling-statistics/anova/basics/what-is-anova/>

### **Atomic Force Microscope**

An instrument used for mapping the atomic-scale topography of a surface by means of the repulsive electronic forces between the surface and the tip of a microscope probe moving above the surface. <http://www.merriam-webster.com/dictionary/atomic%20force%20microscope>

### **Atterberg Limits**

The state of fined grain soils are assessed on the basis of the amount of water in the soil system. The four states of the soil are described in terms of limits: liquid limit is the boundary between the liquid and plastic states; plastic limit is the boundary between the plastic and semi-solid states; shrinkage limit is the boundary between the semi-solid and solid states.

### **Fluid Fine Tailings (FFT)**

A fluid discard from bitumen extraction facilities with more than 1 wt% solids and having an undrained shear strength of less than 5 kPa.

### **Foldover**

Test runs added to a two-level fractional factorial experiment, generated by duplicating the original design by switching levels of one or more factors in all runs (ASTM-E1169 07).

### **Interlamellar**

Spacing between clay layers or lamellae.

### **Isomorphic Substitution**

This is the substitution of one element for another in the clay structure without changing the structure. Charges developed on the clay by isomorphic substitution are permanent and are not pH dependent.

### **Mature Fine Tailings (MFT)**

Tailings that have reached a solids content of about 30 wt% usually within one or two years after being deposited as fluid fine tailings in tailings ponds

### **Montmorillonite**

A clay mineral with a 2 silicon tetrahedral sheets enclosing 1 aluminum octahedral sheet. Expansion caused by water results in this being considered a swelling clay.

### **Raman**

Raman spectroscopy is the measurement of the wavelength and intensity of inelastically scattered light from molecules. The Raman scattered light occurs at wavelengths that are shifted from the incident light by the energies of molecular vibrations. The mechanism of Raman scattering is different from that of infrared absorption, and Raman and IR spectra provide complementary information. Typical applications are in structure determination,

multicomponent qualitative analysis, and quantitative analysis.

[http://www.chemicool.com/definition/raman\\_spectroscopy.html](http://www.chemicool.com/definition/raman_spectroscopy.html)

### **Sequential Sum of Squares (SSQ)**

Sequential sums of squares depend on the order the factors are entered into the model. It is the unique portion of SS Regression explained by a factor, given any previously entered factors.

For example, if you have a model with three factors, X1, X2, and X3, the sequential sums of squares for X2 shows how much of the remaining variation X2 explains, given that X1 is already in the model. To obtain a different sequence of factors, repeat the regression procedure entering the factors in a different order. <http://support.minitab.com/en-us/minitab/17/topic-library/modeling-statistics/anova/anova-statistics/understanding-sums-of-squares/>

### **Signal to Noise Ratio**

One of the most important components of analytical chemistry is maximizing the desired signal while minimizing the associated noise. The analytical figure of merit is known as the signal-to-noise ratio (S/N or SNR). Noise can arise from environmental factors as well as from fundamental physical processes.

[http://en.wikipedia.org/wiki/Analytical\\_chemistry#Signals\\_and\\_noise](http://en.wikipedia.org/wiki/Analytical_chemistry#Signals_and_noise)

### **Small Angle X-Ray Scattering**

Small-angle X-ray scattering (SAXS) is a small-angle scattering (SAS) technique where the elastic scattering of X-rays (wavelength 0.1 to 0.2 nm) by a sample which has inhomogeneities in the nm-range, is recorded at very low angles (typically 0.1 to 10°).

[http://en.wikipedia.org/wiki/Small-angle\\_X-ray\\_scattering](http://en.wikipedia.org/wiki/Small-angle_X-ray_scattering)

### **Sonication**

This is the act of applying sound energy to agitate particles to effect dispersion.

### **Tailings**

Mineral waste from an oil sands processing plant usually deposited in a water medium

### **Tailings Pond**

A man-made impoundment structure which contains tailings.

### **X-Ray Diffraction**

A scattering of X-rays by the atoms of a crystal that produces an interference effect so that the diffraction pattern gives information on the structure of the crystal or the identity of a crystalline substance.

