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16. Abstract The clay contamination of coarse and fine aggregates and its effects on pavement performance of portland cement concrete, bituminous mixes and chip seals is a major concern for Texas Department of Transportation. We proposed (i) to determine what type and concentration of clay mineral will result in poor pavement performance, (ii) to identify a quick field test method to detect the presence of deleterious clay minerals in the stockpile, and (iii) suggest remedial techniques to make the clay contaminated aggregates acceptable for use. The modified methylene blue (MMB) and X-Ray Diffraction (XRD) tests were identified as the most promising methods to identify and quantify clay mineral in aggregate fines. Nearly thirty aggregate sources have been tested using the MMB test. XRD was used to determine the content of different clay minerals present in these samples. A strong positive correlation between expansive clay content and methylene blue value (MBV) was evident which clearly indicates that the MMB test is the most reliable and rapid test method to detect clay minerals in aggregate fines. XRD is an advance research tool which was used to validate the MMB test. The correlation between MBV and concrete performance testing (both PPC and HMA) became the basis to assign a threshold MBV (corresponds to the maximum permissible clay content within the aggregate fines) and categorize aggregates fines with different ranges of MBV. A high MBV indicate increased potential for diminished aggregate performance in asphalt, concrete, and other construction applications. The Methylene Blue Test is sensitive to clays which contribute to stripping in HMA and could be used to eliminate problematic field sand sources. It appears that HMA is more robust and can tolerate higher amounts of clay contamination than PCC, mainly because water is not present in HMA. Although the bar linear shrinkage and sand equivalent tests give good repeatability in the results, these tests fail to provide consistent and accurate indications of clay minerals present in aggregate fines. Based on MMB test, materials that are failed by the current specifications (e.g., aggregate fines with clay size non-clay mineral particles) can be allowed, which promotes sustainability and save money. Therefore, type and concentration of clay minerals present in aggregate fines are very important aspects in relation to pavement performance. The guidelines for controlled use of aggregate fines with varying level of clay contamination have been developed and further research / implementation plan has been proposed.					
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**TREATMENTS FOR CLAYS IN AGGREGATES USED TO PRODUCE CEMENT
CONCRETE, BITUMINOUS MATERIALS. AND CHIP SEALS: TECHNICAL
REPORT**

by

Anal K. Mukhopadhyay
Associate Research Scientist, Texas A&M Transportation Institute

Brandon Pitre
Graduate Assistant Researcher, Texas A&M Transportation Institute

Andrew Russell
Graduate Assistant Researcher, Soil Science Department

Edith Arambula
Associate Research Scientist, Texas A&M Transportation Institute

Cindy Estakhri
Program Manager, Texas A&M Transportation Institute

and

Youjun Deng
Assistant Professor, Soil Science Department

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College Station, Texas 77843-3135

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CHAPTER 1

INTRODUCTION

RESEARCH BACKGROUND

The Texas Department of Transportation (TxDOT) has recently expressed concern about the cost of removing fines from aggregate used in Portland cement concrete (PCC). An internal study was done by TxDOT personnel that showed inclusion of fines above recommended concentrations did not produce detrimental effects to concrete specimens. If the maximum amount of 1.5 percent deleterious materials for PCC aggregates could be relaxed, then the cost of aggregate would be reduced while potentially opening up some new sources of aggregate.

Problems typically arise when the coarse aggregate is contaminated with (1) clay balls, (2) clay minerals present as constituents in the rock (weathering of unstable minerals), or (3) when fines coating the coarse aggregate are composed of deleterious clay minerals. There are 137 aggregate sources on the Concrete Rated Source Quality Catalog, and there are seven others that are not on the QM that are currently being used by TxDOT districts. The aggregates are as variable as the geology of Texas with all major rock types (igneous, metamorphic, and sedimentary) being represented. This variability will yield clay minerals of vastly different compositions and engineering characteristics.

Clay has two definitions. First, clay is used as a size term where anything smaller than 2 μm is considered as clay. The DOTs generally consider anything passing the No. 200 sieve (i.e., 75 μm) as clay or fines (sometimes called microfines). The minus 200 fraction mineralogy can differ significantly from true clay minerals and will vary from one quarry to the next. The second definition of clay refers to a group of minerals also called phyllosilicates, which are very active chemically and often control the properties of materials into which the clays are mixed. The clay minerals are generally very fine-grained (< 2 μm) and include the following minerals: chlorite, smectite, kaolinite, illite, palygorskite, talc, etc. The second definition (clay as a mineral term) is the one we are discussing in this research project.

The properties of coarse and fine aggregates play a major role in the overall performance of Portland cement concrete, hot mix asphalt (HMA), and seal coat. In this study, researchers are focused on the properties of aggregate contaminated by clay. Clay contaminating the aggregate is believed to influence the water demand, drying shrinkage, flexural strength, and tensile strength of Portland cement concrete. HMA and seal coat performance parameters such as permanent deformation, fatigue cracking, raveling, moisture susceptibility (moisture damage), and frictional resistance are believed to be related to clay in the aggregate as well.

RESEARCH OBJECTIVES

The objective of this research project is to (i) come up with a new rapid field technique (i.e., modified methylene blue test) to identify harmful clay minerals that may be contained in aggregates, which may help to determine the suitability of a particular aggregate source, (ii) have the modified methylene blue test to be used in conjunction with existing laboratory tests to detect clay minerals in aggregate, or possibly have the modified methylene blue test replace some of the

existing tests that have proven to be inferior to this new test method, and (iii) establish tolerable limits of clay contamination that can be allowed in aggregates ensuring that they are still considered suitable for use in concrete.

SCOPE OF RESEARCH

The research team has divided the work of the project into a number of Tasks and presented in the report as chapters. Chapter 2 gives the background information based on a literature review of relevant work conducted by other researchers. Chapter 3 provides several advanced research tools that are used to identify and quantify clay minerals along with test results based on standard clay minerals in order to establish which method is more effective. The most effective test methods that are identified in Chapter 3 will be used in Chapter 4 in an attempt to quantify the aggregate fines collected from various quarries. Chapter 5 involves conducting concrete mixing and testing for HMA and PCC using pure standard clay minerals in order to evaluate their effect on concrete performance. Chapter 6 includes using select aggregates from a few quarries to be used in HMA and PCC mixes in order to see if naturally occurring clays in aggregates have an effect on concrete performance. Chapter 7 involves using remedial techniques that can be used to treat and improve the quality of low-quality, or clay-rich, aggregates to make them acceptable for use. Lastly, Chapter 8 provides conclusions and recommendations based on all test results in each section.

CHAPTER 2

LITERATURE REVIEW AND SURVEY

Since it has already been established that clay contamination in aggregates can result in producing poor-performing concrete, the section highlights previous work done by other researchers in this field. This section focuses mainly of the effect of clay minerals in aggregates used in Portland cement concrete, bituminous mixes (HMA), and seal coats.

OCCURRENCES OF CLAY IN AGGREGATES

Based on research done by the authors as well as other researchers (Emry et al. 2006), clay is commonly associated with aggregates in three forms: (1) clay commonly coats the aggregate surface as fines generated during crushing the stone; (2) clay may be present in coarse aggregate as clay balls that are generally entrained in the stockpile from the soil below or overburden above; (3) the clay may be entrained in the aggregate pieces themselves due to chemical weathering.

Most of the literature deals with clay coating the aggregate as fines either generated during crushing at a quarry, or as clay mixed with the sand generally used as a fine aggregate source. Goldbeck (1933) identified seven different surface coatings on coarse aggregate which include: (1) stone dust, (2) clay, (3) organic, (4) alkali and salt, (5) bituminous oil, (6) calcareous, and (7) sugar coatings. Gullerud and Cramer (2002) narrowed the classification of surface coating to three types, which include: (1) dust (rock, quartz, feldspar, etc.), (2) clay minerals (chlorite, smectite, etc.), and (3) carbonate minerals.

SWELLING/EXPANSION OF CLAYS

One unique feature that some 2:1 clay minerals possess is the ability to swell, or expand, in the presence of water. Expansive clays are composed of small, negatively charged plates. Water molecules, which are slightly polarized, are attracted to the clay particles. This can result in the potential for a drastic volume increase when water is absorbed. Engineers are often faced with challenges during construction jobs that take place on soils that are rich in expansive clays from the smectite group. This is caused by the uneven movement induced by the shrink-swell phenomena in these soils that can result in damage to structures or roadways.

There are actually two main types of swelling that can occur in clay minerals when exposed to water molecules: inner crystalline swelling and osmotic swelling (Madsen and Müller-Vonmoos 1989). The inner crystalline swelling occurs as a result of the hydration of exchangeable cations of the dry clay. Osmotic swelling occurs from the large difference in the concentration of ions close to the clay surfaces and in the pore water. In the case of inner crystalline swelling, interlayer cations and the van der Waals attraction tightly hold together the negatively charged clay layers. Upon contact with the water molecules, the cations hydrate and orient themselves on a plane halfway between the two layers. This causes a widening of the spacing between the layers, thus resulting in swelling when water is introduced. Consequently, the layer spacing is reduced upon drying, thus resulting in shrinkage. Smectite minerals are generally smaller than most other clay minerals and tend to be concentrated in the fine clay (< 0.2 μm) fraction of aggregate fines and coatings. This smaller size translates to a higher

surface area, typically in the range of 600 to 800 m²/g. Pronounced shrink–swell and plastic properties (i.e., plasticity index) are brought about by this small size and relatively low layer charge of smectite minerals (Reid–Soukup and Ulery 2002).

EFFECTS OF CLAY IN CONCRETE AGGREGATE

He et al. (1995) evaluated the reactivity of six standard clay minerals added to Portland cement. They additionally calcined the clays at temperatures up to 950°C. Untreated clay minerals had higher water demand and reduced the compressive strengths of the Portland cement mortars, in relation to their surface area. However, the calcined clays had a reduced water demand and reacted with the Portland cement to form new reaction products that actually increased the strength of the mix.

Clay coatings show tendencies near the P200 threshold of 1.5 percent to concentrate air voids around coarse aggregate particles, disrupting the air void system. Clay coatings also significantly impact workability and require additions of water in the field which has the potential to weaken concrete. Furthermore, clay coatings at similarly high levels increase drying shrinkage by around 65 percent and produce noticeable differences in slump and durability.

Gullerud and Cramer (2002) identified three types of surface coatings on concrete aggregate. They identified as either one of the following: (1) dust (rock, quartz, feldspar, etc.), (2) clay (chlorite, smectite, etc.), and (3) carbonate material. They concluded that mineralogy was much more important than fine quantities, and that clay coatings were much more detrimental to durability than dust or carbonate coatings. In fact, the carbonate coatings actually increased strength.

In a subsequent study, Munoz et al. (2010) did more detailed analysis of aggregates from Wisconsin and looked at select clay mineral standards mixed with aggregate prior to addition in PCC. They noted problems with workability and increased water demand with all clay minerals (kaolinite, illite, calcium, and sodium smectite); however, the smectites had the greatest impact. The sodium smectite was very difficult to remove from the aggregate surface with washing and mixing, while much still adhered to the aggregate. Calcium smectite and kaolinite were more easily washed from the aggregate surface and tended to disperse into the cement matrix resulting in a less negative impact on strength. The sodium smectite failed the freeze–thaw durability after 16 cycles while the kaolinite performed well similar to the control with no clay. Munoz et al. (2010) concluded that the methylene blue test was good at identifying the bad fines, but it was not practical for WisDOT to implement.

The American Concrete Pavement Association (Anonymous 2004) issued a technical memorandum on how to prevent and repair clay ball contamination in concrete pavements. They state that management of stockpiles is essential for ensuring clay free aggregate stockpiles. They state that the loader operator is the most important person in producing consistent quality concrete. Clay balls can be problematic when they are numerous and large enough to compromise the structural integrity of the pavement. The void in Figure 2.1 was created by the disintegration of an extremely large clay ball in a Texas pavement.



Figure 2.1. Large Void Generated by Clay Ball in Pavement in Central Texas.

Fernandes et al. (2007) looked at the unconfined compressive strength (UCS) of sand contaminated with 20 percent of each kaolinite and smectite. The workability decreased with addition of clay minerals, and the smectite–contaminated sand required more water to provide adequate workability. The 20 percent smectite–contaminated samples had much lower UCS values than the kaolinite and pure sand samples.

EFFECTS OF CLAY IN BITUMINOUS AND SEAL COAT AGGREGATES

Kandhal and Parker (1998) list several problems caused by clay contaminating the aggregate in HMA. They state that clay coating the aggregate will be more absorptive to asphalt, which leads to lack of coating resulting in more moisture susceptibility and more risk of cracking. There will be more absorption due to clays, so moisture susceptibility will lead to stripping and durability problems during cold weather. Breakdown of weaker aggregate during construction will cause changes in gradation. As a result, the matrix will be unstable and rut–susceptible.

Woodward et al. (2002) conclude that clay derived from weathered basalt increases the stiffness of the asphalt mix. They explained that the increase of stiffness was due to the presence of smectite in weathered basalt. If the seal coat is excessively dirty or dusty, the asphalt binder will not be able to securely hold the aggregate in place. The asphalt will stick to the coating of dirt or dust and with traffic, the aggregate particles will be dislodged (Figure 2.2).



Figure 2.2. (a) Effect of Fines in Seal Coat Aggregate Surface with Excess Fines after Sweeping (b) Surface of Seal Coat with Clean Aggregate.

SUCCESSFUL USE OF CLAY-RICH AGGREGATES

The researchers did a cursory search of the literature to see what was being done to improve the quality of marginal aggregates. New Zealand researchers looked at two greywackes, one basalt, and one andesite quarry (Bartley et al. 2007). They collected fresh, partly weathered, and weathered rock from each quarry and added lime, cement, and durabind (mix of slag plus lime) to the aggregate to see if engineering properties improved. They determined that lime stabilized the weathered aggregate samples best and attributed the effectiveness of lime to the abundant smectite in the weathered aggregate.

Researchers from the University of Texas (Norvell et al. 2007) added methylene blue to aggregates containing clay mineral standards in contents of 1 percent and 4 percent by volume. The methylene blue reduced the demand for water reducing agents, but did not conclusively change compressive strengths in all clays except the montmorillonite treated samples. The compressive strengths in these samples improved slightly, which the researchers attributed to reduced demand for water-reducing additives.

Jeknavorian et al. (2003) experimented with superplasticizers in two natural sands and one laboratory-prepared sand with sodium montmorillonite. Other researchers reported that polycarboxylate-based comb-typed polymers (PCPs) did not work well in certain fine aggregate sources. The findings of previous researchers were confirmed by Jeknavorian et al. (2003) and they also determined that adding sacrificial agents such as polyethylene glycols (PEGs) coupled with the right sequence of material addition helped mitigate the adverse effects that smectite has on concrete mixtures.

ACCEPTABLE CLAY LIMITS IN AGGREGATES

There is not an abundance of information available on acceptable limits of clay in aggregate for use in HMA, seal coats, or PCC. Most state DOT agencies have limits like 1.5 percent by mass of fine materials (material that passes a No. 200 sieve) in the coarse aggregate. The Florida DOT uses 2 percent by mass passing the No. 200 sieve as a limit for coarse aggregate in HMA. No DOTs make any reference to the mineralogy of the fine materials.

The research sponsored by the Wisconsin DOT concluded that 0.7 percent smectite by weight was deleterious for concrete aggregate used in Wisconsin.

Yool et al. (1998) evaluated workability and UCS of different clay minerals in cement mortars. Their research showed that 1 percent of kaolinite by mass of cement causes a 2 percent drop in compressive strength, and 1 percent of smectite by mass of cement causes a 10 percent drop in compressive strength.

ENGINEERING TEST TO IDENTIFY CLAYS IN AGGREGATES

There are some engineering laboratory tests commonly run to identify clays in aggregates for PCC and bituminous mixes including the sand equivalent test (Tex-203-F), plasticity index (PI) (Tex-106-E), methylene blue test (AASHTO TP 57), determination of deleterious materials (Tex-413-A), and the decantation test (Tex-406-A).

The *sand equivalent test* measures the amount of clay-sized material in fine aggregates by mixing a calcium chloride solution with the sand and placing on a mechanical shaker for continuous agitation for a specified period followed by letting the sand/clay mixture settle for a time before obtaining a reading to determine the amount of clay-sized material. This tells you nothing about mineralogy, just the size of the fine material.

The *plasticity index* is an empirical test used to estimate the amount of swelling clay in a sample, where a higher PI indicates more swelling clay is present. This test is fairly good at estimating deleterious clay minerals, but the test results will vary depending on the experience of the technician.

The *methylene blue test (MBV)* is done by dissolving a certain amount of methylene blue dye in an aqueous solution and titrating with rock that has passed a No. 40 sieve. The methylene blue dye absorbs onto the mineral surfaces and into the interlayer region of expansive clay minerals (i.e., smectite). A glass stirring rod is used to dab each aliquot onto white filter paper until a blue halo is observed. When the blue halo is observed, the test is complete. This test can be subjective if the operator is not well versed in the method. Yukselen and Kaya (2008) show that this test does give a good estimate of cation exchange capacity (CEC) and specific surface area (SSA) in soils not containing zeolite minerals. Gullerud and Cramer (2002) determined that the methylene blue value was good at detecting clay coatings on concrete aggregates, and the MBV is related more to durability and not to the strength of concrete. In bituminous mixes, Kandhal and Parker (1998) determined that the methylene blue test is best related to stripping over the sand equivalency and plasticity index tests. The methylene blue test was also favored by NCHRP project 4-19 where they stated that there was a significant relationship between the rutting performance of wet pavements and the MBV.

The *decantation test* refers to the coating of aggregate particles with clays and/or the presence of weak, reactive, or unsound materials. The decant test is simply soaking aggregate in water for a minimum of 12 hours and washing through a No. 200 sieve. The amount lost through the No. 200 sieve is recorded. A similar test is determination of deleterious materials. It is simply spreading out an amount of coarse aggregate on a table and visually separating the clay lumps, shale, soft or friable, and laminated particles and recording the mass of each fraction with

respect to the total mass. Deleterious materials inhibit asphalt binder from coating the aggregate particles and sometime react with the environment. Some examples are clay lumps, friable particles, shale, coal, glassy particles, and free mica. The presence of free mica in HMA mixture is believed to reduce fatigue life and increase rutting (Seigel 1992).

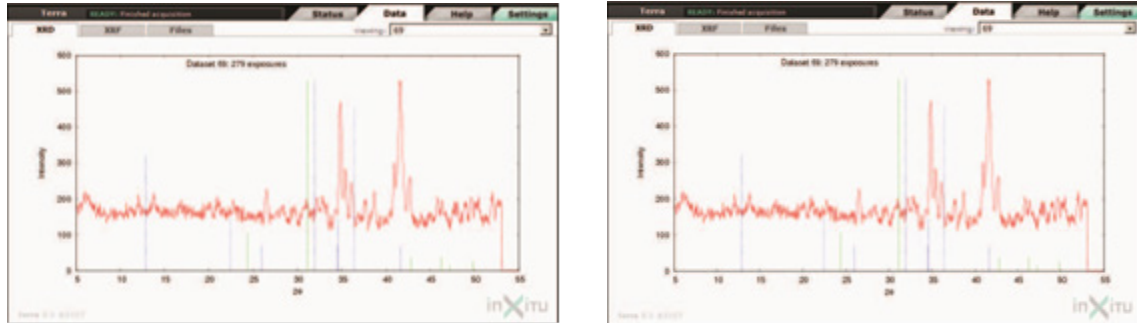
It can be concluded that the test methods mentioned above certainly have limitations in their ability to accurately detect clay minerals in aggregates. On the other hand, there are a few advanced techniques like X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR) and X-ray fluorescence (XRF) used to identify and quantify clay minerals that are present in aggregates. However, the problem with these innovative tools is that they require costly equipment and must be performed in the lab. With that being said, potential new tests (semi-quantitative to quantitative) to detect clay minerals at a field location are examined in this research project. Also, one of the main focuses of this project was to employ a new rapid test (i.e., modified methylene blue test) that can be used to accurately identify clay minerals that may be contained within aggregates.

POTENTIALLY NEW TEST TO IDENTIFY CLAY MINERALS IN AGGREGATE FINES

Soil scientists and geologists use a number of laboratory techniques to identify clay minerals; however, quantitative determination of clay minerals in a sample remains a long, labor intensive process. Therefore, we will focus on potential new tests (semi-quantitative to quantitative) to identify and quantify clay minerals in a sample at a field location.

X-Ray Diffraction and X-Ray Fluorescence

With the decreased size of instrumentation, many X-ray diffraction and X-ray fluorescence (XRD/XRF) analyses can be performed in the field with a portable unit. Terra (InXitu, Inc.) is one of the portable combination XRD/XRF systems; it was initially designed for rock and mineral analysis and can be used to analyze any powder samples. The unit has been tested in many places including remote sites such as the Antarctic. Its 2-D X-ray detector can measure the diffracted beam and the fluorescent X-rays from the sample simultaneously and therefore make it possible to obtain both mineral phase information and elemental composition of the studied phase (Figure 2.3). The data collected can be analyzed with its own or commonly used diffraction pattern processing software to perform mineral identification and quantification. A special model CheMin, with similar design to the commercial model Terra, was included in the payload of Mars 2009 Mars Science Laboratory mission and will be used to investigate soil and rock mineralogy on Mars (Sarrazin et al. 2005). A similar, non-invasive XRD/XRF instrument has been developed and used to study art works (Sarrazin et al. 2009).



(a)

(b)

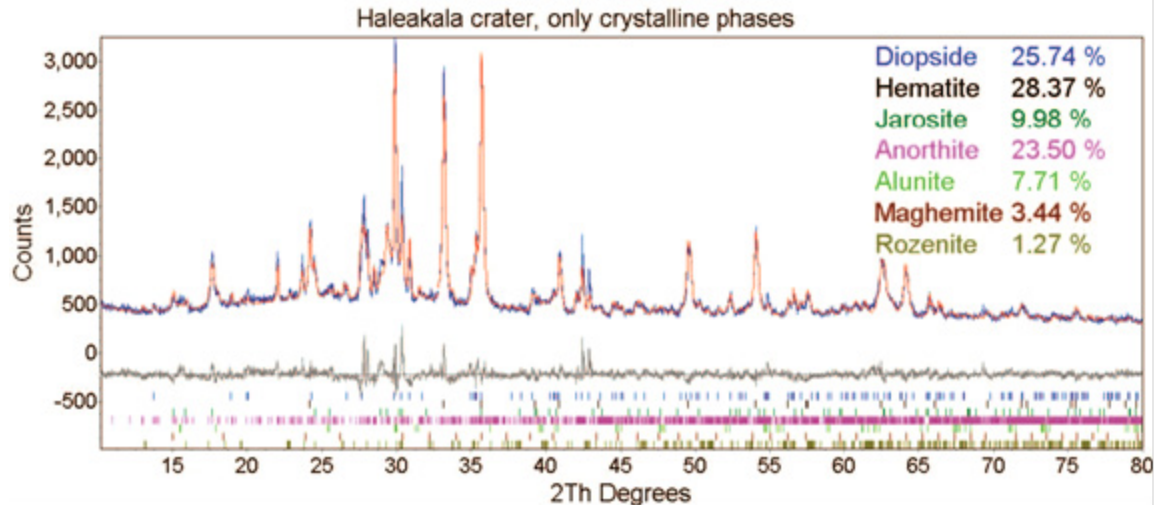
Photo sources: NASA and InXita, Inc.

Figure 2.3. (a) Mineral Analysis (XRD) and (b) Chemical Composition Analysis (XRF) Results from Portable XRD–XRF Combined Unit.

Desktop X–Ray Diffractometers

Several methods can be used to quantify minerals using the collected XRD patterns from the portable, desktop, or laboratory X–ray diffractometers. There is an increasing interest in fitting the observed XRD patterns with calculated patterns. Quantitative mineral composition information can be retrieved based on fitting the calculated patterns with the observed patterns. This approach is an outgrowth of the research of Rietveld (Rietveld 1967, 1969; Young 1993), which was originally used to refine crystal structures using neutron diffraction data. The X–ray diffraction data can be used in the refinement calculation too. This approach is done by minimizing the weighted and squared differences between the calculated and observed diffraction intensities at every step (Figure 2.4).

Most Rietveld refinement software can correct orientation, absorption, peak overlapping, and many other factors that affect the diffraction intensity. The Rietveld refinement can calculate diffraction patterns from crystallographic structures and chemical compositions. This approach works very well for highly crystalline minerals in soil, sediments, and rocks. Current Rietveld software, however, cannot fully model expandable clay minerals, especially the interstratification and disordered layer stacking, and therefore, the method has not been fully adopted by the clay mineralogy community. The XRD patterns of clay minerals can be modeled by 1–D XRD simulation software such as NEWMOD and MUDMASTER.



This example shows the observed and calculated XRD patterns and their difference of a sample taken from a cinder cone in the Haleakala Crater Valley, Maui, Hawaii. Dr. Holger Cordes (Bruker) did the calculation using TOPAS software.

Figure 2.4. Quantitative Analysis of Mineral Composition Based on Rietveld Refinement.

To overcome the accurate model problem in full pattern fitting, some researchers suggest using experimentally recorded diffraction patterns of standard minerals in the fitting (Figure 2.5). Software packages, FullPat (Chiperá and Bish 2002) and RockJock (Eberl 2003) use this approach. The drawback of this approach is that the standard library patterns are instrument-specific and cannot be shared between different laboratories. It also requires that the XRD patterns of the standard minerals are identical or very close to those in a sample.

Portable Infrared and Raman Spectrometers

With spectrum quality comparable to laboratory infrared and Raman spectrometers, many handheld portable infrared and Raman spectrometers have been developed and can be used in situ to detect and quantify interested minerals, chemicals, or other compounds. For example, the hand portable FT-IR spectrometer (Model 102) from D&P Instruments (Figure 2.6A) is a rugged remote sensing field and industrial instrument with the following features: lightweight, single package design, thermally stabilized interferometer, embedded computer, calibrated output with optional thermally stabilized blackbody, “through-the-lens” viewing of targets, high sensitivity and throughput, real-time on-screen spectra, and math processing, etc. The PerkinElmer Raman IdentiCheck (Figure 2.6B) combines the convenience of a portable, handheld triggered probe system with the performance of a highly specified laboratory instrument. It is an ideal choice for in situ Raman analyses performed in the field whereas the quality of the spectra is still guaranteed. The Raman IdentiCheck is packed into a portable, wheeled case, with retractable handle suitable for transportation. Jehlicka et al. (2009a) have observed well-resolved Raman spectra of sulfate minerals (gypsum, anglesite, barite) by a portable Raman instrument: the Ahura First Defender XL. Jehlicka et al. (2009b) also have reported recording Raman spectral signatures in situ for a series of minerals in outcrops using portable Raman instruments. Cerussite, anglesite, wulfenite, titanite, calcite, tremolite, andradite, and quartz were detected using the portable Raman spectrometer.

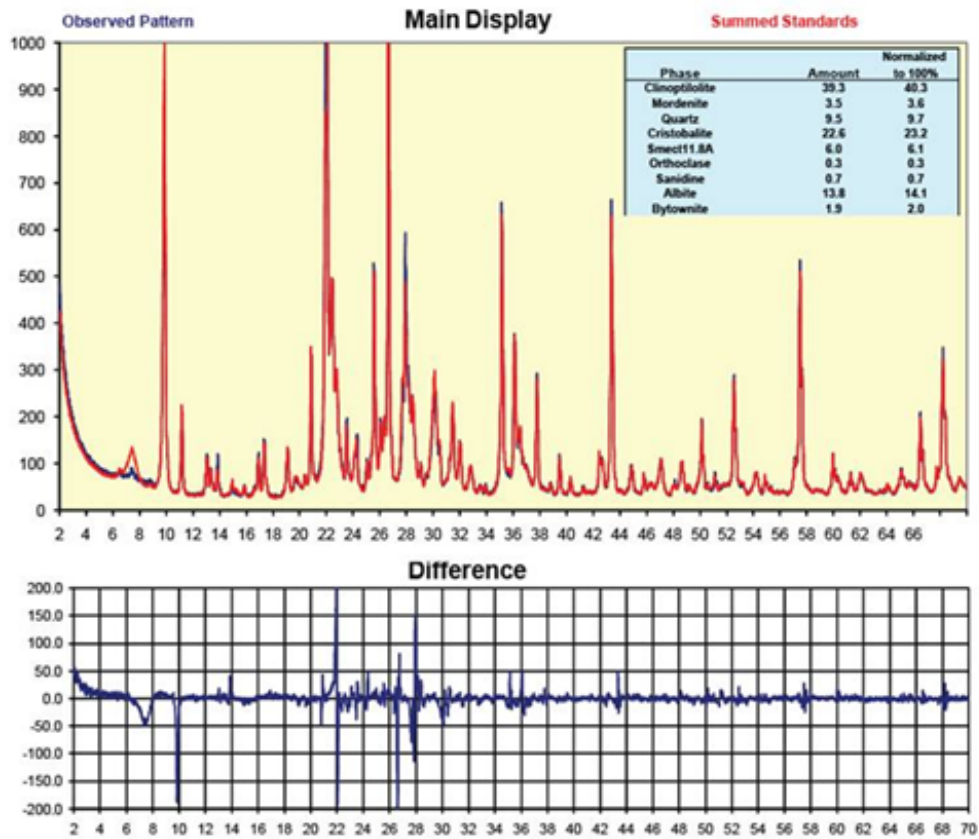


Figure 2.5. Observed and Calculated XRD Patterns and Their Difference in Program FullPat (Chipera and Bish 2002).

There is another Raman device called the Rockhound that contains a library of Raman Spectra for approximately 500 minerals and rocks. This device can be transported to the field to analyze samples at the stockpile. After talking to a representative from DeltaNu (Rockhound manufacturer), he stated that the 785-nm excitation of the Rockhound causes fluorescence and interferes with the signal from clay minerals. However, he mentioned another Raman device that has a 1064-nm excitation that does not fluoresce with clay minerals and may work in quantifying the clay minerals. This is a benchtop unit and is not conducive to use in the field.



(Photo sources: D&L Instruments and Perkin–Elmer, respectively).

Figure 2.6. (a) A Hand–Portable FT–IR Spectrometer from D&P Instruments (Model 102) and (b) a Portable Raman Spectrometer (Raman IdenticCheck) from PerkinElmer.

Diffuse Reflectance Spectroscopy

Diffuse reflectance spectroscopy is a rapid and economical analytical method that has been broadly used in industry, geology, soil survey, and research laboratories to analyze both inorganic and organic compounds. Many companies have developed portable visible–near infrared spectrometers for quality control, product screening, breeding selection, etc. One example of the portable visible–near infrared spectrometer AgriSpec from ASD Inc. is shown in Figure 2.7. This field portable Vis/NIR analyzer is designed specifically for analysis of a wide range of organic and inorganic materials in soils. It measures the intact soil samples without grinding or drying but still provides results similar to more processed samples for a wide range of soil properties. The instrument is also well suited for rapid in–field chemical and mineralogical composition analysis of sediments which, when measured by NIR, are similar to those measured in soils. It has been successfully used in predicting numerous soil properties such as clay content, organic carbon, total nitrogen, cation exchange capacity, sand fraction, silt fraction, clay fraction, copper, zinc, chromium, nickel, cadmium, and manganese (Viscarra Rossel et al. 2006, Bray et al. 2009, Viscarra Rossel et al. 2009).

The diffuse reflectance spectra in the visible–near infrared (vis–NIR: 400–2500 nm) and mid infrared (mid–IR: 2500–25000 nm) regions of the electromagnetic spectrum can be easily collected with the portable or laboratory spectrometers (Figure 2.8). Data acquisition is fast, accurate, and more economical than many other time–demanding methods. The spectrum bands are characteristic to organic and inorganic compounds in soils and sediments making them powerful for mineral quantification. The mid–IR contains more information about the minerals and organic compounds than the vis–NIR because there are more resolved fundamental vibration bands in the mid–IR range from inorganic and organic compounds. The bands in the

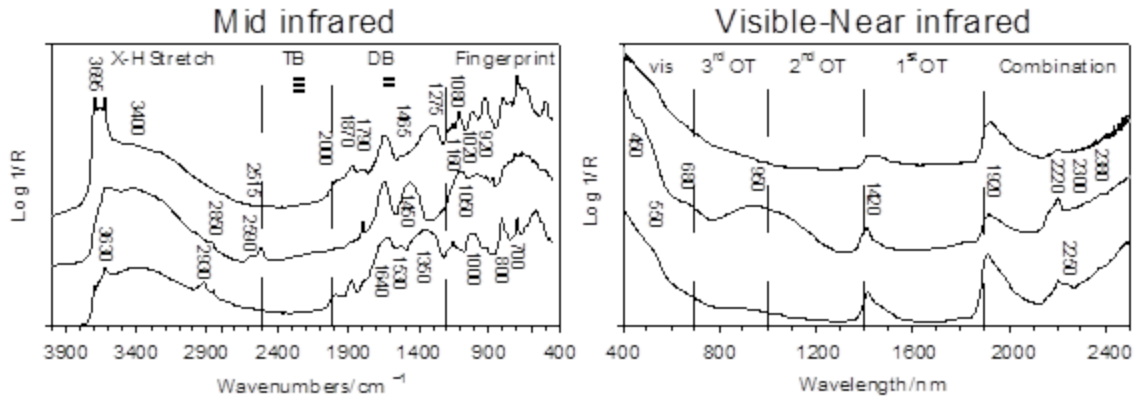
NIR range are the overtones or combinations of the fundamental vibrations, and many of them overlap with each other making the NIR bands broader, smoother, and much less abundant. Therefore, more robust calibration using mid-IR spectra can be performed across a wide range of samples (Viscarra Rossel and McBratney 2008).



Figure 2.7. A Portable Visible–Near Infrared Spectrometer from ASD Inc. (Model AgriSpec).

The success of the application of diffuse reflectance spectra in predicting mineral composition or other properties of soils and sediments relies on the establishment of chemometrics and multivariate statistical techniques in analytical chemistry. Chemometrics extract information from chemical systems by data-driven means using methods frequently employed in core data-analytic disciplines such as multivariate statistics, applied mathematics, and computer-science. Multivariate calibration refers to the use of empirical data and prior knowledge to predict an unknown property y from many spectroscopic measurements x_1, x_2, \dots, x_k , simultaneously via a mathematical transfer function (Viscarra Rossel and McBratney, 2008). Principal components regression and partial least squares regression are probably the most commonly used in the multivariate analysis. Other methods, such as multiple linear regression, step-wise multiple linear regression, radial basis function networks, multivariate adaptive regression splines, and artificial neural networks have been employed by many research groups too (Viscarra Rossel and McBratney 2008). Several commercial software and shareware such as ParLeS (Viscarra Rossel 2008) have been developed in recent years to maximize the accuracy of the prediction on a variety of samples.

The VIS–NIR spectroscopy method is easy to use and has been successfully used to predict many soil properties and clay mineralogy composition, while the major hurdle for implementation of this method in mineral quantification is to get the calibration library. To establish that library, many samples, up to hundreds, if not thousands, need to be fully analyzed using other methods such as Rietveld refinement and chemical analyses. The specimens used in the library must have similar properties as the unknown samples that are going to be analyzed. Unfortunately, there is no easy and quick quantitative method for full mineral quantification yet.



DB: Double Bond, TB: Triple Bond, and OT: Overtone (Viscarra et al. 2008).

Figure 2.8. Soil Diffuse Reflectance Spectra in the Mid Infrared (left) and Visible–Near Infrared Range (right).

Staining Tests

There are some simple staining tests that have proven useful for identifying poor quality aggregate. Alizarin Red–S and potassium–ferricyanide were used by Wojakowski and Hossain (1996) to identify poor quality limestone aggregates in concrete pavements in Kansas. If the aggregate stained purple, then it was good; if the aggregate stained blue or yellow, then it was a poor carbonate aggregate. They did not state what caused the aggregate to perform poorly. Later, research by the Kansas DOT showed the staining techniques to be too variable in predicting aggregate quality. Bartley et al. (2007) report using methylene blue to stain thin–sections of weathered basalt for deleterious clay minerals (smectite); they indicate that the basalt altered to smectite can be distinguished in thin–section by the blue stain of the methylene blue. However, this technique does not lend itself to use in the field since preparation of thin–sections is time consuming and reserved for the laboratory.

Gamma Ray Scintillometer

A new technique proposed by researchers for the Kansas DOT is the use of a spectral gamma ray logging tool to detect deleterious clay minerals (Emry et al. 2006). A spectral gamma ray scintillometer can measure potassium, uranium, and thorium which are major sources of gamma radiation in rocks. The observations on the use of gamma ray scintillometry by Emry et al. (2006) are: (1) clay Minerals have significantly higher potassium content than carbonates; (2) clay minerals are often associated with organic matter that fixes uranium; and (3) some clay minerals can absorb thorium (Doveton, 1994). They used the GF Instruments GRM 260 scintillometer to measure potassium, uranium, and thorium in one–foot intervals at the working face of 10 area quarries. They concluded that the potassium content best reflected aggregate durability (determined by the Freeze Thaw test) and developed an Excel spreadsheet to calculate durability based on potassium content measured by the scintillometer.

A gamma ray scintillometer is different from a Geiger counter in the way that it detects X–rays. Geiger counters have a cylindrical detector filled with an inert gas (e.g., He, Ar) with a wire placed in the center of the cylinder. X–ray photons enter the cylinder and interact with the gas to form He⁺ and an electron called a primary ion pair. The electron is attracted to the

positively charged wire in the center of the cylinder. If a voltage is applied to the wire, the electrons moving to the center wire are accelerated to a point where they can collide with and ionize other filler gas molecules (Robinson 1970) and generate secondary ion pairs. At a high enough voltage, small changes in voltage do not affect the current. At that point, the current is dependent on changes in the X-ray intensity which is the basis for the Geiger counter (Robinson 1970).

In a scintillation detector, X-ray radiation hits compounds that emit visible light when bombarded by the radiation (Robinson 1970). The light is detected by a photomultiplier and quantified based on the amount of light emitted. This detector is more sensitive than a Geiger counter and can differentiate between different elements that emit gamma-ray radiation (i.e., potassium, uranium, thorium).

Modified Methylene Blue Test

As mentioned previously, there is a currently used laboratory procedure that involves using methylene blue dye to identify clays in aggregates. The methylene blue dye absorbs onto the mineral surfaces and into the interlayer region of expansive clay minerals such as smectite. However, this test method is fairly user-subjective; therefore, there is the potential for high variability in the test results.

There is a new test procedure developed by W.R. Grace, the modified methylene blue test, which involves a similar methylene blue dye to identify clay minerals in aggregates based on the amount of absorbance as measured by colorimeter. The modified methylene blue test is simpler and quicker to run than the existing methylene blue test. The test also has merits to replace some of the existing test methods to identify clays in aggregates, as the test has given accurate results with good repeatability. More of this test method will be presented in Chapter 3, and more extensively in Chapter 4, where the test procedure along with results will be presented. Table 2.1 gives a summary of the potentially new tests to identify clays in aggregates.

RESULTS OF THE WEB SURVEY TAKEN BY TXDOT EMPLOYEES

There was a survey that the research team submitted to the 25 TxDOT districts in attempt to assess the problems the districts are experiencing with clays/fines in aggregate sources. Eleven questions were asked related to testing and performance of aggregates in HMA, seal coats, and PCC. There were a total of 17 respondents to the survey (Appendix A). Results from the survey tell the research team that most districts (12 responses) are not aware of durability issues with aggregates used in HMA, seal coats, or PCC. Eight districts did not take the survey, so we can only assume that they are not aware of any problems caused by clay in the aggregates. The question the researchers ask is how do the districts know that there is not a problem with durability if they do not do any durability testing with the finished product (asphalt, seal coats, or concrete)?

Table 2.1. Potentially New Tests to Identify Clays in Aggregates.

POTENTIAL TEST	LOCATION WHERE USED	DETAILS
Portable XRD/XRF unit	Field	Gives both mineral phase information and elemental composition of the test sample – may not be very effective to detect clay minerals.
Desktop XRD unit (with Rietveld refinement)	Lab	Patterns collected can be used in crystalline phase identification, quantification, and structural analysis. The method has not been fully adopted by the clay mineralogy community.
Portable infrared and Raman spectrometers	Field	Can be used in situ to detect and quantify minerals, chemicals, or other compounds – may work in quantifying the clay minerals.
Diffuse reflectance spectroscopy	Field	Well–suited for rapid in–field chemical and mineralogical composition analysis of sediments or soils. It has been successfully used in predicting clay content/clay fraction, organic carbon, cation exchange capacity etc.
Spectral gamma ray scintillometer	Field	Used to detect clay minerals through the measurement of potassium, uranium, and thorium (major sources of gamma radiation) – some non–clay minerals could be a potential source of these elements, too.
Modified methylene blue test	Lab or field	Used to detect clay minerals in aggregates based on level of dye absorbance as measured by colorimetry.

CHAPTER 3

MINERALOGICAL EVALUATION AND QUANTIFICATION OF PURE CLAYS IN AGGREGATE FINES USING ADVANCED RESEARCH LABORATORY TOOLS

POTENTIAL TEST METHODS

The quantification of clay minerals in rock and soils is very difficult and time consuming (Dixon and White 1999). Proper identification requires some expertise in mineralogy and various analytical techniques that provide complimentary information. The results are semi-quantitative estimates at best using current technology. The Texas Department of Transportation is interested in evaluating different test procedures that will estimate the quantity of deleterious clay minerals in an aggregate sample. To be of benefit to TxDOT, the test needs to be simple to run and preferably be run in the field. To achieve this goal, the researchers evaluated two clay mineral standards using various analytical techniques.

Two clay minerals were chosen that are ubiquitous in Texas weathered aggregates and soils to evaluate the different test procedures for quantification of the clay minerals. A kaolin deposit from Georgia and a bentonite from Gonzales, Texas were characterized using standard procedures outlined in Dixon and White (1999). The primary mineral in the Georgia Kaolin is kaolinite, and the Gonzales bentonite is dominated by a calcium-saturated smectite.

Currently, the best way to quantify clay minerals in aggregates is involved wet chemical pretreatments on the aggregate to remove cementing agents like carbonates and organic matter, and then the clays must be dispersed with water of pH 10 and centrifuged to separate the different size fractions (i.e., sand, silt, coarse, and fine clay). Appendix B contains a detailed explanation of the steps necessary to fractionate the different particle sizes (e.g., sand, silt, and clay) in order to identify and quantify clay minerals in an aggregate fine sample. X-ray diffraction (XRD) is used as the main tool to accurately quantify clay minerals. In order to prepare samples for XRD testing, there are a few steps involved to get the samples ready for testing. These steps include the following: pretreatments for clay mineralogy, dispersion and fractionation, and preparation for XRD analysis (Appendix B).

In addition to XRD quantification, the research team also used other advanced techniques to identify and quantify pure clay minerals. These other methods included X-ray fluorescence (XRF), fourier transform infrared spectroscopy (FTIR), and turbidity methods. The main practical laboratory test used in this chapter was the modified methylene blue (MMB) test, with the hopes of finding a strong correlation based on the results of the advanced quantification techniques. A strong correlation between MMB test results and the results from the advanced techniques will support the MMB's accuracy in detecting clay minerals along with differentiating between the two pure standard clays used (bentonite as swelling vs. kaolinite as non-swelling clay).

CHARACTERIZATION OF THE PURE CLAYS

Grain Size Analysis

Results of the detailed analyses of the two clay mineral standards are presented here. Table 3.1 lists the grain size analyses of the two standard materials; the kaolinite is dominated by coarse clay while the bentonite has a surprisingly large concentration of minerals in the silt size range. However, the fine clay fraction makes up over 23 percent of the sample. The CEC of the kaolinite is low which is expected, and the bentonite has a CEC typical of a sample dominated by smectite.

Table 3.1. Clay Mineral Standards' Grain Size Data.

Sample Name	Grain Size				CEC
	Sand (%)	Silt (%)	Coarse Clay (%)	Fine Clay (%)	
Georgia Kaolinite	0	22.2	63.8	14	6.7
Texas Bentonite	1.1	45.6	29.6	23.7	77.6

X-Ray Diffraction Testing

For the clay mineral standards, the chemical pretreatments were not performed because the standard minerals were processed before the researchers received them. The kaolinite was dispersed with distilled water, and two separate aliquots were placed on glass and vycor slides for XRD analysis. The kaolinite was saturated with magnesium and potassium, but the cation saturation does not influence peak position because these cations do not substitute in the kaolinite structure and will not affect the XRD pattern of the kaolinite.

As seen in Figure 3.1, the sample is monomineralic according to the XRD analysis. The pattern shows peaks at 7.167 and 3.569 angstroms (\AA), which are diagnostic of kaolinite. The peaks do not shift upon ethylene glycol solvation, and the 7 \AA peak disappears upon heat treatment at 550°C. This XRD pattern is very simple and easy to interpret, which is exactly what we want for our clay mineral standards.

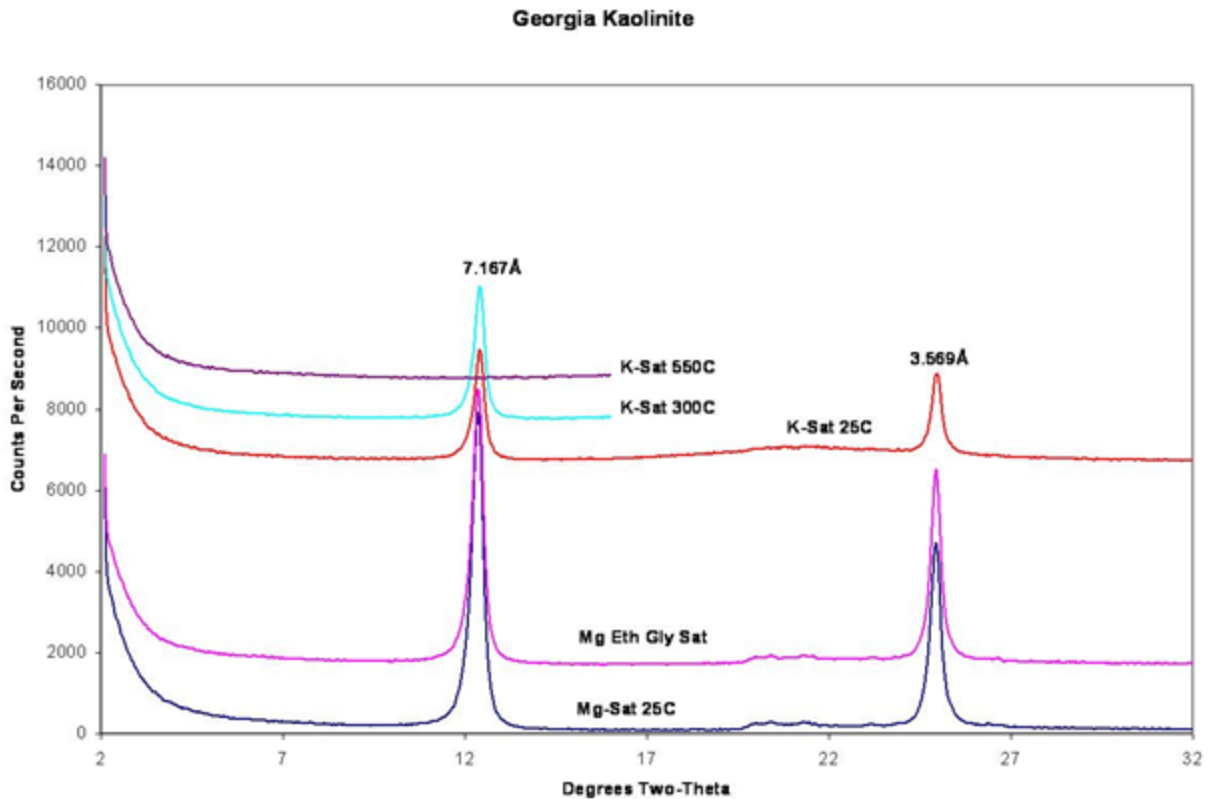


Figure 3.1. XRD Pattern of Oriented Kaolinite Standard Mineral.

The Texas bentonite standard is shown in Figure 3.2 and shows a pattern that is a little more complex. Note how the 15.4Å peak shifts upon ethylene glycol solvation to 16.5Å. The expansion of the d-spacing tells us that the sample has expansive clay (i.e., smectite). Upon heat treatment, the 15.4Å peak collapses to 9.7Å. The patterns for the bentonite sample are relatively clean (i.e., not many peaks), which indicate that the bentonite is predominantly smectite in composition.

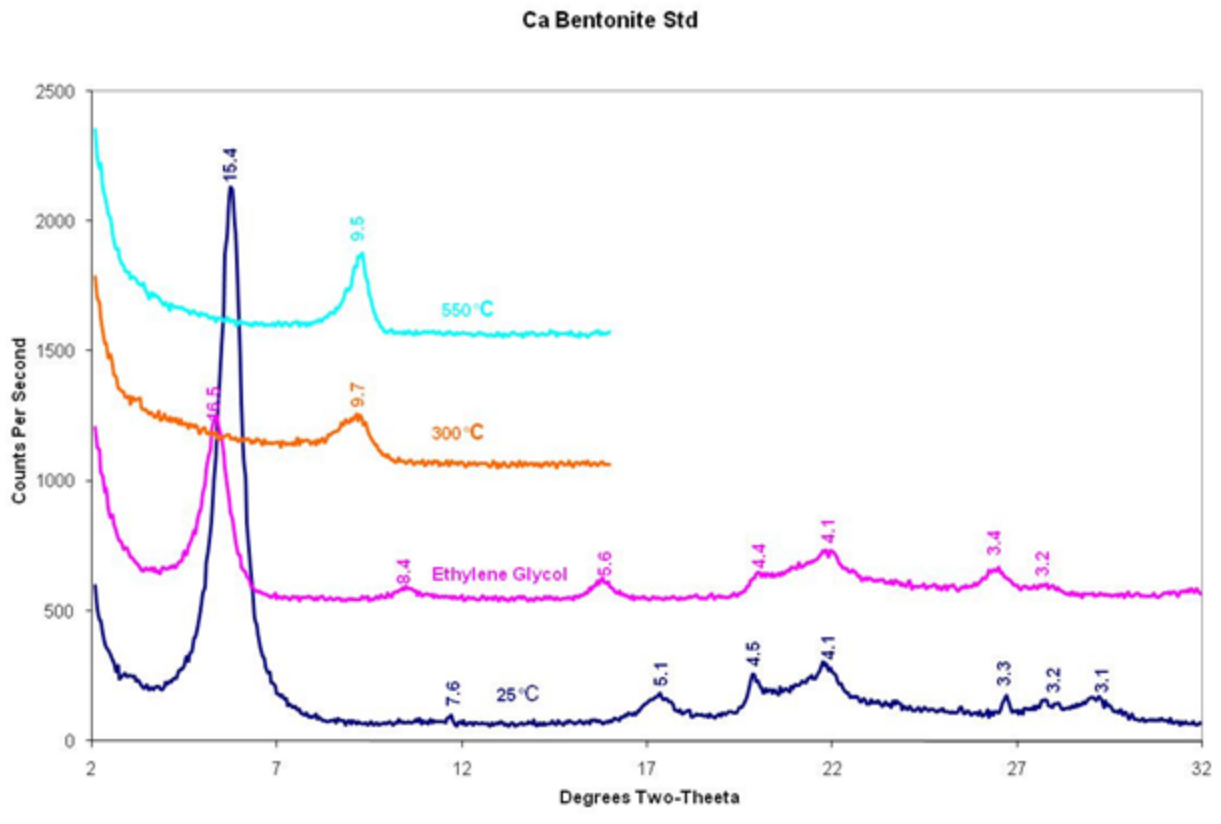


Figure 3.2. XRD Pattern of Oriented Bentonite Standard Material.

Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR data for the two clay mineral standards were collected on a Perkin Elmer Spectrum 100 FT–IR under atmospheric conditions using a diffuse reflectance sampling accessory (DRIFT). Each sample was prepared by mixing 5 mg of clay with 300 mg of potassium bromide (KBr). Figure 3.3 shows the FTIR pattern for the Georgia kaolinite standard clay. The sharp peak at an absorbance of 3686 cm^{-1} is diagnostic of the OH–stretching band for kaolinite and can be used to identify kaolinite in a sample. As will be seen later, kaolinite may be detected in minute percentages using this technique if there are not many other minerals to interfere with absorbance bands of kaolinite.

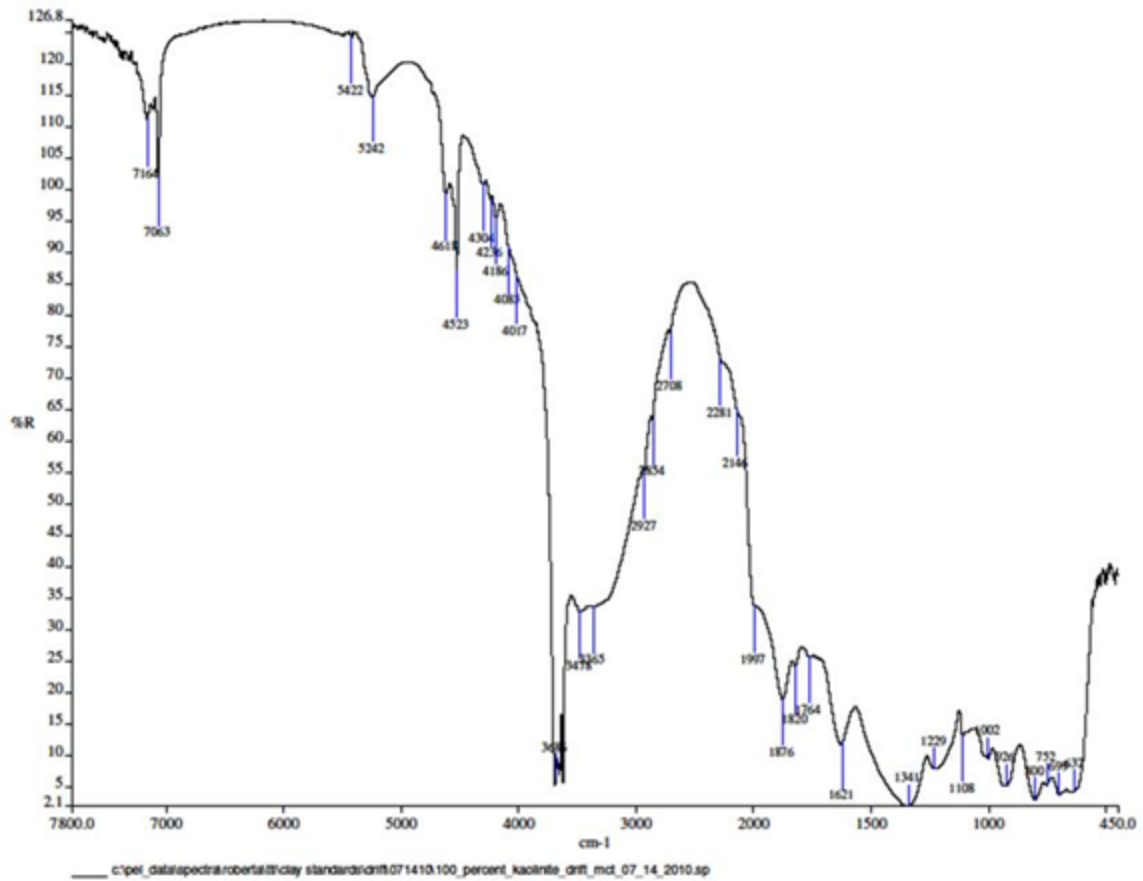


Figure 3.3. FTIR Data for Kaolinite Standard Material.

Figure 3.4 is the FTIR pattern for the Texas Bentonite standard. The broad band at 3416 cm⁻¹ is from adsorbed water. The band at 3629 cm⁻¹ suggests that the octahedral sheet is predominantly composed of aluminum. As other minerals are added to these patterns, there is a significant amount of peak overlap, so interpretation of the patterns becomes more difficult.

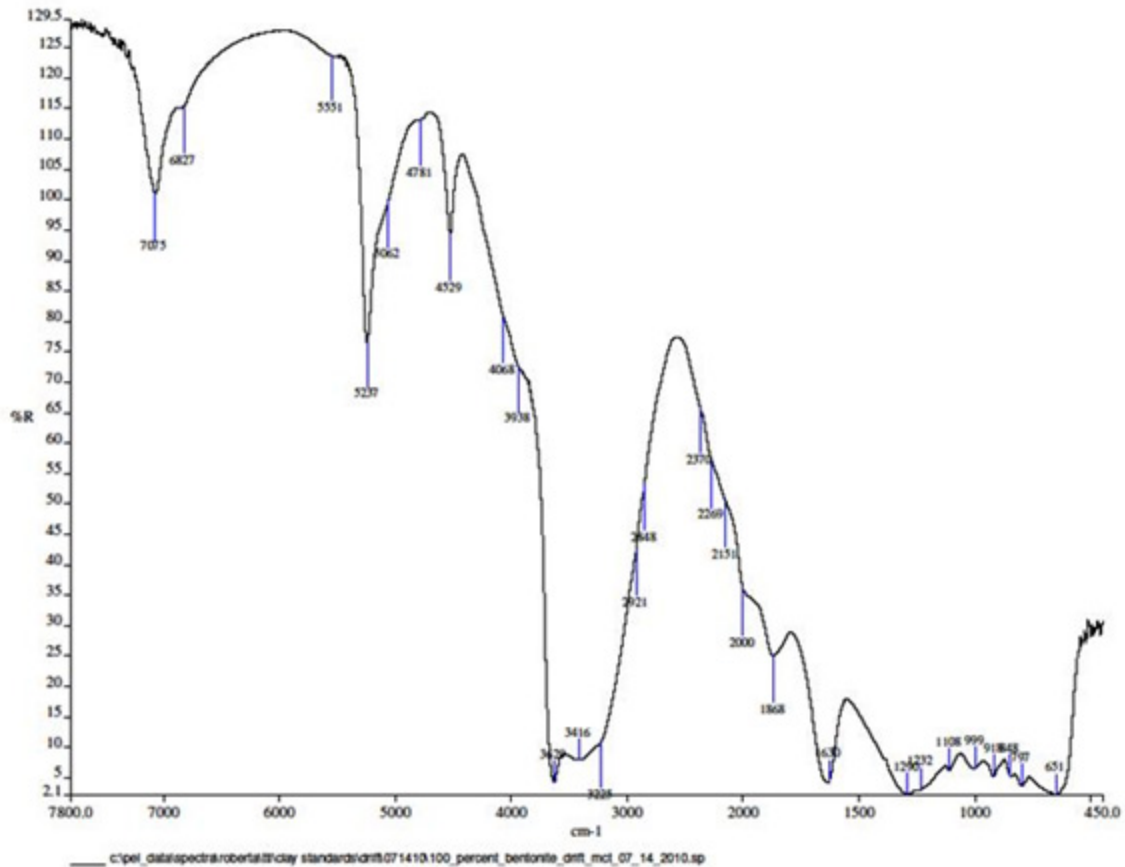


Figure 3.4. FTIR Data for Bentonite Standard Material.

Differential Scanning Calorimetry (DSC)

DSC is commonly used to measure the heat flux in an unknown sample relative to a standard material. One gets peaks and valleys in the curve (Figure 3.5) that represent endothermic and exothermic reactions. An endothermic reaction (valley) is where more heat is required to change the material from one phase to another. An example of this is removal of free water from smectite, which usually occurs at around 100°C. The bentonite shows a doublet in the low temperature (~120°C) range that has been attributed to divalent interlayer ions. The endothermic peak at about 700°C has been attributed to the loss of the hydroxyl radical (Kerr et al. 1949). The kaolinite has an endothermic peak centered around 520°C and an exothermic peak around 990°C. The endothermic peak has been used to tell about grain size with lower temperatures equating to finer grain sizes (Kerr et al. 1949). The peak at 990°C has been attributed to crystallization of a new phase from the kaolinite and is diagnostic.

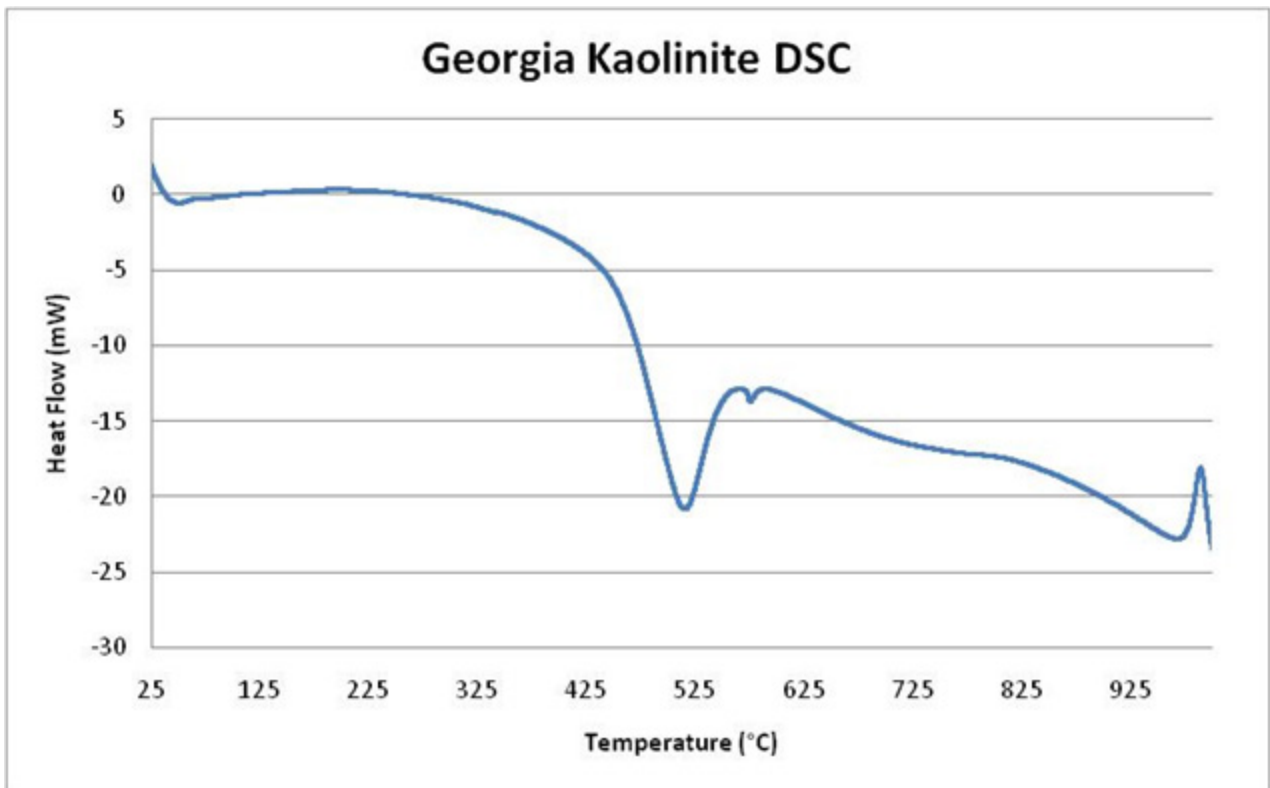
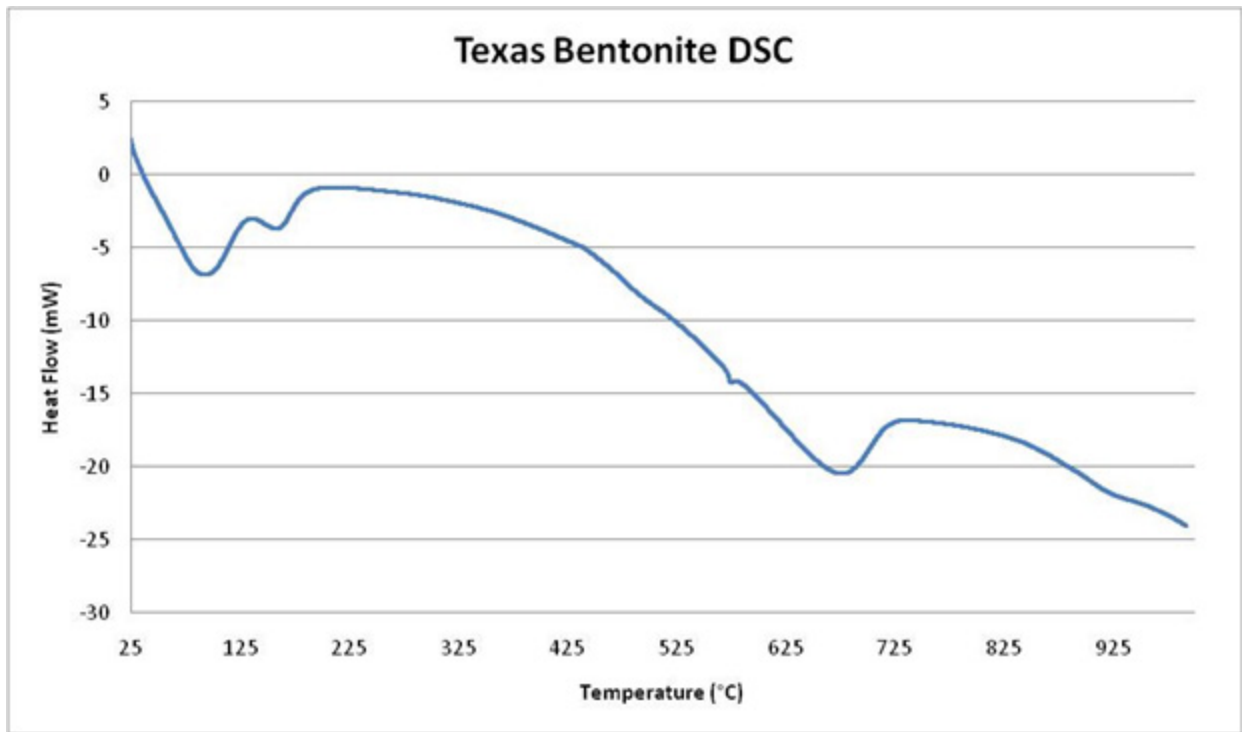


Figure 3.5. DSC Data for the Texas Bentonite (top) and the Georgia Kaolinite (bottom).

After the full mineralogical characterization of the two clay mineral standards (presented above), the research team wanted to employ similar testing methods to quantify different

percentages of the clay mineral standards mixed with another pure material (i.e., quartz sand from Carthage, Illinois). Quartz was chosen because it is ubiquitous in rocks and soil environments. It generally dominates the XRD patterns of most soil and rock samples. Techniques like XRD/XRF, FTIR, turbidity, and the MMB test were also used to quantify the clay minerals standards combined with the quartz sand.

QUANTIFICATION OF PURE CLAY MINERALS IN STANDARD MIXES

X-Ray Diffraction Testing

XRD analysis is one of the ultimate standard methods for mineral identification and quantification. Yet, direct mineral quantification using XRD for complex samples such as natural soils, sediments, or dusts, is still challenging. This is because several factors can interfere with the XRD peak width and intensity and thus the quantification. These factors include: particle size, crystallinity, structural defects in natural samples that are difficult to model, overlap of peaks from different minerals, and chemical composition variations of a particular mineral (i.e., solid–solution series).

To explore the feasibility of using XRD for direct clay mineral quantification, we artificially mixed reference clays: a bentonite from Gonzales, Texas, and a kaolin from Georgia, both with quartz sand. The clay contents in the mixtures were varied from 1, 2, 4, 6, 8, and 10 percent. Their XRD patterns were recorded on a Bruker D8 ADVANCE X-ray diffractometer with Cu K α X-ray source operated at 35 kV and 40 mA. Sample radiation length was set to 12 mm during the XRD analysis.

The XRD patterns (Figures 3.6 and 3.7) of both clays suggest that a minimum of 4 percent of clay must be present in the mixture in order to show visible characteristic diffraction peaks of the clay minerals, such as the (001) diffraction peak of kaolinite at 7.1 Å and the (001) diffraction peak of smectite at about 15 Å. As most aggregates used by TxDOT are gravels or sands, it is very unlikely that those aggregates will have such a high concentration of smectite or kaolinite. Direct XRD analysis of the bulk samples will not be adequate for clay mineral quantification in the aggregates. To quantify the clay minerals using XRD, the clay minerals have to be concentrated and go through the series of standard treatments outlined at the beginning of this chapter.

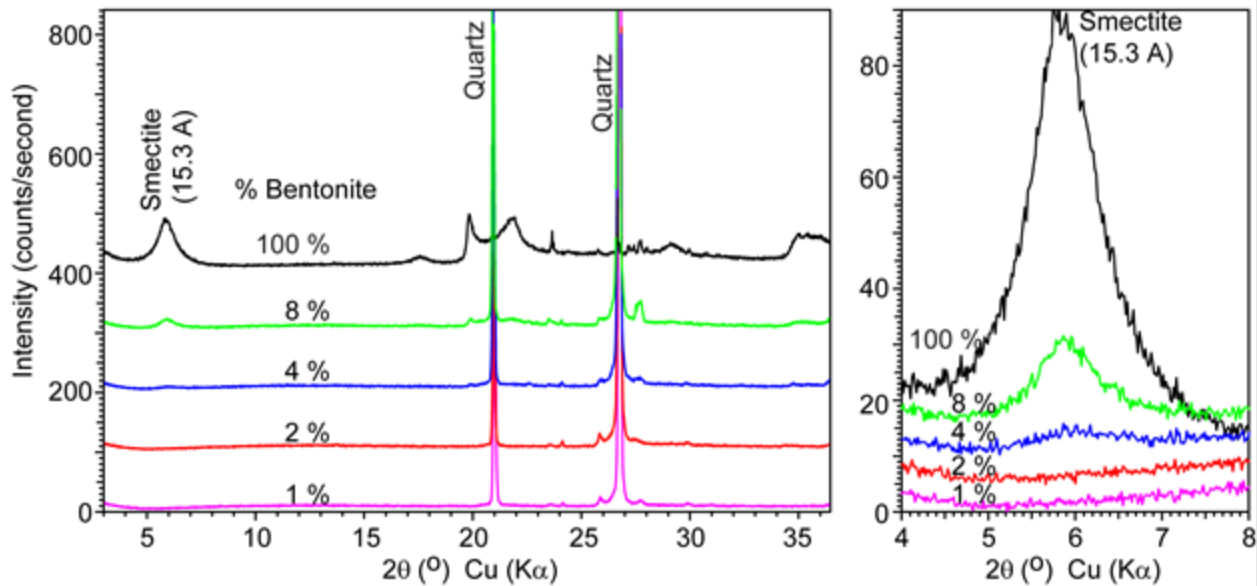


Figure 3.6. XRD Patterns of Artificial Mixtures of Bentonite Clay and Quartz Sand.

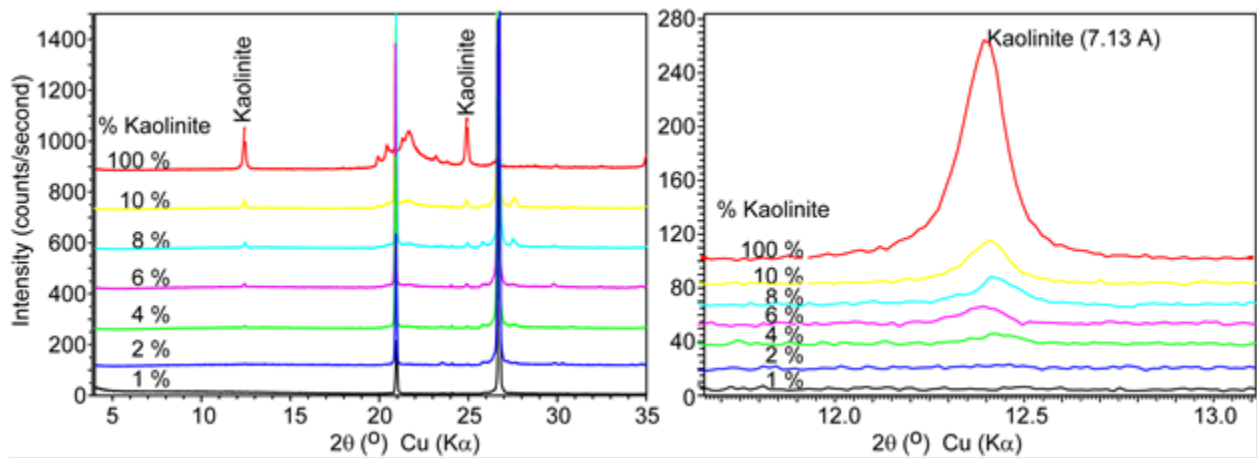


Figure 3.7. XRD Patterns of Artificial Mixtures of Kaolin Clay and Quartz Sand.

X-Ray Fluorescence

XRF is used to detect elemental composition of a bulk sample. It cannot tell anything about crystalline structure. The researchers used a ThermoFisher handheld XRF unit to try detecting different clay minerals mixed in low concentrations with the quartz sand. Initially, we thought that radioactive elements like potassium, thorium, or uranium may be used to detect different clay minerals. We also thought that titanium may be used as a proxy for clay content.

Table 3.2 presents averages of five analyses of four different elements that the researchers thought may be used to estimate the amount of different clay minerals present in an aggregate sample. Data were collected in Soils Mode for 120 seconds for each of the analyses. Titanium was high in both clay mineral standards, so it would not be good to differentiate between clay minerals. Potassium was high in the sand as well as the clay minerals due to the presence of feldspar minerals, so feldspars preclude using potassium content as a proxy.

Thorium was detected at 42 ppm in the 100 percent bentonite; however, in the samples where the bentonite was at 6 percent or less of the total sample, thorium was not detected. XRF really did not provide any unique elemental combinations that could be used to distinguish different clay minerals.

Table 3.2. Elemental Concentration of Standard Clays Using Handheld XRF Unit.

Sample	Ca (ppm)	Ti (ppm)	K (ppm)	Th (ppm)
Bentonite				
1%	1112	367	3302	ND
2%	803	409	3680	ND
4%	348	444	3364	ND
6%	735	452	3220	ND
100%	10053	1336	2323	42
Kaolinite				
1%	1120	466	2991	ND
2%	258	775	3400	ND
4%	0	558	3074	ND
6%	0	671	2843	ND
100%	428	1862	0	18
St Peter Sd				
100%	ND	296	3519	ND

Fourier Transform Infrared Spectroscopy

FTIR can be used to analyze materials regardless of their crystalline status. We attempted using attenuated total reflection infrared spectroscopy to analyze the above artificial bentonite–quartz sand and kaolin–quartz sand mixtures, but the spectra were too noisy to be used for adequate identification and quantification. However, when the samples were analyzed in the diffuse reflection mode, high–quality spectra were successfully obtained (Figure 3.8).

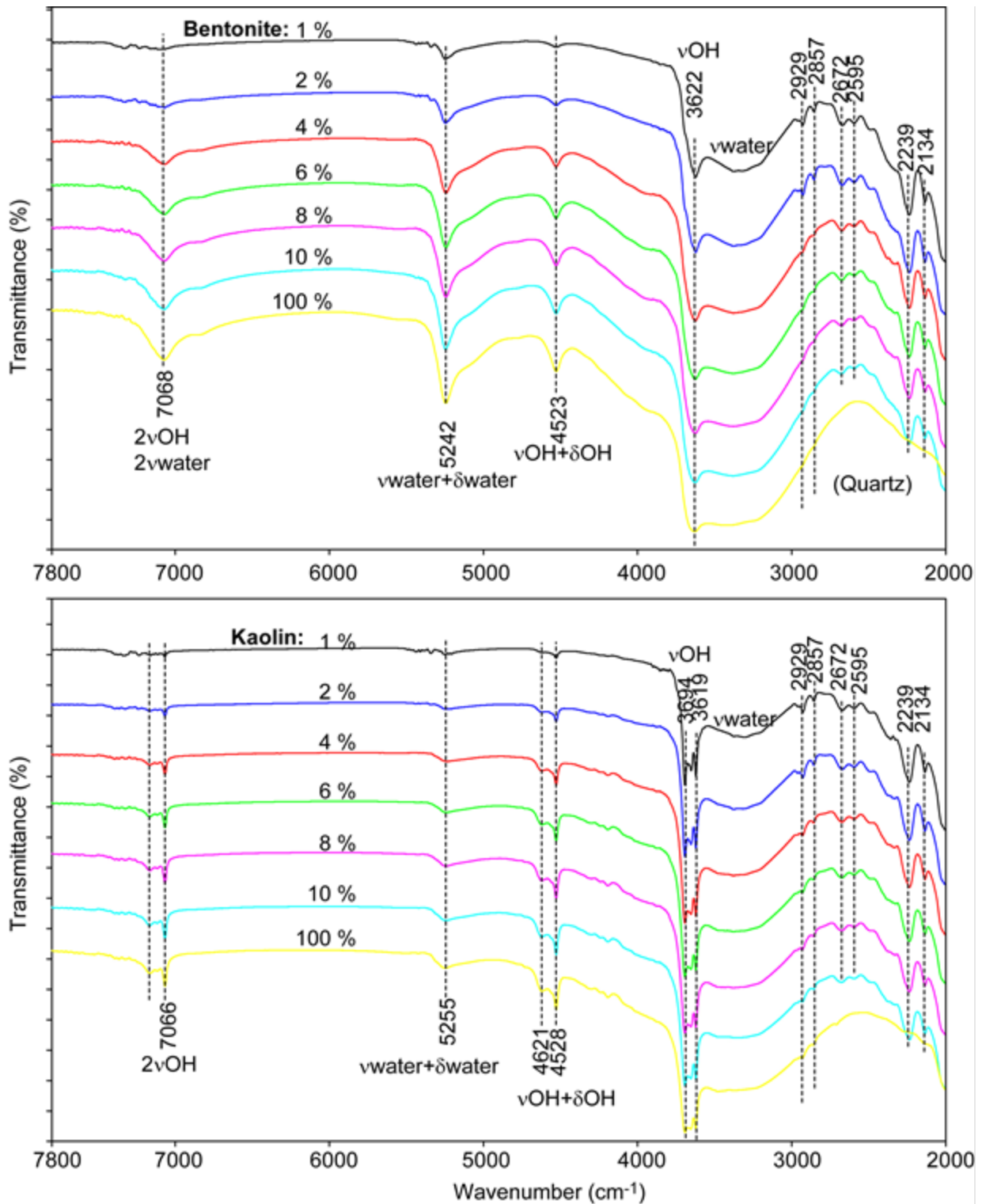


Figure 3.8. Diffuse Reflection Infrared Spectra of Artificial Mixtures of Bentonite with Quartz Sand (top) and of Artificial Mixtures of Kaolin with Quartz Sand (bottom).

Contrary to XRD analysis, the infrared spectroscopy is very sensitive in detecting kaolinite and smectite. In the simple artificial mixtures, very distinct smectite and kaolinite

infrared bands can be detected at the 1% clay level. For example, very intense infrared bands were observed at 7068, 5242, 4523, and 3622 cm^{-1} in all of the bentonite–quartz sand mixtures (Figure 3.8, top). The 3622 cm^{-1} band is due to the stretching vibration of octahedral OH group in smectite; the 7068 cm^{-1} is the overtone of this stretching vibration. The 4523 cm^{-1} band is due to stretching and bending combination of the OH group. Smectites can adsorb substantial water, and the adsorbed water molecules have broad infrared bands at about 3400 cm^{-1} and 5242 cm^{-1} .

Intense infrared bands of kaolinite can also be detected at low kaolinite levels: the characteristic bands at 3695, 3670, 3650, and 3619 cm^{-1} , which due to the OH stretching vibrations of various phase relationships of the inner surface OH groups, were very intense in all of the kaolin–quartz sand mixtures (Figure 3.8, bottom). The overtones of these stretching vibrations occurred in the 7173–7066 cm^{-1} range, and the combinations of the stretching and bending vibrations occurred in the 4621–4528 cm^{-1} range, even though these bands were less intense than the fundamental stretching vibrations.

Positive correlations exist between the clay content and the integrated absorbance of the infrared bands (Figure 3.9), yet the correlations are not simple, linear correlations in the clay content ranges tested. It appears that good linear correlations between kaolinite content and the 4493–4581 bands or 7043–7092 bands can be obtained when kaolinite content is less than 4 percent. We expect the bands in the range 3600–3700 will be more sensitive for kaolinite. Smectite bands are generally much broader than the kaolinite bands. The fundamental stretching band at 3622 cm^{-1} of the bentonite is more sensitive.

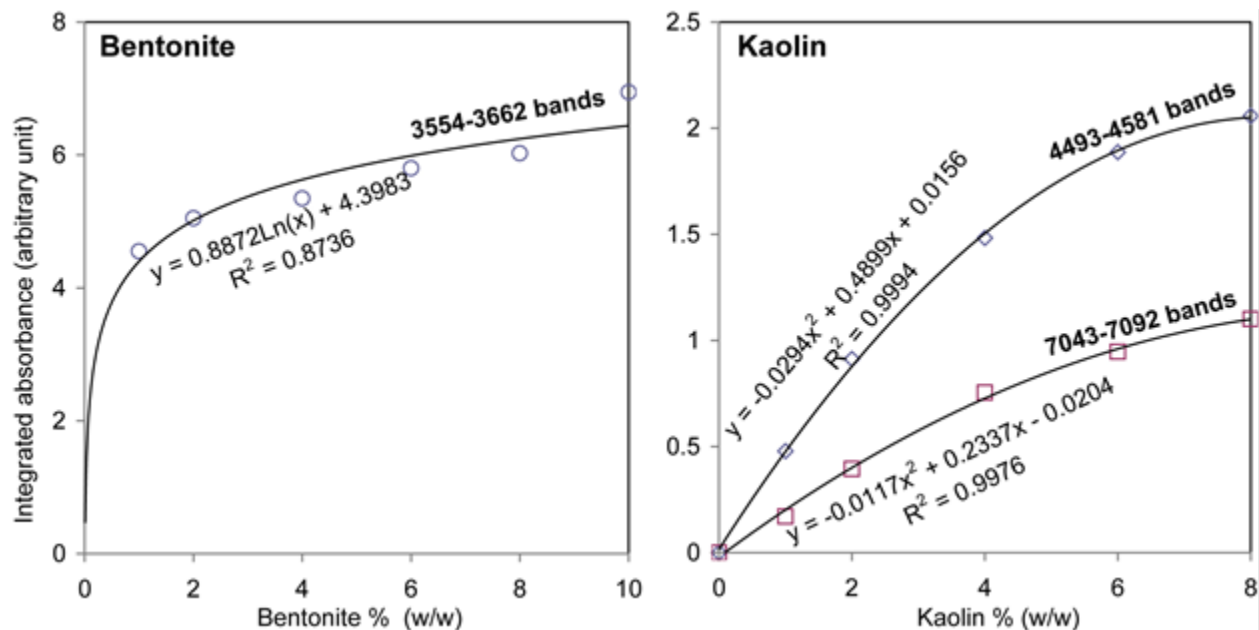


Figure 3.9. Correlations of Integrated Infrared Absorbance and Contents of Clays in Artificial Bentonite–Quartz and Kaolin–Quartz Mixtures.

The high sensitivity of infrared spectroscopy and the positive correlations of the infrared absorbance and clay content suggest that the infrared analysis can be a candidate method for clay

quantification. The major challenge of using this method will be the overlap of the infrared bands of several minerals in the natural samples. For example, the bands at about 3620 cm^{-1} are common to nearly all layer silicate minerals that have dioctahedral sheets in their structures. Adsorbed water bands occurring around 3640 cm^{-1} can interfere with the intensity of this band. Similarly, the overtones and the combinations of the stretching–bending of the clay minerals overlap. More sophisticated statistical methods, such as multivariate analysis and chemometrics using partial least–squares regression (PLSR), need to be investigated to deal with the natural samples. The PLSR analysis is becoming increasingly popular in rapid quantification of inorganic and organic components in soils, ores, and sediments. This method, however, needs a large reference library to create the calibration curves. This might be a research area for TxDOT if the rapid field mineral quantification method is critical for aggregate evaluation.

Turbidity

Since turbidity is evaluated as a method to rapidly and accurately quantify clay minerals, we explored the correlation between turbidity and concentration of two standard clay minerals, smectite and kaolinite. We collected the ($< 2\ \mu\text{m}$) clay fractions of a Texas Bentonite (Southern Clay Productions, Inc., Gonzales, TX) and a Georgia kaolin to get relatively pure smectite and kaolinite specimens.

The original bentonite and kaolin samples were treated similarly with pH 5 sodium acetate (NaOAc) solutions to remove carbonate minerals. The treatment was repeated three times. Then the samples were dispersed in pH10 Na_2CO_3 solution and were passed through 325 mesh sieves to separate the sand fraction ($> 50\ \mu\text{m}$). The remaining clay and silt mixtures were transferred to 250–mL centrifuge tubes. The clay ($< 2\ \mu\text{m}$) and silt ($2\text{--}50\ \mu\text{m}$) fractions were separated by centrifuge at 750 rpm for 3.2 minutes. The clay fractions suspended in the solution and were collected in 4–liter plastic beakers. The separation by centrifugation was repeated several times until the supernatant became clear.

Diluted smectite and kaolinite suspensions were prepared with deionized water. A series of 3.7–mL clay suspensions containing up to 1.0 mg/L clay were transferred to 1 cm by 1 cm disposable cuvettes and covered with parafilm to avoid evaporation. When the cuvettes are inserted into the sample holder of a UV–Visible spectrometer (Beckman DU 600), the beam strikes the suspension at the same 3.0 cm depth. Before measurement, the suspension in the cuvettes was shaken by hand to achieve homogenous dispersion. The absorbance of the clay suspension was monitored at different light wavelengths. The corresponding absorbance versus clay concentration is plotted in Figure 3.10. In general, the absorbance of clay suspensions increases with clay concentration and decreases with light wavelength. Excellent linear correlations exist when the absorbance is lower than 1. When clay concentration is lower than 0.5 mg/L, the linear regression coefficients between the absorbance and clay concentration are greater than 0.995. At longer wavelengths, better linear correlation is achieved. Figure 3.10 also shows that kaolinite has an absorbance three to four times higher than smectite at the same wavelength and with the same concentration. The linear correlation at low clay concentration and longer wavelength suggests that turbidity (absorbance) can be used to quantify the clay minerals when a suspension contains only one clay mineral.

The linear correlations between turbidity and concentration of pure clay minerals (Figure 3.10) suggest the potential of turbidity as clay mineral quantification methods for the aggregates. However, the aggregates generally contain several minerals and amorphous phases in the clay fraction. Iron oxides, organic matter, and manganese oxides strongly absorb the UV–Visible light, therefore interfering with the turbidity measurement. These interference components might be removed by chemical methods such as sodium dithionite–citrate–bicarbonate solution and hydrogen pyroxide.