<http://www.merriam-webster.com/dictionary/x-ray%20diffraction>

## **11.2 Acronyms**

Adj SS

Adjusted Sum Of Squares

COSIA	Canada's Oil Sands Innovation Alliance
CSR	Clay to Solids Ratio
CWR	Clay Water Ratio
D&S	Dean and Stark
DOE	Design of Experiment
EP	End Point
MB	Methylene Blue
MBI	Methylene Blue Index
MFT	Mature Fine Tailings
NAIT	Northern Alberta Institute of Technology
NARCOSS	NAIT Applied Research Centre for Oil Sands Sustainability
NMR	Nuclear Magnetic Resonance (spectroscopy)
OSRIN	Oil Sands Research and Information Network
PB	Plackett-Burman
R <sup>2</sup>	Coefficient of determination
SEE	School of Energy and the Environment
Seq SS	Sequential Sum Of Squares

### 11.3 Chemicals

Fe <sub>2</sub> O <sub>3</sub>	Iron (III) Oxide
I <sub>2</sub>	Iodine
KI	Potassium iodide
NaOH	Sodium Hydroxide
NaHCO <sub>3</sub>	Sodium Bicarbonate

## LIST OF OSRIN REPORTS

OSRIN reports are available on the University of Alberta's Education & Research Archive at <http://hdl.handle.net/10402/era.17209>. The Technical Report (TR) series documents results of OSRIN funded projects. The Staff Reports (SR) series represent work done by OSRIN staff.

### **OSRIN Technical Reports – <http://hdl.handle.net/10402/era.17507>**

BGC Engineering Inc., 2010. Oil Sands Tailings Technology Review. OSRIN Report No. TR-1. 136 pp. <http://hdl.handle.net/10402/era.17555>

BGC Engineering Inc., 2010. Review of Reclamation Options for Oil Sands Tailings Substrates. OSRIN Report No. TR-2. 59 pp. <http://hdl.handle.net/10402/era.17547>

Chapman, K.J. and S.B. Das, 2010. Survey of Albertans' Value Drivers Regarding Oil Sands Development and Reclamation. OSRIN Report TR-3. 13 pp. <http://hdl.handle.net/10402/era.17584>

Jones, R.K. and D. Forrest, 2010. Oil Sands Mining Reclamation Challenge Dialogue – Report and Appendices. OSRIN Report No. TR-4. 258 pp. <http://hdl.handle.net/10402/era.19092>

Jones, R.K. and D. Forrest, 2010. Oil Sands Mining Reclamation Challenge Dialogue – Report. OSRIN Report No. TR-4A. 18 pp. <http://hdl.handle.net/10402/era.19091>

James, D.R. and T. Vold, 2010. Establishing a World Class Public Information and Reporting System for Ecosystems in the Oil Sands Region – Report and Appendices. OSRIN Report No. TR-5. 189 pp. <http://hdl.handle.net/10402/era.19093>

James, D.R. and T. Vold, 2010. Establishing a World Class Public Information and Reporting System for Ecosystems in the Oil Sands Region – Report. OSRIN Report No. TR-5A. 31 pp. <http://hdl.handle.net/10402/era.19094>

Lott, E.O. and R.K. Jones, 2010. Review of Four Major Environmental Effects Monitoring Programs in the Oil Sands Region. OSRIN Report No. TR-6. 114 pp. <http://hdl.handle.net/10402/65.20287>

Godwalt, C., P. Kotecha and C. Aumann, 2010. Oil Sands Tailings Management Project. OSRIN Report No. TR-7. 64 pp. <http://hdl.handle.net/10402/era.22536>

Welham, C., 2010. Oil Sands Terrestrial Habitat and Risk Modeling for Disturbance and Reclamation – Phase I Report. OSRIN Report No. TR-8. 109 pp. <http://hdl.handle.net/10402/era.22567>

Schneider, T., 2011. Accounting for Environmental Liabilities under International Financial Reporting Standards. OSRIN Report TR-9. 16 pp. <http://hdl.handle.net/10402/era.22741>