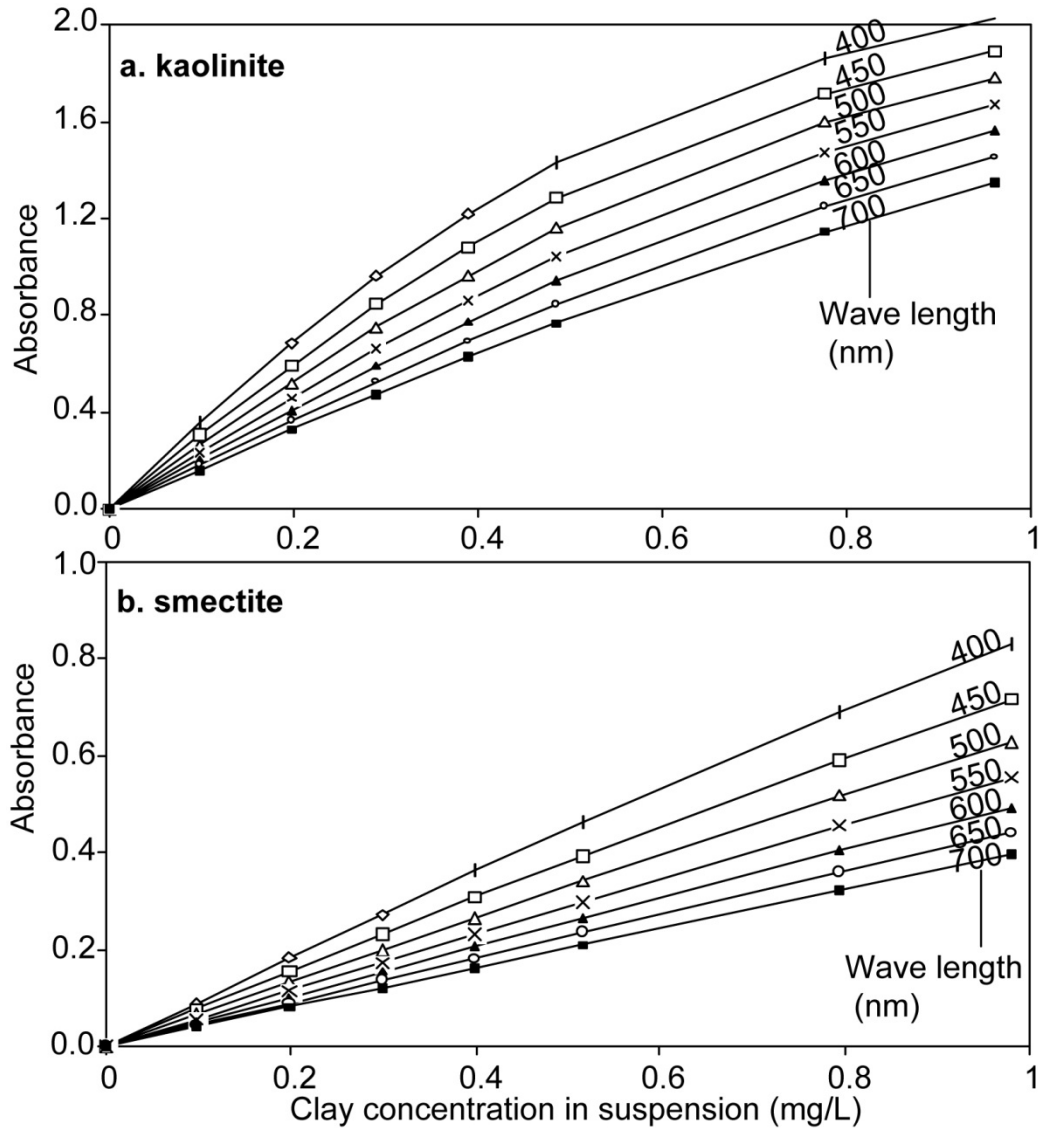


Figure 3.10. Absorbance (Turbidity) of Kaolinite (a) and Smectite (b) Suspensions as a Function of Clay Concentration and Light Wavelength.

As smectite is the major concern in the aggregates, it will be attractive to let other minerals settle down but suspend only smectite in the suspension so that it can be quantified by turbidity. We attempted using polymer solutions to achieve this goal. We tested the stability of smectite and kaolinite suspensions in the presence of 0 to 160 ppm polyacrylamide (PAM)

(Magnifloc, Cytec Industries Inc. West Paterson, NJ) solutions. In preliminary trials, we found that the positively charged and neutral polyacrylamide solutions actually flocculated the clay suspensions, but the anionic PAM 836A can increase the stability of the suspensions. In the test, kaolinite and smectite clay suspensions were prepared in the presence of the polymers. Similar to the turbidity monitoring experiment, a 3.7-mL each suspension was transferred to a cuvette, and the concentration of the clays at the 3-cm depth was calculated based on its absorbance at 600 nm and the linear relationships shown in Figure 3.10. Without the polymer (0 ppm PAM in Figure 3.11), both clays could suspend in water for several days, yet increasing amount of clays settled with time, and kaolinite settled faster than the smectite. After 10 days, kaolinite essentially settled completely, whereas about 10 percent of the smectite remained in suspension. Introducing the anionic polymer into the suspensions increased the stability of both clays, particularly the kaolinite, where about 80 percent of the kaolinite was still suspended in solution even after one month's settlement (Figure 3.11). Only about 20 percent smectite remained in the suspension after the one-month period.

The suspension stability revealed by Figure 3.11 suggests that it would be difficult to separate smectite from kaolinite by simple sedimentation methods in a short time period (e.g., within hours). Introducing the stabilizing polymer into the suspensions actually reduced the separation tendency of the two clay minerals. Even though this method cannot be used to quantify smectite in an aggregate, it suggests that turbidity may be used to quantify the total clay content of the aggregates.

Modified Methylene Blue (MMB) Test

The existing methylene blue test has been used by several researchers to estimate the amount of clay in a sample. It is accomplished by methylene blue dye being adsorbed onto the surface of the clay. It has been used as a proxy for the surface area of a sample as well. A detractor of this test has been that it depends on a person's eyesight or visual judgment to determine when the endpoint is reached. This often results in poor repeatability between different operators. On the other hand, a new technique has been proposed where the human guesswork has been removed, and the methylene blue concentration is read by a colorimeter, which allows for more consistent results between different users.

The researchers added different concentrations of the two clay mineral standards to a clean quartz sand and determined the methylene blue values (MBV). Table 3.3 shows the results of this testing. Results in the table are an average of three analyses. Note how the methylene blue values for the smectite/bentonite are extremely high for even very small contents of the clay. Also, note that the methylene blue values for the kaolinite are very low, indicating that it does not adsorb nearly the amount of methylene blue dye as does the bentonite.

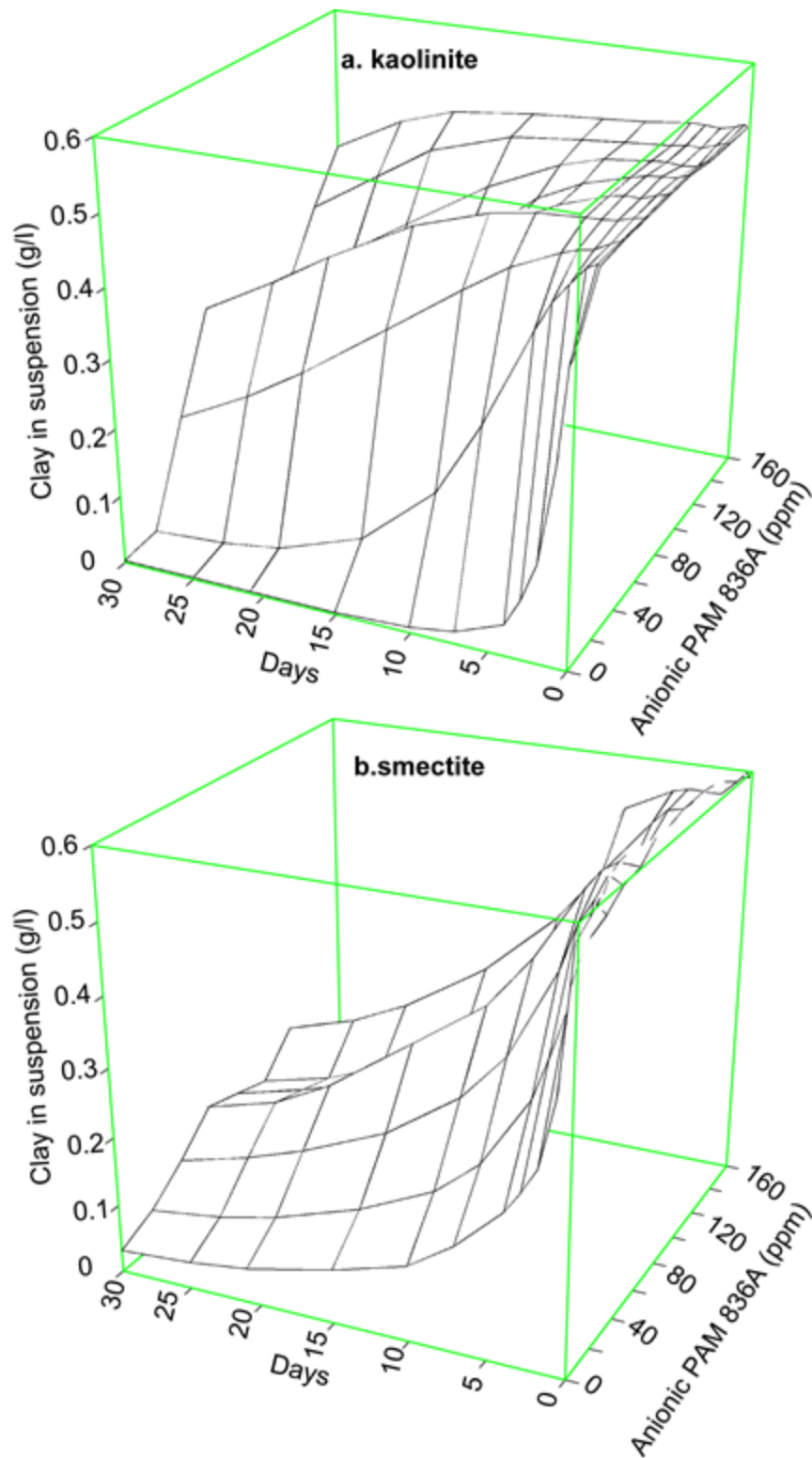


Figure 3.11. Remaining Smectite and Kaolinite Concentrations in Solutions in the Presence of Anionic PAM 836.

Table 3.3. Methylene Blue Values Obtained for Pure Clay–Sand Mixtures.

Bentonite		Kaolinite	
% Added	MBV (mg/g)	% Added	MBV (mg/g)
1	2.66	1	0.36
2	4.96	2	0.68
3	6.76	3	0.9
4	9.98	4	1.08
5	11.21	5	1.28

Based on the test results, it is obvious that the MMB test can differentiate swelling (i.e., bentonite) from non–swelling clays (i.e., kaolinite). Figure 3.12 below shows the relationship between MBV and clay content for both clays.

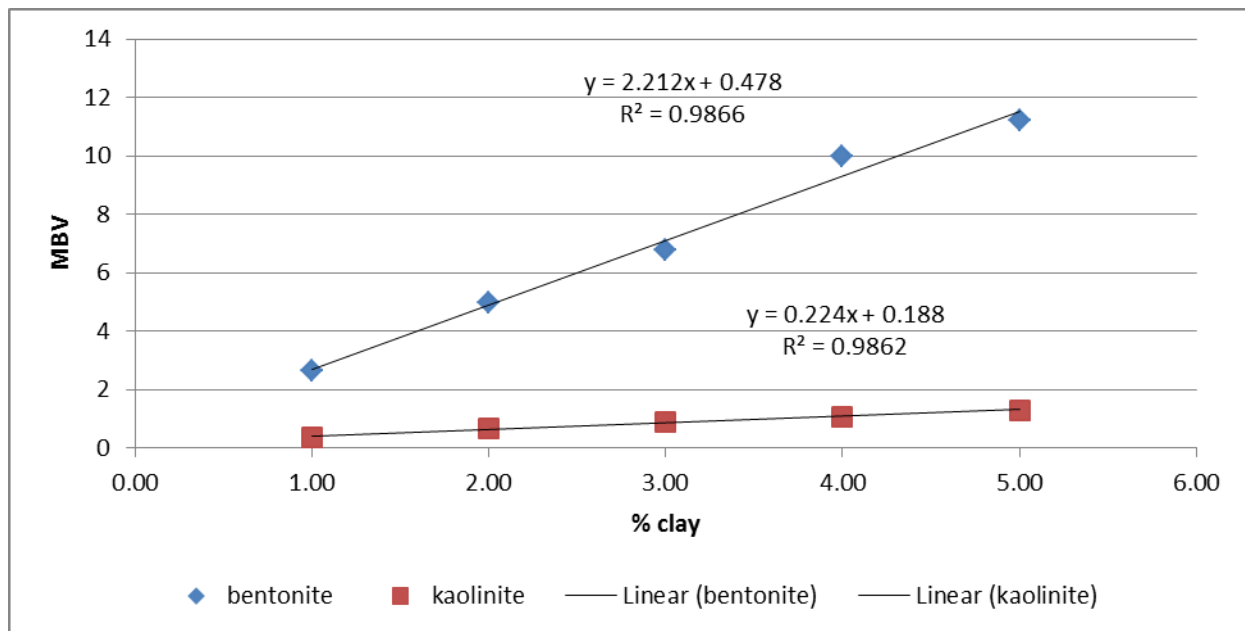


Figure 3.12. Relationship between MBV and Clay Content for Bentonite and Kaolinite.

SUMMARY AND CONCLUSIONS

Results of the testing involved in this chapter tell us that direct *X–ray diffraction testing* and analysis of the bulk samples will not be adequate for clay mineral quantification in the aggregates. To quantify the clay minerals using XRD, the clay minerals have to be concentrated and go through the series of standard treatments outlined at the beginning of this chapter. Moreover, it requires special training to interpret data.

X–ray Fluorescence is also a poor candidate to quantify the deleterious clay in an aggregate sample because there are too many elements in common with many different minerals. There was not a good correlation with any particular element dealing with pure clay mineral standards, so it would be impossible to detect clay mineral unknowns with this technique.

FTIR data look good using pure clay mineral standards where there are not many different minerals providing bands that overlap with the pure clays. However, quantifying unknown clay minerals becomes more difficult due to many of the clays having peaks in the same region. This technique may work, but considerably more research would need to be done to try and model the resultant bands from multiple minerals in a sample.

Using a *turbidity* technique, the researchers were able to get linear concentration gradients at low concentrations; however, the ability to differentiate between different clay types is not possible at this time.

The *modified methylene blue* technique seems to be the test method with the most promise based on testing with clay mineral standards. It is very simple to run and can be run in a few minutes. There is a good linear correlation between clay content and MBV with both the smectite and kaolinite. Additionally, the smectite values are orders of magnitude greater than the kaolinite, which will allow differentiation between the different clay minerals.

CHAPTER 4

QUANTIFICATION AND CHARACTERIZATION OF FINES AT AGGREGATE QUARRIES

Following the literature review, web survey results from the TxDOT districts, and the meeting with key TxDOT personnel involved in concrete research, the researchers determined a new approach was needed to address the needs of TxDOT. In this section, aggregate fines from all quarries that have had difficulty meeting the fines requirements needs were evaluated. Geology plays a significant role in the quality of aggregates. As part of this study, problematic crushed stone quarries/gravel pits from all districts with quarries that have problems meeting current fines requirements were visited by the researchers to determine the natural variations in clay content (due primarily to weathering or deposition in sedimentary rocks). The main purpose of this chapter is to present information on the aggregate fines collected from different quarries and characterize the fines by different test methods identified in chapter 3. XRD and CEC testing were used to identify and quantify the clay minerals in aggregate fines directly, whereas the modified methylene blue (MBB) test was used to detect the presence of clay minerals indirectly. XRD (an advanced research tool) was used to establish the MBB test. The method of sample preparation and testing for XRD is provided in Appendix B. CEC method was also used as a supporting tool for MBB method. Sand Equivalent (SE), Bar Linear Shrinkage and PI tests were subsequently included based on TxDOT's recommendation, which were not proposed originally.

MATERIALS SELECTION AND COLLECTION

The aggregate fine materials (mostly pit run/screening materials) from a total of 30 quarries [25 quarries in Texas covering 11 districts (Abilene, Atlanta, Austin, Bryan, El Paso, Ft. Worth, Lubbock, Odessa, San Antonio, Waco, and Yoakum Districts), 3 in Arkansas, and 2 in Oklahoma] were collected. Some of the materials were known to contain deleterious materials/harmful clay minerals. Pit run/screening materials represent materials that were collected from the pit/quarry before washing or any other treatment. Stockpiled materials are the final finished product after washing (if washing or any other treatment is applied). Obviously, the content of clay minerals should be higher in pit run/screening materials than that of stockpiled materials if the source of the clay minerals is in the quarry itself. The idea of collecting pit run/screening materials was to identify and quantify the clay minerals present in the selected quarries. If the presence of harmful clays is confirmed in the pit (before washing) there is a high probability that those clays may be present in some batches of the final stockpiled materials, depending on the efficacy of treatment process (e.g., washing) and amount and type of clay minerals present. Table 4.1 below provides the aggregate sources along with available lithological information.

Table 4.1. Aggregate Sources and Their Composition.

Aggregate Pit	Rock Type
Wood Pit	015–Partly Crushed Siliceous and Limestone Gravel
Rankin Pit	'018–Crushed Limestone
South Noodle	'025–Partly Crushed Limestone and Siliceous Gravel
Smith Buster	'029–Crushed Sandstone
Bird Hill	'050–Trap Rock
La Burrita	'015–Partly Crushed Siliceous and Limestone Gravel
Fordyce Murphy	Siliceous river gravel
Cemex McKelligon Dolomite	El Paso Limestone, '019–Crushed Dolomite
Whitney Pit	'023–Limestone and Siliceous Gravel
Jones Mill	Martin Marietta Materials, Atlanta
McKelligon Granite	Franklin Red Granite, '051–Crushed Granite
Cemex South	Hueco Limestone, 018/019 crushed L.st./dolomite
Vulcan Helotes	'018–Crushed Limestone
Pit #365	'021–Crushed Limestone Gravel
North Troy	Kincaid Fm, '019–Crushed Dolomite
Delta (Brownlee)/Austin, Capitol	'029–Crushed Sandstone
Marble Falls, Capitol. Austin	'019–Crushed Dolomite
Black Lease, Abilene, Vulcan	'018–Crushed Limestone
Texas Crushed Stone	no info for quarry/pit
Bridgeport	'018/019–Crushed Limestone/Dolomite
Little River	'012–Partly Crushed Siliceous Gravel
Scarmardo	Siliceous and limestone gravel
Super Crushed Stone I	'018–Crushed Limestone
Super Crushed Stone II	'018–Crushed Limestone
Yarrington	'022–Partly Crushed Limestone Gravel
Hoot	No info for quarry/pit
Vulcan Huebner	'018–Crushed Limestone

The test methods that were used to quantify clay minerals in aggregates fines in this chapter are (1) identification and quantification of clay minerals by XRD, (2) Cation Exchange Capacity (CEC), (3) Infrared Absorption Spectroscopy, and (4) Modified Methylene Blue

(MBB) Test. Test procedures, sample preparation, results, and discussion for each method are presented below.

IDENTIFICATION AND QUANTIFICATION OF CLAY MINERALS BY XRD

X-ray diffraction is one of the most powerful methods for identifying and quantifying minerals in aggregate fine samples. Quantitative XRD was the primary method used to measure clay mineral quantities in aggregate fines in this study. It was established in Chapter 2 that clay minerals cannot be detected by XRD in a powder mixture with pure quartz below the detection limit (< 5 percent). Therefore, separation of a fraction of smaller-sized particles was performed to concentrate the clay minerals above the detection limit. In the pretreatment process, cementing materials in aggregate such as carbonate minerals, iron and manganese oxides, and organic matter are dissolved and removed from the samples to liberate clay minerals bound by those materials. Then, size-fractionation of the aggregate materials was performed to isolate a small particle, “clay” fraction (particle size < 2 μm diameter). The steps involved in preparing samples for XRD are described in detail in Appendix B. Separation of clay fractions, identification of clay minerals after saturation with cations, and quantification by NEWMOD simulation is a time-consuming but established and reliable method for clay mineral identification and quantification. Without the separation of clay fractions (< 2 μm) and fixing of layer thickness with magnesium and potassium cationic solutions, correct identification of clay minerals is not possible using the XRD method.

A Bruker D8 Advanced X-ray diffractometer was used to record the diffraction patterns. Diffraction parameters included: Cu $K\alpha$ source, 35 kV and 45 mA beam energy, variable Soller and antiscatter slit length, 0.05° step size, 3-second dwell time, 30 rpm disc rotation, and SolX energy-dispersive, solid-state radiation detector. The diffractometer is semi-automated, with Bruker software capable of running 90 samples in succession via a robotic sample loader. After generating the diffractions patterns for all 27 aggregate samples, XRD analysis was performed to identify and quantify the clay minerals present. The identification of clay minerals was performed after stacking the five patterns into a single figure, as shown in Figure 4.1 below. Smectite is identifiable by layer thickness of 14 to 15 Angstroms (\AA) in the magnesium saturation treatment that expands to approximately 18 \AA in the magnesium glycerol treatment. This is observable in Figure 4.2 in the prominent peak at 14.6 \AA in the bottom pattern that moves to 17.9 \AA in the second pattern from the bottom. Vermiculite, however, does not undergo a peak shift in the glycerol treatment, and it is identifiable from the glycerol treatment’s 14.4 \AA peak. However, vermiculite layer thickness collapses to 10 \AA upon potassium treatment and heating to 330°C and 550°C. The 14.4 \AA peak in the potassium 550°C treatment is attributable to chlorite minerals. Kaolinite is identifiable from a peak in the 7 \AA region, visible in the lower four patterns that disappears in the 550°C treatment. Illite is visible as a shoulder of the smectite peak at approximately 10 \AA in the magnesium and potassium treatments. Because smectite, vermiculite, and chlorite all have peaks in the 14 \AA region with no saturations or magnesium treatment, all five treatments are necessary. The XRD patterns (stacking of five patterns for each sample) of all the samples are provided in Appendix D.

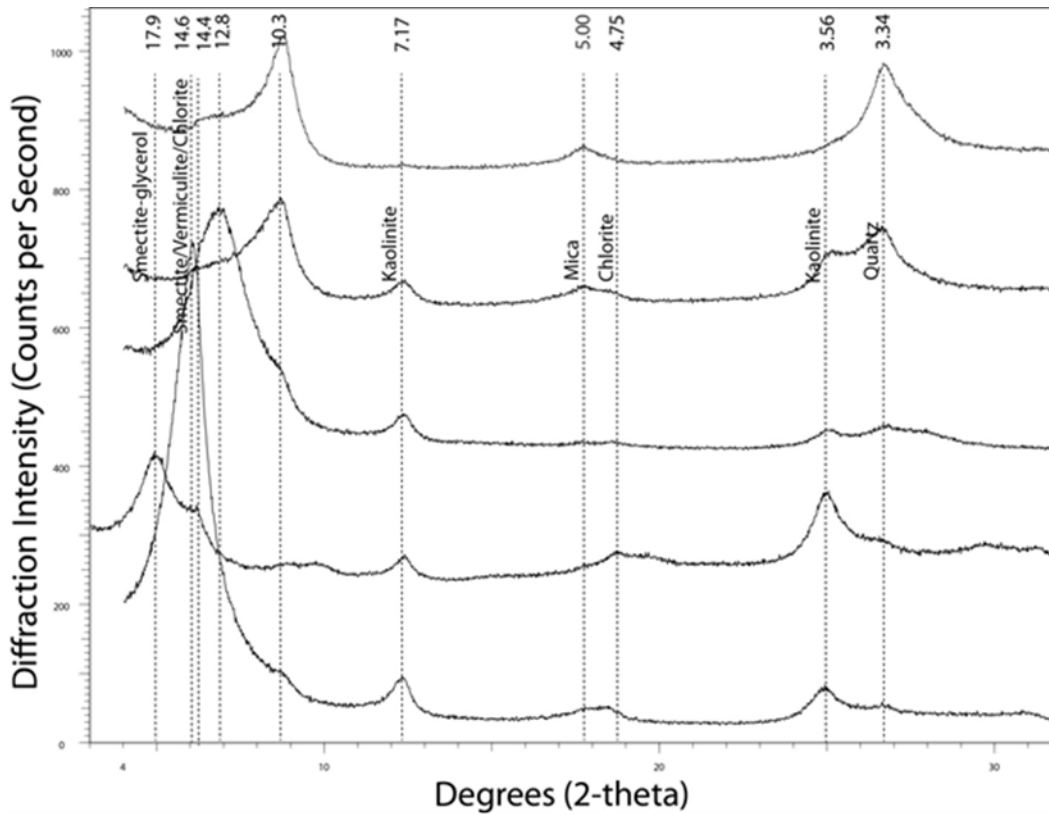


Figure 4.1. Clay Minerals Identified from XRD Pattern of Jones Mill Fine Clay Fraction.

Results and Discussion

The quantification results based on NEWMOD simulation are presented in Table 4.2. The results are also presented graphically in Figures 4.2, 4.3, and 4.4. The weight percentages of different clay minerals were calculated with reference to the starting material quantify of -2 mm size. ‘Clay’ refers to total < 2 μm fraction recovered. Clay mineral names are abbreviated as follows: ‘Smec’ for smectites, ‘Verm’ for vermiculite, ‘Kaol’ for kaolinite, ‘Chlor’ for chlorites, ‘HIS/HIV’ for hydroxy–interlayered smectite or vermiculite, ‘I–S’ for interstratified clay minerals, and ‘Paly/Sep’ for palygorskite and sepiolite.

The main observations are described below:

- The specimens analyzed came from the “pit run” and not aggregate stockpiles – they did not undergo washing or standard clay removal treatment at their quarries. Therefore, values for clay content may be elevated from what is typically encountered in the stockpiled materials.

Table 4.2. NEWMOD Quantification Results, Percent Clays in Aggregate Fraction < 2 mm.

Aggregate	Clay	Smec.	Verm.	Illite	Kaol.	Chlor.	HIS/HIV	I-S	Paly./Se
Blum	1.26	0.96	—	0.14	0.16	—	—		
Hoot	0.71	0.34		0.07	0.29	—	—		
Jarrell 1	0.37	0.27		0.01	0.09	—	—		
Jarrell 2	0.89	0.65	0.08	0.01	0.06	—	—		
Jones Mill	5.98	1.70	2.53	0.47	1.10	0.19	—		
Little River	1.52	0.58	0.12	0.35	0.47	—	—		
McKelligon Granite Granite	3.86	2.70	0.16	0.57	0.44	—	—		
Pit 365	28.0	18.2	—	4.3	5.6	—	—		
Scarmardo	0.21	0.16	—	0.03	0.03	—	—		
South Noodle	16.6	8.3	—	7.1	1.2	—	—		
Tolar	8.01	0.2	—	4.3	0.3	—	1.7		
Whitney	5.2	3.2	—	1.1	0.9	—	—		
Wood	4.8	4.5	—	1.1	0.9	—	—		
Yarrington	7.5	4.2	—	1.4	1.7	—	—		
Armor	3.0	1.0				—	—		2.0
Black Lease	1.8	0.6	—	0.3	0.9	—	—		
Texas Crushed Stone	0.9	0.5	—	0.1	0.2	—	—		
Bridgeport	3.3	—	—	0.5	2.4	—	—	0.4	
Buster/Bird	3.3	—	—	0.5	2.4	—	0.4		
McKelligon Dolomite	13.5	—	—	13.5	—	—	—		
Bird Hill	6.6	—	—	1.0	3.6	—	2.0		
Huebner	3.1	1.4	—	0.4	1.3	—	—		
Rankin	6.9	0.2	—	2.0	2.0	—	2.7		
Helotes	3.3	1.7	—	0.3	1.3	—	—		
Cemex South	3.1	—	—	1.5	0.4	—	—	1.2	
North Troy	3.5	0.1	—	0.5	2.6	—	0.3		

- Smectite is the class of expandable clay mineral with the highest capacity to adsorb water and to affect concrete workability. It has strong shrink–swell properties that undermine concrete performance and durability and high CEC (100–150 meq./100g). Vermiculite has medium to low shrink–swell potential and high CEC (100–160 meq./100g). Kaolinite and Illite have very low CEC (10–5 meq./100g) and almost no swelling potential. I–S is characterized by medium CEC (40–60) and moderate swelling potential. HIS–HIV show moderate to high CEC (50–70) and low swelling potential whereas Paly./Sep. show low to moderate CEC (20–40) but low swelling potential. HIS–HIV mineral can absorb MB but may not be expansive (false positive, Rankin).

- In order to speed dissolution of carbonates, several samples, asterisked in Table 4.3, were ground to pass through a 140–mesh sieve ($< 105 \mu\text{m}$). This may have resulted in higher quantities of quartz and other crystalline materials in the clay fraction after grinding, in which case clay mineral quantities may be overestimated.
- An aggregate may have a high content of fine–sized particles and still have low quantities of harmful clay minerals, such as smectite, for instance, in the McKelligon Dolomite sample. Conversely, some aggregates have low quantities of clay–sized particles with relatively high smectite content, such as in Blum Pit.
- Six aggregates contained less than 1 percent total recovered clay fraction by mass. Nine aggregates contained greater than 1 percent smectite. One aggregate contained greater than 1 percent vermiculite, and three contained greater than 1 percent hydroxy–interlayered clay minerals, which have high cation exchange capacities, and therefore, may be at greater risk of producing false positives. These minerals were less common than smectite was in the samples.

In order to validate the accuracy of the NEWMOD quantification method, three artificial mixtures were prepared with recorded quantities of standard kaolinite and smectite minerals. Mixtures underwent a 0.5 M magnesium chloride saturation treatment identical to the treatment performed on all aggregate clay specimens. Diffractometer parameters were also identical to the aggregate clay analysis: Cu K α source, 35 kV and 45 mA beam energy, variable divergence and antiscatter slit lengths, 0.05° step size, 3–second dwell time, 30 rpm disc rotation, and a SolX energy–dispersive, solid–state radiation detector. According to Moore and Reynolds (1989) ± 10 percent accuracy for quantification of each major clay mineral phase and ± 20 percent accuracy for each minor clay mineral phase present (i.e., components that make up less than 20 percent weight fraction of the specimen) is a good result. An accuracy of ± 3 percent for clay mineral phases is considered a very good result.

NEWMOD was used to achieve good accuracy in quantification of clay minerals in the standard mixtures. Slight underestimation of smectite quantities versus kaolinite was observed (Table 4.3). There may be several causes of this overestimation of kaolinite quantities. There may be some overlap of the 002 diffraction peak for smectite peak with the kaolinite 001 peak, but a low–order kaolinite peak was also modeled and included in the analysis to attempt to address this problem. In addition, the kaolinite standard was a dried powder whereas the smectite standard was a dilute suspension, and some of the kaolinite may have formed difficult–to–disperse aggregates that would increase diffraction intensity.

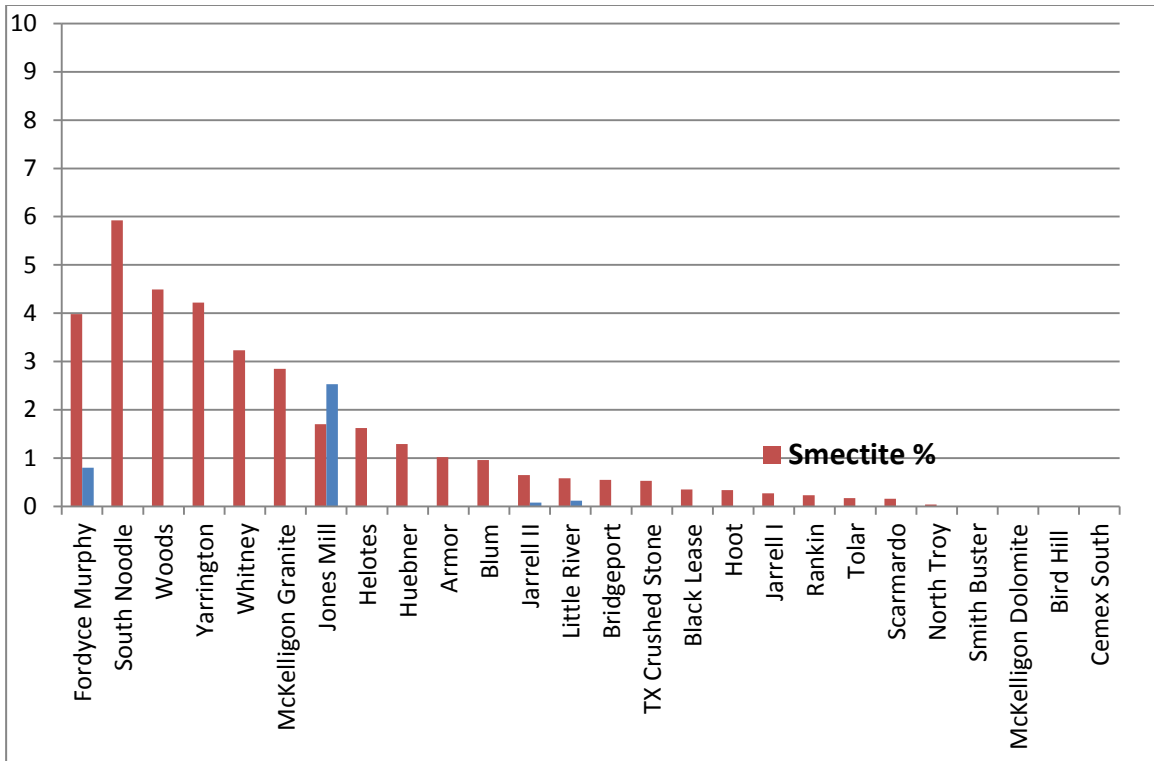


Figure 4.2. Smectite and Vermiculite Contents as Percentage of Aggregate, < 2 mm Fraction.

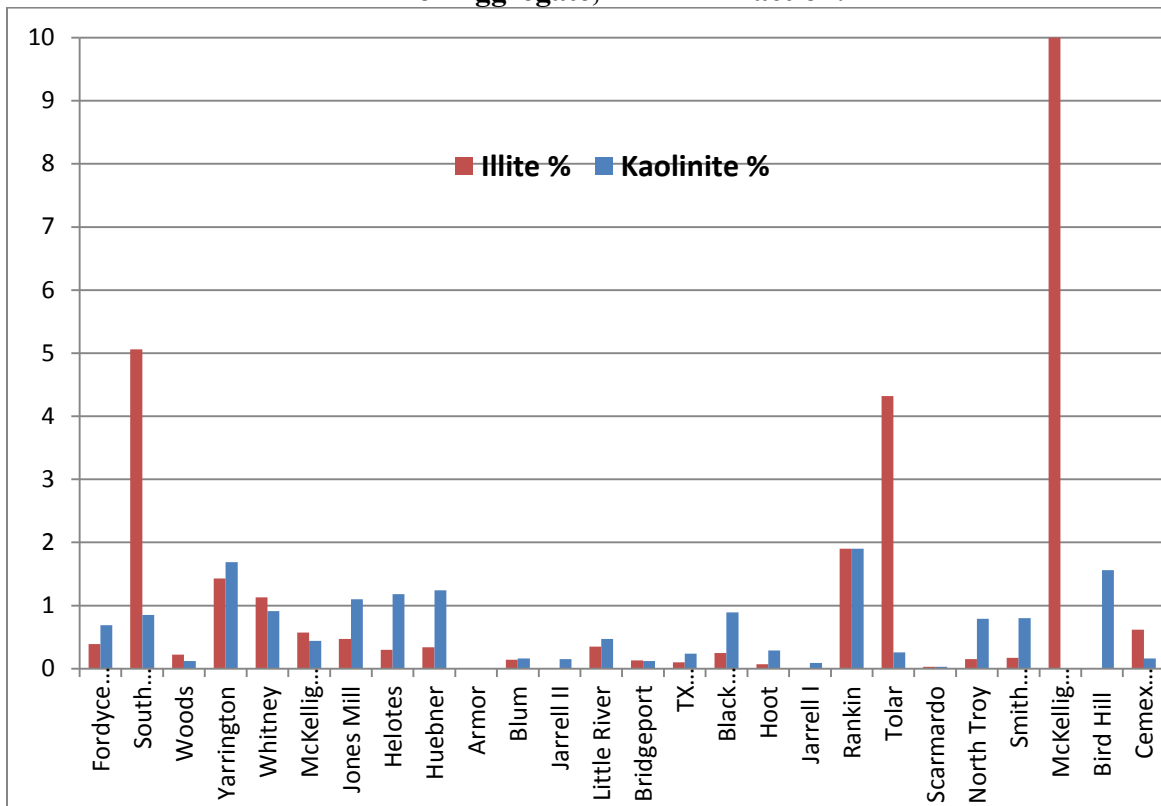


Figure 4.3. Illite and Kaolinite Contents as Percentage of Aggregate, < 2 mm Fraction.

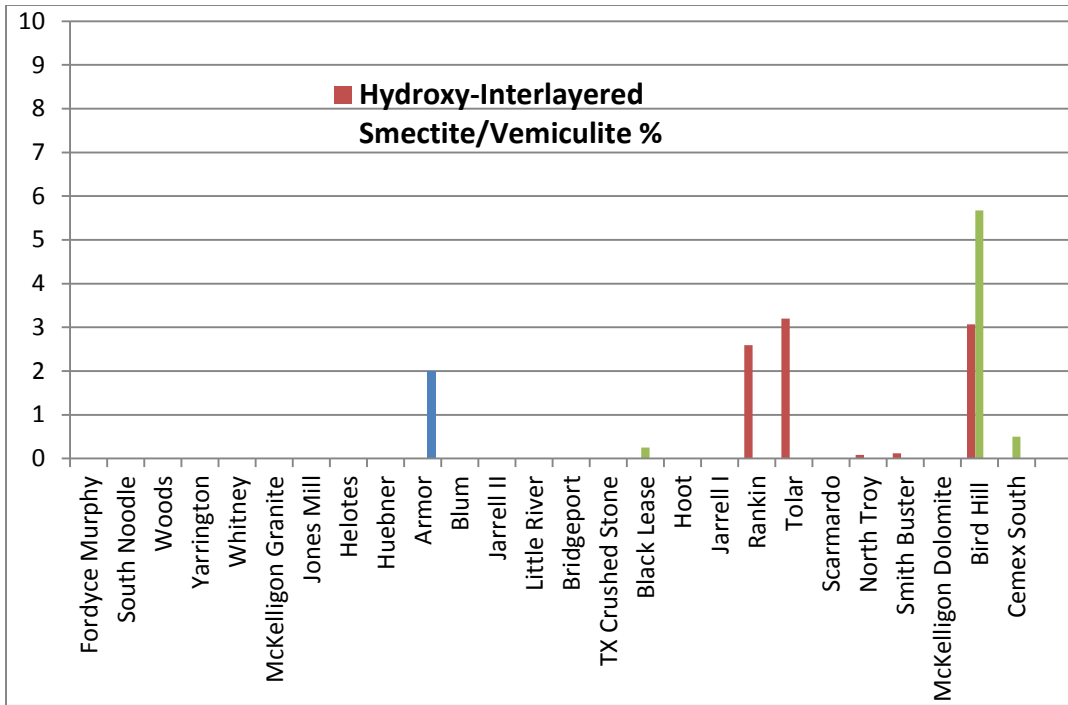


Figure 4.4. HISV, ISI, and Palygorskite / Sepiolite Contents as Percentage of Aggregate, < 2 mm Fraction.

Table 4.3. NEWMOD Validation Quantification Results.

Specimen	Recorded Smectite (%)	NEWMOD Smectite (%)	Accuracy NEWMOD (%)
Mixture 1	47.9	45.0	-6.1
Mixture 2	54.7	52.8	-3.5
Mixture 3	78.4	71.7	-8.5

Rietveld Refinement Quantification

The Rietveld method is a full-pattern simulation that utilizes a least square difference of statistical analysis in conjunction with models calculated from crystallographic data of real mineral samples. Online databases of crystal structures are contributed to by researchers around the world and are readily accessible. In addition, most mineralogy labs catalog standard mineral diffraction patterns and use the crystal structure data in Rietveld modeling (Figure 4.5). Quantification by the Rietveld method works by minimizing the difference between actual and modeled diffraction patterns. Researchers work to identify the minerals and select the appropriate crystal models from a database or lab mineral reference library. The software program then runs a full pattern simulation, modeling all of a mineral's diffraction peaks (Young 1993). In modeling, all peaks, even the weaker peaks in a diffraction pattern, the Rietveld approach resolves the significant issue of peak overlap that complicates quantification by other methods, such as the Reference-Intensity-Ratio method (RIR).



Figure 4.5. Bruker's TOPAS Program Interface for Rietveld Analysis from Crystal Structures.

The major limitation of the Rietveld method is that it calculates diffraction patterns assuming 3-dimensional periodicity in sample crystal structure. This condition, however, is only true for highly crystalline materials or minerals, such as quartz and calcite. Clay mineral structure exhibits ordered arrangement of atoms in two dimensions along the X and Y axes, but between layers there is disordered stacking. In addition, crystallite size is much smaller in clay minerals than in more crystalline minerals, and chemical variation by isomorphic substitution is common in clay minerals as well. The lack of 3-dimensional diffraction characteristics and variability in structure and chemical composition of clay minerals means that the development of crystal structure models for Rietveld analysis of clays is an area of ongoing research among clay researchers. Crystalline structure is less definable due to the variable layer thickness, interstratification of clay minerals, and difference angles of layer sheet stacking. In a Rietveld total-sample quantification, clay minerals may not be easily identifiable because the interference of multiple crystalline phases and the difficulty of definitively identifying individual minerals with similar layer thickness or peak spacing. A detailed procedure of the Rietveld method is presented in Appendix E.

Results and Discussion

The spray-dryer method yielded good particle size and shape for reducing orientation effects for powder x-ray diffraction quantification. For highly crystalline minerals, choosing an appropriate crystal model is straightforward. However, for the clay minerals, correct mineral identification is infeasible without separation of clay fractions and cation saturations. Crystal models for clay minerals may also be imprecise due to the occurrence of interstratifications and

randomness of layer orientations, as well (Brindley and Brown 1980). The quantification results based on the Rietveld method are presented in Table 4.4. Unidentified may refer to clay minerals, amorphous materials, or minerals that were present but not identified and/or modeled using relevant crystal models. Fifteen aggregates underwent quantification using the spray dryer and Rietveld methods. The spray–dryer method was still experimental when this project began, and the methods to get good sample recovery had to be developed by trial and error. Four of the 15 tested samples contained greater than 95 percent quartz, and four contained greater than 85 percent calcite. Quartz–rich aggregates were composed of river gravel, and calcareous aggregates were made from crushed limestone. There is currently no procedure in place for identifying expandable clay minerals from the Rietveld method alone. At the current time, more groundwork needs to be put in place to explore quantifying clay minerals with the Rietveld method, but this is a very promising procedure for future projects.

Table 4.4. XRD Quantification Results Based on Rietveld Method.

Aggregate	Quartz	Calcite	Feldspars	Mica	Kaolinite	Unidentified
Blum	0.47	85.6	—	—	—	13.9
Murphy	95.7	4.3	—	—	—	—
Hoot	97.4	—	2.6	—	—	—
Jarrell 1	0.9	95.1	—	—	—	4
Jarrell 2	0.9	92.5	0.0	—	—	6.5
Jones Mill	18.4	6.0	46.7	4.7	—	24.2
Little River	96.4	—	1.3	—	0	2.3
McKelligon Granite	16.6	4.0	27.3	9.0	—	20.0
Pit 365	8.9	58.0	1.0	6.2	—	25.9
Scarmardo	95.1	3.5	1.4	—	—	—
South Noodle	65.7	17.6	1.6	—	—	15.2
Tolar	7.2	68.8	—	—	—	23.8
Whitney	64.3	2.4	9.3	5.2	—	14.8
Wood	65.0	6.4	13.4	2.5	—	12.7
Yarrington	2.7	91.7	—	—	—	5.6

Cation Exchange Capacity (CEC)

Cation exchange capacity is a measurement of the chemical reactivity of materials and may be an important property in concrete design. Expandable layer silicate minerals such as smectite and vermiculite have relatively high CEC, exceeding 100 meq/100 g. CEC is a useful test for identifying and quantifying clay minerals in aggregate fines. However, CEC is not exactly proportional to expandable clays such as smectite, as non–expandable clays, non–clay minerals, and other materials have CEC as well. In this procedure, the CEC of treated and separated clay fractions (< 2 μm) was determined.

Procedure

One repetition or duplicate of each clay fraction is typically completed for each sample to reduce experimental error. For each treatment, 100 mg clay each was treated three times with a 0.5 M calcium chloride solution to ensure Ca-saturation, treated three times with a 0.005 M calcium chloride solution (CaCl_2) to bring the interstitial solution to a known Ca concentration, and then treated four times with 0.5 M magnesium chloride (MgCl_2) solution followed to replace Mg^{2+} for Ca^{2+} on the cation exchange sites in the clay interlayer and particle edge sites. After each washing with magnesium chloride solution, supernatant containing the displaced calcium ions was collected and set aside. Calcium concentration in the magnesium solution was determined by atomic absorption spectroscopy (AAS) analysis with an acetylene flame. CEC was calculated in units of milliequivalents positive charge per 100 grams sample.

Results and Discussion

CEC was determined for 21 out of the 27 separated aggregate clay fractions, based on availability of sufficient clay material for each aggregate. CEC of -40 size materials was also measured in order to establish a correlation with MBV of -40 size materials (described later). Most of the aggregates' CEC values ranged between 20 and 30 meq /100 g clay (< 2 μm size). For two of the aggregates, McKelligon Granite and Wood Pit, bulk separated clay was further separated into coarse clay (2–0.2 μm) and fine clay (< 0.2 μm) fractions. The fine clay fraction was used to complete the CEC test for these two aggregates, which have a higher CEC than if the total clay fraction was used. This is due to the larger surface area of small particles and concentration of smectites and other high-CEC minerals as seen in Table 4.5.

CEC can be used as an approximate estimation of expandable clay mineral quantities in a sample, but it does not allow for the distinction between expansive minerals and non-expansive minerals with high CEC like smectite and vermiculite. CEC determination is a powerful tool, but its focus is narrow, and it cannot be used for accurate identification and quantification of clay minerals without other data. Thirteen of the 21 clays tested had CECs between 20 and 36 meq/100 g clay. Four aggregates had CEC of 15 or below: two of the four were siliceous river gravels with relatively small clay fractions. On the high end, Fordyce Murphy had the highest CEC of any of the total clay fractions. Its clay was composed almost entirely of smectite. The aggregates whose fine clays were used because the coarse and fine clays were pre-separated had higher CECs because the particle size was smaller, which tends to contain greater smectite quantities and have particles with greater surface area. Since the majority of CEC values were so similar, overall trends that apply to all aggregates are not immediately apparent.

Table 4.5. Cation Exchange Capacity of Aggregate Clay Fractions (< 2µm) and –No. 40 Screenings.

Aggregate	CEC of –No. 40 screenings (meq/100 g)	CEC of clays (< 2 µm) (meq/100 g)
South Noodle	5.7	34.0
Armor	4.4	31.7
Rankin	1.5	29.8
McKelligon Dolomite	2.2	20.1
McKelligon Granite	4.6	–
McKelligon Granite Fine Clay (< 0.2 µm)	–	58.0
Helotes	1.5	31.7
Volclay Montmorillonite Standard	–	95.0
Cemex South	2.5	14.5
Lake Bridgeport	0.8	27.2
Wood Fine Clay (< 0.2 µm)	–	87.0
Bird Hill	24.7	28.0
Huebner	2.3	35.5
Black Lease	–	30.0
Smith Buster/Bird	0.6	8.9
Fordyce Murphy	–	50.0
North Troy	1.1	7.5
Little River	–	13.5
Jones Mill	14.9	28.2
Yarrington	2.1	20.9
Pit 365	15.2	32.0
Whitney	3.4	26.8
Hoot	–	15.2

Infrared Absorption Spectroscopy

Infrared absorption analysis (FTIR–ATR) measures absorbance of infrared radiation of different wavenumbers, the inverse of wavelength, through diverse materials of organic and mineral origin. A plot of absorbance versus wavenumber may be generated, and the resulting graph is used to identify what minerals or other materials are present in a specimen. Many minerals may be identified by their characteristic absorption of infrared radiation, or “bands,” but not all clay minerals are easily identified by this method. In particular, there is no unique IR peak for the class of expandable layer minerals known as smectites, which this study is seeking to identify. However, there is a characteristic peak for water, or water–adsorbing minerals.

Procedure

A small specimen of separated and dried clay was oven–dried and analyzed by an attenuated total reflectance (ATR) technique between 650 and 2000 cm^{-1} wavenumber. The sample stage was cleaned in between samples with methanol. Identification of minerals was undertaken with pertinent reference books containing standard absorption data for clay minerals. Infrared absorption patterns were recorded for 11 of the 27 aggregate clays.

Results and Discussion

The Figure 4.6 shows FTIR pattern for clay fraction in Blum aggregate fines. This FTIR utilized the same clay fractions that had undergone cementing agent removal and chemical separation of the clay fractions. This procedure was not continued for the remaining of the 27 aggregates due to its limitations as a primary source of data for clay mineral identification. Its insensitivity to distinguish smectite, the primary expansive clay mineral or interest in the project, from illite, a non–expansive or poorly–expansive clay mineral, was a critical factor in this conclusion. Because the IR procedure is relatively brief in duration and portable technologies are commercially available for work in the field, if the smectite–sensitivity limitation could be overcome, it might still be a promising tool for future projects.

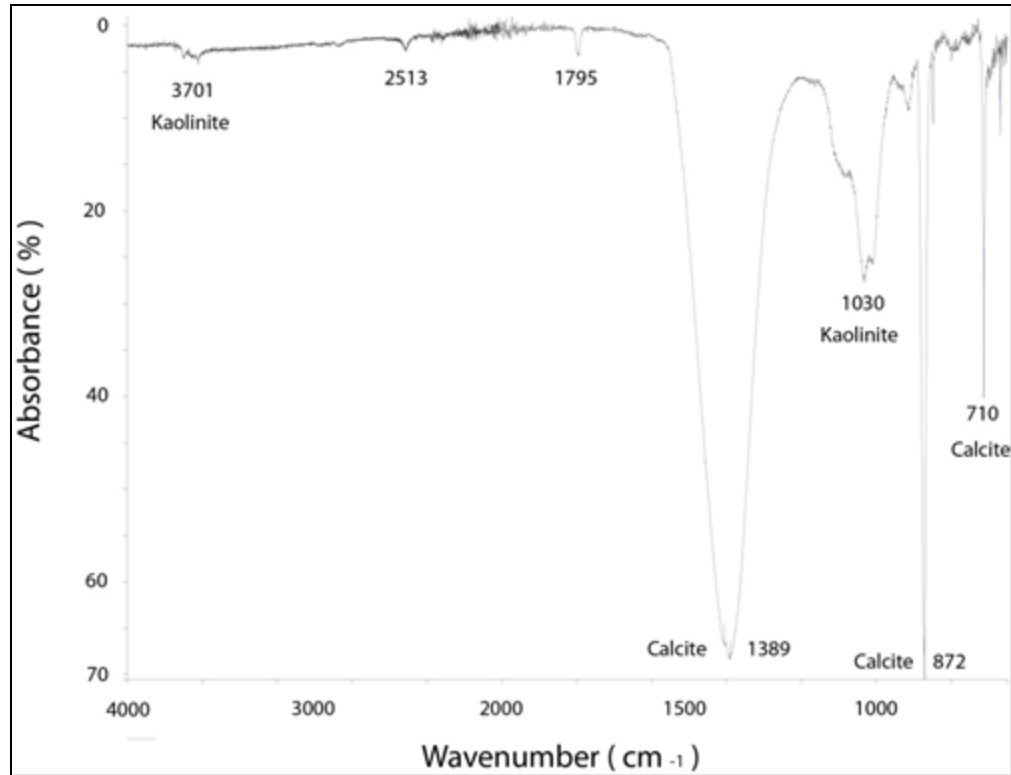


Figure 4.6. Infrared Absorption Spectrum of Blum Clay Fraction.

SUMMARY AND CONCLUSIONS

The following conclusions can be made based on the results of clay mineral quantification by the above methods (i.e., XRD, CEC, and FTIR):

- Several potential methods of expansive clay mineral identification and quantification are reviewed in this report. XRD method including separation of clay fractions from bulk aggregate material, fixation of clay interlayer thickness with cation saturation, and use of commercial modeling software appeared to be the most complete and reliable method during the study period. Twenty–seven aggregates underwent the NEWMOD analysis, and of those, Fordyce Murphy, Wood Pit, South Noodle, and Yarrington pits had smectite content greater than 4 percent in pit run –10 mesh size fractions.
- Cation exchange capacity determination was performed on 21 aggregate clay fractions. CEC data were used to support evidence of expansive clay minerals in aggregate clays; these target minerals have high CEC. Eight of the 21 clays exhibited high CEC (e.g., 30 meq/100 g or greater), and three of the four aggregates with greater than 4 percent smectite also had CEC greater than 30. However, non–expansive clay minerals, certain non–clay minerals, and organic compounds also have high CEC. The potential for false positives in using this method on its own to predict clay mineral contamination is high. Vermiculite, a non–expansive clay mineral, exhibits higher CEC than smectite, for instance. This problem is evidenced in the inconclusive correlation between smectite content of –10 mesh (i.e., 2 mm) fraction and CEC of < 2 μm fraction.

- FTIR–ATR is a potentially very rapid field method that, like CEC, does not provide definitive evidence of expansive clay minerals such as smectite in soils and geologic samples. This method is not as powerful of a tool for mineral identification and quantification as XRD. Experimental results were inconclusive for expansive clay mineral analysis and not presented in this report.
- The Rietveld quantification method (another way to quantify clay minerals in XRD) is a promising, rapid quantification method that requires careful attention to identification of mineral crystal models for accurate diffraction pattern simulation. Currently, modeling clay minerals by the Rietveld method requires the separation of clay fractions and fixation of layer thickness for mineral identification. Mineral identification is necessary to select appropriate crystal structure parameters for Rietveld calculations, and this is the most time–consuming step of the procedure. Rietveld quantification was undertaken for 15 of the 27 aggregate materials, and the crystalline minerals (e.g., quartz and calcite) proved straightforward to model and quantify. Of particular interest are the relative quantities of silicate and carbonate minerals in the aggregates viewable in Table 4.4. In the future, methods may be developed for identification of clay minerals in bulk sample, but in Chapter 3, it was found that smectite was not detectable in quantities below 5 percent in quartz. It may always be necessary to separate clay fractions for clay mineral identification, which is a significant time commitment.

Modified Methylene Blue Test

Currently, there are different methods to detect the presence of clay minerals in aggregate fines, directly or indirectly. Some of currently used methods are the sand equivalent (SE) test, plasticity index (PI) and shrinkage measurements. These methods are sometimes not very accurate in detect the presence of clay minerals in aggregate fines, as they are better suited in identifying only clay–like or clay–sized particles. Moreover, these methods are somewhat operator–subjective. The XRD method is the best method to identify and quantify the clay minerals in aggregate fines with reasonably good accuracy, but this method is cumbersome and requires advanced training to operate. The MMB test has been shown to be a quick and effective way of detecting the presence of clay minerals in aggregate fines. One of the greatest advantages of the MMB test is that it can be performed by nearly anyone and only takes a few minutes to perform. The modified methylene blue test procedure is presented in Appendix C.

MMB Test Procedure

In the modified methylene blue method, a sample of fine aggregate is combined with a methylene blue solution and mixed for a prescribed period of time. The solution from resulting mixture of MB solution and sand size sample is filtered and diluted. A colorimeter is used to determine the absorbance of the final solution, which is correlated with the concentration of methylene blue prior to dilution. The change in concentration in methylene blue prior to dilution is converted to a MBV and reported. The test procedure with further details is described below:

Step 1: Sand

Weigh 20 grams of dry sand (passing No. 4 sieve) for testing.

Step 2: Sand and Solution Batch

Accurately weigh 30 grams of methylene blue test solution (0.5 percent w/v solution) in a 45-mL testing tube (Figure 4.7). The methylene blue solution that was purchased from VWR was with 1 percent solution concentration. A stock solution of 0.5 percent was prepared from the 1 percent solution and used in step 2 for all the aggregate fines. Carefully add the 20 grams of the sand to the test solution and cap the tube.

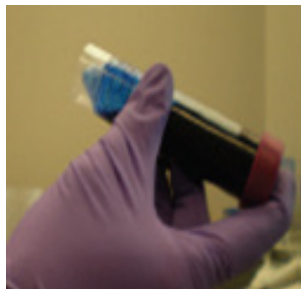


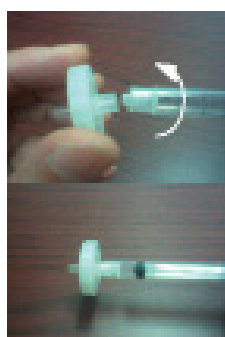
Figure 4.7. Methylene Blue Solution and Sand Samples in a 45-mL Test Tube.

Step 3: Mixing (1-3-1 min.)

Shake the sample for 1 minute, and then allow it to rest for 3 minutes. After the 3-minute rest period, shake the sample for an additional minute.

Step 4: Solution Filtration

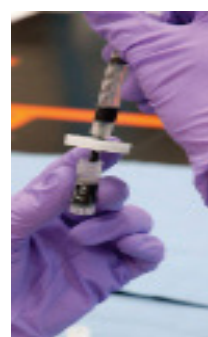
Remove the plunger from the enclosed 3-mL syringe and place a filter on the luer-lok fitting (Figure 4.8a). Using a plastic eyedropper, add approximately 2 mL of the test solution to the syringe and replace the plunger (Figure 4.8b). Slowly filter 0.5-1 mL of the test solution into a new clean 1-mL plastic tube (Figure 4.8c).



(a)



(b)



(c)

Figure 4.8. Different Stages of Solution Filtration.

Step 5: Dilution

Tare a new clean 45-mL sample tube on the balance. Using a micropipette, transfer 130 μ L of the filtered solution into the sample tube (Figures 4.9a and 4.9b). Dilute the 130- μ L

aliquot with water to accurately total 45 grams using a balance (Figures 4.9c and 4.9d). Cap the tube and mix the sample.

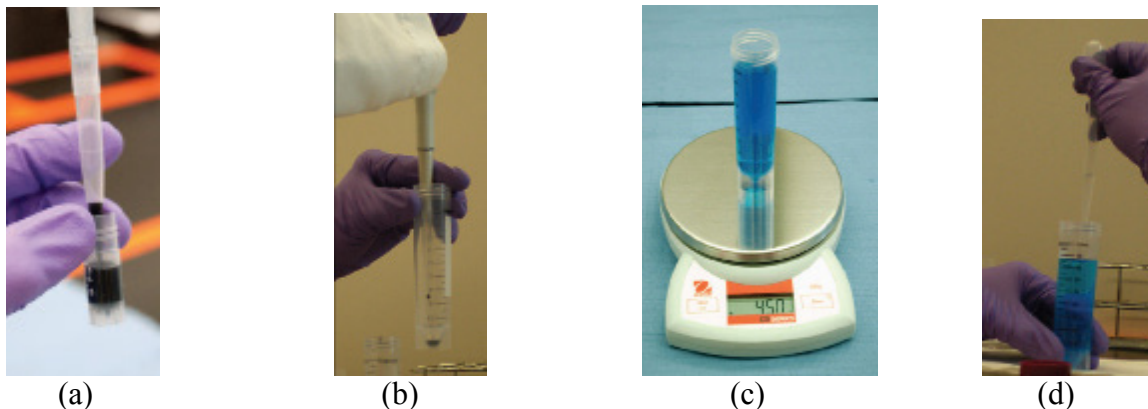


Figure 4.9. Different Stages of Dilution.

Step 6: Transfer to Test Tube

Fill a glass test tube with the newly diluted test sample and cap the tube. The solution is now ready to be measured by the colorimeter.

The following procedure pertains to the operation of the Hach DR 850 colorimeter:

Step 1: Start-up

Remove the instrument cover. Insert the 16 mm test tube adapter into the cell compartment and rotate until it drops into the alignment slots (Figure 4.10). Finish the installation by gently pushing down on the adaptor until it snaps into position. Turn on the power to the colorimeter (top right-hand button).



Figure 4.10. Installation of the Tube Adaptor.

Step 2: Method 107

Press the PRGM button and type in “107” then hit the ENTER key.

Step 3: Water Calibration

Place a glass test tube filled with water into the tube adapter and place cover over the tube. Press the ZERO key. The instrument will display a value a 7.50.

Step 4: Sample Measurement

Remove the glass test tube filled with water and replace with the test tube filled with the diluted sample (Figure 4.11). Take a measurement and record the absorbance. Next, rotate the glass tube within the meter a quarter revolution and take another measurement. Repeat a total of four times and take the average of the four values.



Figure 4.11. A Sample Tube Is Inserted into the Tube Adapter.

The MBV is a function of the initial and final methylene blue concentrations and is determined by the following equation:

$$\text{MBV} = [\{ (C_i - C_f) (30 \text{ mL}) \} / 20\text{g}] \times 1000$$

where:

C_i = Initial methylene blue concentration.

C_f = final methylene blue concentration.

The MBV value is reported as mg/g unit. If the MBV is ≥ 7.5 mg/g, report the MBV as greater than 7.5. The test may be repeated using only 10 g of sand. In this case, the MBV should be doubled. If the MBV is still ≥ 15 mg/g, the MBV is outside of the range of the instrument's tolerance.

Relating MBV to Clay Content

In order to relate the MBV to clay content, it is necessary to generate the relationship between MBV and standard clay of known quantity, as done in Chapter 3 (Figure 3.12). These are also referred to as calibration curves. In order to do this, we used a 20-gram sample of a pure siliceous sand (zero clay content) and replaced a portion of the sand by a standard clay mineral (bentonite and kaolinite) with 1 percent increments. In general, the higher the MBV, the higher the clay content is. Bentonite is a swelling clay, and it absorbs more methylene blue (i.e., high MBV) than kaolinite clay (non-swelling type). Therefore, MBV measurement can be a good indicator of the type and content of clay minerals present. The calibration curves based on standard clay mineral can be used to estimate clay content from MBV, provided aggregate fines contain primarily the same clay mineral (e.g., bentonite or kaolinite), which is used for the calibration. However, aggregate fines generally contain more than one clay mineral along with some non-clay minerals. Therefore, MBV vs. standard clay content relationship can be used for

rough estimation of clay content at the best. For a more accurate estimation of clay content, calibration curves representing type and amount of clay minerals present in aggregate fines in a particular region or location must be generated.

Results and Discussion

The MB values for the aggregate fines from 33 different sources were determined using the procedure described above, and the results are presented in Tables 4.6 and 4.7. Table 4.6 represents the MBV of pit run/screening materials, and Table 4.7 represents the MBV of stockpiled materials. A comparative assessment between MBV of pit run/screening and MBV of stockpiled materials is an effective way to monitor the clay content in the stockpiled materials and can serve as an effective quantify control measure. Because of the above reasons, a large number of pit run/screening materials were tested in the project.

WR Grace recommends MB testing using a sand-sized sample (i.e., passing the No. 4 sieve). However, we also tested at the P40 (passing No. 40 sieve) size as well since that is the same size used for the PI and bar linear shrinkage tests. Grace also suggests any aggregates with a MBV of 5 or greater can be problematic and should be cleaned further, as a significant amount of clay particles may still be present. The colorimeter has a peak value of 7.5, which corresponds to the water used to zero the colorimeter. In the case of really high clay amounts, all the methylene blue dye is absorbed by the clay minerals, thus giving a clear diluted solution, and the highest MBV around 7.5 is measured. It is recommended to report MBV of > 7.5 in this case. When this occurs, it is advisable to reduce the sample size from 20 g to 10 g and determine the MBV using 10 g of sample and 10 g of inert filler (i.e., clean silica sand with “zero” MBV). When using this 10–10 dilution method, the value displayed on the colorimeter needs to be doubled to get the real MBV for the sample. The 10–10 dilution method was used for Wood Pit, South Noodle, Bird Hill, Fordyce Murphy, Jones Mill, Vulcan Huebner, Armor, and Tolar. For some samples (e.g., Whitney Pit, South Noodle, and Pit #365), a 5–15 dilution method was used to obtain a representative MBV, as the 10–10 dilution method was still not sufficient to obtain that.

Table 4.6. MBV for Pit Run/Screening Materials.

Screenings	MBV (-4)	MBV (-40)	COV (-4) %	COV (-40) %
Pit #365	≥ 15**		6.3	
Whitney Pit	14.76*	≥ 15 **	1.5	0.9
South Noodle	13.16*	≥ 15 **	5.9	1.8
Armor	12.43*	13.66*	4.7	0.6
Tolar	11.79*		8.1	
Wood Pit	6.45	14.72*	4.6	0.5
Little River	6.28	10.59*	3.5	2.9
Bird Hill	5.35	11.78*	0.8	0.1
Jones Mill	4.67	9.76*	4.1	2.0
McKelligon Granite	2.95	6.71	3.8	0.4
Yarrington	2.63	3.99	2.7	2.4
Blum	2.45	4.64	2.9	1.3
Super Crushed Stone II	1.86	4.36	4.3	3.9
Rankin Pit	1.78	3.96	2.1	1.4
Hoot	1.2	1.84	0.7	0.5
McKelligon Dolomite	0.8	2.79	12.2	9.2
Super Crushed Stone I	0.73	1.71	2.7	1.9
Scarmardo	0.67	1.51	1.3	1.1
Fordyce Murphy		9.35*		3.3
Vulcan Huebner		9.15*		2.6
Beckman		6.25		1.3
Cemex South		5.48		2.2
La Burrita		5.34		3.1
Texas Crushed Stone		4.18		0.8
North Troy		2.96		2.4
Bridgeport		1.55		0.7
Smith Buster		1.27		1.5

Table 4.7. MBV for Stockpile Materials.

Stockpile	MBV (-4)	MBV (-40)
Wood Pit	6.28	13.66*
Armor	6.09	12.85*
Pit #365	4.61	9.39*
Bird Hill	3.31	10.25*
Beckman	1.02	4.13
Vulcan Helotes	0.98	2.86
Marble Falls		4.42
Delta		4.3

Note: * indicates 10–10 dilution method (10 g of aggregate fines + 10 g of inert siliceous sand)

** MBV \geq 15 with 10–10 dilution indicates MBV is outside the range of the instrument's tolerance

Table 4.8. PI and Bar Linear Shrinkage Results.

Aggregate Type		Liquid Limit	Plastic Limit	Plasticity Index (PI)		Linear Shrinkage (%)	COV %
				Value	Type		
Woods Pit	1st bucket	19	12	7	Low plasticity	6.33	9.12
	2nd bucket	18	13	5	Slightly plastic	5.00	0.00
Rankin Pit		13	9	4	Slightly plastic	3.00	0.00
South Noodle		N/A	7	N/A	Nonplastic	0.00	0.00
Smith Buster		N/A	17	N/A	Nonplastic	1.00	0.00
Bird Hill	1st test	17	17	0	Nonplastic	4.17	6.93
	2nd test	18	16	2	Slightly plastic	4.17	6.93
La Burrita		N/A	20	N/A	Nonplastic	0.00	0.00
Fordyce Murphy		N/A	11	N/A	Nonplastic	0.00	0.00
Cemex Mckelligon Dolomite	1st bucket	15	13	2	Slightly plastic	3.67	7.87
	Mixed 3 buckets	14	13	1	Slightly plastic	3.00	0.00
Whitney Pit		15	15	0	Slightly plastic	0.00	0.00
Jones Mill		16	16	0	Nonplastic	3.83	7.53
Mckelligon Granite		17	17	0	Nonplastic	3.17	9.12
Cemex South		16	15	1	Slightly plastic	3.90	9.25
Vulcan Helotes		14	14	0	Nonplastic	2.93	3.94
Pit #365		34	23	11	Medium plasticity	11.30	6.19
Martin Marietta North Troy		13	13	0	Nonplastic	2.67	10.83
Vulcan Huebner	1st bag	N/A	13	N/A	Nonplastic	2.17	13.32
	Mixed 4 bags	N/A	N/A	N/A	Nonplastic	2.00	0.00
Texas Crushed Stone		14	13	1	Slightly plastic	2.00	0.00
Bridgeport		N/A	N/A	N/A	Nonplastic	0.00	0.00
Marble Falls		15	13	2	Slightly plastic	N/A	N/A
Black Lease		15	14	2	Slightly plastic	4.33	13.32
Armor		32	18	14	Medium plasticity	11.00	0.00

After extensive testing using the modified methylene blue test method, there are a few key observations worth noting:

- A perusal of Tables 4.6 and 4.7 indicates an increase of MBV with decreasing particle size [(i.e., from -4.74 mm ($-$ No. 4 sieve) to 0.425 mm ($-$ No. 40 sieve)]. Figure 4.12 shows the comparison of MBV for screening materials tested at the two different sizes, and Figure 4.13 shows the comparison of MBV for stockpile materials tested at the two different sizes. In both the figures, a consistent trend of increasing MBV with decreasing particle size is clearly manifested. The higher concentration of clay particles in the finer fraction during sieving is the main cause of this kind of relationship between MBV and particle size. Also, a lower COV was found with the smaller particle size. It seems MBV of both -4 and -40 sizes are useful to categorize aggregate fines with varying clay contents, with the following notes:
 - For screening materials, -4 size is more representative. None of the samples tested with -4 size except Pit #365 show ≥ 15 MBV with 10–10 dilution, whereas some of the samples with -40 size (e.g., Whitney Pit, South Noodle) show ≥ 15 MBV with 10–10 dilution (i.e., outside of the range of the instrument’s tolerance).
 - For stockpiled materials, MBV of both -4 and -40 sizes can be used to categorize aggregate fines. None of the samples with -40 size show ≥ 15 MBV with 10–10 dilution. Also, less variation of the results has been typically noticed with the sample of smaller particle size (-40 sieve size).
- The samples with high range of MBV should be correlated with high amount of swelling clays. The relationship between amount of swelling type clay (as determined by QXRD and discussed earlier) and MBV are plotted for both -4 and -40 size fractions and presented in Figures 4.14 and 4.15, respectively. A fairly strong correlation ($R^2 \sim 0.64-0.84$) is observed for both the size fractions. The relationship, i.e., the higher the MBV the higher the amount of swelling clay, which was observed with standard bentonite clay, is valid in natural aggregate fines. Therefore, MBV is a true representation of type and amount of clay present.

Plasticity Index and Bar Linear Shrinkage

The plasticity index of a soil (AASHTO T 89) is the numerical difference between its liquid and plastic limits. It is generally used as a means to characterize the soil based on its clay content. The lowest water content determined by this test procedure at which the soil remains plastic is the *plastic limit*. The water content determined by this test procedure at which the soil passes from a plastic state to a liquid state is the *liquid limit*. Similarly with the PI test, the bar linear shrinkage (Tex–107–E) of a soil gives an idea of how much clay is contained within the test sample by determining the linear shrinkage. As one would expect, higher amounts of clay present will result in more shrinkage.

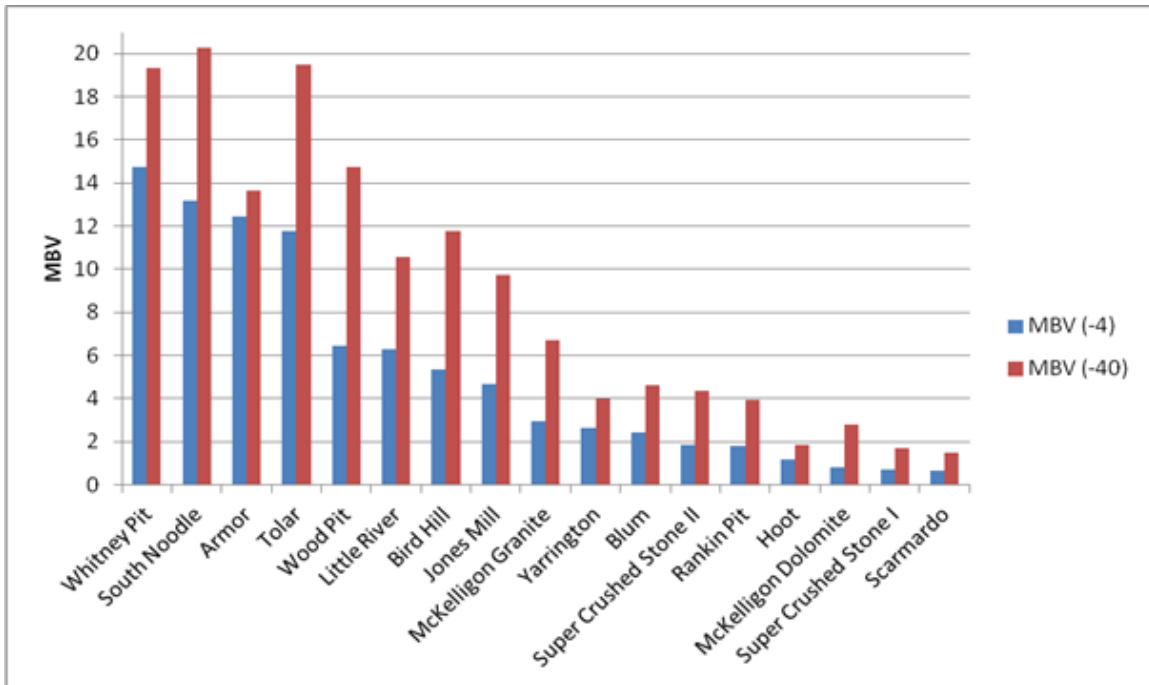


Figure 4.12. Effect of Particle Size on MBV for Screening Material.

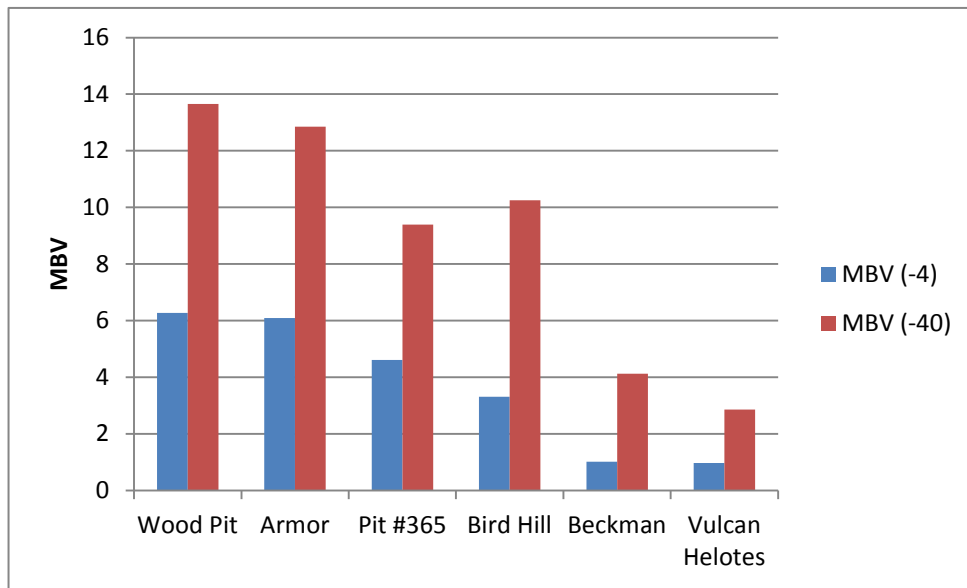


Figure 4.13. Effect of Particle Size on MBV for Stockpile Material.

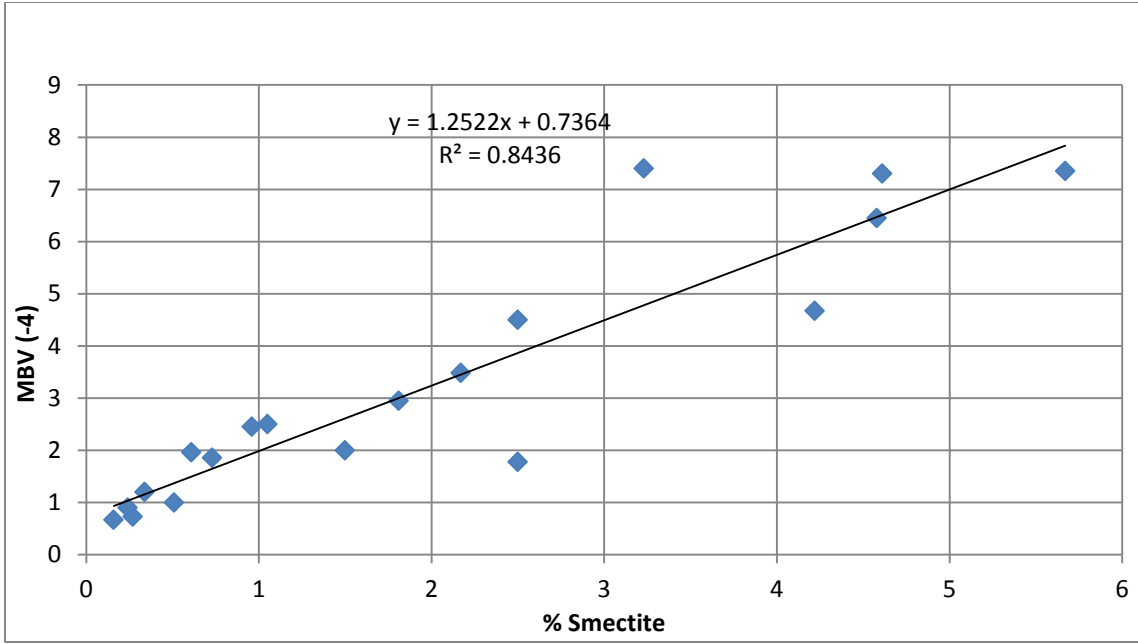


Figure 4.14. Relationship between Clay Content and MBV for Materials of -No. 4 Sieve Size.

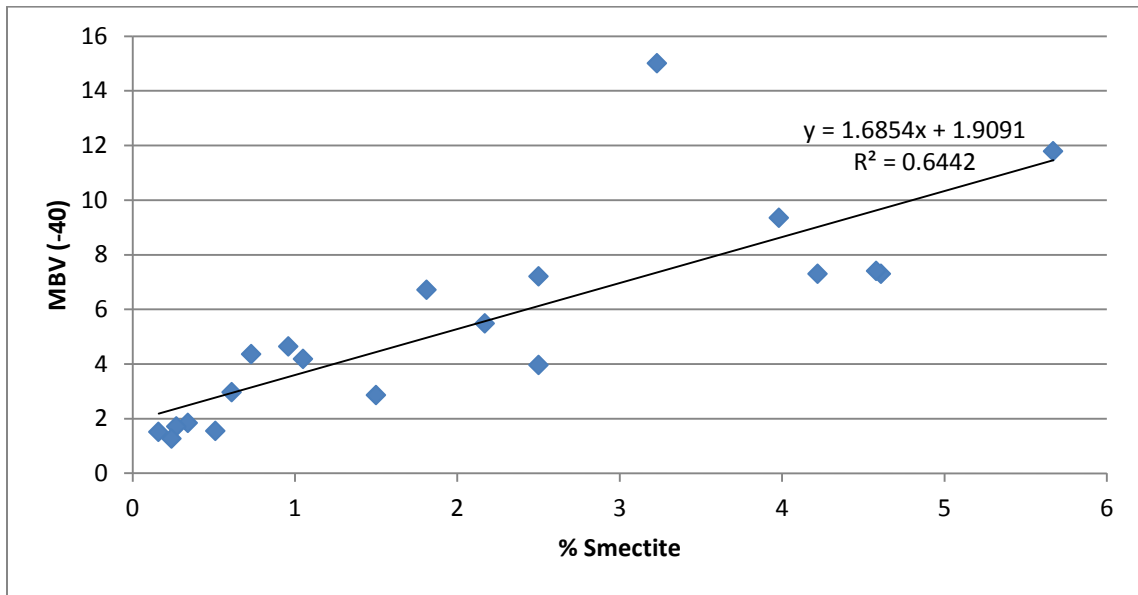


Figure 4.15. Relationship between Clay Content and MBV for Materials with -No. 40 Sieve Size.

Table 4.7 shows the PI and bar linear shrinkage results. The repeatability within the lab was calculated based on three replicas, and the COV was within 4 percent for all the results. The aggregates with the highest PI values are Wood Pit, Pit #365, and Armor Pit. There also appears to be a direct relationship between PI and bar linear shrinkage; thus, these aggregates have the highest bar linear shrinkage. For the most part, the higher MBVs for these aggregates seem to support the higher PI values and shrinkage. Figure 4.16 shows the relationship between bar

linear shrinkage and clay content. There seems to be a slight increase in shrinkage with an increase in clay content, but there is no strong consistent and positive correlation to support this reasoning.

Sand Equivalent Test

The procedure of sand equivalent (SE) test (Tex-203-F) is used to determine the relative proportion of detrimental fine dust or clay-like particles in soils or fine aggregates. Currently, the SE test is used as a preliminary test to detect clay-like particles in aggregate fines that are to be used in HMA mix design.

The SE test results are summarized in Table 4.8 shown below. Figure 4.17 shows the relationship between clay content and SE value. It is clear that even though there seems to be a gradual decrease in SE value with increasing clay content, there is no strong and consistent correlation to support this reasoning. This poor correlation provides evidence that the SE test is not a reliable test procedure to detect clay minerals in aggregate fines. However, the repeatability of this test is pretty good, with a COV within 3.2 percent for all the test results.

It seems the SE test fails to distinguish whether the clay-sized particles in the test sample are dust fines or actual clay minerals. Even though a higher amount of these clay-sized fines will yield a “bad” (i.e., lower) SE value, previous research has shown that clay-sized fines can actually be beneficial to the HMA in acting as mineral fillers while aiding in reducing air voids. Similarly, having a permissible amount of clay-sized particles or non-expansive clay minerals can help in PCC mixes as well. It is only the swelling clay minerals that can be problematic in HMA or PCC mixes. The SE test cannot distinguish the difference between a non-swelling (i.e., kaolinite) and swelling (i.e., bentonite); it will simply give a low SE value for both cases if either type of clay mineral is present (discussed later in Chapter 5).

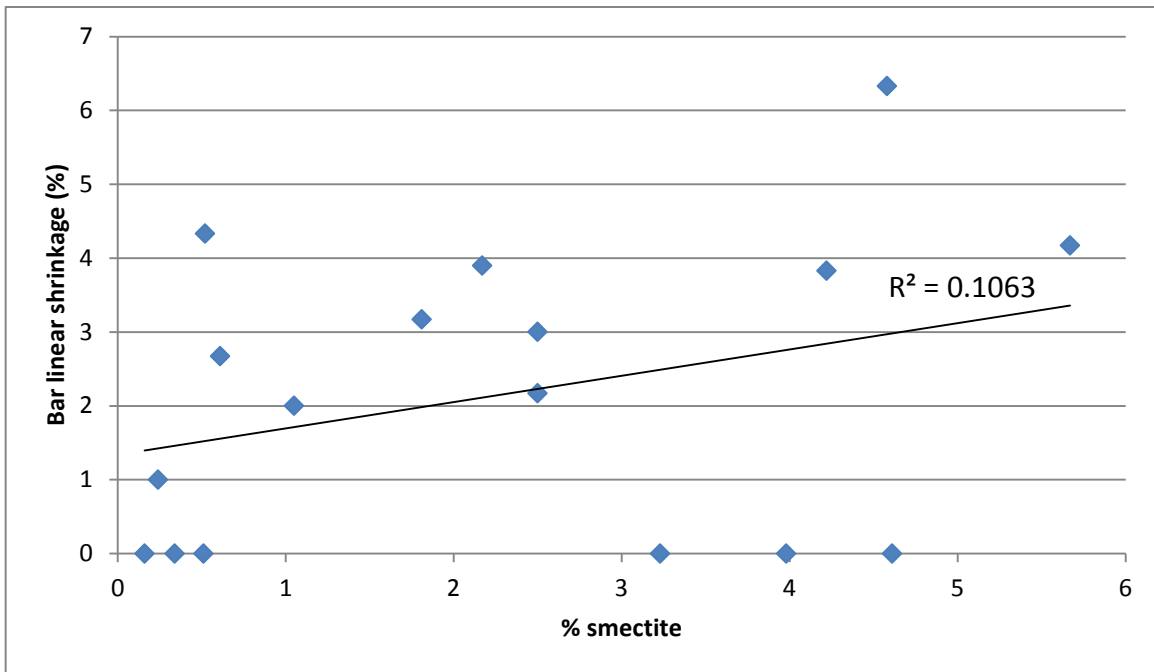


Figure 4.16. Relationship between Clay Content and Bar Linear Shrinkage.

Table 4.9. SE Test Results.

Aggregate Pit	1st reading	2nd reading	3rd reading	Avg. SE value	STD	COV %
JONES MILL	53.3	51.2	54.6	53	1.7	3.2
CEMEX SOUTH	68.5	71.7	70.4	70	1.6	2.3
MCKELIGON DOLOMITE	75	78.4	78	77	1.9	2.4
FORDYCE MURPHY	60.7	58.2	59.1	59	1.3	2.1
RANKIN	64	62.2	62.7	63	0.9	1.5
WOOD PIT	40.9	42.2	42	42	0.7	1.7
WHITNEY PIT	29.7	31.3	30.2	30	0.8	2.7
SOUTH NOODLE	93.6	93.1	93.8	94	0.4	0.4
BIRD HILL	52.4	50.7	51.4	52	0.9	1.6
McKELIGON GRANITE	58.7	58.3	58	58	0.4	0.6
La BURRITA	87.8	86.3	87.1	87	0.8	0.9
NORTH TROY	70.3	70.2	70.1	70	0.1	0.1
SMITH/BUSTER BYRD PIT	26.7	25.7	25.3	26	0.7	2.8
HELOTES	80.3	81.6	80.9	81	0.7	0.8
DELTA	66.1	65.9	66.4	66	0.3	0.4
MARBLE FALLS	53.1	52.8	53.3	53	0.3	0.5
MINE SERVICES #365	12.7	12.9	12.6	13	0.2	1.2
BLACK LEASE	30	30.7	29.8	30	0.5	1.6
MARTIN MARIETTA	59.3	60.1	60.4	60	0.6	0.9
HOOT PIT	98.1	95.6	96.4	96	1.3	1.3
SCARMARDO	96.3	98.2	97.7	97	1.0	1.0
ARMOR	16	14.4	14.9	15	0.8	5.5
VULCAN HUEBNER	67.3	66.8	68.1	67	0.7	1.0
TEXAS CRUSHED STONE	74.1	73.5	73.9	74	0.3	0.4
BRIDGE PORT	93.5	93.8	93.1	94	0.4	0.4

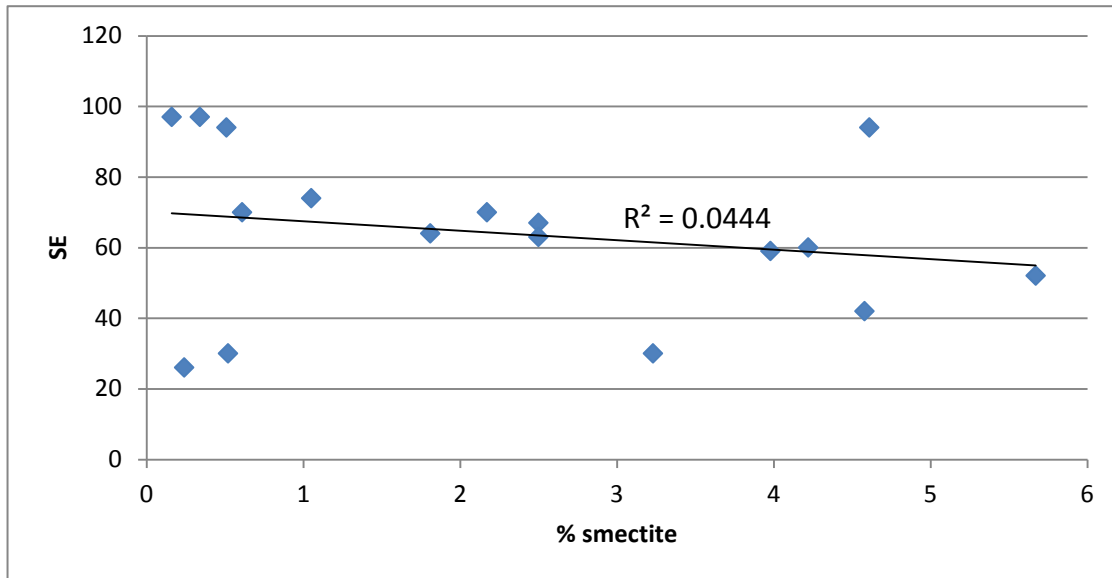


Figure 4.17. Relationship between Clay Content and SE Value.

SUMMARY AND CONCLUSIONS

The following conclusions can be made based on the results of methylene blue, bar linear shrinkage, and sand equivalent tests:

- A strong positive correlation between clay content (determined by QXRD) and MBV is evident (Figures 4.14 and 4.15), which clearly indicates that the MMB test is the most reliable and rapid best method to detect clay minerals in aggregate fines. Although the bar linear shrinkage and sand equivalent tests give good repeatability in the results, both the bar linear shrinkage and the sand equivalent tests fail to provide consistent and accurate indications of clay minerals present in aggregate fines (Figures 4.16 and 4.17).
- Furthermore, the MMB test procedure has several advantages over the bar linear shrinkage and sand equivalent tests.
 - The MMB test procedure is easy to follow and can be performed in the field.
 - It can be performed by nearly anyone and does not require any advanced training for operation.
 - The entire test can be completed in about 10 minutes.
 - The test consistently gives good results with low variability.
- MBV of both –4 and –40 sizes can be used to categorize aggregate fines for stockpiled materials.
- A correlation between MBV and concrete performance testing (discussed further in chapters 5 and 6) will become the basis to categorize aggregates fines with different ranges of MBV. An attempt will be made to establish threshold MBV based on concrete performance (both HMA and PCC).