Davies, J. and B. Eaton, 2011. Community Level Physiological Profiling for Monitoring Oil Sands Impacts. OSRIN Report No. TR-10. 44 pp. <http://hdl.handle.net/10402/era.22781>

- Hurdall, B.J., N.R. Morgenstern, A. Kupper and J. Sobkowicz, 2011. Report and Recommendations of the Task Force on Tree and Shrub Planting on Active Oil Sands Tailings Dams. OSRIN Report No. TR-11. 15 pp. <http://hdl.handle.net/10402/era.22782>
- Gibson, J.J., S.J. Birks, M. Moncur, Y. Yi, K. Tattrie, S. Jasechko, K. Richardson, and P. Eby, 2011. Isotopic and Geochemical Tracers for Fingerprinting Process-Affected Waters in the Oil Sands Industry: A Pilot Study. OSRIN Report No. TR-12. 109 pp. <http://hdl.handle.net/10402/era.23000>
- Oil Sands Research and Information Network, 2011. Equivalent Land Capability Workshop Summary Notes. OSRIN Report TR-13. 83 pp. <http://hdl.handle.net/10402/era.23385>
- Kindziarski, W., J. Jin and M. Gamal El-Din, 2011. Plain Language Explanation of Human Health Risk Assessment. OSRIN Report TR-14. 37 pp. <http://hdl.handle.net/10402/era.23487>
- Welham, C. and B. Seely, 2011. Oil Sands Terrestrial Habitat and Risk Modelling for Disturbance and Reclamation – Phase II Report. OSRIN Report No. TR-15. 93 pp. <http://hdl.handle.net/10402/era.24547>
- Morton Sr., M., A. Mullick, J. Nelson and W. Thornton, 2011. Factors to Consider in Estimating Oil Sands Plant Decommissioning Costs. OSRIN Report No. TR-16. 62 pp. <http://hdl.handle.net/10402/era.24630>
- Paskey, J. and G. Steward, 2012. The Alberta Oil Sands, Journalists, and Their Sources. OSRIN Report No. TR-17. 33 pp. <http://hdl.handle.net/10402/era.25266>
- Cruz-Martinez, L. and J.E.G. Smits, 2012. Potential to Use Animals as Monitors of Ecosystem Health in the Oil Sands Region – July 2013 Update. OSRIN Report No. TR-18. 59 pp. <http://hdl.handle.net/10402/era.25417>
- Hashisho, Z., C.C. Small and G. Morshed, 2012. Review of Technologies for the Characterization and Monitoring of VOCs, Reduced Sulphur Compounds and CH<sub>4</sub>. OSRIN Report No. TR-19. 93 pp. <http://hdl.handle.net/10402/era.25522>
- Kindziarski, W., J. Jin and M. Gamal El-Din, 2012. Review of Health Effects of Naphthenic Acids: Data Gaps and Implications for Understanding Human Health Risk. OSRIN Report No. TR-20. 43 pp. <http://hdl.handle.net/10402/era.26060>
- Zhao, B., R. Currie and H. Mian, 2012. Catalogue of Analytical Methods for Naphthenic Acids Related to Oil Sands Operations. OSRIN Report No. TR-21. 65 pp. <http://hdl.handle.net/10402/era.26792>
- Oil Sands Research and Information Network and Canadian Environmental Assessment Agency, 2012. Summary of the Oil Sands Groundwater – Surface Water Interactions Workshop. OSRIN Report No. TR-22. 125 pp. <http://hdl.handle.net/10402/era.26831>
- Valera, E. and C.B. Powter, 2012. Implications of Changing Environmental Requirements on Oil Sands Royalties. OSRIN Report No. TR-23. 21 pp. <http://hdl.handle.net/10402/era.27344>

- Dixon, R., M. Maier, A. Sandilya and T. Schneider, 2012. Qualifying Environmental Trusts as Financial Security for Oil Sands Reclamation Liabilities. OSRIN Report No. TR-24. 32 pp. <http://hdl.handle.net/10402/era.28305>
- Creasey, R., 2012. Professional Judgment in Mineable Oil Sands Reclamation Certification: Workshop Summary. OSRIN Report No. TR-25. 52 pp. <http://hdl.handle.net/10402/era.28331>
- Alberta Innovates – Technology Futures, 2012. Investigating a Knowledge Exchange Network for the Reclamation Community. OSRIN Report No. TR-26. 42 pp. <http://hdl.handle.net/10402/era.28407>
- Dixon, R.J., J. Kenney and A.C. Sandilya, 2012. Audit Protocol for the Mine Financial Security Program. OSRIN Report No. TR-27. 27 pp. <http://hdl.handle.net/10402/era.28514>
- Davies, J., B. Eaton and D. Humphries, 2012. Microcosm Evaluation of Community Level Physiological Profiling in Oil Sands Process Affected Water. OSRIN Report No. TR-28. 33 pp. <http://hdl.handle.net/10402/era.29322>
- Thibault, B., 2012. Assessing Corporate Certification as Impetus for Accurate Reporting in Self-Reported Financial Estimates Underlying Alberta’s Mine Financial Security Program. OSRIN Report No. TR-29. 37 pp. <http://hdl.handle.net/10402/era.29361>
- Pyper, M.P., C.B. Powter and T. Vinge, 2013. Summary of Resiliency of Reclaimed Boreal Forest Landscapes Seminar. OSRIN Report No. TR-30. 131 pp. <http://hdl.handle.net/10402/era.30360>
- Pyper, M. and T. Vinge, 2013. A Visual Guide to Handling Woody Materials for Forested Land Reclamation. OSRIN Report No. TR-31. 10 pp. <http://hdl.handle.net/10402/era.30381>
- Mian, H., N. Fassina, A. Mukherjee, A. Fair and C.B. Powter, 2013. Summary of 2013 Tailings Technology Development and Commercialization Workshop. OSRIN Report No. TR-32. 69 pp. <http://hdl.handle.net/10402/era.31012>
- Howlett, M. and J. Craft, 2013. Application of Federal Legislation to Alberta’s Mineable Oil Sands. OSRIN Report No. TR-33. 94 pp. <http://hdl.handle.net/10402/era.31627>
- Welham, C., 2013. Factors Affecting Ecological Resilience of Reclaimed Oil Sands Uplands. OSRIN Report No. TR-34. 44 pp. <http://hdl.handle.net/10402/era.31714>
- Naeth, M.A., S.R. Wilkinson, D.D. Mackenzie, H.A. Archibald and C.B. Powter, 2013. Potential of LFH Mineral Soil Mixes for Land Reclamation in Alberta. OSRIN Report No. TR-35. 64 pp. <http://hdl.handle.net/10402/era.31855>
- Welham, C. and B. Seely, 2013. Oil Sands Terrestrial Habitat and Risk Modelling for Disturbance and Reclamation: The Impact of Climate Change on Tree Regeneration and Productivity – Phase III Report. OSRIN Report No. TR-36. 65 pp. <http://hdl.handle.net/10402/era.31900>