CHAPTER 5

TESTS WITH EXPERIMENTAL AGGREGATE SAMPLES (IMPACT ON ENGINEERING PROPERTIES)

The goal of this section was to conduct an extensive laboratory test program to determine the level of standard clay contamination where the critical engineering properties are impacted. This section involves PCC and HMA mixing and performance testing using pure reference clays. It was proposed to use experimental aggregate samples in order to develop the best testing procedure to follow in Chapter 6 where real aggregate samples have been used. Different percentages of pure clays (Georgia kaolinite and Gonzales, Texas, smectite) were added (0, 1.5, 3, 5 percent by wt.) during mixing of bituminous and Portland cement concrete and the effects on selective fresh and hardened properties were measured. A clean sedimentary dolomitic aggregate was selected from the Hanson–Burnet quarry for the PCC testing, and an igneous rock was selected from a Martin Marietta–Jones Mill quarry for the HMA testing. The same smectite and kaolinite clay mineral standards that are used in Chapter 3 are also used in this chapter.

PORTLAND CEMENT CONCRETE MIXES

A conventional concrete mix design was used in this section. Table 5.1 shows relevant mix design information specific to the components of the mix. Table 5.2 shows the relevant aggregate properties required for mix design. The amounts of each component in the mix based on 1 yd³ (27 ft³) are presented in Table 5.3.

Table 5.1. Mix Design Parameters.

w/c ratio	Fly ash	Coarse aggregate factor	Cement factor
0.42	20% class F	0.68	6

Table 5.2. Aggregate Properties.

	Specific Gravity (BSG _{OD})	Dry Rodded Unit Weight (DRUW) –lb/ft ³	Absorption Capacity (AC %)
Coarse Aggregate	2.74	100.5	0.89
Fine Aggregate (sand)	2.63	112.2	0.52

Table 5.3. Batch Weight (Based on 27 ft³).

Mix component	Cement	Fly ash (class F)	Coarse aggregate	Fine aggregate (sand)	Water	Air entraining admixture (mL)
Amount (lb)	451.2	112.8	1860.3	1316.9	237.8	180.5

A clean, sedimentary dolomitic aggregate from the Hanson–Burnet quarry was used as coarse aggregate, and a clean siliceous natural sand from Knife River was used as fine aggregate (Table 5.2). The control mix (Table 5.3) does not contain any clay. For the mixtures with standard pure clays (bentonite and kaolinite), 1.5 and 3 percent of coarse aggregate weight was replaced by the standard clay minerals. The control mix provided around 1–in. slump. Due to the high water demand caused by the incorporation of the bentonite (i.e., smectite clay), it was decided to add more water (i.e., 0.49 w/c with 1.5 percent clay and 0.6 w/c with 3 percent clay) in the mixes with bentonite clays in order to achieve the same workability (i.e., around 1–in. slump). However, the concrete mixtures with kaolinite clay (both 1.5 and 3.0 percent replacement levels) provided the same workability (i.e., around 1–in. slump) with a 0.42 w/c as kaolinite is a non–swelling type clay. Drying shrinkage and flexural strength were measured for each mix. The test results are presented in the sections below.

EFFECT ON DRYING SHRINKAGE

Drying shrinkage was measured according to ASTM C 157 for all the mixtures. Specimens were cast, covered, and then stored in a 100 percent RH environmental chamber to cure for 24 hours. After the 24–hour curing period, specimens were de–molded then placed in lime–saturated water for 30 minutes. The samples were then measured to get their original length using the comparator. Next, the specimens are stored in the 50 percent RH environmental chamber at 23°C. The length change was monitored for each specimen until drying for 28 days. The test results are presented below in Figure 5.1.

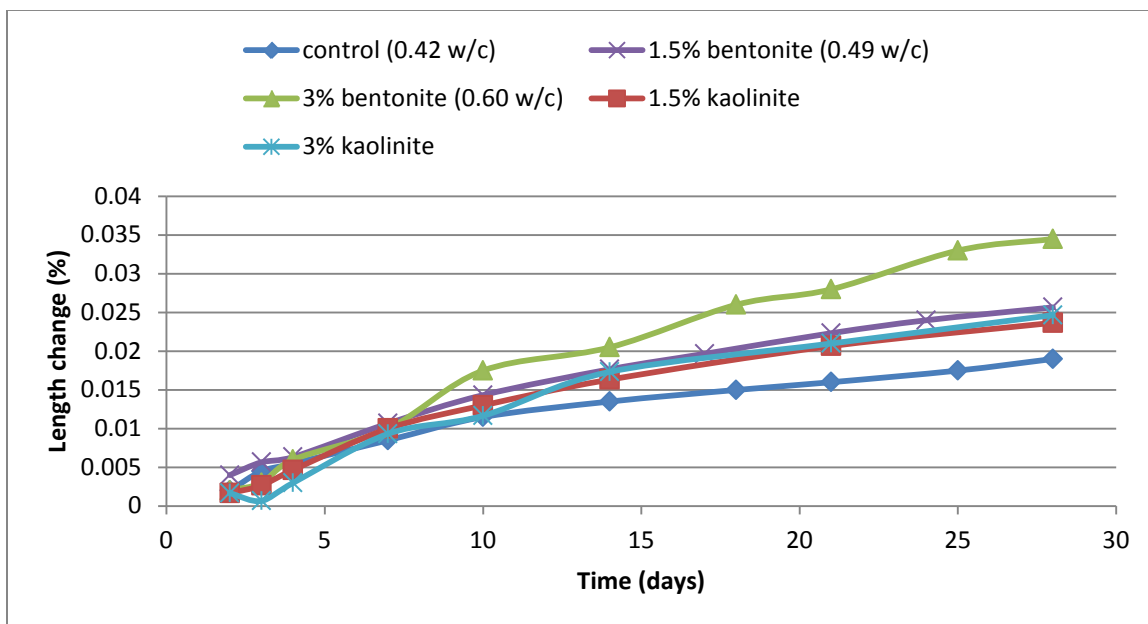


Figure 5.1. Drying Shrinkage Results for Bentonite and Kaolinite–Rich PCC Mixes.

Based on the results in Figure 5.1, it can clearly be seen that the incorporation of an expansive clay mineral like bentonite causes an increase in drying shrinkage. The addition of an appreciable amount of an expansive clay mineral (i.e., up to 3 percent) to a PCC mix greatly increases the water demand. In order to allow for adequate mixing and sample casting, the w/c

has to be raised from 0.42 to 0.49 and 0.60 for the mixes containing 1.5 and 3 percent bentonite, respectively. While there is a significant increase in the shrinkage going from 1.5 to 3 percent bentonite, the mixes with 1.5 and 3 percent kaolinite had essentially the same degree of drying shrinkage. A perusal of Figure 5.1 indicates the change in length of the concrete containing 1.5 percent bentonite was nearly the same as the concrete containing 3 percent kaolinite at 28 days (roughly 0.025 percent).

EFFECT ON FLEXURAL STRENGTH

The flexural strengths at 7 and 28 days were determined according to ASTM C 78 for all the concrete mixes and are presented in Table 5.4 and Figure 5.2. Figure 5.2 shows an overall comparison in flexural strength at 7 and 28 days for both the bentonite-rich and kaolinite-rich mixes. Table 5.4 also gives the percentage decrease in flexural strength in comparison with control mix both at 7 and 28 days.

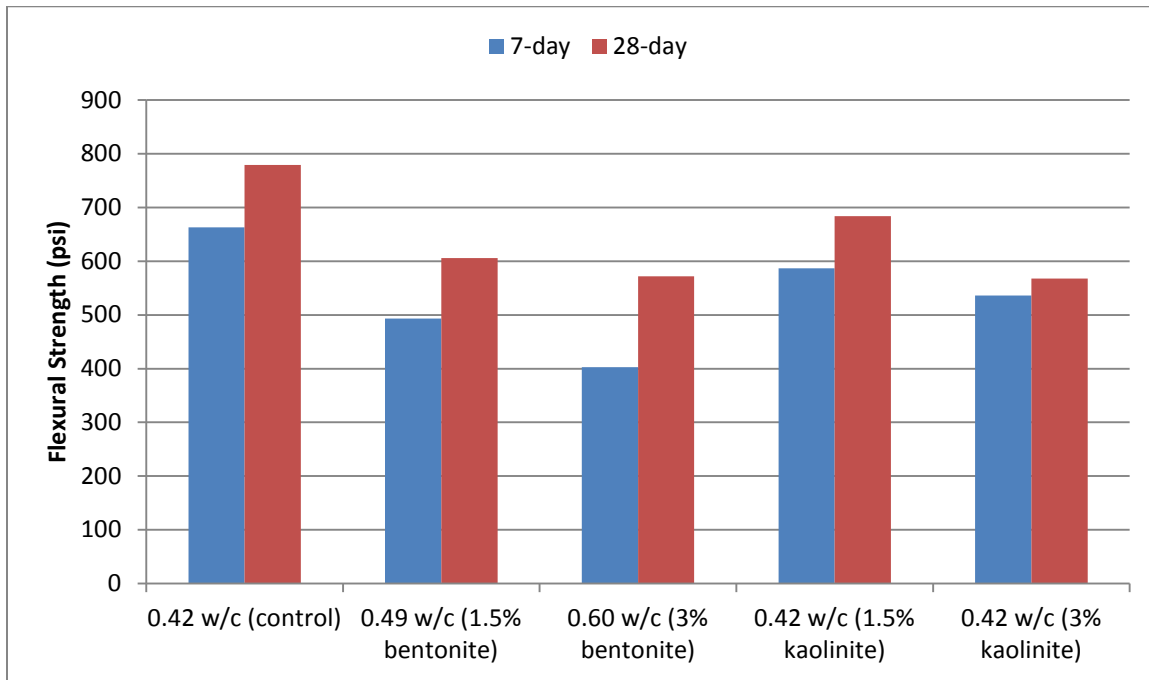


Figure 5.2. Flexural Strength Results at 7 and 28 Days.

Table 5.4. Flexural Strength Comparison.

Mix	7-day strength (psi)	28-day strength (psi)	% decrease in 7-day strength	% decrease in 28-day strength
Control	663	779		
1.5% bentonite	493	606	25.6	22.2
3% bentonite	404	572	39.0	26.6
1.5% kaolinite	587	684	11.5	12.2
3% kaolinite	536	668	19.1	14.2

As expected, the highest strength can be seen in the control mix. Incorporating 1.5 percent bentonite causes a 25 and 22 percent reduction in flexural strength at 7 and 28 days (Table 5.4), respectively. On the other hand, adding 3 percent bentonite causes a 39 and 26 percent reduction in flexural strength at 7 and 28 days, respectively. In contrast, the flexural strength of the mixes containing kaolinite clay was not compromised as much compared to the control mix. For example, there was only about an 11 percent reduction in 7–day strength and about a 12 percent reduction in 28–day strength for the mix with 1.5 percent kaolinite. The mix with 3 percent kaolinite shows a slightly higher reduction in strength (e.g., 19 percent at 7 days and 14 percent at 28 days) compared to the 1.5 percent case. It is likely that the greater reductions in flexural strength (in case of mixes with bentonite clay) can be attributed to the increased water demand (i.e., higher w/c) needed to allow for adequate mixing and specimen compaction.

THRESHOLD MBV

Figure 5.3 shows the change in strength, as compared to the control, at 7 days for the mixes containing 1.5 and 3 percent bentonite. Figure 5.4 shows the change in strength at 7 days for the mixes containing 1.5 and 3 percent kaolinite. From Figure 5.3, a PCC mix can tolerate roughly 1.2 percent bentonite and still give acceptable 7–day strength (i.e., 555 psi). Figure 5.4 shows that satisfactory flexural strength can be achieved with a PCC mix that contains up to about 2.3 percent kaolinite, approximately double the permissible amount of bentonite. The data in Figure 5.5 below were generated using concrete sand similarly as the MBV versus clay content calibration curves were developed in Chapter 3 using pure silica sand. The different percentages of sand (i.e., 0, 1.5, and 3 percent) were replaced by standard clays. This way we are able to establish a more accurate correlation between clay content and MBV in defining threshold MBV based on flexural strength testing. Based on this reasoning, an MBV of about 3.7 or below (with respect to expansive bentonite clay, Figure 5.5) would satisfy the TxDOT minimum 7–day flexural strength requirement of 555 psi.

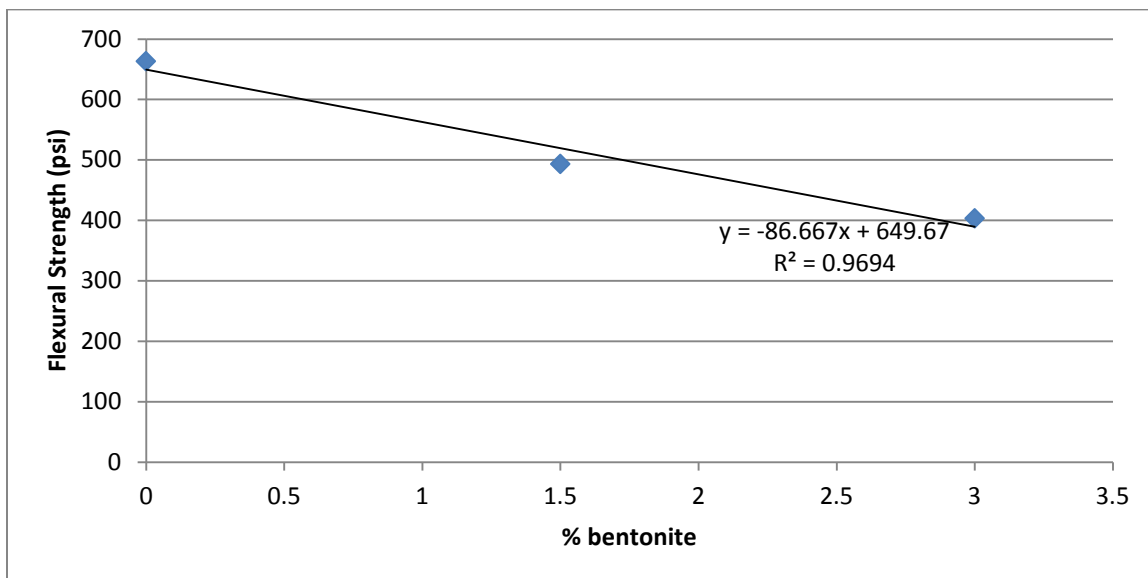


Figure 5.3. Flexural Strength Results for Bentonite–Rich PCC Mixes at 7 Days.

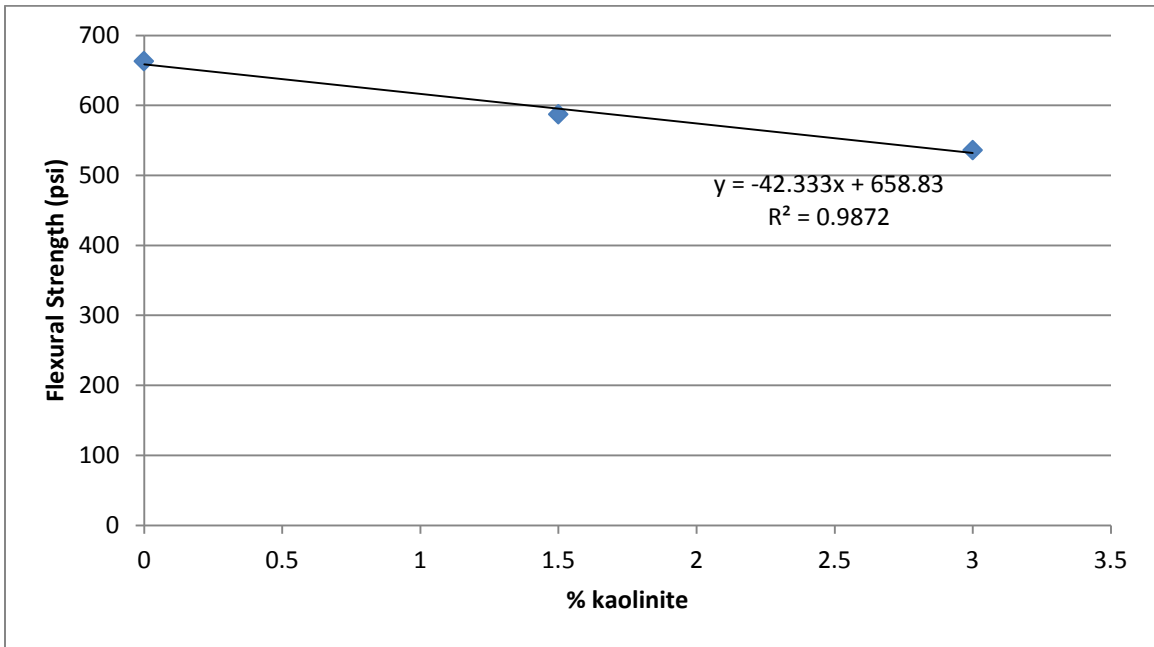


Figure 5.4. Flexural Strength Results for Kaolinite–Rich PCC Mixes at 7 Days.

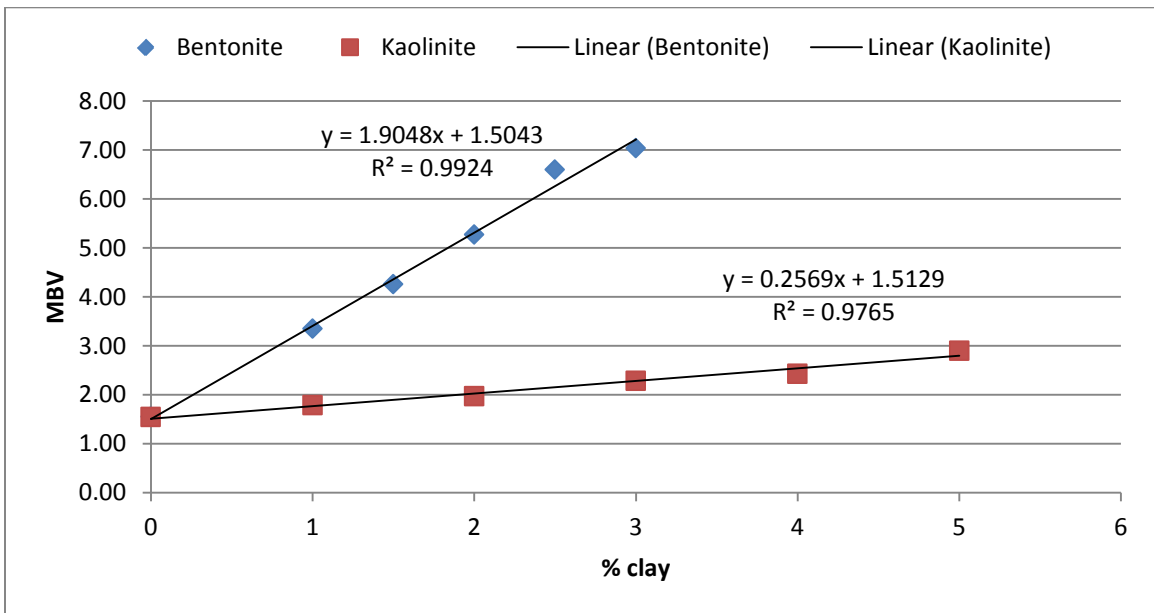


Figure 5.5. Effect of Clay on MBV for Concrete Sand.

RELATIONSHIP BETWEEN REDUCTION IN STRENGTH AND INCREASE IN SHRINKAGE

The addition of bentonite has greatly increased the water demand whereas the addition of kaolinite showed only a marginal effect on water demand. Adequate mixing and sample compaction was still possible without adding any additional water (higher than w/c 0.42) for kaolinite mixes.

Figures 5.6 through 5.9 show the relationship between the percent increase in drying shrinkage and percent decrease in flexural strength over time until 28 days. Figures 5.6 and 5.7 show this relationship for the mixes with 1.5 percent bentonite and 3 percent bentonite, respectively. Figure 5.6 shows that there was approximately a 21 percent increase in drying shrinkage along with about a 22 percent decrease in flexural strength when the coarse aggregate fraction was replaced by 1.5 percent by wt. of bentonite. Figure 5.7 shows that there was roughly up to an 80 percent increase in drying shrinkage along with about a 27 percent decrease in 28-day flexural strength with a 3 percent replacement of bentonite for the coarse aggregate fraction. Figures 5.8 and 5.9 show how the drying shrinkage and flexural strength were affected by the addition of kaolinite to the concrete. Figure 5.8 shows about a 23 percent increase in drying shrinkage along with a decrease in flexural strength of about 12 percent. Based on Figure 5.9, the 3 percent kaolinite caused the drying shrinkage to be increased by nearly 30 percent, and the flexural strength is compromised by 14 percent at 28 days.

At 1.5 percent replacement level, the percentage increase of shrinkage was slightly higher for bentonite (30–35 percent) than kaolinite (15–25 percent) but percent strength reduction was much higher in bentonite (25–22 percent) mixture than that at kaolinite mixture (~10 percent). Therefore, a non-favorable crack pattern, with respect to crack spacing and width, is expected with 1.5 percent bentonite mixture provided around 25 percent strength reduction is not permissible (discussed in details next). At 3 percent replacement level, the bentonite mixture shows very high percent increase of shrinkage along with reasonably high percent reduction of strength (Figure 5.7) in comparison with kaolinite mixture (Figure 5.9). An uncontrolled pattern of crack formation with respect to spacing and width is unavoidable with 3 percent bentonite mixture. It is expected that a reasonably high percent of shrinkage increase (~ 30 percent) in kaolinite mixture (3 percent) may not affect the crack pattern development much as percent strength reduction (18–12 percent) is still low. In all cases, the shrinkage increase is more than the strength decrease.

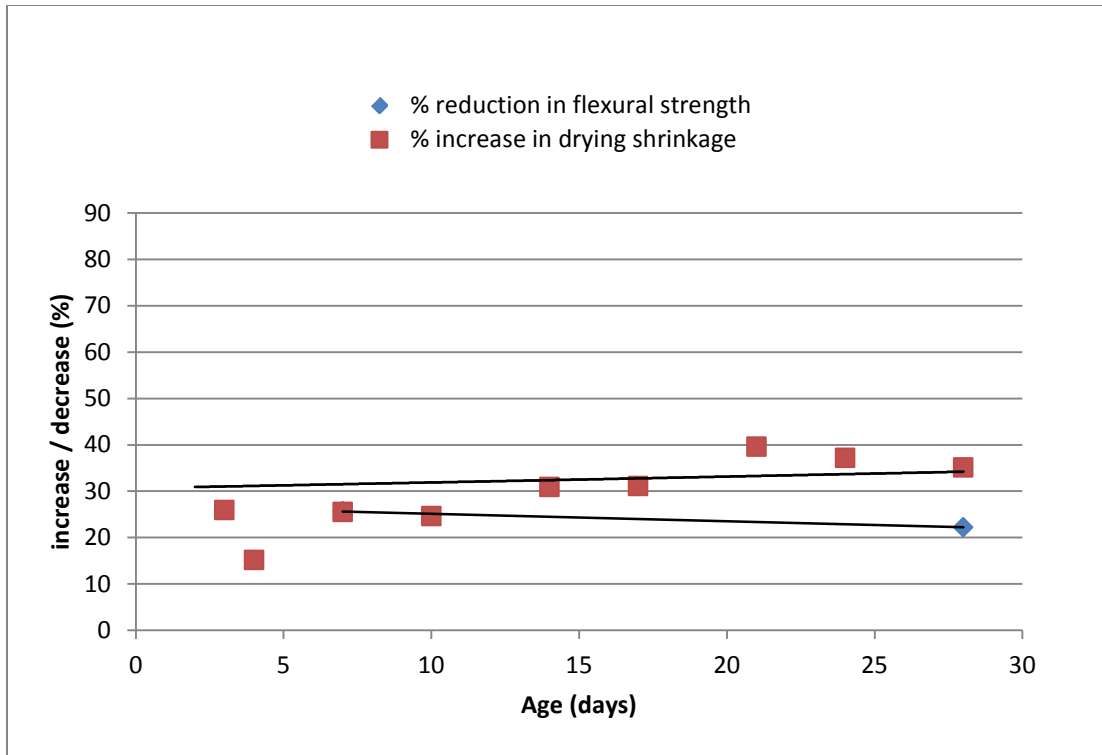


Figure 5.6. Drying Shrinkage Increase versus Flexural Strength Decrease in PCC with 1.5 Percent Bentonite Clay.

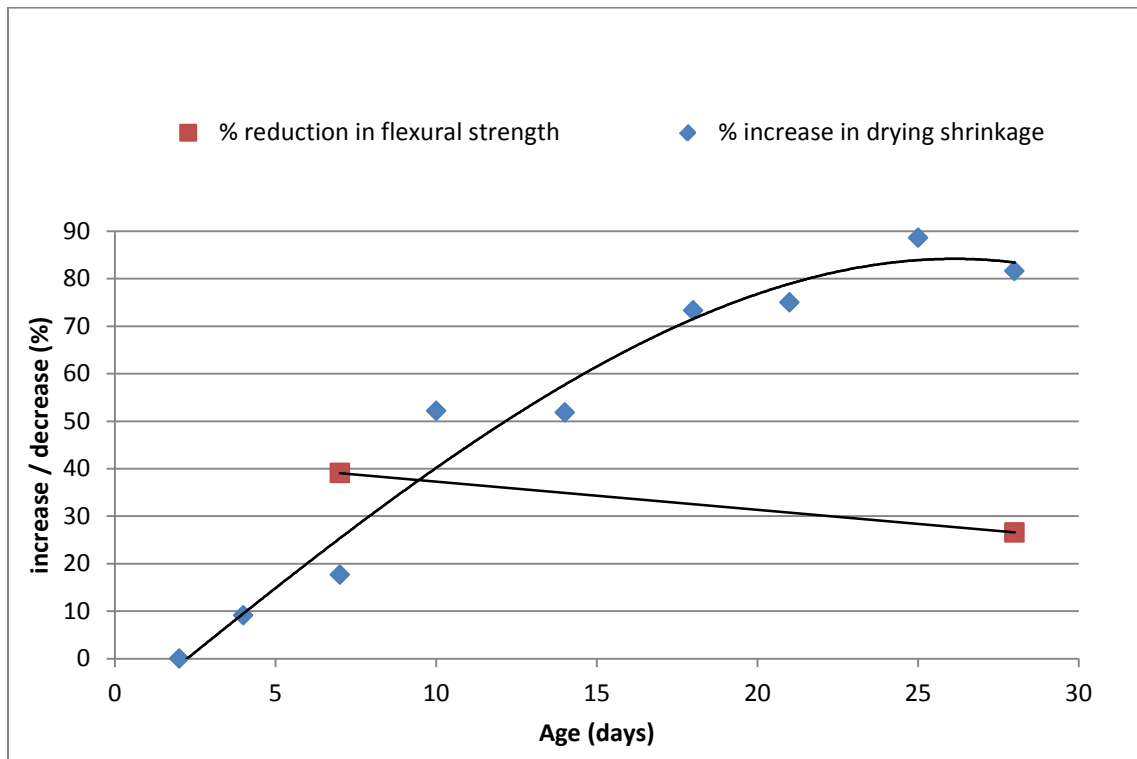


Figure 5.7. Drying Shrinkage Increase versus Flexural Strength Decrease in PCC with 3 Percent Bentonite Clay.

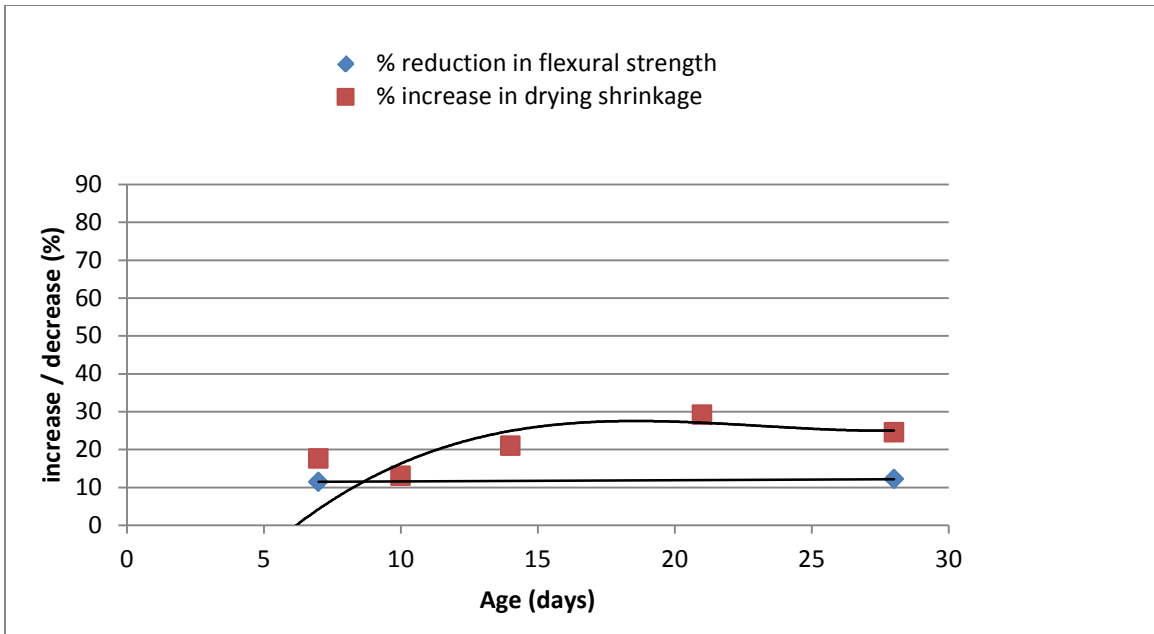


Figure 5.8. Drying Shrinkage Increase versus Flexural Strength Decrease in PCC with 1.5 Percent Kaolinite Clay.

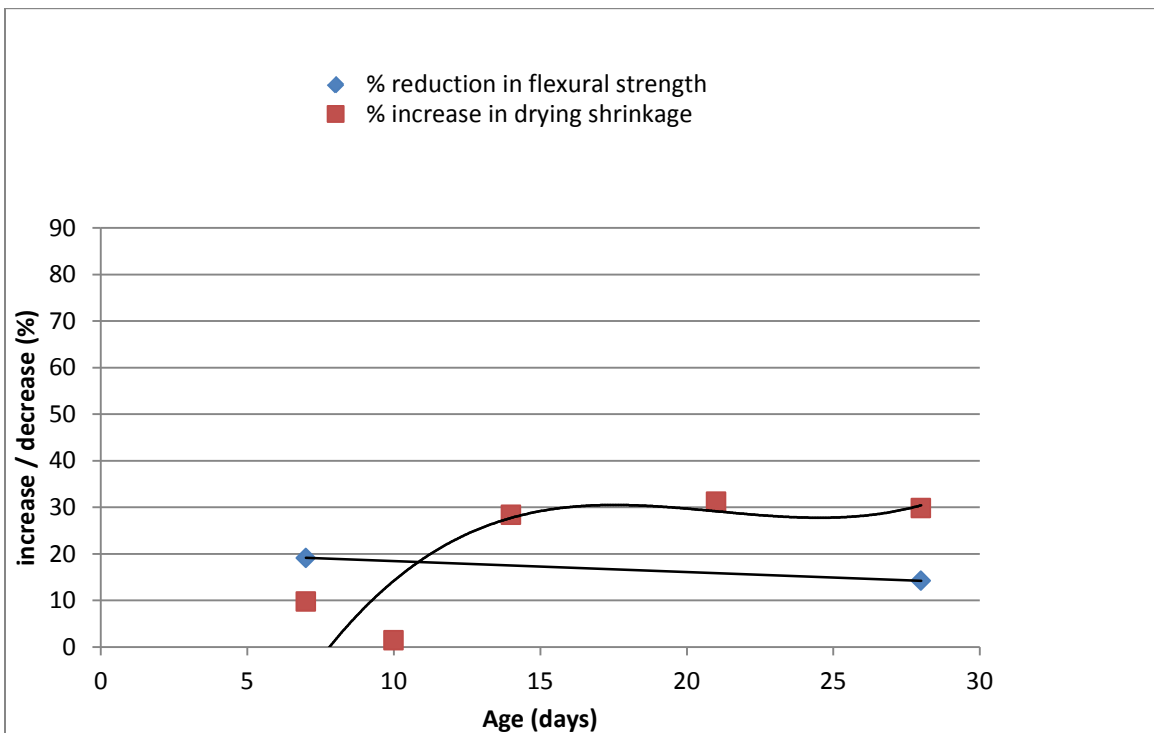


Figure 5.9. Drying Shrinkage Increase versus Flexural Strength Decrease in PCC with 3 Percent Kaolinite Clay.

Figures 5.10 and 5.11 show the relationship between MBV vs. percent decrease of strength and MBV vs. percent increase of shrinkage, respectively. Interestingly, MBV shows a good correlation with both percent reduction in strength and increase in shrinkage. Based on the threshold MBV of 3.7 obtained earlier, we can relate this to the permissible amount of flexural strength reduction (Figure 5.10) and drying shrinkage increase (Figure 5.11). For example, an MBV of 3.7 corresponds to strength reduction of about 25 percent and a shrinkage increase of about 11 percent. If the assignment of these permissible limits is good, then 3 percent bentonite mixture is above the permissible limit for percent reduction in strength and percent increase in shrinkage (Figure 5.7). These values are based on 7–day test results, as the TxDOT flexural strength requirement is based on 7–day strength.

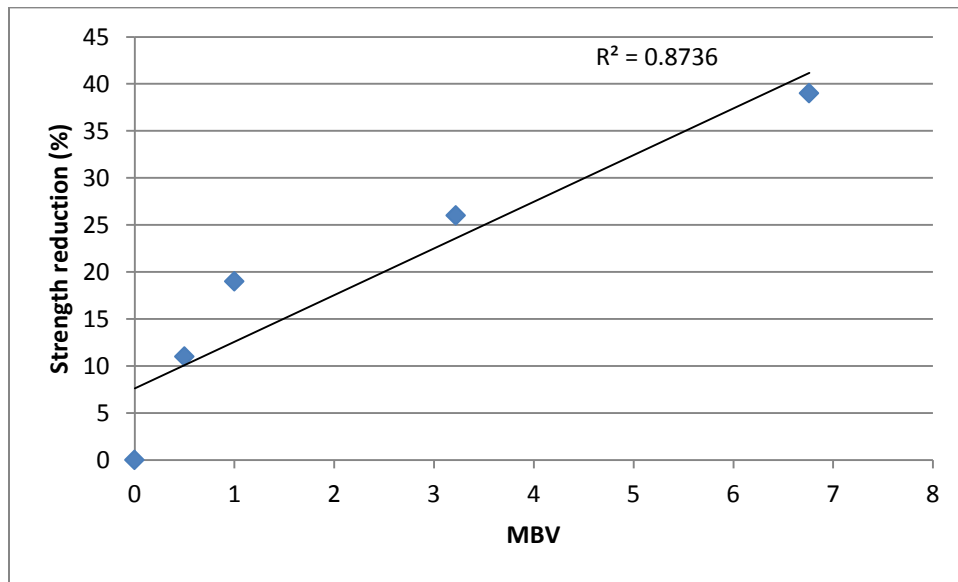


Figure 5.10. Relationship between MBV and Flexural Strength Reduction at 7 Days.

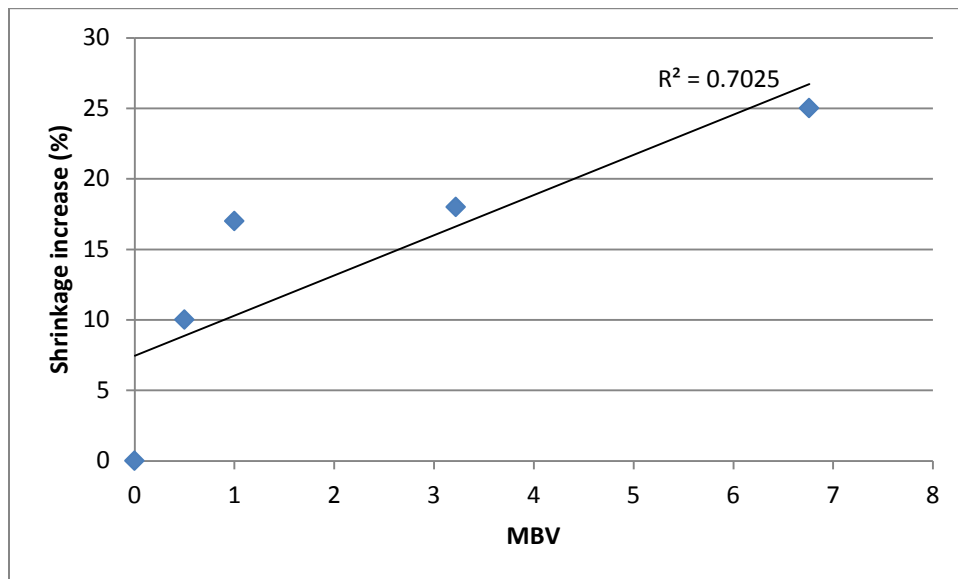


Figure 5.11. Relationship between MBV and Drying Shrinkage Increase at 7 Days.

SUMMARY AND CONCLUSIONS

The incorporation of an expansive clay mineral like bentonite causes an increase in drying shrinkage and reduction in strength of PCC mixtures. It is likely that the greater reductions in flexural strength and increase in shrinkage (in case of mixes with bentonite clay) can be attributed to mainly the increased water demand (higher w/c) needed to allow for adequate mixing and specimen compaction. This is an indirect effect due to the presence of expansive clay minerals in aggregate fines. The main direct effect is causing poor bond between aggregate and paste. Concrete testing using a fixed w/c (~ 0.45) will enable us to study the direct effect alone.

A threshold MBV of around 3.7 is obtained based on (i) percent bentonite vs. flexural strength and (ii) percent bentonite vs. MBV relationships. A similar method in developing a threshold MBV will be examined in Chapter 6 based on concrete testing with the selected five different natural stockpile aggregates as part of the test factorial.

MBV shows a good correlation with both percent reduction in strength and increase in shrinkage of the corresponding PCC mixtures. The permissible percent strength reduction and percent shrinkage increase at threshold MBV of 3.7 are 25 percent and 11 percent, respectively.

BITUMINOUS MIXES

The goals of this section were to determine the effect of different clay types and various amounts of clay contamination on the moisture susceptibility and cracking potential of asphalt mixtures and to identify a laboratory test method that can be used to detect the type and level of clay contamination in the aggregate in an accurate and simple way. An igneous aggregate: Jones Mill produced by Martin Marietta was used to prepare asphalt mixture specimens following a specified Type D mixture design. The combined aggregate gradation is shown in Figure 5.12. The mixture design prescribed the use of a liquid anti-stripping agent; however, because one of the objectives of the study was to evaluate the moisture susceptibility of the mixtures with added clay, no anti-stripping additives were included. The type of asphalt used to prepare the mixtures was a Wright/Valero PG 76-22.

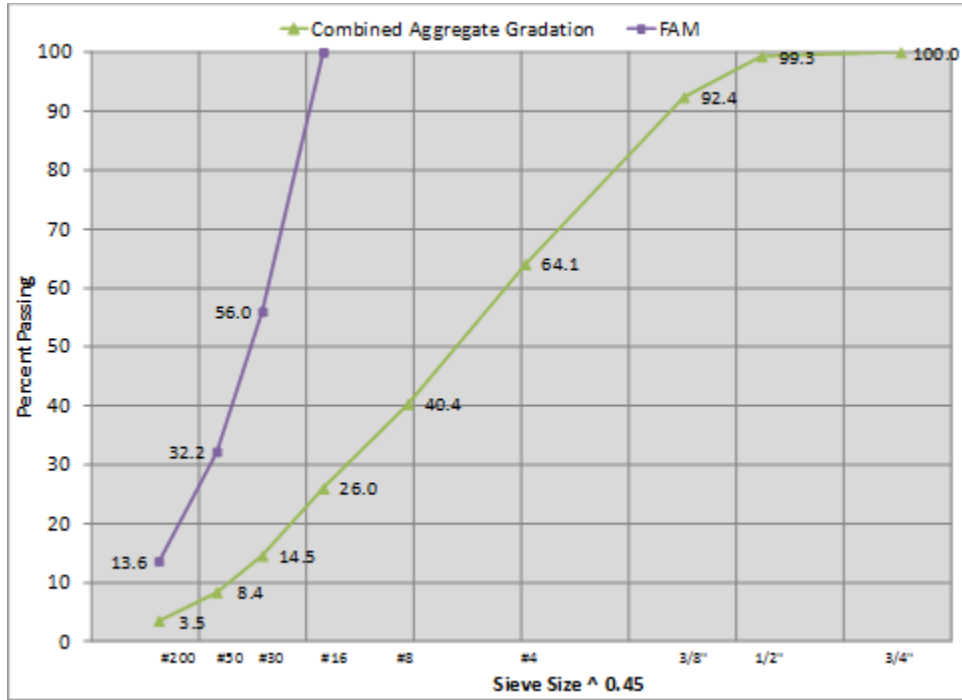


Figure 5.12. Full and Fine Aggregate Combined Aggregate Gradations.

Two types of clay were added to the mixtures as powder coatings: Gonzales, Texas smectite and Georgia kaolinite. Several amounts of clay (1, 3, and 5 percent) were intermixed with the Jones Mill material passing sieve No. 4, and the samples were tested by the sand equivalent test procedure (Tex 203–F). The results are shown in Figure 5.13. Using linear regression, the amounts of clay to produce SE values between 25 and 65 percent were determined. This range was selected around TxDOT’s minimum SE test requirement value of 45 percent. Results are presented in Table 5.5.

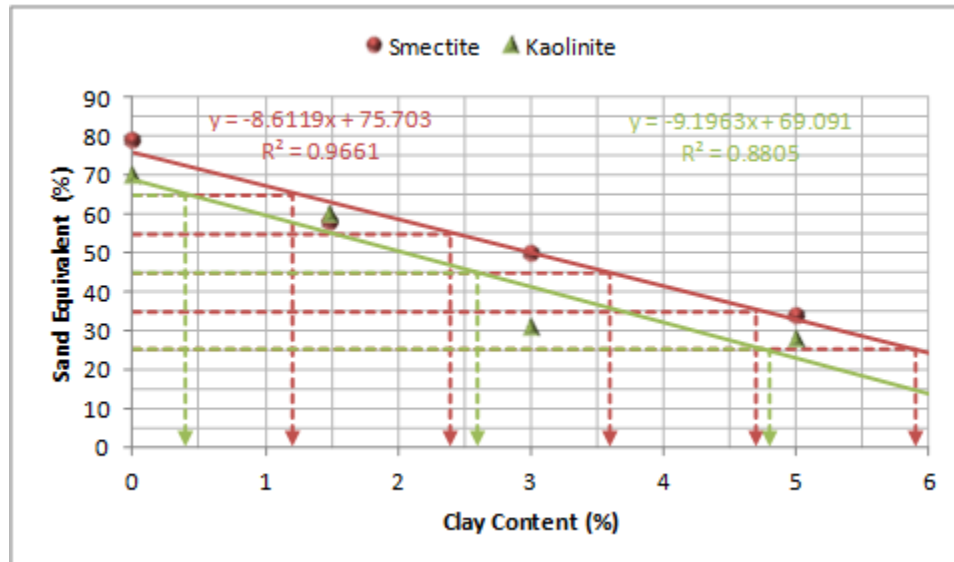


Figure 5.13. Sand Equivalent Test Results for Jones Mill Aggregate Samples without Clay and with Various Amounts of Smectite and Kaolinite Clay.

Table 5.5. Required Clay Contents to Achieve Target Sand Equivalent Values.

Clay Type	Sand Equivalent (%)	Clay Content (%) ^A	Binder Content for the Full Mixture (%)	Binder Content for the FAM mixture
Smectite	25	5.9	5.7	13.0
	35	4.7	5.5	12.7
	45	3.6	5.4	11.1
	55	2.4	5.3	—
	65	1.2	5.3	—
Kaolinite	25	4.8	5.3	—
	45	2.6	5.5	—
	65	0.4	5.7	—

^A Calculated using the linear regression equations shown in Figure 5.13

In addition to measuring SE, the methylene blue value (MBV) was also measured for the same samples. The relationship between the MBV and the SE results for each clay type are illustrated in Figure 5.14. As can be observed, contrary to the SE test, the MMB test was able to differentiate between clay types, yielding very distinct values for each material. The MBV for the Jones Mill material with no clay added was 2.51 mg/g. For the smectite clay, the range of MBVs was from 4.76 to 7.20 mg/g. For the kaolinite clay, on the other hand, the MBVs ranged from 2.63 to 3.64 mg/g. A perusal of Table 5.5 clearly indicates that the kaolinite content is less than smectite content at any levels of SE values. The SE test proves that it cannot differentiate between expansive (smectite) and non-expansive clay (kaolinite). Based on SE test, kaolinite is more harmful than smectite, which is certainly not true.

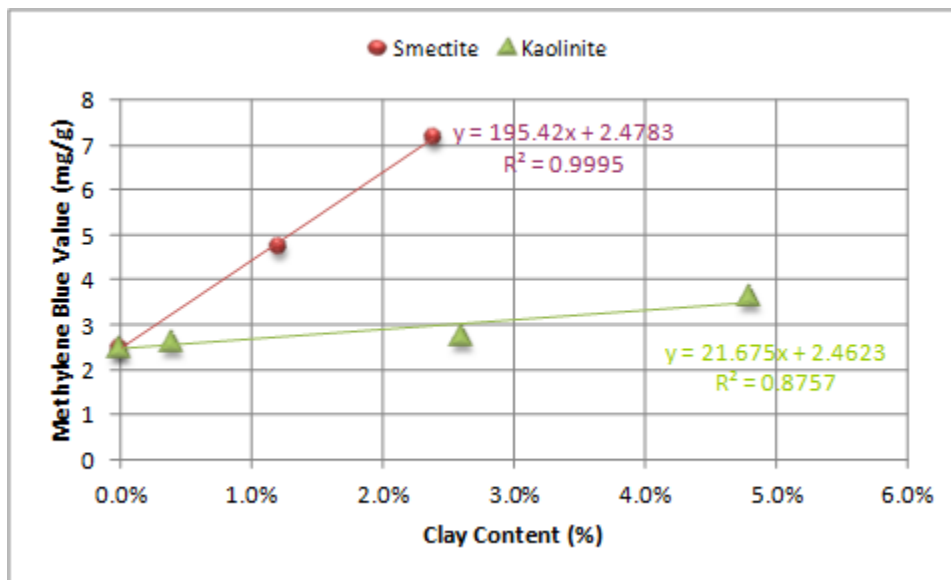


Figure 5.14. MBV Results for Jones Mill Aggregate Samples without Clay and with Various Amounts of Smectite and Kaolinite Clay.

Of greater importance was to establish a relationship between the measured MBVs and the SE test measurements. This relationship is crucial to identify a laboratory test method that

can be used to detect the level of clay contamination in the aggregate in an accurate and simple way. The relationship between these two variables is illustrated in Figure 5.15. The numbers next to the data points indicate the level of clay. A different fitted line between MBV and SE was established for each type of clay because of the dissimilar range of values that was obtained, as explained previously. The regression line obtained for the smectite clay was projected beyond the value of 2.4 percent clay in an attempt to estimate MBVs for lower SE values; however, caution should be used when estimating MBVs using the projected regression line. Figure 5.15 clearly indicates that smectite and kaolinite mixtures with similar level of clay addition can produce similar SE values but their MBV are distinctly different. Therefore, MMB test is the most reliable method to detect the level of clay contamination in aggregate fines.

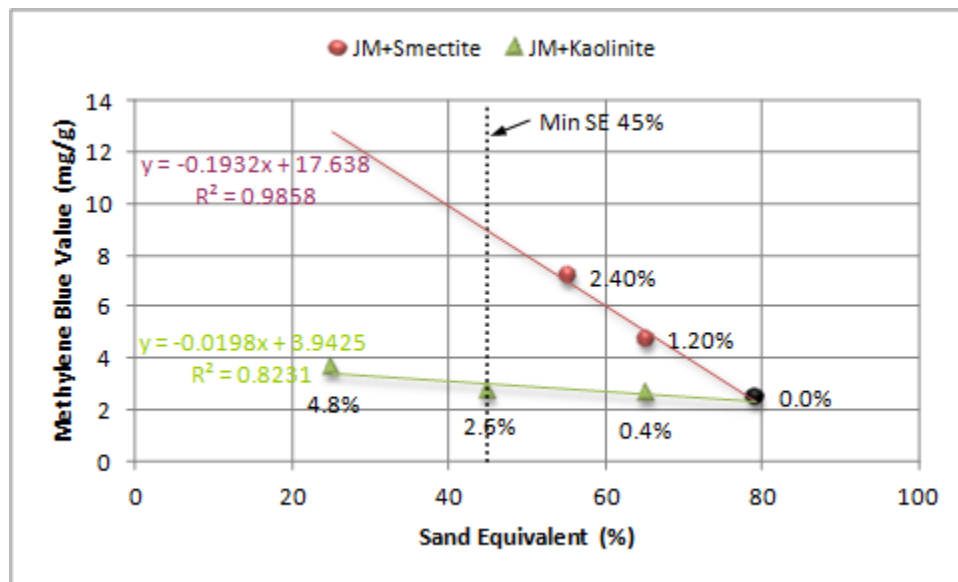


Figure 5.15. Relationship between MBV and SE Test Results for Jones Mill Aggregate Samples without Clay and with Various Amounts of Smectite and Kaolinite Clays.

Another test performed on the Jones Mill material passing sieve No. 40 with the various amounts of clay was the Bar Linear Shrinkage Test (Tex 107–E), which along with the SE is also part of the Aggregate Quality Requirements prescribed test in TxDOT specifications. The maximum linear shrinkage allowed is 3 percent. The results of this test are shown in Figure 5.16. As expected, with additional amounts of clay, the shrinkage increased. The values for both types of clay follow a common linear trend. They are described with a single regression equation since the linear shrinkage test is not able to differentiate between the two types of clay.

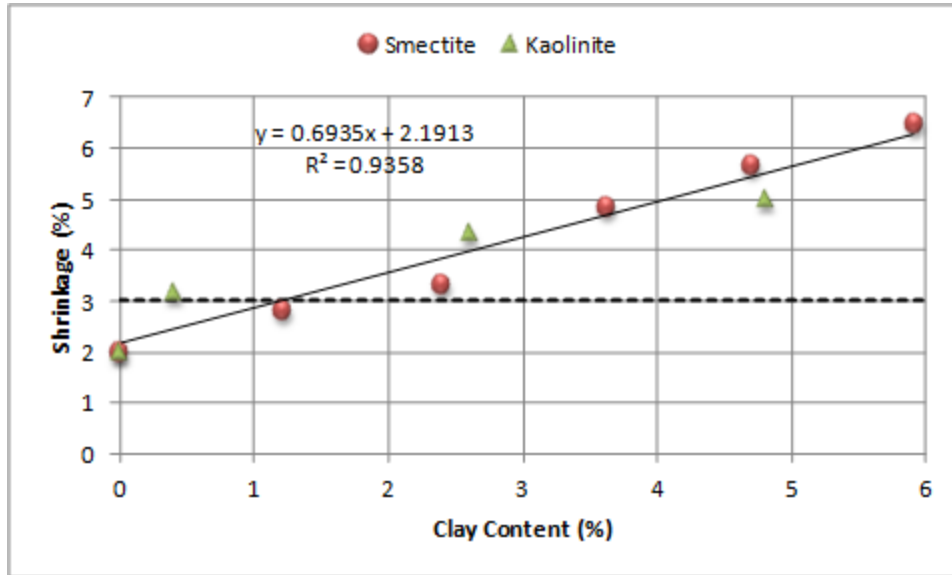


Figure 5.16. Bar Linear Shrinkage Test Results for Jones Mill Aggregate Samples with Various Amounts of Smectite and Kaolinite Clay.

SPECIMEN PREPARATION

With the amounts of clay indicated in Table 5.5, the Texas Gyrotory Compactor was used to determine the design binder content of the asphalt mixtures at 4 percent air voids. The results are also listed in Table 5.5. For the smectite clay, the required binder content increased with added clay contamination, while for the kaolinite clay, the design binder content was higher for the lowest amount of clay and decreased with added clay content. For the Jones Mill mixture with no added clay, the design binder content was 5.3 percent.

Once the design binder contents were determined, several specimens were prepared to conduct the Boil Test (Effect of Water on Bituminous Mixtures – Tex 530–C) on the loose mixture and the Hamburg Wheel–Tracking Test (Tex 242–F), and the Overlay Test (Tex 248–F) on compacted specimens. During compaction, it was noted that the mixtures felt stiffer, yet the number of Superpave Gyrotory Compactor (SGC) gyrations reduced with added amounts of clay. This translates into more workability. Figure 5.17 shows the number of gyrations for each mixture. The numbers above the bars represent the average air voids of three replicate specimens.

The results of the Boil, Hamburg, and Overlay tests are discussed in subsequent sections. The objective of these tests was to estimate the moisture susceptibility and cracking potential of the mixtures.

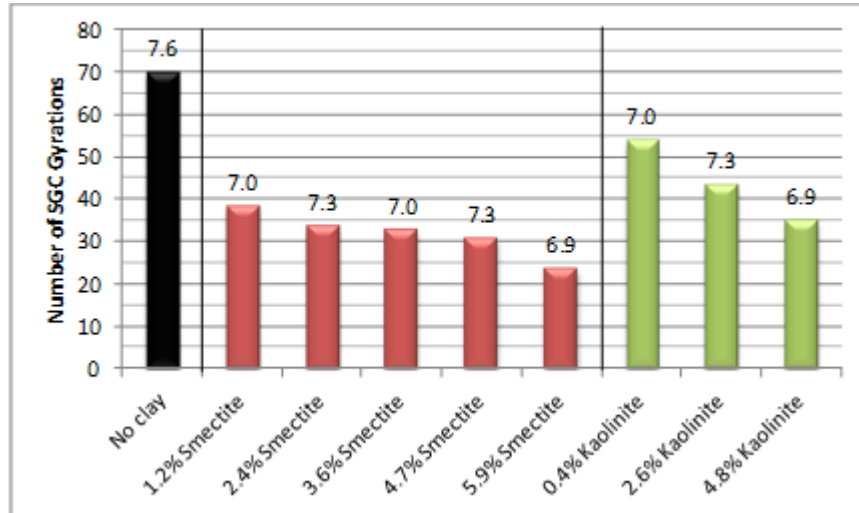


Figure 5.17. Number of SGC Gyration for Jones Mill Aggregate Samples without Clay and with Various Amounts of Smectite and Kaolinite Clay.

In addition, for the mixtures with 3.6, 4.7, and 5.9 percent added smectite clay, the fine portion of the mixture (defined as the material passing sieve No. 16) was estimated from the full aggregate gradation (labeled as FAM in Figure 5.12) and used to prepare fine aggregate mixture (FAM) specimens for the Dynamic Mechanical Analyzer (DMA) test. The design binder content for the FAM specimens was estimated by preparing and sieving loose asphalt mixture through sieves No. 8 and No. 16. The material passing sieve No. 16 was collected and burned in the ignition oven. With the difference in weight before and after burning, the design binder content was calculated. The results are listed in Table 5.5.

The FAM specimens were compacted in the SGC until refusal (i.e., no change in specimen height with additional gyrations). Afterward, the SGC specimens were trimmed and cored to obtain DMA test specimens 12–mm diameter by 50–mm height. About 30 DMA specimens were obtained from a single SGC sample, but only six were selected for testing. Half of those six DMA test specimens were subjected to a moisture conditioning protocol by submerging the specimens in water and applying vacuum for about 1 minute. The conditioned specimens were left to air dry before gluing on the end caps for testing.

Test Results

The results of the Boil Tests on the specimens showed no difference in performance (Figure 5.18). The only appreciable difference was that the loose mixture with added clay was less shiny than the mixture with no clay and some of the larger rocks demonstrate stripping of the asphalt binder from the aggregate. However, the stripping was not very evident or extensive.

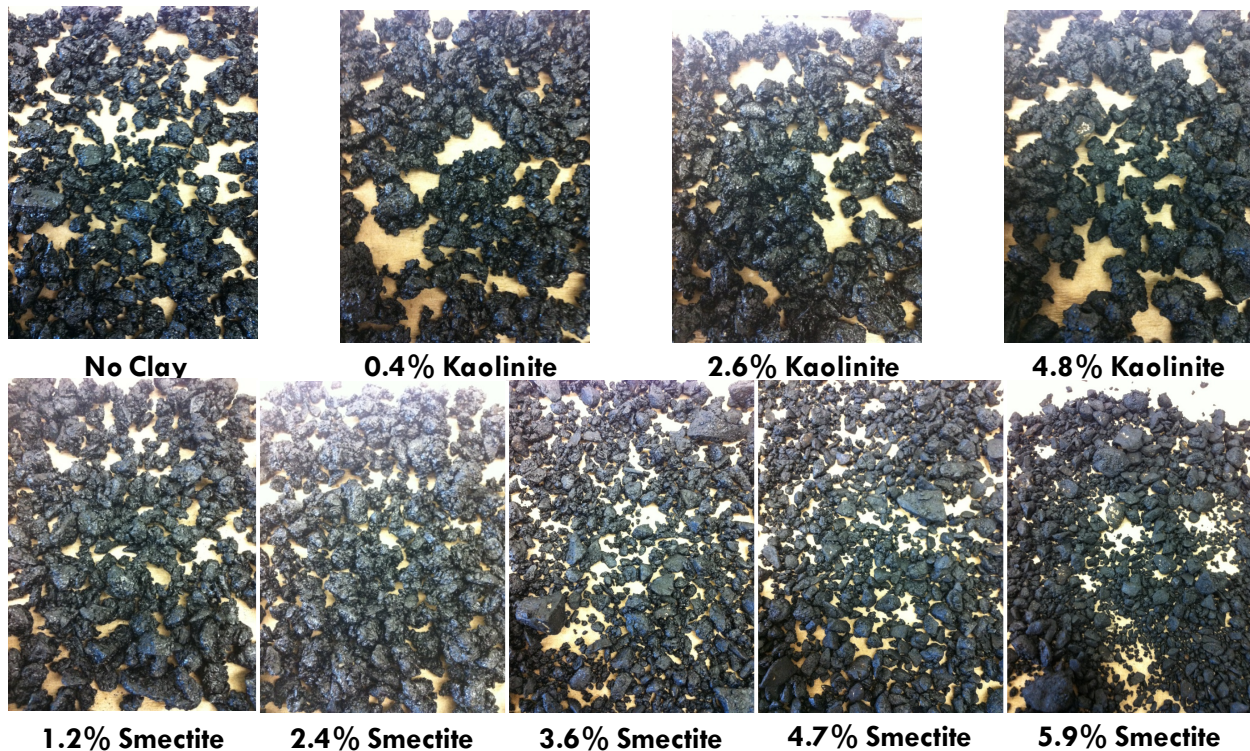


Figure 5.18. Boil Test Results for the Jones Mill Material without Clay and with Various Amounts of Smectite and Kaolinite Clay.

The HWTT results are illustrated in Figure 5.19. From the trends, it is clear that the type and amount of clay had a significant effect on the performance on the asphalt mixtures. The mixture with no clay, despite not including the anti-stripping agent prescribed in the mixture design, performed adequately, showing no signs of stripping and achieving 20,000 load cycles with minimal rutting. The mixtures with smectite clay were more sensitive to rutting and moisture damage. The mixtures with lower clay amounts (i.e., 1.2 and 2.4 percent) showed adequate performance, although the curve for the 2.4 percent smectite clay started to decline toward the end of the test, which is an indication of stripping. The mixtures with the higher smectite clay amounts performed poorly, not complying with the minimum HWTT requirement of less than 12.5 mm rut depth after 20,000 load cycles. On the other hand, the mixtures with the kaolinite clay performed adequately, showing minimum rutting and no signs of stripping.

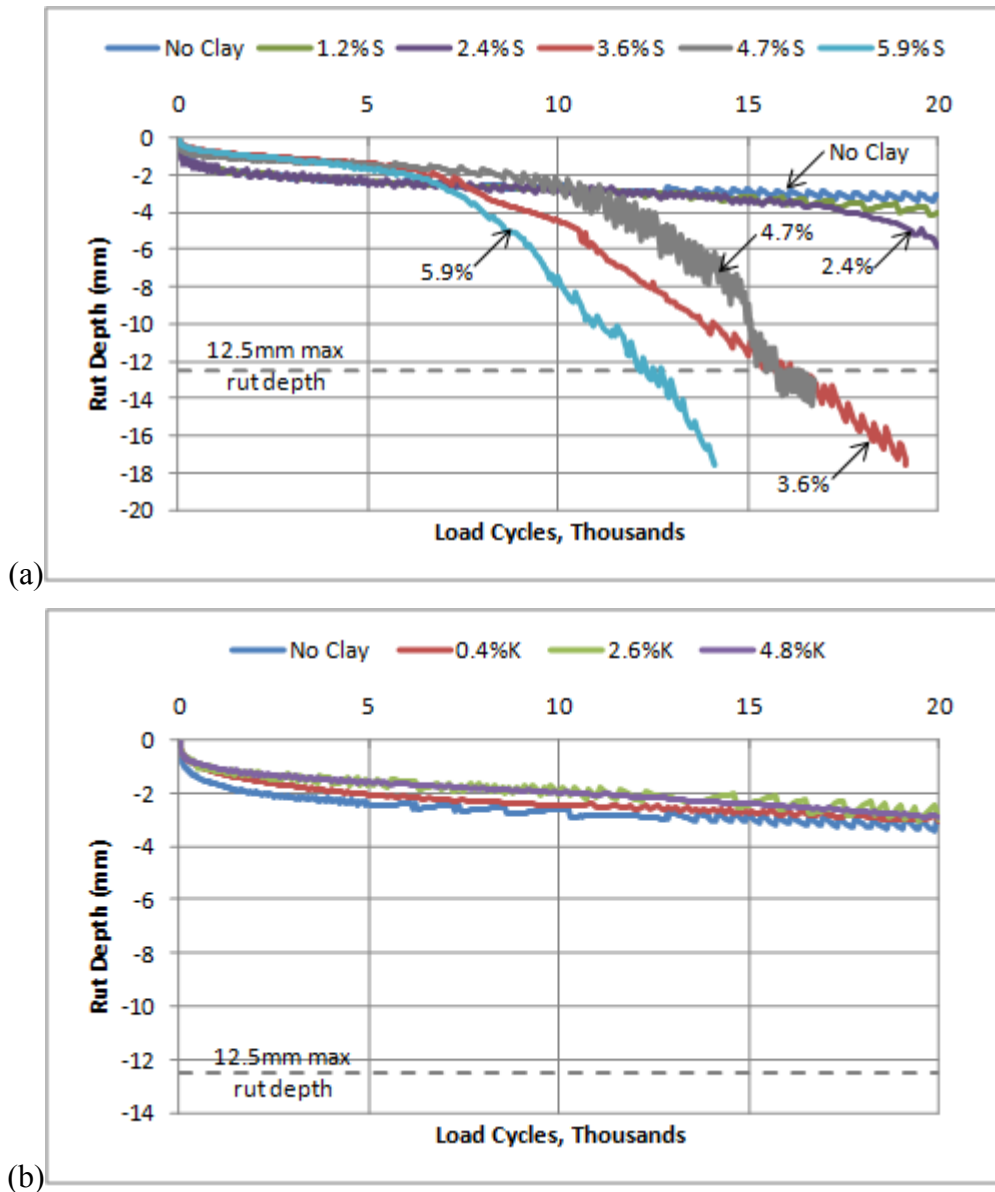


Figure 5.19. Hamburg Wheel–Tracking Test Results for the Jones Mill Mixtures with Various Amounts of Clay; (a) Smectite, (b) Kaolinite.

The stripping inflection point (SIP) of the mixtures (i.e., the number of cycles when the initial creep slope intersects the stripping slope) was also estimated. The results are shown in Table 5.6. From these values, it is evident that the smectite clay had a negative effect on the mixture, especially when 3.6 percent or more clay was added. The evolution of damage with load cycles and number of cycles to failure is illustrated in Figure 5.20. At about 5000 load cycles, all mixtures had equivalent rutting depths. The mixtures with high smectite clay contents had even lower rut depths than the other mixtures, but with additional load cycles the progression of rutting was more significant for the mixture 5.9 percent smectite clay, failing (i.e., reaching 12.5 mm rut depth) after about 12,800 load cycles. Mixtures with 3.6 and 4.7 percent smectite clay behaved similar in terms of rutting progression and total number of load cycles to failure: 15,950 and 15,650, respectively. The mixtures with kaolinite clay performed the best, with

rutting values at the end of the 20,000 load cycles that were even lower than those recorded for the mixture with no clay.

Table 5.6. Calculated SIP for the Jones Mill Material with Various Amounts of Smectite.

Clay Type	Clay Content (%)	Stripping Inflection Point (# Cycles)
—	None	>20,000
Smectite	1.2	>20,000
	2.4	22,946
	3.6	9,594
	4.7	12,050
	5.9	8,323
Kaolinite	0.4	>20,000
	2.6	>20,000
	4.8	>20,000

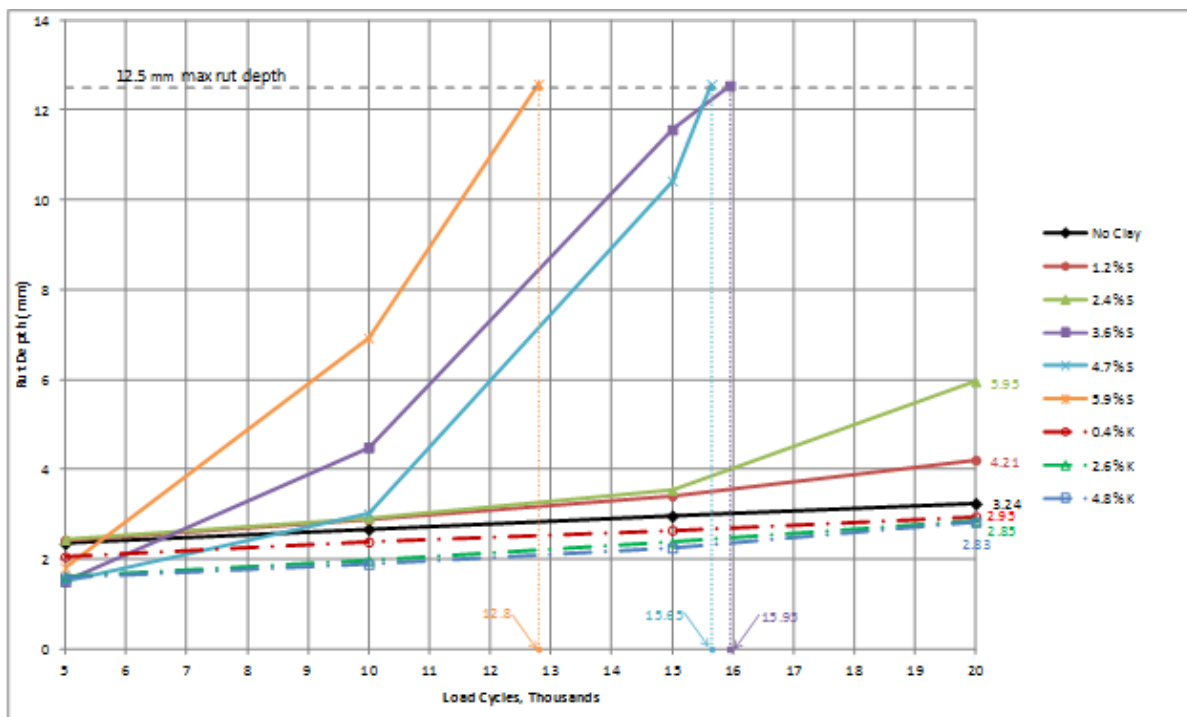


Figure 5.20. Evolution of Rutting and Number of Load Cycles to Failure for the Jones Mill Mixtures without Clay and with Various Amounts of Smectite and Kaolinite Clay.

The Overlay Test results for the Jones Mill mixtures are presented in Figure 5.21. The bars represent the average number of loads cycles to failure, defined as a 93 percent reduction in the peak load. The numbers on top of the bars are the average air voids of the three replicate specimens used in the test. The dots represent the peak load achieved during the first load cycle for each of the mixtures. Based on the trends, the conclusion is that the stiffness of the mixtures increases with added clay contents, as demonstrated by the higher peak load values. This usually translates into lower resistance to repeated loading by the mixtures with added clay for the

kaolinite mixtures, although for the smectite mixtures, the reduction in load cycles does not follow a consistent downward trend due to the variability in the test results. The most significant reduction in the number of cycles to failure in comparison to the mixture with no clay was experienced by the mixtures with 2.4 percent and 4.7 percent smectite and 4.8 percent kaolinite.

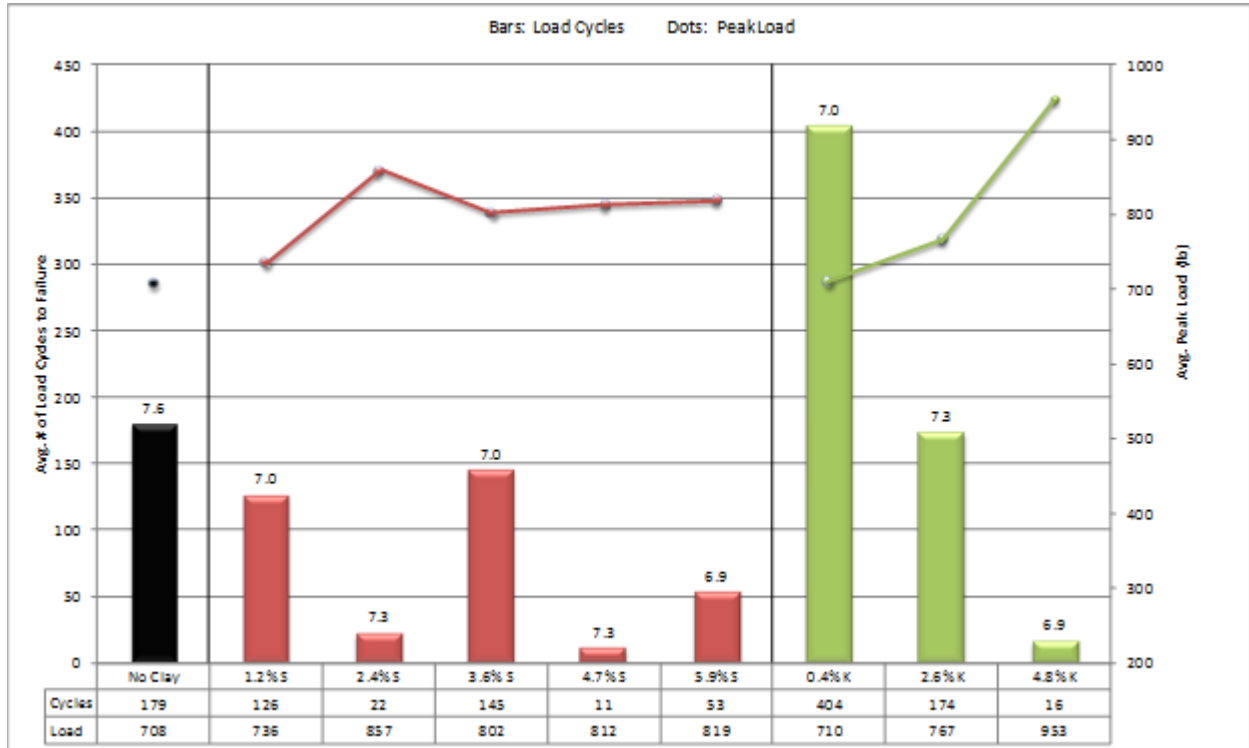


Figure 5.21. Overlay Test Results for the Jones Mill Mixtures without Clay and with Various Amounts of Smectite and Kaolinite Clay.

SUMMARY AND CONCLUSIONS

Increasing clay contents in the Jones Mill Type D mixture increased the perceived stiffness of the mixture, although the workability improved, as demonstrated by the lower number of SGC gyrations needed to compact the specimens.

Results thus far indicate that the addition of smectite clay to asphalt mixtures has a negative effect on their performance in terms of rutting, moisture susceptibility, and cracking resistance. This is somewhat abnormal since the typical observed behavior is that mixtures with good rutting performance have poor cracking resistance, and vice versa. However, for the smectite mixtures the presence of the clay negatively affected both characteristics. The mixtures with added kaolinite, on the other hand, had inadequate cracking performance at the higher clay levels, but good moisture susceptibility and rutting values were obtained.

The SE test was not able to differentiate between clay types, and the pass/fail test results from the HWTT were inconsistent with the specification limit of 45 percent minimum SE. That is, some mixtures with SE values of 45 percent or less passed HWTT while others failed (Figure 5.22). The same is true for the results of the Bar Linear Shrinkage test, which was not

able to differentiate between clay types, and most of the results were above the prescribed limit of 3 percent maximum shrinkage (Figure 5.23).

The results of MMB test were the most promising because the test was able to differentiate between clay types. Based on the pass/fail HWTT results, a preliminary threshold MBV of 7.2 mg/g with corresponding SE threshold value of 55 percent are proposed (Figure 5.24). Additional mixture types should be tested to verify these proposed thresholds.

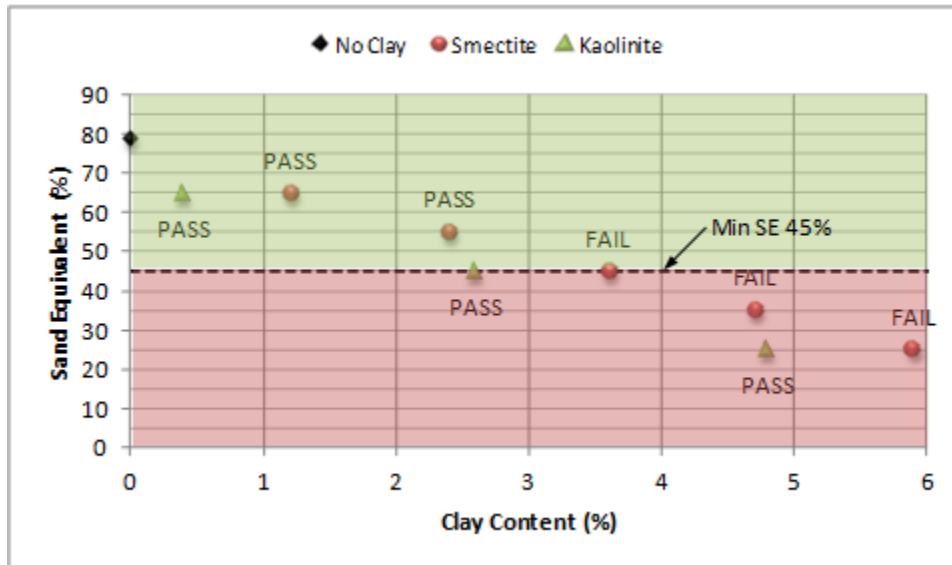


Figure 5.22. SE Test Results for Jones Mill Aggregate Samples Showing Poor Correlation to HWTT Pass/Fail Criteria.

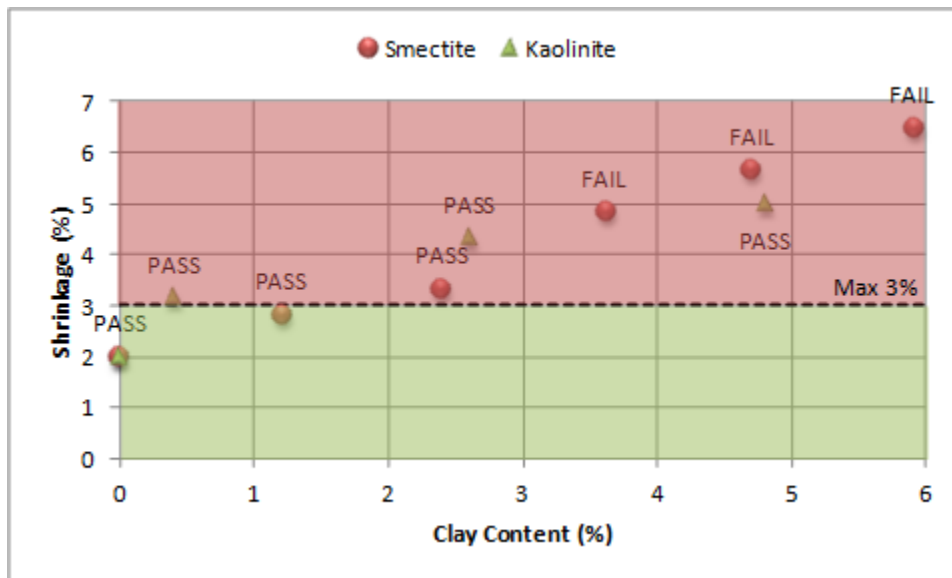


Figure 5.23. Bar Linear Shrinkage Test Results for Jones Mill Aggregate Samples Showing Poor Correlation to HWTT Pass/Fail Criteria.

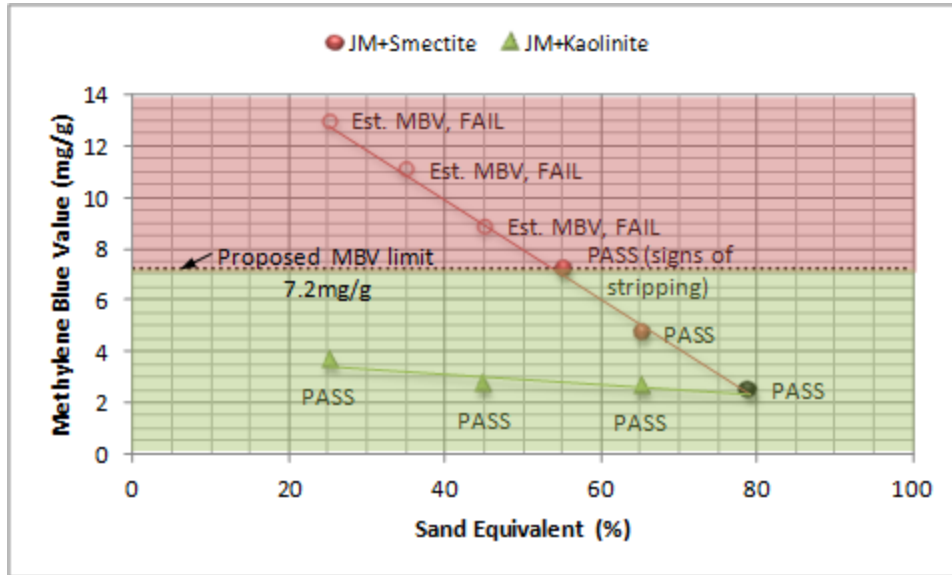


Figure 5.24. MBV Test Results for Jones Mill Aggregate Samples Showing Good Correlation to HWTT Pass/Fail Criteria.

CHAPTER 6

PERFORMANCE EVALUATION OF PCC AND HMA MIXES WITH NATURAL CLAY/AGGREGATE COMBINATIONS

The objective of this section was to quantify the effect of the existing type and amount of clay minerals found in Texas aggregates on the engineering properties of PCC and HMA mixes. Similarly as done in chapter 5, a control mix using a clean (free of deleterious matter) sedimentary dolomitic aggregate from Hanson quarry in Burnet was used. There were five natural aggregates selected for this task in which their performance was compared with that of the control mix. These five aggregate sources are Armor Pit, Beckman, Bird Hill, Wood Pit, and Pit #365. These quarries/gravel pits were known to contain a high amount of fines which could have deleterious clay minerals in the aggregate, as identified by previous evaluation of clay mineralogy (Chapter 4). It has been widely reported that the presence of clay minerals in concrete can reduce the compressive and flexural strengths while increasing drying shrinkage.

PCC MIXES

Similarly as done in Chapter 5, a conventional concrete mix design was used for the concrete mixing necessary in this section. Table 6.1 below shows relevant mix design information specific to the components of the mix. Table 6.2 shows the necessary aggregates properties of all aggregates used in this section as required for mix design. Although our concrete batches were only 3.3 ft³, Table 6.3 is provided to give an idea of the amount of what an equivalent batch of 1 yd³ (or 27 ft³) would be since most paving jobs are done on a per cubic yard basis.

Table 6.1. Mix Design Information.

w/c ratio	Fly ash	Coarse aggregate factor	Cement factor
0.42	20% class F	0.68	6

Table 6.4 below provides the workability of each of mix based on the slump test (ASTM C 143). The aim was to produce each mix with at least a 1–in. slump based on our control mix in order to ensure uniform mixing and adequate casting and compaction of the concrete specimens. The mixes containing aggregate from Armor and Bird Hill seemed to have slightly higher water demand, thus, they showed slightly lower slump values than the others. This is likely caused by the higher amount of fines, or even micro fines, prevalent in both aggregates. In contrast, the mix containing aggregate from Wood Pit provided the highest workability with a 2–in. slump. This aggregate source is mainly a river gravel material and contains particles which are very rounded or spherical–shaped, and this lack in angular aggregate particles would explain a slightly higher slump since aggregate geometry is a factor of the slump test.

Table 6.2. Aggregate Properties.

	Specific Gravity (BSG_{0D})	Dry Rodded Unit Weight (DRUW)– (lb/ft³)	Absorption Capacity (AC, %)
Fine Aggregate (sand)	2.63	112.2	0.52
Sed. Dolomite	2.74	100.5	0.89
Armor	2.34	84.2	3.72
Beckman	2.51	97.0	2.08
Bird Hill	2.98	109.7	1.35
Wood Pit	2.55	102.4	1.40
Pit #365	2.50	94.3	2.80

Table 6.3. Batch Weights (Based on 27 ft³).

Mix component	Cement	Fly ash (class F)	Coarse aggregate	Fine aggregate (sand)	Water	Air entraining admixture (mL)
Amount (lb)	451.2	112.8	1860.3	1316.9	237.8	180.5

Table 6.4. Slump Data.

Coarse Agg.	Sed. Dolomite	Armor	Beckman	Bird Hill	Wood Pit	Pit #365
Slump (in.)	1	0.75	1	0.75	2	1

EFFECT ON DRYING SHRINKAGE (ASTM C 157)

Similarly as performed in Chapter 5, drying shrinkage and flexural strength testing was conducted for all the mixtures in this section. The test results are presented in Figure 6.1. In order to get more accurate detection of concrete shrinkage, strain gauges (from Tokyo Sokki Kenkyujo Co.) were used. The results of these measurements are presented in Figure 6.2. It should be noted that these shrinkage strain measurements are based on seven days of data.

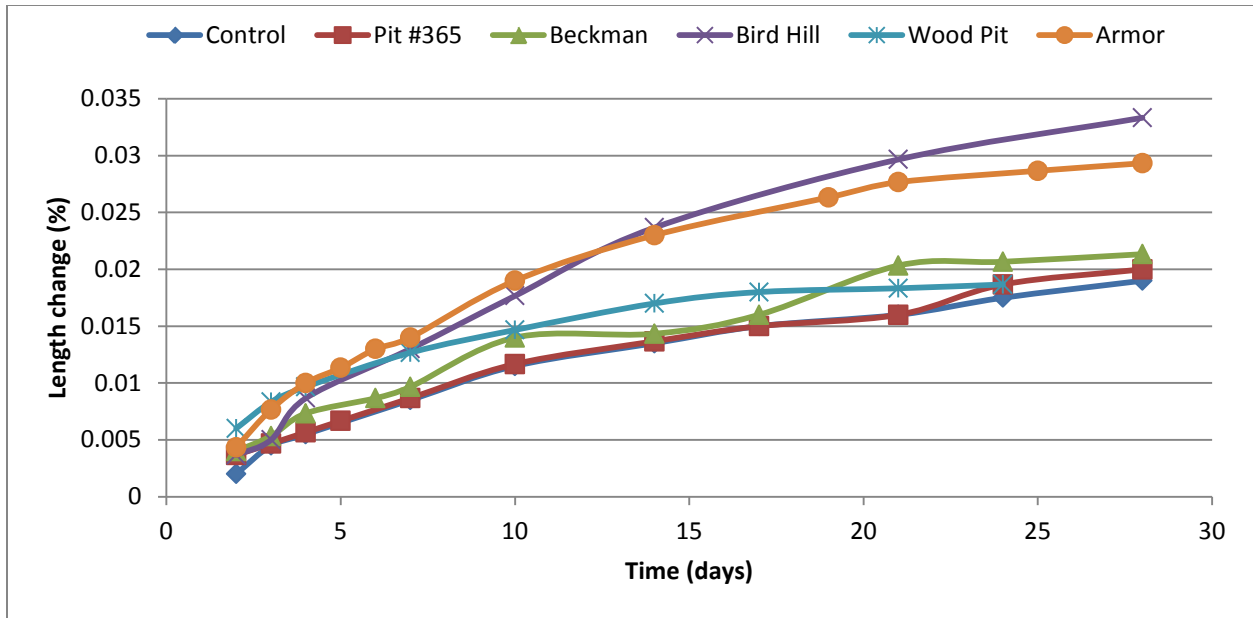


Figure 6.1. Drying Shrinkage Comparison.

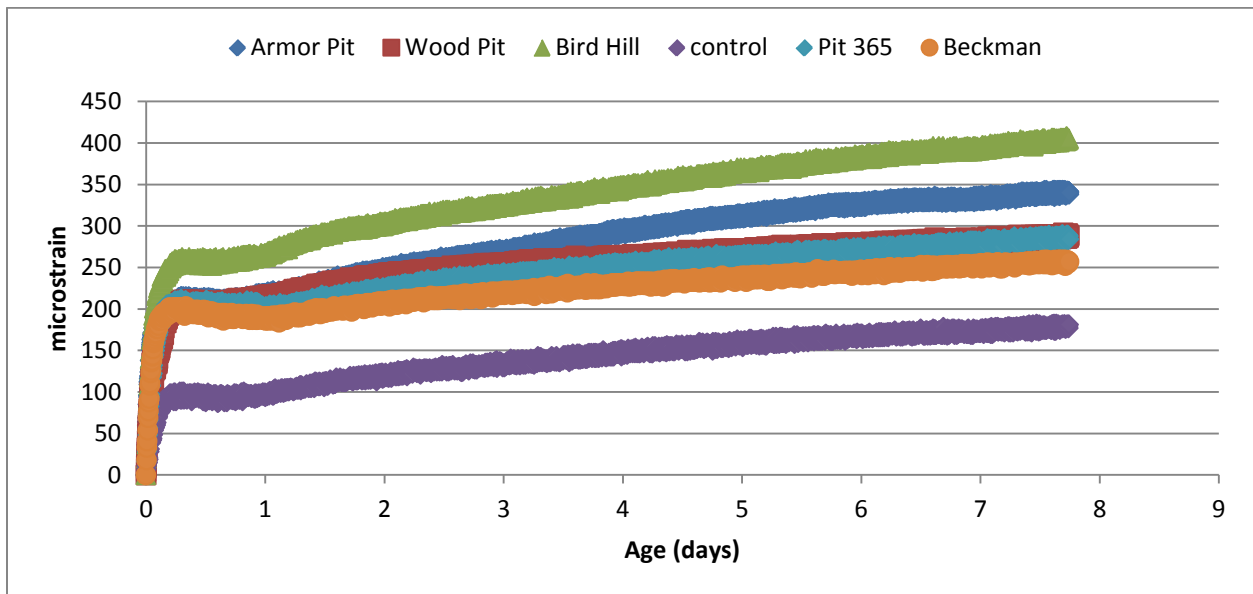


Figure 6.2. Shrinkage Strain Comparison.

RESULTS AND DISCUSSION

Based on the results in Figure 6.1, it can be seen that the control mix gave the lowest amount of drying shrinkage through 28 days. The mix with aggregate from Pit #365 has undergone almost identical amount of drying shrinkage over time when compared to the control mix. Both of these mixes experienced a length change of approximately 0.02 percent after 28 days of drying. The mixes containing aggregates from the Beckman and Wood Pit quarries gave slightly higher amounts of drying shrinkage, at about 0.022 and 0.024 percent, respectively, at

28 days. The specimens that experienced the higher amount of drying shrinkage were from the mixes having coarse aggregate from the Bird Hill and Armor Pit quarries. Both of these specimens underwent a much higher early-age drying shrinkage, and that trend continued until 28 days. The Armor test specimen felt nearly a 0.03 percent change in length at 28 days, and the Bird Hill test specimen experienced about a 0.034 percent change in length at 28 days. These last two mixes with the highest amount of drying shrinkage were also the least workable of all the mixes. It is also probable that aggregate fines and micro fines from these stockpiles caused a higher degree of drying shrinkage. Furthermore, if the micro fines contain a significant amount of clay minerals, it can reduce the amount of mix water available for the cement hydration reactions, thereby producing a decrease in workability.