- Eaton, B., T. Muhly, J. Fisher and S-L. Chai, 2013. Potential Impacts of Beaver on Oil Sands Reclamation Success – an Analysis of Available Literature. OSRIN Report No. TR-37. 65 pp. <http://hdl.handle.net/10402/era.32764>
- Paskey, J., G. Steward and A. Williams, 2013. The Alberta Oil Sands Then and Now: An Investigation of the Economic, Environmental and Social Discourses Across Four Decades. OSRIN Report No. TR-38. 108 pp. <http://hdl.handle.net/10402/era.32845>
- Watson, B.M. and G. Putz, 2013. Preliminary Watershed Hydrology Model for Reclaimed Oil Sands Sites. OSRIN Report No. TR-39. 193 pp. <http://hdl.handle.net/10402/era.34250>
- Birks, S.J., Y. Yi, S. Cho, J.J. Gibson and R. Hazewinkel, 2013. Characterizing the Organic Composition of Snow and Surface Water in the Athabasca Region. OSRIN Report No. TR-40. 62 pp. <http://hdl.handle.net/10402/era.36643>
- De Corby, R.G., 2013. Development of Silicon-Based Optofluidic Sensors for Oil Sands Environmental Monitoring. OSRIN Report No. TR-41. 19 pp. <http://hdl.handle.net/10402/era.36936>
- Iqbal, M., T.K. Purkait, J.G.C. Veinot and G.G. Goss, 2013. Benign-by-Design: Synthesis of Engineered Silicon Nanoparticles and their Application to Oil Sands Water Contaminant Remediation. OSRIN Report No. TR-42. 30 pp. <http://hdl.handle.net/10402/era.37308>
- Oil Sands Research and Information Network, 2013. Future of Shrubs in Oil Sands Reclamation Workshop. OSRIN Report No. TR-43. 71 pp. <http://hdl.handle.net/10402/era.37440>
- Smreciu, A., K. Gould and S. Wood, 2013. Boreal Plant Species for Reclamation of Athabasca Oil Sands Disturbances. OSRIN Report No. TR-44. 23 pp. plus appendices. <http://hdl.handle.net/10402/era.37533>
- Pereira, A.S. and J.W. Martin, 2014. On-Line Solid Phase Extraction – HPLC – Orbitrap Mass Spectrometry for Screening and Quantifying Targeted and Non-Targeted Analytes in Oil Sands Process-Affected Water and Natural Waters in the Athabasca Oil Sands Region. OSRIN Report No. TR-45. 33 pp. <http://hdl.handle.net/10402/era.37793>
- Liang, J., F. Tumpa, L.P. Estrada, M. Gamal El-Din and Y. Liu, 2014. Ozone-Assisted Settling of Diluted Oil Sands Mature Fine Tailings: A Mechanistic Study. OSRIN Report No. TR-46. 43 pp. <http://hdl.handle.net/10402/era.38226>
- Rochdi, N., J. Zhang, K. Staenz, X. Yang, D. Rolfson, J. Banting, C. King and R. Doherty, 2014. Monitoring Procedures for Wellsite, In-Situ Oil Sands and Coal Mine Reclamation in Alberta. OSRIN Report No. TR-47. 156 pp. <http://hdl.handle.net/10402/era.38742>
- Taheriazad, L., C. Portillo-Quintero and G.A. Sanchez-Azofeifa, 2014. Application of Wireless Sensor Networks (WSNs) to Oil Sands Environmental Monitoring. OSRIN Report No. TR-48. 51 pp. <http://hdl.handle.net/10402/era.38858>
- Marey, H.S., Z. Hashisho and L. Fu, 2014. Satellite Remote Sensing of Air Quality in the Oil Sands Region. OSRIN Report No. TR-49. 104 pp. <http://hdl.handle.net/10402/era.38882>

Li, C., A. Singh, N. Klammerth, K. McPhedran, P. Chelme-Ayala, M. Belosevic and M. Gamal El-Din, 2014. Synthesis of Toxicological Behavior of Oil Sands Process-Affected Water Constituents. OSRIN Report No. TR-50. 101 pp. <http://hdl.handle.net/10402/era.39659>

Jiang, Y. and Y. Liu, 2014. Application of Forward Osmosis Membrane Technology for Oil Sands Process-Affected Water Desalination. OSRIN Report No. TR-51. 27 pp. <http://hdl.handle.net/10402/era.39855>

Zhu, L., M. Yu, L. Delgado Chávez, A. Ulrich and T. Yu, 2014. Review of Bioreactor Designs Applicable to Oil Sands Process-Affected Water Treatment. OSRIN Report No. TR-52. 39 pp. <http://hdl.handle.net/10402/era.39903>

Oil Sands Research and Information Network, 2014. Oil Sands Rules, Tools and Capacity: Are we Ready for Upcoming Challenges? OSRIN Report No. TR-53. 120 pp. <http://hdl.handle.net/10402/era.39985>

Iqbal, M., T.K. Purkait, M. Aghajamali, L. Hadidi, J.G.C. Veinot, G.G. Goss and M. Gamal El-Din, 2014. Hybrid Aerogel SiNP Membranes for Photocatalytic Remediation of Oil Sands Process Water. OSRIN Report No. TR-54. 29 pp. <http://hdl.handle.net/10402/era.40004>