Upon observation of Figure 6.2, it is obvious that the concretes containing aggregates from the Bird Hill and Armor quarries yielded the highest levels of shrinkage strain (~ 400 and 350 microstrain at 7.5 days, respectively). The control mix gave the lowest amount of shrinkage strain of approximately 190 microstrain at 7.5 days. Although no connection between the measurement units from the two figures (6.1 and 6.2) is made, the results in Figure 6.2 support the results in Figure 6.1 with respect to which concrete underwent the most and least amounts of shrinkage, whether it be bulk change in length or internal shrinkage strain.

EFFECT ON FLEXURAL STRENGTH (ASTM C 78)

Figure 6.3 below shows the results of 7-day and 28-day flexural strength testing for all the concrete mixes. Table 6.5 gives the flexural strength values obtained from the various mixes that were tested at 7 and 28 days. It also gives the amount (%) decrease in flexural strength. These amounts are based on the amount of flexural strength decrease compared to the strength values obtained from the control mix.

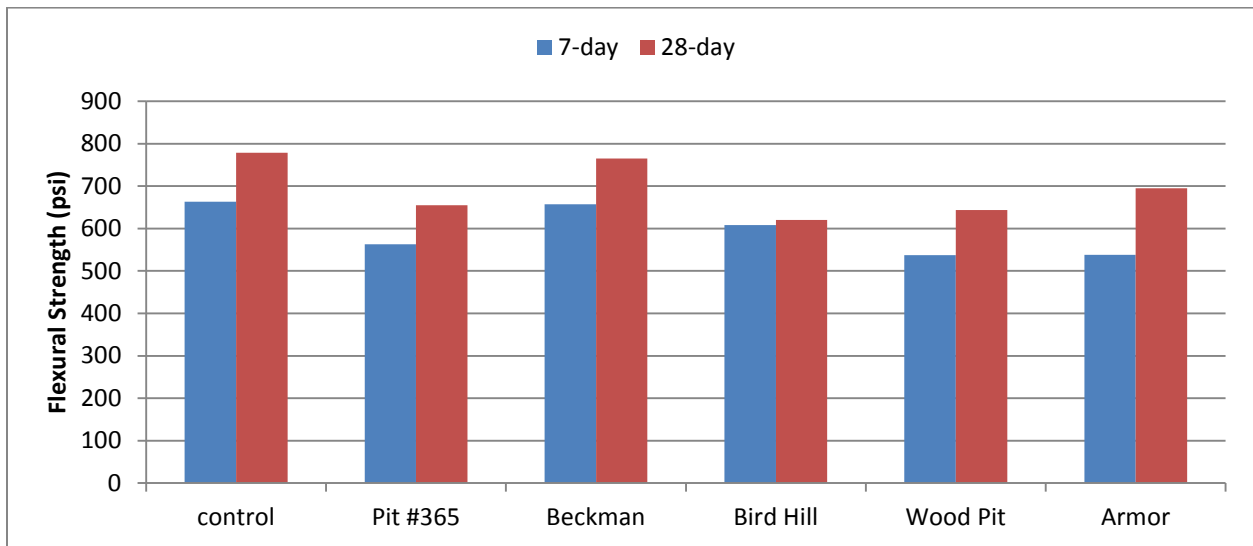


Figure 6.3. Flexural Strength Comparison.

Table 6.5. Flexural Strength Reduction.

Mix	7-day strength (psi)	28-day strength (psi)	Decrease in 7-day strength (%)	Decrease in 28-day strength (%)
Control	663	779		
Pit #365	563	655	15.1	15.9
Beckman	657	765	0.9	1.8
Bird Hill	608	620	8.3	20.4
Wood Pit	537	644	27.9	24.6
Armor Pit	538	695	18.9	10.8

Additionally, a relationship between flexural strength and MBV was established according to the test results based on the MBV of the P4 and P40 size fractions of the stockpiled aggregates, as shown in Figure 6.4.

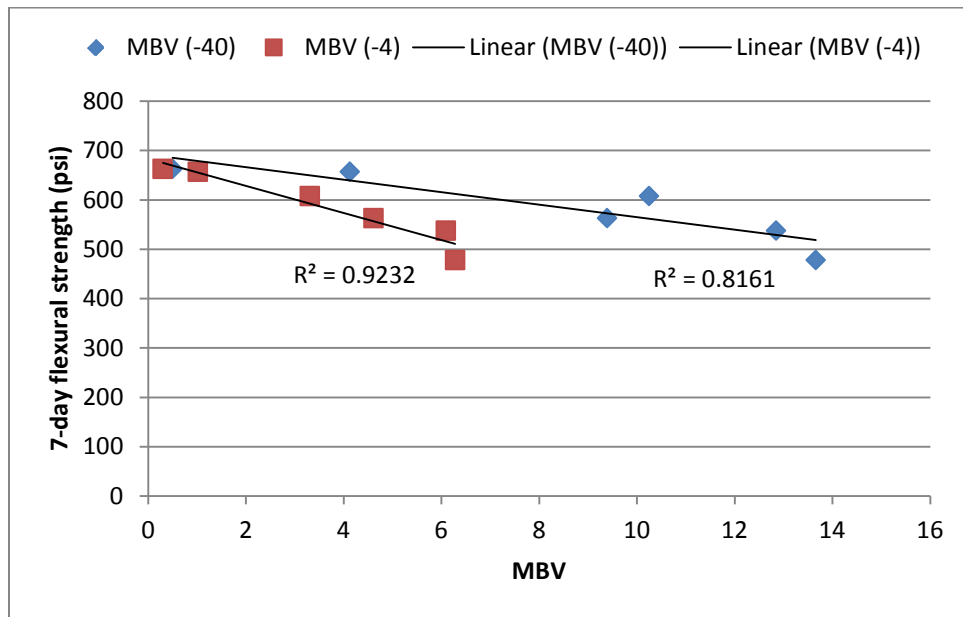


Figure 6.4. Relationship between MBV and Flexural Strength at 7 Days.

Similarly, Figure 6.5 shows a strong correlation between MBV and the percent reduction of flexural strength. It is clearly shown in both Figures 6.4 and 6.5 that flexural strength is reduced with increasing MBV of the aggregate fines.

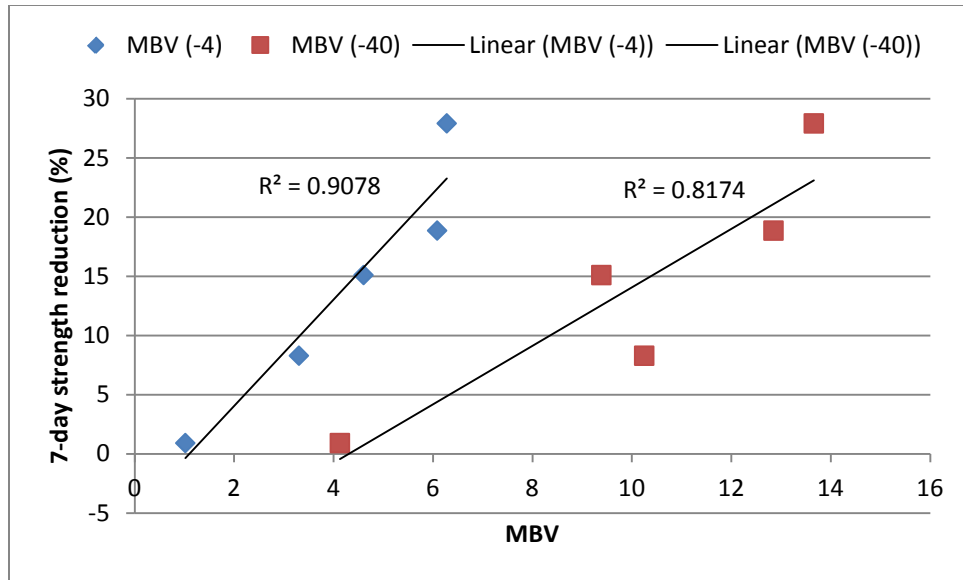


Figure 6.5. Relationship between MBV and Flexural Strength Reduction at 7 Days.

Threshold MBV

Figure 6.4 was established by plotting the flexural strength values obtained from all the mixes (shown in Table 6.5) against their corresponding MBV. From this figure, we can see that based on the TxDOT minimum 7-day flexural strength requirement, this indicates that threshold MBVs of 4.5 and 11 can be agreed for the P4 and P40 size fractions, respectively. Similarly, this logic was followed in Chapter 5 in deciding on a threshold MBV based on strength of pure clay mixtures, and that MBV (P4) was about 3.7. An MBV (P4) of 4.5 or below for stockpile aggregate fines would indicate that the aggregate is free from a significant amount of deleterious matter (i.e., harmful clay minerals). However, this value is somewhat conservative and solely based on MMB testing of the coarse aggregate fraction and not considering what contribution the fine aggregate fraction (e.g., concrete sand) would make. To obtain a more precise determination of a permissible MBV, MMB testing would need to be conducted on both the coarse and fine aggregates used in making the concrete. Unless the sand used in the concrete is totally inert (giving “0” MBV), the permissible or threshold MBV would be slightly higher, depending on the cleanliness or quality of the sand. We can now correlate the allowable amount of flexural strength reduction, as shown in Figure 6.5. As one would expect and based on Figure 6.4, an increase in MBV yields higher strength reduction. MBVs of 4.5 and 11 for P4 and P40 sizes, respectively, correspond to approximately a 15 percent reduction in flexural strength at 7 days. The percent reduction of strength at 7 days for Woods pit (28 percent) and Armor pits (19 percent) are above this permissible limits.

Relationship between Reduction in Strength and Increase in Shrinkage

Relationships among flexural strength reduction and drying shrinkage increase when compared with the control strength and shrinkage were established, which are shown in Figures 6.6–6.10 below. Since the coarse aggregate from the Beckman stockpile appeared to be a clean and good quality aggregate to be used in making concrete (low MBV), the strength reduction for its mix was marginal compared to the control. As shown in Figure 6.6, it only

experienced about a 0.9 and 1.8 percent reduction in flexural strength at 7 and 28 days, respectively. Furthermore, there was about a 20 percent increase (average) in drying shrinkage. The concrete that contained coarse aggregate from the Bird Hill stockpile (Figure 6.7) witnessed a decrease in flexural strength of 8.3 and 20.4 percent at 7–day and 28–day testing, respectively. Its drying shrinkage gave about an 80 percent increase. Figure 6.8 shows that the concrete tested with aggregate from the Wood Pit quarry underwent a reduction in flexural strength of nearly 28 percent at 7 days and a 24.6 percent decrease at 28 days. Its corresponding increase in drying shrinkage was about 30 percent. When aggregate from Pit #365 was used, the resulting concrete experienced a fairly consistent reduction in flexural strength of between 15 and 16 percent, as indicated in Figure 6.9. It also shows an increase of drying shrinkage never exceeding 10 percent when compared to the control mix. Lastly, Figure 6.10 shows how the reduction in strength and increase in shrinkage of the Armor mix compared with the testing results for the control mix. Based on the test results, there was nearly a 19 percent decrease in 7–day flexural strength and almost an 11 percent decrease in 28–day flexural strength. There was a corresponding increase in drying shrinkage of about 70 percent compared to the control. It seems concrete containing Woods Pit and Armor are problematic, whereas concretes made with Beckman and Pit #365 aggregate give normal, acceptable performance.

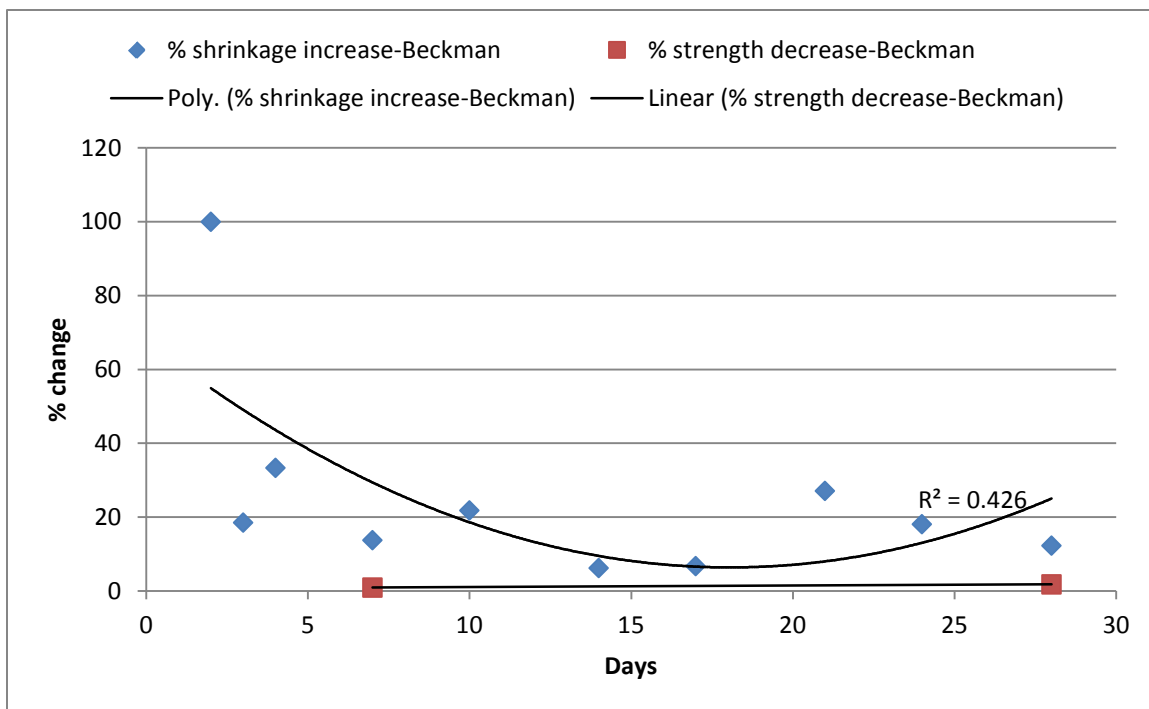


Figure 6.6. Increase in Shrinkage and Reduction in Strength for Beckman.

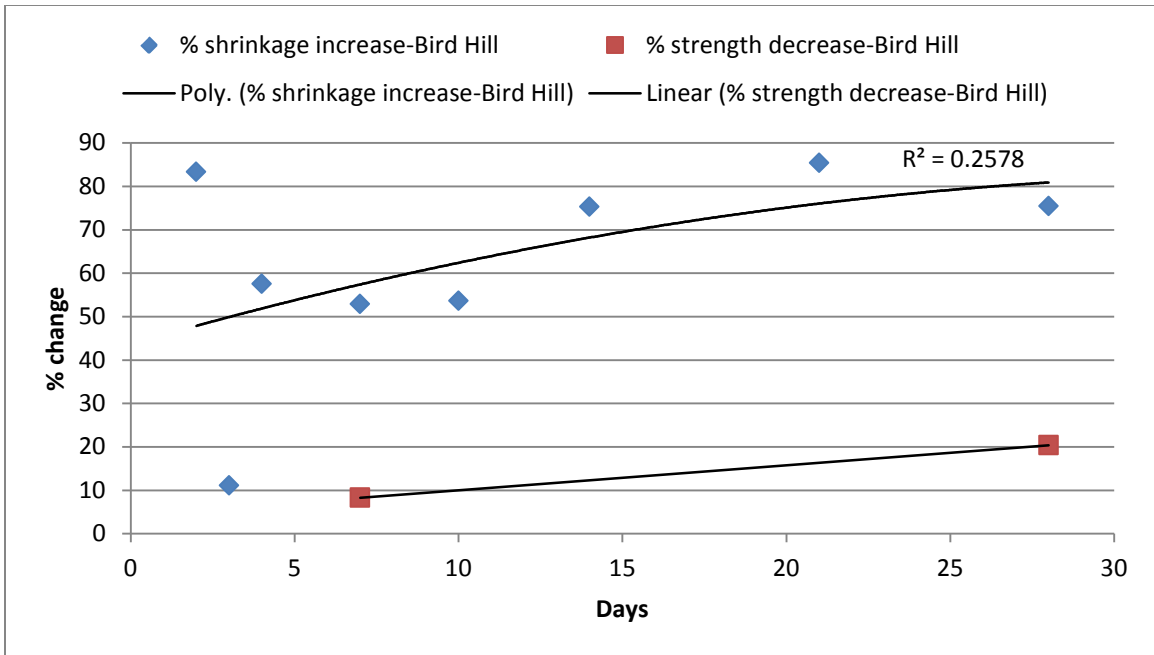


Figure 6.7. Increase in Shrinkage and Reduction in Strength for Bird Hill.

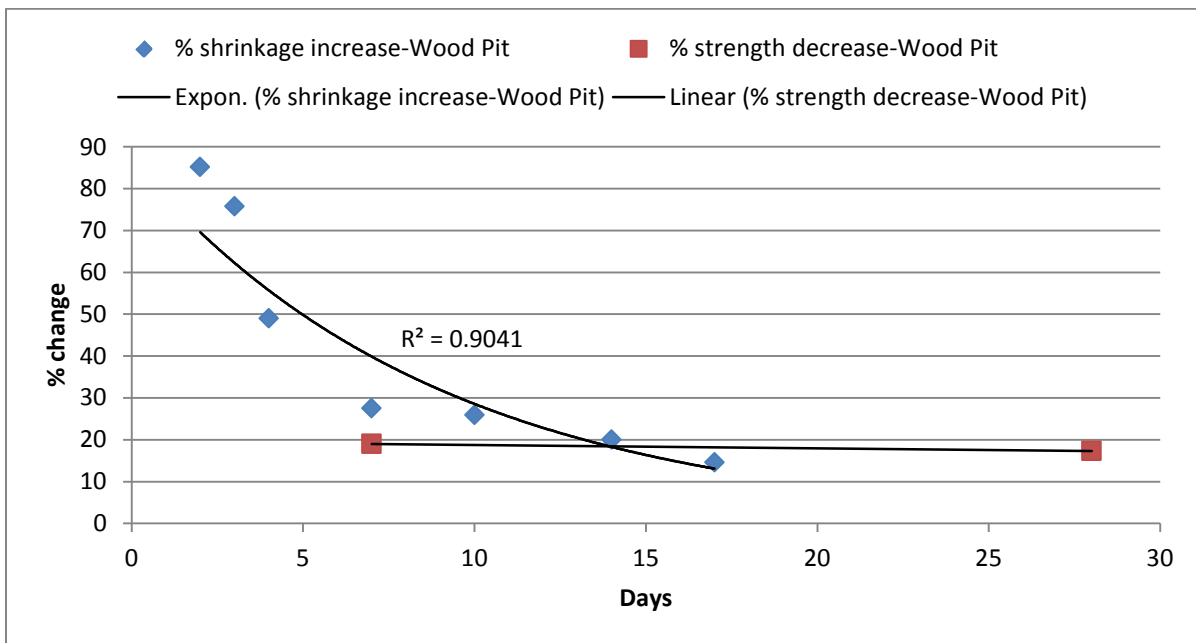


Figure 6.8. Increase in Shrinkage and Reduction in Strength for Wood Pit.

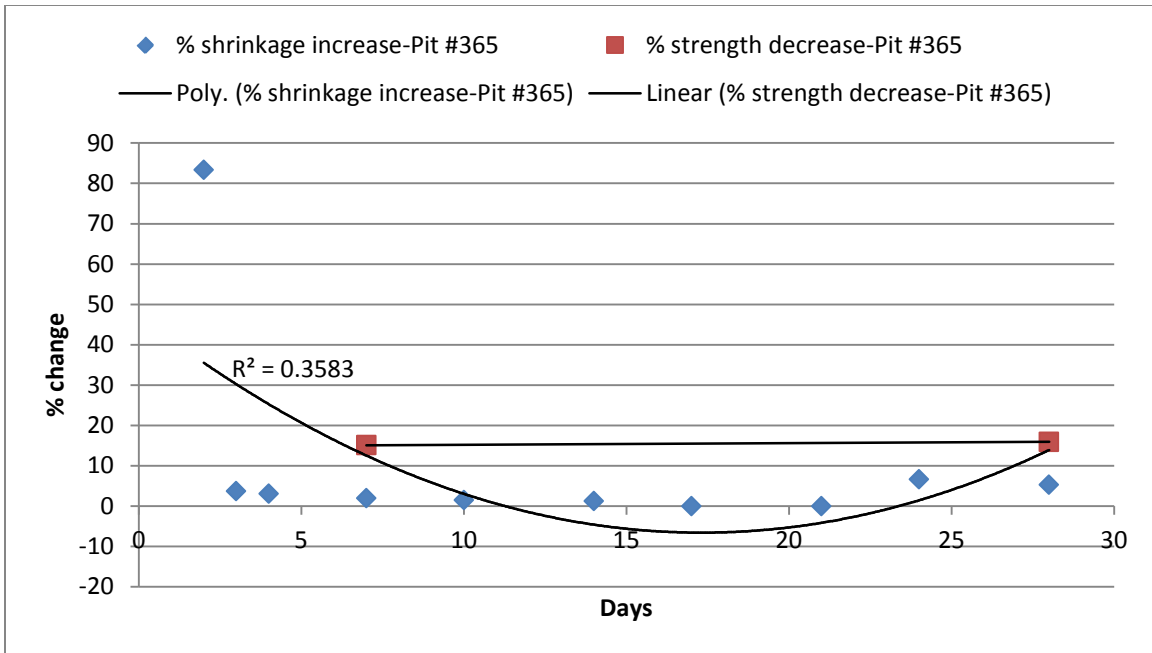


Figure 6.9. Increase in Shrinkage and Reduction in Strength for Pit #365.

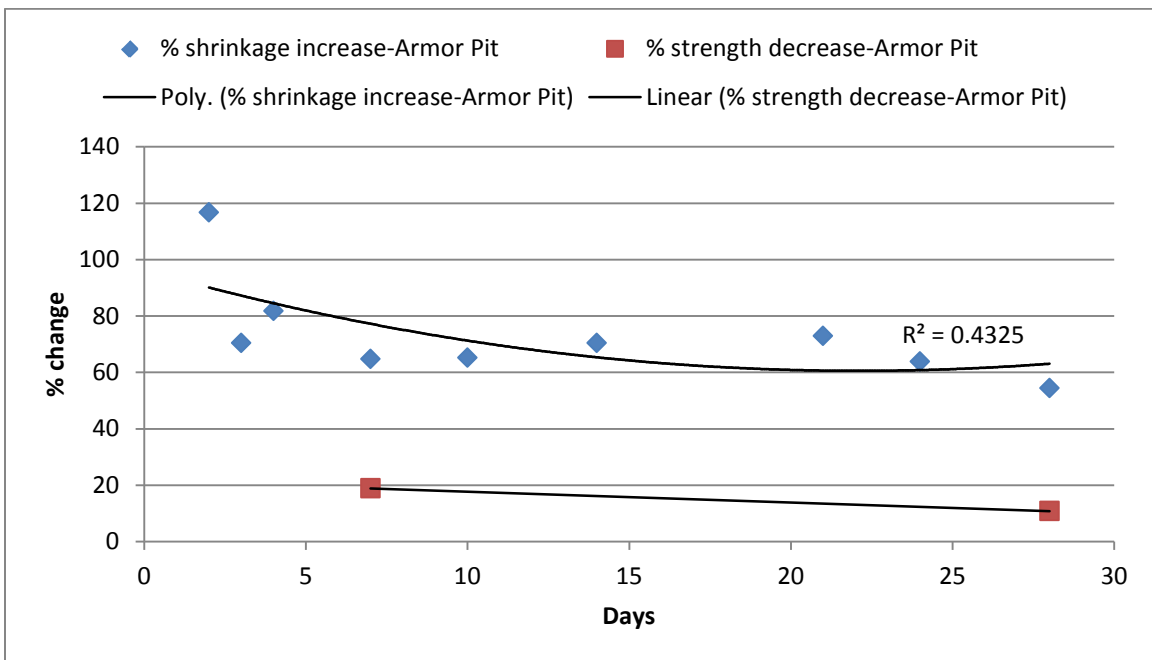


Figure 6.10. Increase in Shrinkage and Reduction in Strength for Armor Pit.

Categorization of Aggregate Fines Based on MBV

An attempt has been made to categorize the aggregate fines based on their MBV. The third column in Table 6.6 is based on concrete performance testing results (strength and shrinkage results). A correlation between MBV and concrete performance testing (discussed above) became the basis to categorize aggregates fines. Tables 6.7 and 6.8 below show the

ranges for MBV to represent different ranking/category (i.e., normal, poor, very poor, etc.) for stockpile aggregate fines (both -4 and -40 sieves). As screening materials were not used to do concrete performance testing, categorization is not possible for the screening materials. Moreover, screening materials are not the materials that are actually used in concrete making. It is also noteworthy that the ranges are different for the two sizes (-4 and -40 sieves), i.e., higher MBV with smaller particle size (i.e., -40). This difference is obvious based on the fact that MBV increases as particle size decreases (mentioned previously). But MBV of both -4 and -40 sizes provide almost the same performance category (Tables 6.6, 6.7, and 6.8). The ranges are arbitrary in nature at this time as these are based on the MBV of only 5–6 stockpiled materials. A large number of aggregate stockpiled materials need to be tested for their MBV in both -4 and -40 sizes along with corresponding concrete performance testing in order to assign more accurate MBV ranges.

Table 6.6. MBV for Stockpile Materials.

Stockpile	MBV (-4)	MBV (-40)	Performance category - 4) / (-40)
Wood Pit	6.28	13.66*	Poor/poor
Armor	6.09	12.85*	Poor/poor
Pit #365	4.61	9.39*	Poor-normal/normal
Bird Hill	3.31	10.25*	Normal/normal
Beckman	1.02	4.13	Normal/normal
Vulcan Helotes	0.98	2.86	Normal/normal
Marble Falls		4.42	Normal/normal
Delta		4.3	Normal/normal

* indicates 10–10 dilution method (10 g of aggregate fines + 10 g of inert siliceous sand), ** MBV ≥ 15 with 10–10 dilution indicates MBV is outside the range of the instrument's tolerance

Table 6.7. Performance Category Based on MBV (-4).

MBV (-4)	Category
<4.5	normal
4.5 – 6.5	poor
>6.5	very poor

Table 6.8. Performance Category Based on MBV (-40).

MBV - (40)	Category
<11	normal
11 – 14	poor
>14	very poor

Summary and Conclusions

As previously mentioned, the goal of this section (Chapter 6) was to conduct concrete performance testing (drying shrinkage and flexural strength testing) using five different stockpiled coarse aggregates in Texas. Some of these aggregates contained many fines and micro fines that seemed to compromise, or at least have a negative effect, on performance. For example, the aggregate that was used from the Bird Hill stockpile showed the least amount of strength gain between 7 and 28 days. This could likely have been caused by the interference of the micro fines on the cement hydration. These micro fines may contain non-swelling clay minerals that readily detach from the aggregate and increase the rate of the hydration reaction, thus only contributing to early strength gain. Overall, with the exception of the concretes using aggregate from Wood Pit and Armor Pit (Table 6.5), all the other concrete mixes passed the 7-day minimum flexural strength requirement as set by TxDOT.

There is also a strong correlation between MBV and flexural strength. As MBV increased, flexural strength decreased in a linear fashion. This provides some supporting evidence that the MB test can accurately detect clay minerals which may hinder concrete strength. However, there seemed to be no strong correlation between MBV and drying shrinkage. This is likely due to the fact that the comparator to measure change in length used in accordance with ASTM C 157 does not consistently give accurate results for measuring drying shrinkage. Another main problem when using the comparator is its lack of sensitivity. In order to achieve a better estimation of shrinkage, strain gages were also used, as they are usually very accurate and can detect much smaller increments of shrinkage than the comparator gauge. Nonetheless, all mixes in this chapter experienced higher amounts of drying shrinkage when compared to the control mix.

HMA Mixes

This section includes HMA performance testing in attempt to quantify the effect of the existing type and amount of clay in typical Texas field sands on the engineering properties of HMA mixes. A field sand from a gravel pit located near FM 50 in Hearne, Texas, was selected for this portion of the study based on field observations reporting high clay contents on the material. The gradation of the field sand material along with the modified full mixture gradation needed to accommodate 14 percent added field sand is presented in Figure 6.11.

A field sand from a gravel pit located near FM 50 in Hearne, Texas, was selected for this portion of the study based on field observations reporting high clay contents on the material. The gradation of the field sand material along with the modified full mixture gradation needed to accommodate 14 percent added field sand is presented in Figure 6.11.

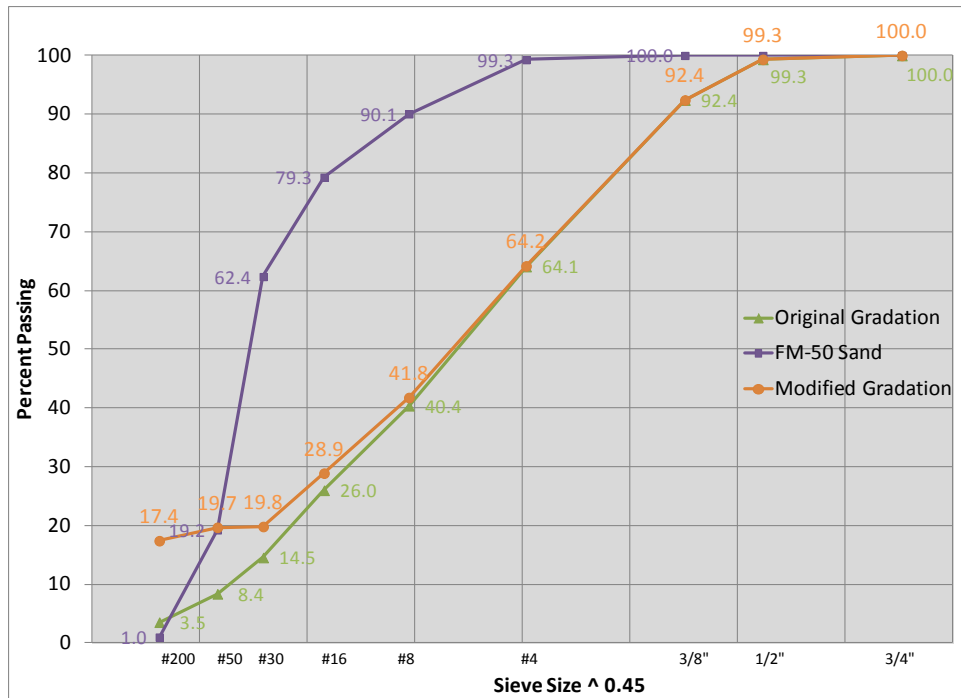


Figure 6.11. Combined Aggregate Gradations for the Original Full Mixture, Modified Full Mixture, and FM-50 Field Sand.

During compaction, the mixture with the field sand proved to be the best compaction aid, with SGC gyrations of around 17 for specimens with average 7.7 percent air voids. The SE test results for the field sand and the Jones Mill material + 14 percent field sand were 48 and 73 percent, respectively, both higher than the minimum of 45 percent prescribed by TxDOT. The bar linear shrinkage for the Jones Mill aggregate passing No. 40 with 14 percent added field sand was 3.50 percent, which is beyond the maximum allowed by TxDOT specifications and significantly higher than the 2.0 percent obtained for the material with no field sand.

The MBV of the Jones Mill aggregate passing No. 4 with 14 percent field sand resulted in a value of 3.66 mg/g, which is not much higher than the result obtained for the Jones Mill aggregate with no contamination (3.51 mg/g). The MBV for only the field sand, however, was 5.57 mg/g, which is about equivalent to the values obtained for the Jones Mill with 1.2 percent smectite and much higher than any of the MB values obtained for the mixtures with kaolinite clay. The MBV vs. SE test results are illustrated (Figure 6.12) along with the values obtained for the Jones Mill mixtures with added smectite and kaolinite clay amounts (Chapter 5) for reference.

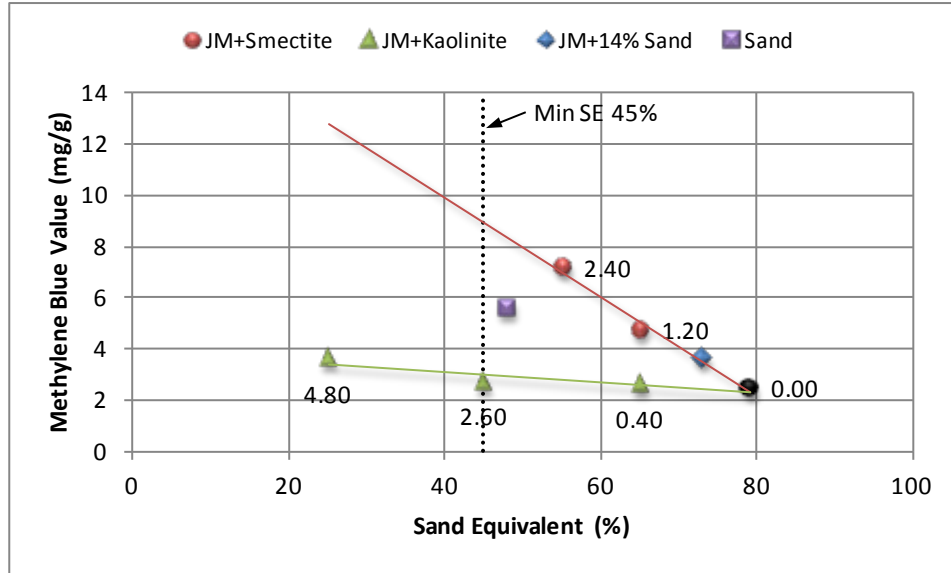


Figure 6.12. Relationship between MBV and SE Test Results for the Field Sand and Jones Mill Aggregate Samples.

The same performance tests performed in Chapter 5 were performed for the Jones Mill mixture specimens with 14 percent field sand, including:

- Boil Test (Effect of Water on Bituminous Mixtures) – Tex 530–C on the loose mixture.
- Hamburg Wheel–Tracking Test (HWTT)–Tex 242–F.
- Overlay Test–Tex 248–F on compacted specimens.

The results of the boil test are illustrated in Figure 6.13. As with the mixtures with added clay amounts, there was no apparent difference between the asphalt mixtures after boiling.

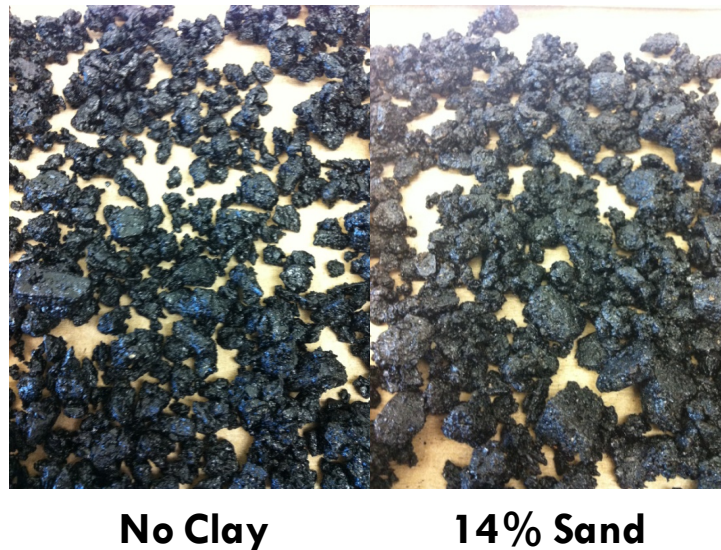


Figure 6.13. Boil Test Results for the Jones Mill Material without Field Sand and with 14 Percent Field Sand.

The HWTT results are illustrated in Figure 6.14. The rutting and moisture susceptibility of the mixture with field sand was adequate, showing no signs of stripping (SIP > 20,000 cycles) and developing minimum rutting after 20,000 load cycles.

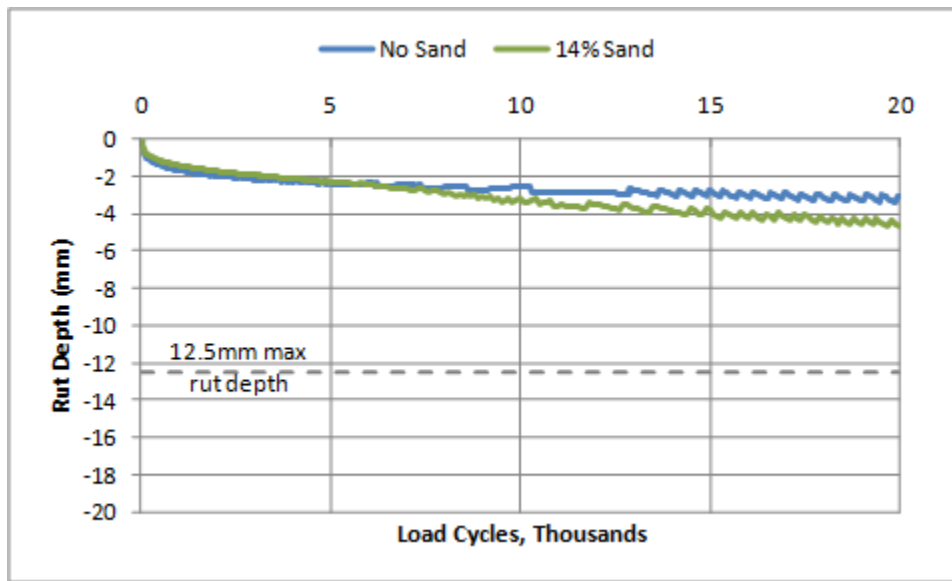


Figure 6.14. Hamburg Wheel–Tracking Test Results for the Jones Mill Mixtures without Field Sand and with 14 Percent Field Sand.

The evolution of damage with load cycles and number of cycles to failure is presented in Figure 6.15. At about 5000 load cycles, both mixtures had equivalent rutting depths. Afterward, the mixture with added field sand had a faster rate of rutting. Yet, both mixtures had less than 5 mm rut depth after 20,000 load cycles.

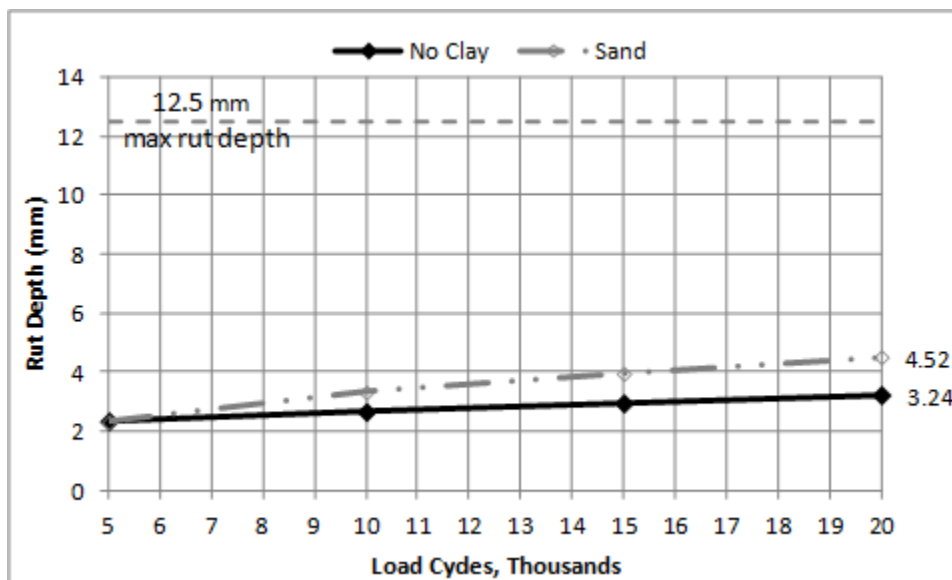


Figure 6.15. The Evolution of Damage with Load Cycles and Number of Cycles to Failure in Hamburg Wheel–Tracking Test.

The overlay test results are summarized in Figure 6.16. Both mixtures with and without field sand had equivalent performance in terms of the number of cycles to failure, although the field sand had a lower peak load versus the mixture without sand.

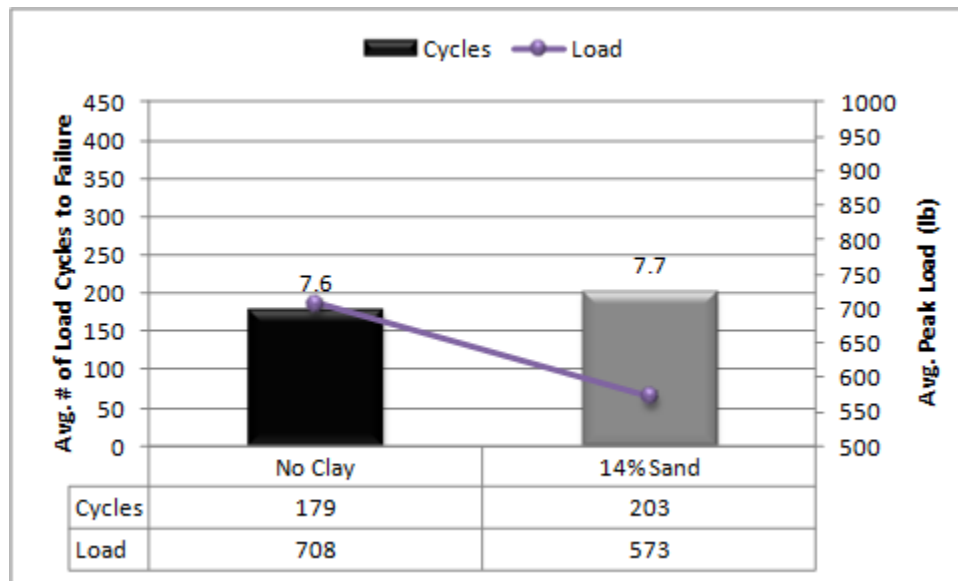


Figure 6.16. Overlay Test Results for the Jones Mill Mixtures without Field Sand and with 14 Percent Field Sand.

SUMMARY AND CONCLUSIONS

The performance of the Jones Mill aggregate with 14 percent field sand proved adequate. Initially, this clay was labeled as problematic due to its perceived high clay content based on field observations. However, the MBV and SE test results on the Jones Mill material + 14 percent sand were 3.66 mg/g and 74 percent, respectively, both below the proposed threshold of 7.2 mg/g and 55 percent SE. Therefore, given the adequate performance of the mixture, the proposed MBV and SE thresholds need to be considered as preliminary estimation. It is recommended that additional field sands be tested to further validate the selected criteria.

CHAPTER 7

REMEDIAL TECHNIQUES FOR CLAY-RICH AGGREGATES

At most quarries, it is currently standard procedure to have aggregates go through a series of washing during production before they are placed in stockpiles in order to remove any deleterious matter that may have been incorporated at the quarry site. In many cases, this technique is quite effective at removing this deleterious matter from the aggregates, but depending on the nature and degree of the clay contamination, sometimes this method fails to remove the harmful clay minerals that can be contained within the fines; therefore, improved techniques may be required. The deleterious matter and clay minerals may be either contained within the aggregate source or collected from the ground during stockpiling operations.

Clay minerals have high cation exchange capacities and large surface areas, thus are ideal as sorbents for surface modification. In recent years, many studies have been focused on using surfactant-modified clay minerals (often called organoclays) to remove hydrophobic organic contaminants from water (Boyd et al. 1988, Zhang et al. 1993). Hexadecyl trimethylammonium (HDTMA) bromide was used to modify the surface of clay minerals such as kaolinite and montmorillonite. Montmorillonite adsorbed a quantity of HDTMA equivalent to its cation exchange capacity. Kaolinite adsorbed relatively small amounts of the surfactant (Krishna et al. 2001). Therefore, adsorption of cationic surfactants such as HDTMA by clay minerals was mainly attributed to cation exchange.