Schoonmaker, A., J-M. Sobze, E. Fraser, E. Marenholtz, A. Smreciu, C.B. Powter and M. Mckenzie, 2014. Alternative Native Boreal Seed and Plant Delivery Systems for Oil Sands Reclamation. OSRIN Report No. TR-55. 61 pp. <http://hdl.handle.net/10402/era.40099>

Aguilar, M., E. Glucksman, D. Bass and J.B. Dacks, 2014. Next Generation Sequencing of Protists as a Measure of Microbial Community in Oil Sands Tailings Ponds: Amplicon Versus Metagenomic Approaches. OSRIN Report No. TR-56. 24 pp. <http://hdl.handle.net/10402/era.40100>

Alessi, D.S., M.S. Alam and M.C. Kohler, 2014. Designer Biochar-Coke Mixtures to Remove Naphthenic Acids from Oil Sands Process-Affected Water (OSPW). OSRIN Report No. TR-57. 38 pp. <http://hdl.handle.net/10402/era.40122>

Oil Sands Research and Information Network, 2014. Survey of Oil Sands Environmental Management Research and Information Needs. OSRIN Report No. TR-58. 67 pp. <http://hdl.handle.net/10402/era.40128>

Huang, Q., H. Wang and M.A. Lewis, 2014. Development of a Toxin-Mediated Predator-Prey Model Applicable to Aquatic Environments in the Athabasca Oil Sands Region. OSRIN Report No. TR-59. 59 pp. <http://hdl.handle.net/10402/era.40140>

**OSRIN Videos** – <http://hdl.handle.net/10402/era.29304>

Rooney Productions, 2012. [Assessment Methods for Oil Sands Reclamation Marshes](#). OSRIN Video No. V-1. 20 minutes. Also available on the [University of Alberta You Tube Channel](#) (recommended approach).

Rooney Productions, 2012. [Assessment Methods for Oil Sands Reclamation Marshes](#). OSRIN Video No. V-1. Nine-part mobile device version. Also available on the University of Alberta You Tube Channel ([link to Part 1](#) - recommended approach).

**OSRIN Staff Reports – <http://hdl.handle.net/10402/era.19095>**

OSRIN, 2010. Glossary of Terms and Acronyms used in Oil Sands Mining, Processing and Environmental Management – December 2013 Update. OSRIN Report No. SR-1. 123 pp. <http://hdl.handle.net/10402/era.17544>

OSRIN, 2010. OSRIN Writer’s Style Guide – November 2013 Update. OSRIN Report No. SR-2. 29 pp. <http://hdl.handle.net/10402/era.17545>

OSRIN, 2010. OSRIN Annual Report: 2009/2010. OSRIN Report No. SR-3. 27 pp. <http://hdl.handle.net/10402/era.17546>

OSRIN, 2010. Guide to OSRIN Research Grants and Services Agreements - June 2011 Update. OSRIN Report No. SR-4. 21 pp. <http://hdl.handle.net/10402/era.17558>

OSRIN, 2011. Summary of OSRIN Projects – October 2014 Update. OSRIN Report No. SR-5. 113 pp. <http://hdl.handle.net/10402/era.20529>

OSRIN, 2011. OSRIN Annual Report: 2010/11. OSRIN Report No. SR-6. 34 pp. <http://hdl.handle.net/10402/era.23032>

OSRIN, 2011. OSRIN’s Design and Implementation Strategy. OSRIN Report No. SR-7. 10 pp. <http://hdl.handle.net/10402/era.23574>

OSRIN, 2012. OSRIN Annual Report: 2011/12. OSRIN Report No. SR-8. 25 pp. <http://hdl.handle.net/10402/era.26715>

OSRIN, 2013. OSRIN Annual Report: 2012/13. OSRIN Report No. SR-9. 56 pp. <http://hdl.handle.net/10402/era.31211>

OSRIN, 2014. OSRIN Annual Report: 2013/14. OSRIN Report No. SR-10. 66 pp. <http://hdl.handle.net/10402/era.38508>