Recently, Li and Gallus (2007) pointed out that both cation exchange and hydrophobic interaction played an important role in cationic surfactant adsorption on negatively charge clay mineral surfaces. The intercalation of cationic surfactants changes the surface properties of clay minerals from hydrophilic to hydrophobic (Xi et al. 2010). Comparing with original clay minerals, modification with HDTMA decreased the specific surface areas. Based on the above previous work it can be concluded that cationic surfactant can be used to neutralize the negative charges of clay minerals through mainly cation change phenomena which mitigates the swelling potential of clay minerals. Changing the surface properties from hydrophilic to hydrophobic and decreasing surface areas could be additional benefits in mitigating the swelling potential of clay minerals. Jeknavorian et al. (2003) determined that adding sacrificial agents such as polyethylene glycols (PEGs), coupled with the right sequence of material addition, helped mitigate the adverse effects that smectite had on concrete mixes.

Surfactants can be added during concrete mixing or dispersants can be used during washing in aggregate producing plant. The approach of using dispersants may be helpful if simply washing with water is not effective enough to provide a clean, high-quality aggregate suitable to be used in concrete.

USE OF CATIONIC SURFACTANTS

The use of cationic surfactants and their effectiveness to combat the harmful effects induced by swelling clay was explored in this study. The current study was mainly focused on determination of optimum dosage of surfactants based on (i) calculation of charge balance with known CEC of respective clay minerals – the level of effect of these surfactants is based on charge balance, and (ii) determination of optimum dosage in terms of % charge balance by MBB

test. The concrete workability and water demand test were conducted at optimum surfactant dosage to verify the benefits of adding surfactants. The goal was to lower the water demand that the clay minerals would have on the concrete not treated with any surfactants. Since negatively charged clay particles attract the cations from the surfactants, their charge becomes balanced, reducing the clay's affinity to water molecules. This happens when the cations from the surfactant occupy the clay mineral and prohibit the positively charged ions from the water molecules occupying the interlayer region of the clay mineral.

DETERMINATION OF OPTIMUM SURFACTANT DOSAGE

XRD Method

A small quantity of pure bentonite clay (mention the amount) was mixed with different amounts of surfactants (corresponding to the different levels of charge balance) in a test tube followed by adding water to a certain level of the test tube. The test tube was centrifuged to disperse the clay sample properly as well as enhance the reaction between clay and the added surfactant. At high degree of charge neutralization by surfactant, the clay particles should float and move to the top surface. This has been clearly observed with the high dosage of surfactant (i.e., high charge balance). The reacted clay particles were separated through decantation procedure and dried before XRD testing. The XRD testing was conducted for all the reacted clay at different levels of charge balance for the three selected surfactants and presented in Figures 7.1–7.3. The degree of disappearance of the prominent bentonite peak at 14 Å is a function of surfactant dosages and was monitored for all three surfactants. The important observations are listed below:

- At 60 percent charge balance, both ARQUAD T50 and HDTMA show very effective disappearance of bentonite peak at 14 Å – (a) most of 14 Å peaks is gone at 60 percent charge balance with T 50 surfactant. Smaller layer thickness change causes difficulty in measuring remaining expandable smectite quantities (Figure 7.1), (b) HDTMA appears to cause complete disappearance of 14 Å expandable–layer smectite peak at 60 percent calculated charge compensation. HDTMA appears to be the best–performing surfactant. This is an indication that 60 percent charge balance should be sufficient to change expandable bentonite clay completely to a non–swelling type organoclay (especially with HDTMA). It is important to mention that complete disappearance of bentonite peak at 14 Å is not needed as concrete can tolerate some amount of expansive clay minerals without facing any harmful effects. Therefore, it is recommended to consider dosage corresponding to 40 percent charge balance as a practical limit where significant disappearance of bentonite peak is noticed (Figures 7.1–7.3).
- ARQUAD 2HT–75E compound was not found effective to completely remove the 14 Å peak of expandable bentonite even at 100 percent charge balance. Expandable clay peak still present at calculated 100 % charge balance (Figure 7.3).

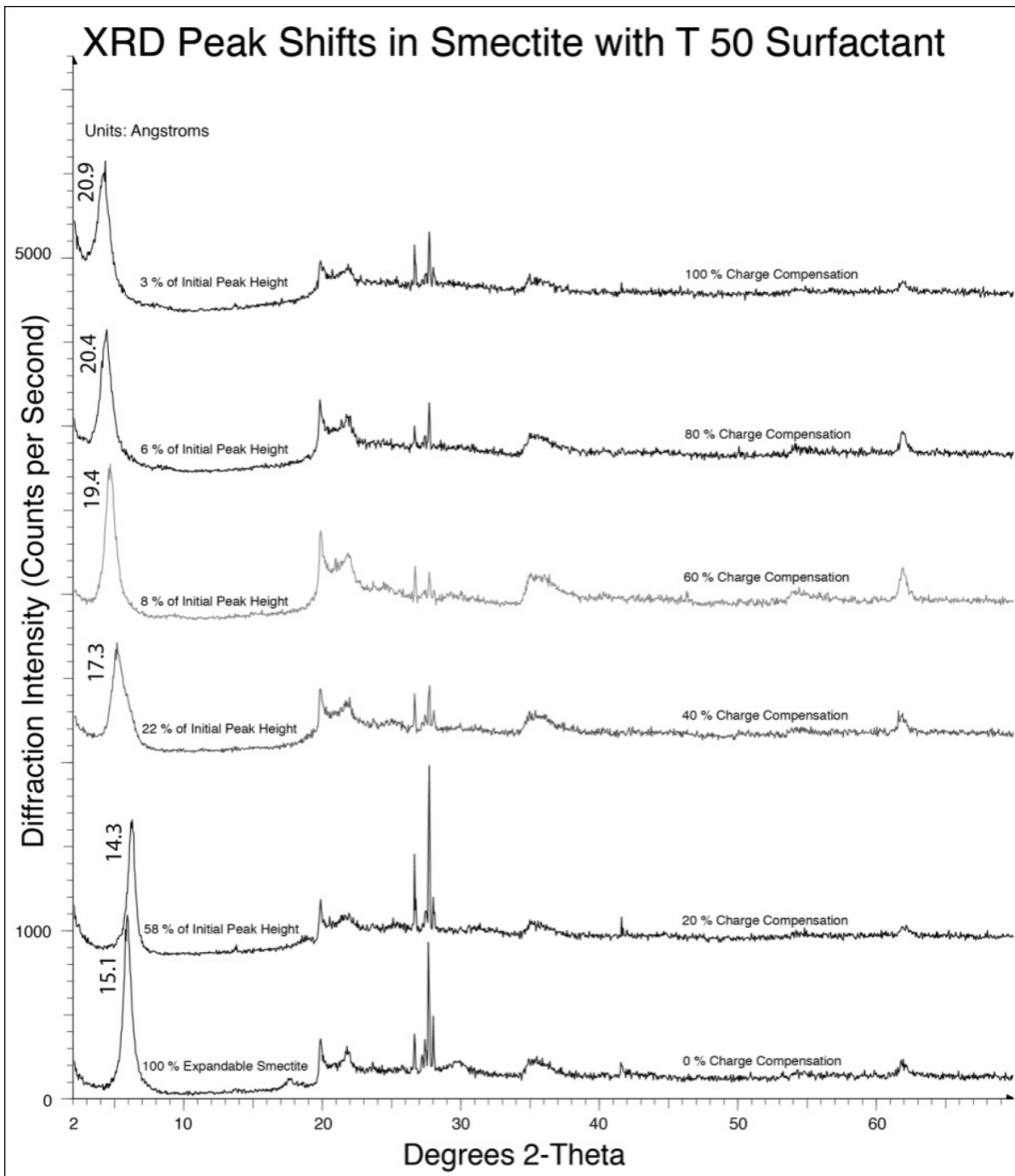


Figure 7.1 Arquad T 50 Surfactant Treatments of Bentonite.

XRD Peak Shifts in Smectite with HDTMA Surfactant

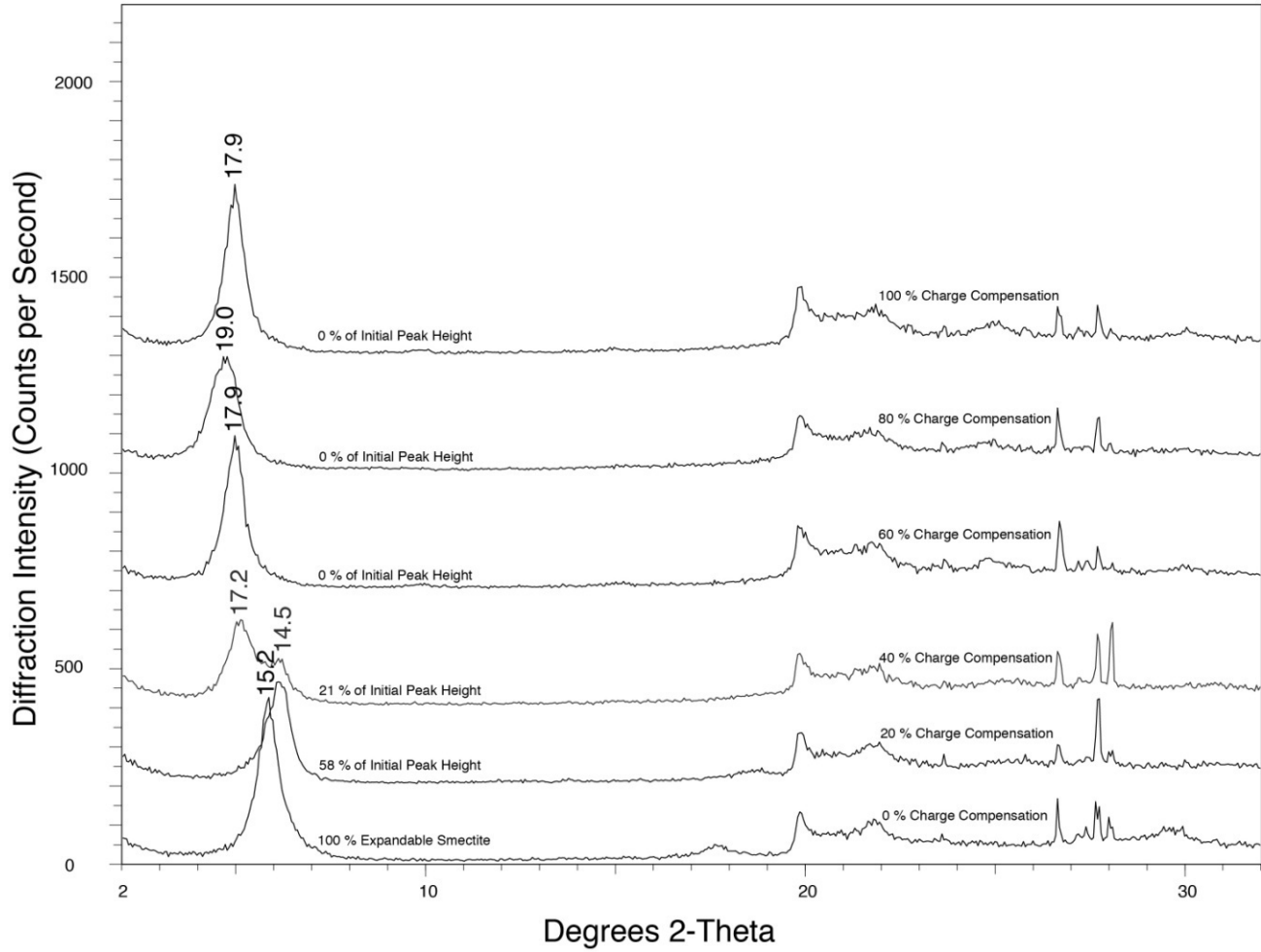


Figure 7.2 HDTMA Surfactant Treatments of Bentonite.

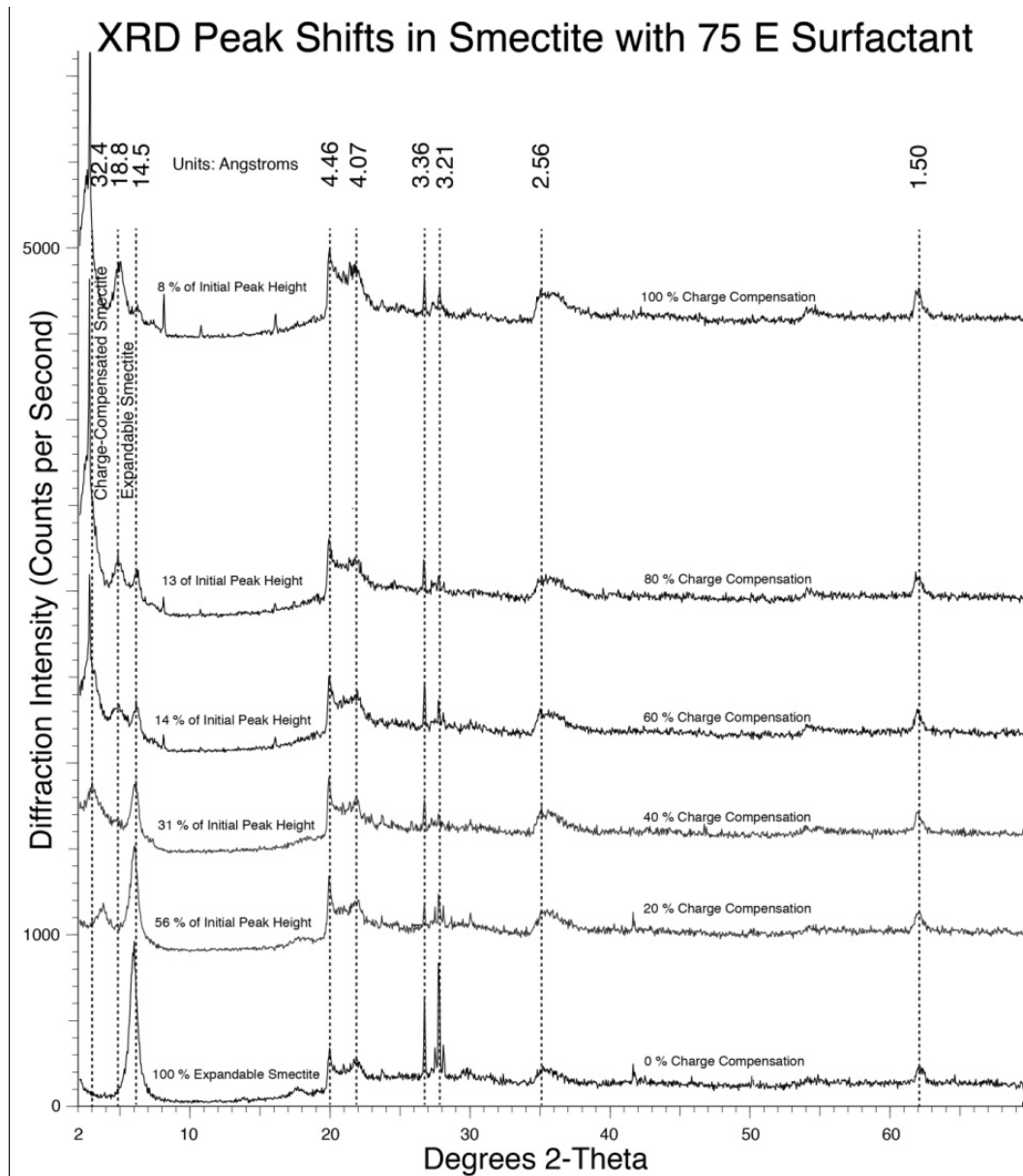


Figure 7.3 Arquad 2HT–75E Surfactant Treatments of Bentonite.

ARQUAD T50 and HDTMA were identified as effective surfactants to neutralize bentonite (expansive) clay with 40–60 percent charge balance and were considered for further studies (linear bar shrinkage, MMB, and water demand tests).

MBB Method

The MMB test was employed for both pure smectite clay and field screening materials containing smectite clay to see if the surfactants were effective, giving lower MBVs than the untreated samples. The idea was to determine which dosage is sufficient to reduce the MBV below the threshold value (i.e., 4.5 for –4 size and 11 for –40 size). Mixtures were developed using (i) pure silica sand (–4 mesh, ~ 80 g) + pure smectite clay (3 percent) + surfactants (T50

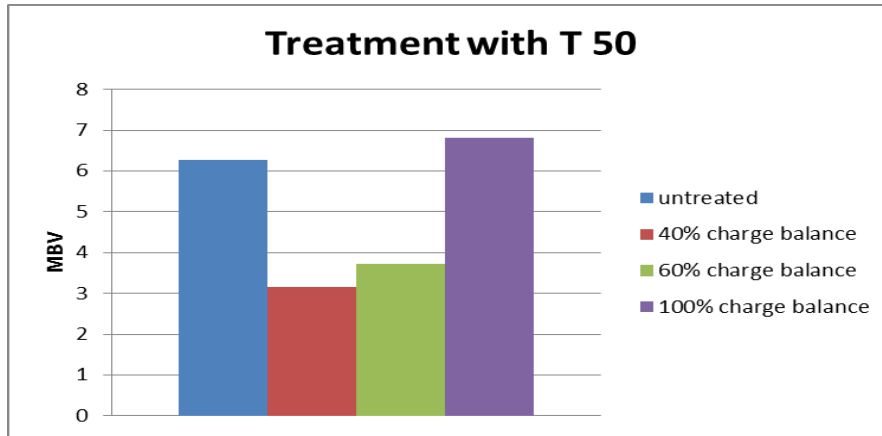
and HDTMA with dosage corresponding to 40 and 60 percent charge balance) + water, (ii) aggregate fines (e.g., -40 size mesh material of around 80 g) form fields + surfactants (both T50 and HDTMA with 40 and 60 percent charge balance) + water. The quantity of water for each mixture was fixed based on the procedure of linear bar shrinkage method, i.e., quantity needed to make the mixture with sufficient wetability. The mixtures were kept under typical lab conditions (i.e., 23°C and ~60 percent RH) for 2–3 hours followed by under oven (60°C) overnight. MBB test was conducted for all the mixtures the next day. The results for pure smectite clay are presented in Figures 7.4 and Table 7.1 and for fines from screening materials are presented in Figures 7.5 and Table 7.2. In order to compare with the shrinkage results (presented next in Table 7.3), MBB test was conducted with -40 size materials.

By examination of the test results for pure clay (Figures 7.4 and Table 7.1), it is evident that the surfactant dosage based on 40 percent charge balance is the most effective in reducing the MBV below the threshold value of 3.8 (Chapter 5). Furthermore, Table 7.1 also provides data showing the percent reduction of MBV with both 40 percent and 60 charge balance for each of the two surfactants used.

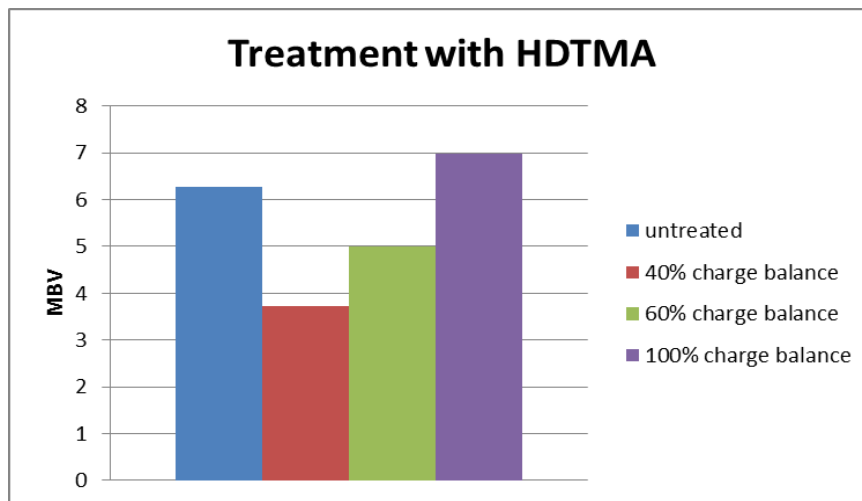
For screening materials (Figure 7.5 and Table 7.2), the same dosage (i.e., dosage corresponding to 40 percent charge balance) as used in the pure clay system was identified as the optimum dosage of the two tested surfactants.

The percent reduction of MBV in pure clay system (Table 7.1) is higher than that for screening materials (Table 7.2). In pure clay system, surfactants get easy access to the clay minerals (freely available). This causes the effective charge balance of clay minerals, which is manifested as significant reduction of MBV in the treated samples. On the other hand, not all clay minerals are freely available in the screening materials and, therefore, the charge balance reaction by the surfactants may not be very effective. This possibly causes less % reduction of MBV in case of screening materials (Table 7.2).

Both XRD and MBB methods have provided a similar range of optimum surfactant dosage (i.e., 40–60 percent charge balance). XRD is an advance research tool and is not a recommended field technique. On the other hand, MBB test is a reliable method and can easily be performed in the field. Therefore, it is recommended to use MBB test to determine the optimum dosage needed.



(a)



(b)

Figure 7.4. MBV Before and After Treatment for Pure Smecite (3 Percent) and Silica Sand Mixtures, (a) ARQUAD T 50 and (b) HDTMA.

Table 7.1 Effect of Surfactants on MBV for Pure Smecite (3 Percent) and Silica Sand Mixtures.

Untreated	Treated							
	MBV (T 50)		% Reduction of MBV (T 50)		MBV (HDTMA)		% Reduction of MBV (HDTMA)	
6.2	40% CB	60% CB	40% CB	60% CB	40% CB	60% CB	40% CB	60% CB
	3.0	3.5	52%	44%	3.6	5.0	42%	20%

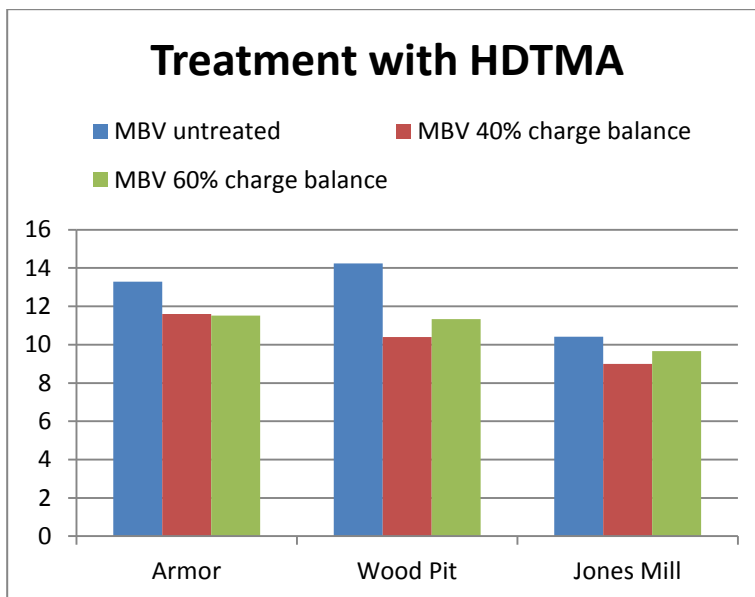
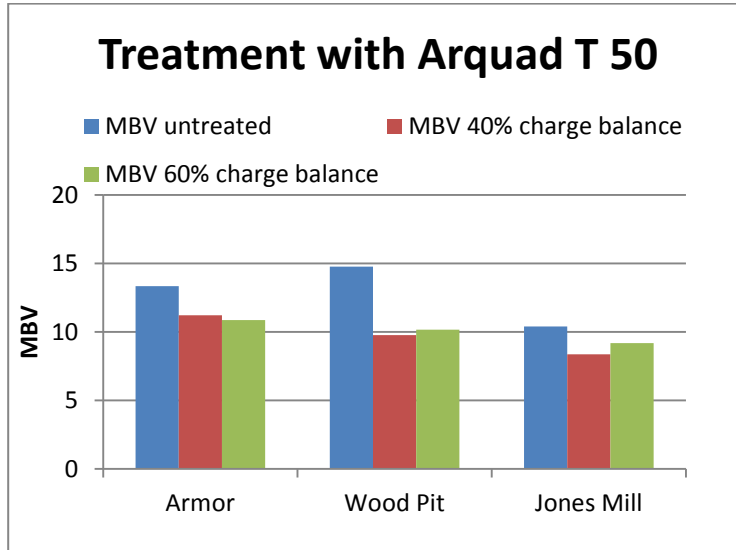


Figure 7.5. MBV Before and After Treatment for Mixtures with Screening Materials, (a) ARQUAD T 50 and (b) HDTMA.

Table 7.2 Effect of Surfactants on MBV for Screening Materials (–40 size).

Sample	Untreated	Treated							
		MBV (T 50)		% Reduction of MBV (T 50)		MBV (HDTMA)		% Reduction of MBV (HDTMA)	
		40% CB	60% CB	40% CB	60% CB	40% CB	60% CB	40% CB	60% CB
Armor	13.66	11.21	10.87	18%	20%	11.6	11.52	15%	16%
Wood	14.72	9.78	10.16	34%	31%	10.4	11.34	29%	23%
Jones Mill	10.39	8.36	9.18	20%	12%	9.0	9.66	13%	7%

Effect on Bar Linear Shrinkage

Similarly as done in Chapter 4, bar linear shrinkage was measured for untreated samples along with samples treated for 40 and 60 percent charge balance (as in Table 7.2). This was performed based on the assumption that the treated samples would yield lower amounts of shrinkage. The test results for the three samples are presented in Table 7.3. Based on the test results, there is no clear and consistent reduction in shrinkage after treatment. Therefore, the shrinkage test is not a recommend method to determine the optimum dosage of surfactant.

Table 7.3 Effect of Surfactants on Bar Linear Shrinkage for the Three Selected Screening Materials.

Sample	Untreated	Treated			
		Shrinkage (T 50)		Shrinkage (HDTMA)	
		40% CB	60% CB	40% CB	60% CB
Armor	6.0	5.0	4.5	5.0	5.0
Wood	4.0	4.5	4.0	3.5	4.0
Jones Mill	2.5	2.5	3.0	2.5	2.5

Effect on Water Demand in PCC Mixes

While the MBV can be used to identify an effective surfactant and to determine its optimum dosage in the lab, additional testing for concrete (e.g., reduction in water demand, strength increase and shrinkage reduction) made with the same aggregate (coarse or fine) and the recommended dosage of surfactant is highly needed to verify the benefits. For this reason, some concrete mixing was carried out using the method presented in Chapter 5. It was previously determined that aggregates containing 1.5 percent by weight of bentonite, required a water content equivalent to a 0.49 w/c in order to provide adequate workability (i.e., around a 1–in. slump). Since the AT–50 surfactant was the most effective, it was selected to be used in concrete containing 1.5 percent bentonite with hopes of reducing the water demand.

There were two methods of the surfactant addition to the concrete mixer that were explored (Table 7.4) in this study. Time of addition of surfactant with possible mechanisms and effectiveness are provided in Table 7.4. The methods of addition of the AT–50 surfactant to the

concrete should be considered as satisfactory if it provides considerable reduction of water demand in comparison with controls. A dosage equivalent to 60 percent charge balance was required for option 1 to maintain a constant workability (i.e., 1-in. slump). On the other hand, a dosage corresponding to 40 percent charge balance was found to be optimum for Option 2. With each method of addition, the w/c was effectively reduced from 0.49 to 0.46, while giving adequate workability and slump of over 1 inch. It seems Option 2 is more effective than Option 1 in this situation. Additionally, Option 2 should be the recommended choice if fine aggregate is contaminated with clay minerals.

Table 7.4 The Methods of Surfactant Addition.

	Option 1	Option 2
Time of addition of surfactant	Adding raw surfactant directly to coarse aggregate with clay contamination and 20–30% water (first stage of a conventional mixing sequence)	Adding raw surfactant during the final stage of a conventional mixing (e.g., after adding all the concrete ingredients)
Mechanisms	Surfactant reacts with expansive clay present in coarse aggregate fines before the addition of other concrete ingredients (e.g., cement, fine aggregate, admixtures)	(i) Clay in fines consumes some water and causes mix to be less workable at the beginning, (ii) surfactant interact with the water-filled clays subsequently and expels the consumed water and makes the mix workable with the normal range of w/c
Effectiveness	Should be good provided coarse aggregate doesn't absorb surfactant (remote possibility)	The interaction (if any?) between surfactant and Fly ash/cement/AEA will be more than option 1 – may reduce the effectiveness of the main reaction between surfactant and clay minerals (need further investigation)

GUIDELINES FOR MITIGATION

The use of cationic surfactants seems to have some potential to treat aggregate fines with high content of expansive clay minerals. The current study was mainly focused on (i) determining optimum dosage of cationic surfactants, (ii) developing procedure to add surfactant during concrete mixing (Table 7.4), and (iii) measuring water demand of concrete. The mitigation guidelines for PCC based on the work performed in this project and recommended future work are provided below.

Surfactant Dosage Calculation

Step 1: Conduct MMB test of the aggregate fines (both –4 and –40 sizes) from stockpile materials and determine the MBVs. If the MBVs are higher than the threshold values (i.e., 4.5 for –4 size and 11 for –40 size), then proceed to Step 2.

Step 2: Estimate % smectite from the measured MBV by using the relationship between smectite content vs. MBV that was developed in Chapter 4 (Figures 4.14 and 4.15).

Step 3: Calculate the dosage of the selected surfactant with different levels of charge balance (i.e., 40, 60, and 100 percent) using the given Excel spreadsheet. The required inputs for the spreadsheet are percent smectite (determined in Step 2), sample size (pounds of coarse or fine aggregate per yard of concrete depending on whether the swelling clays are introduced through coarse or fine aggregates).

Step 4: Run the MBB test (as described previously in this chapter) to determine the optimum surfactant dosage. i.e., the dosage needed to reduce the MBV below the threshold value. The dosage corresponding to 40 percent charge balance was found to be a standard practical dosage for concrete. However, it is recommended to do the MBB testing whenever new stockpile material is encountered.

Adding Surfactant to PCC during Mixing

Step 5: Select the method of addition (according to Table 7.4) of the selected surfactant of required dosage (determined in Steps 3 and 4) during concrete mixing. Option 2 should be the preferable way to add surfactant. However, Option 1 can also be used depending on its effectiveness. It is necessary to verify the applicability of both these options in the context of typical concrete batch plant operation. The option that goes well with the existing operation of a batch plant (without any special requirement) will be the most preferable option to add surfactant.

PCC Performance Verification

Step 6: Conduct testing to determine fresh concrete properties (measure slump and water demand). Considerable reduction of water demand should be achieved in comparison with the control mix without any surfactant

Step 7: Conduct testing to determine hardened concrete properties (strength and shrinkage testing) – considerable increase of strength and reduction of shrinkage should be achieved in comparison with the control mix without any surfactant in order to justify the use of surfactant.

More research is needed (Steps 1–7) using problematic stockpiled materials to verify the effectiveness of different surfactants and other effective chemicals. It is recommended to do the work under Steps 5, 6, and 7 in the field lab before applying the surfactant in the batch plant for large scale production to make sure that surfactant is providing the expected beneficial effects.

Use of Dispersants in Aggregate Producing Plant during Washing

- It is also recommended to explore the possibility of adding dispersant with the water during washing (if any) in the aggregate producing plant. The presence of dispersant with washing water may be useful to remove clay minerals effectively. No investigation has been done in this aspect.

- If significant removal of clay minerals by washing with water plus dispersant is achieved during aggregate production then the use of surfactant during concrete mixing in the batch plant may not be needed.

Guidelines for Controlled Use of Aggregate Fines with Varying Clay Contamination

Guidelines for Portland cement concrete based on threshold MBV ranges and total permissible fine contents in comparison with the current specifications are developed (Table 7.5) and summarized below:

- Conduct the MBB testing of the stockpiled materials and determine the performance category based on MBV ranges (according to Tables 6.7 and 6.8 in Chapter 6).
- Assess the pass/fail situation based on a comparative assessment between MBV and the current practice (first and second columns in Table 7.5).
- Determine the total allowable fine contents with respect to either –4, or –40 sieve sizes (the third column in Table 7.5). Research is needed to assign the total permissible fine contents with respect to percent retained on either –4 or –40 sieve sizes or both of the siezes.
- Determine the effective treatment for cases where aggregate fines failed by MBV criteria but passed/failed by the current practices (3rd and 4th rows in Table 7.5). Determine the type and dosage of surfactant or other effective chemicals according to the mitigation guidelines provided above.
- Cost benefit analysis – Use the provided excel spread sheet to calculate the cost of adding surfactant per yard of concrete (Table 7.6 as an example). The additional cost of using surfactants needs to be justified by making good quality durable concrete with a long service life.

Table 7.5 Guidelines of Using Aggregate Fines Based on MBV and Total Fine Contents.

MBV (-4) /(-40)	Current Methods (e.g., contents of -200 sieve)	Total Permissible Fine (-4 or -40) Contents	Treatment Recommendation	Remarks
≤ 4.5 or ≤ 11 PASS	Within the permissible limit (PL) PASS	Total fine content can be increased	No treatment	Flexibility in controlling the fine contents
≤ 4.5 or ≤ 11 PASS	Above the PL FAIL	-More than the limits specified by the current methods and / or -Higher than the upper limits of the current specified gradation ▲	No treatment	Allowing a material which is unnecessarily failed by current specification(s) – sustainable approach, save money ♣
4.5 – 6.5 OR 11.0–14. 0 MARG.	Within the PL PASS	≤ Upper limit of the current specification ▲ ≤ Lower limit of the current specification ▲	Use of surfactant (e.g., Arquad T50, HDTMA) with recommended dosage (i.e., correspond to 40% charge balance) during concrete mixing	Not allowing a material which is passed by the current specification(s) without any treatment – good control to make durable concrete
≥ 6.5 OR ≥ 14 FAIL	Within the PL PASS			
≥ 6.5 or) ≥ 14 FAIL	Above the PL FAIL	≤ lower limit of the current specification ▲ OR Restricted use of fines of specific size(s) ▲	Use of surfactant with high dosage during concrete mixing ♥ And / or Treatment in the aggregate plant – add surfactant with washing water ♥	A bad material can still be used with proper treatment – sustainable approach

♣ICAR research showed that addition of non-clay fines (manufactured fines, e.g., limestone fines) more than the recommended limit doesn't impose any harmful effects, ▲ Research is needed to assign the total permissible fine contents with respect to representative sieve size(s); ♥ whichever is effective and economic – washing with surfactant can only be attempted if clay minerals in aggregate fines comes from pit/quarry

Table 7.6. Amount of Surfactant and Associated Cost per Cubic Yard of Concrete.

Arquad T 50			HDTMA		
Dosage	Amount needed	Cost per yd ³	Dosage	Amount needed	Cost per yd ³
40% charge balance	6.6 lb	\$15.00	40% charge balance	3.6 lb	\$8.00
60% charge balance	10 lb	\$22.00	60% charge balance	5.5 lb	\$12.00

CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

This section summarizes the main findings of the study and offers recommendations for further investigation of clay contamination of stockpiled aggregates. Within these detailed conclusions, some limitations are also highlighted.

CONCLUSIONS

PCC

Based on the results obtained from this study, there are two conclusive observations that are readily apparent: some existing test methods like the SE test and PI test fail to consistently detect the presence of clay minerals in aggregate fines, and the MMB test proves itself to be more rapid and reliable in identifying the presence of clay minerals in aggregate fines with strong supporting evidence from XRD quantification results. The primary findings in this study include:

- A strong positive correlation between expansive clay content (determined by QXRD) and MBV is evident (Figures 4.14 and 4.15 in Chapter 4), which clearly indicates that the MMB test is the most reliable and rapid test method to detect clay minerals in aggregate fines. MMB test also offers an improvement over the existing methylene blue (MB) test (AASHTO T 330), which can often give erroneous results with high variability since the current MB test is quite subjective, depending on the operator.
- X-Ray Diffraction method is an advance research tool, which was used to establish the MMB method in this study. XRD is the best research tool to identify and quantify clay minerals with reasonably good accuracy. However, the XRD method is not recommended as a field method.
- Furthermore, the MMB test procedure has several advantages over the bar linear shrinkage and sand equivalent tests. For examples, (i) the MMB test procedure is easy to follow and can be performed in the field, (ii) the use of colorimeter to read the MB concentrations minimizes human error, (iii) it can be performed by nearly anyone and doesn't require any advanced training for operation, (iv) the entire test can be completed in about 10 minutes, (v) the test consistently gives good results with low variability.
- Although the bar linear shrinkage and sand equivalent tests give good repeatability in the results, both the bar linear shrinkage and the sand equivalent tests fail to provide consistent and accurate indications of clay minerals present in aggregate fines (Figures 4.16 and 4.17).
- The SE test fails to distinguish between clay-sized particles and actual clay minerals. Furthermore, the SE test is not effective to differentiate between expansive (smectite) and non-expansive clay minerals (Kaolinite).
- The bar linear shrinkage test should not be viewed as a consistently reliable tool to obtain an estimate of clay content, as it certainly has its own limitations. Problems like uneven amounts of shrinkage and bowing that may occur upon drying make for getting an accurate "linear" measurement difficult. There may also be some degree of restrained movement of the test specimens upon drying.

- The MMB test can be performed on aggregate fines passing both No. 4 (P4) and No. 40 sizes (P40). Lower variability (i.e., low COV percent) was observed with the test results of the P 40 size materials than P4 size materials.
- Both the MBV of the P4 and P40 sizes can be used to categorize aggregate fines with the following notes:
 - For pit run/screening materials, the P4 size is more representative. None of the samples tested at the P4 size, with the exception of sample Pit # 365, show a $MBV \geq 15$ using the 10–10 dilution method, whereas some of the samples tested at the P40 size (Pit #365, South Noodle, Whitney Pit) P2 and P3 give a $MBV \geq 15$ using the 10–10 dilution method. It is to be noted that pit run or screening materials are not the actual materials that will be tested in future. Moreover, the sample from Pit #365 is an unrealistic, biased sample of screening materials (clay-rich).
 - For stockpiled materials, the MBVs of both the P4 and P40 sizes can be used to categorize the aggregate fines as none of the samples tested at the P40 size show a $MBV \geq 15$ with 10–10 dilution.
- The need of adding an inert filler (e.g., pure silica sand) during testing with the dilution method (10 g sample + 10 g inert filler or 5 g sample + 15 g inert filler) is not mandatory. The direct use of a 10 or 5 g sample without using any inert filler is equally good to generate representative MBV. Note that the final MBV will have to be multiplied by 2 (for 10 g sample) or 4 (for 5 g sample) to obtain a representative MBV. The manipulation (i.e., multiplying by a factor) error using a 10 g sample is less (double) than that using a 5 g sample (possibly 4–5 times). The MBVs with a 10 g sample (≤ 14.5) is acceptable without compromising much with the data accuracy. However, the MBVs with 5 g sample need to be used with caution as the manipulation error is often very high. Moreover, using a sample size of 5 g is not suggested by the manufacturer as it is outside the detection range of the colorimeter.
- MBV shows a good correlation with both percent reduction in strength and increase in shrinkage of the corresponding PCC mixtures using pure clays. A threshold MBV of around 3.7 is obtained based on (i) percent pure bentonite vs. flexural strength and (ii) percent bentonite vs. MBV relationships.
- There is also a strong correlation between MBV and flexural strength using stockpiled materials. As MBV increased, flexural strength decreased in a linear manner. This provides some supporting evidence that the MB test can accurately detect clay minerals, which may hinder concrete strength. The correlation between MBV and concrete performance testing became the basis to assign threshold MBV and categorize aggregate fines with different ranges of MBV (Chapters 5 and 6). A threshold MBV of 4.5 for P4 size materials or 11 for P40 size materials was established based on performance testing of PCC mixes. (Tables 6.7 and 6.8 in Chapter 6). The ranges are arbitrary in nature at this time as these are based on the MBV of limited stockpiled materials. A large number of aggregate stockpiled materials need to be tested for their MBV in both –4 and –40 sizes along with corresponding PCC performance testing in order to assign more accurate MBV ranges.
- Some materials may fail by currently used methods/specifications in detecting clay, but these samples may pass based on the MMB test. This would indicate more material with

a high fine content would actually be allowable (Table 7.5, Chapter 7). Therefore, a material which is unnecessarily failed by current specification(s) can be allowed. This promotes sustainability and saves money.

- The MMB test can identify some materials as “failed” although other tests may pass them. This indicates that the MMB test is not considering them acceptable without additional washing or treatment (Table 7.5, Chapter 7). That means a material which is passed by the current specification(s) will not be allowed without any treatment which needs to be considered as a good control to make durable concrete.

HMA

The findings in HMA are summarized below:

- Results thus far indicate that the addition of smectite clay to asphalt mixtures has a negative effect on their performance in terms of rutting, moisture susceptibility, and cracking resistance. This is somewhat abnormal since the typical observed behavior is that mixtures with good rutting performance have poor cracking resistance, and vice versa. However, for the smectite mixtures the presence of the clay negatively affected both characteristics. The mixtures with added kaolinite, on the other hand, had inadequate cracking performance at the higher clay levels, but good moisture susceptibility and rutting values were obtained.
- The SE test was not able to differentiate between clay types, and the pass/fail test results from the HWTT were inconsistent with the specification limit of 45 percent minimum SE. That is, some mixtures with SE values of 45 percent or less passed HWTT while others failed (Figure 5.22 in Chapter 5). The same is true for the results of the Bar Linear Shrinkage test, which was not able to differentiate between clay types, and most of the results were above the prescribed limit of 3 percent maximum shrinkage (Figure 5.23).
- The results of the MMB test were the most promising because the test was able to differentiate between clay types. The Methylene Blue Test is sensitive to clays which contribute to stripping in HMA and could be used to eliminate problematic field sand sources. Based on the pass/fail HWTT results, a preliminary threshold MBV of 7.2 mg/g with corresponding SE threshold value of 55 percent are proposed (Figure 5.24). Additional mixture types should be tested to verify these proposed thresholds. It appears that HMA is more robust and can tolerate higher amounts of clay contamination than PCC, mainly because water is not present in HMA.
- Improvement in workability with increasing clay content (of any type) in the HMA mix has been observed. Therefore, increase in workability of today’s stiff mixes with the addition of clay is a potential benefit in HMA.
- The stiffening effects of RAP/RAS in HMA could potentially mask effects of problematic clays (field sands) in the Hamburg Test.
- The Methylene Blue test could allow the “design” of an optimum quantity and type of anti-stripping additive for a particular HMA (instead of common practice, i.e., 1 percent lime).

High methylene blue values indicate increased potential for diminished aggregate performance in asphalt, concrete, and other construction applications. This test method provides a rapid and reliable field method for determining changes in the quality of aggregates during production or placement.

The research team has fine tuned and verified the MMB test procedure/parameters originally developed by WR Grace and continued with an extensive additional study in the following areas:

- Large number of testing: 35 aggregate fines with 3 replicas.
- The effect of size: (i) –No. 4, (ii) –No. 40 and (iii) –No. 200 sieve sizes.
- The effect of dilution – i.e., using 20, 10, 5 g of sample. The dilution using a sample of up to 5 g works for pure clay and silica sand mixtures. However, the MMB test using 5 g of natural clay–rich materials (e.g., screening materials) introduced significant errors.
- Theoretical calculation of MBV based on amount, type and CEC of clay minerals, molecular weight of MB – helps to verify the measured MBV.
- Clay mineral quantification of 27 samples by XRD and establish a relationship between % swelling clay minerals vs. MBV.
- Establish a relationship between MBV and PCC/HMA performance testing and assign a meaningful threshold MBV for both PCC and HMA.
- Use of MBV to assign optimum dosage of cationic surfactants to neutralize clay charge – a potential remedial approach.

The research work performed in the above areas has increased our knowledge significantly on the applicability/suitability of the MMB test to find an optimum particle size and dilution level and generate a representative threshold MBV.

RECOMMENDATION

Further Research for PPC

The following are the areas of further research for PCC:

1. It is highly recommended to complete the fine tuning of the threshold MBV by performing the following work:
 - a. MB Testing for more stockpiled materials. Collect more stockpiled materials based on the information pertaining to (i) current issues with the fines, (ii) aggregate type and mineralogy, (iii) type of variability in the source quarry/pit (horizontally/vertically), (iv) type of clay/shale in the quarry, and (v) clay contamination during stockpiling.
 - b. Conduct MB testing at two different sizes (–No. 4 and No. 40) and assign a threshold MBV for both the sizes. Finally, select the most representative size fraction for MB testing.
 - c. Conduct concrete performance testing. Conduct more concrete performance testing in terms of measuring strength and shrinkage to justify the threshold MBV.

2. Determine total permissible fine contents. The MMB test detects the presence of clay minerals more accurately but it does not say anything about the total permissible fine contents in different sizes. Therefore, further research is needed to define the total allowable fine contents (i.e., the gradation limits of each size fraction of the aggregates, namely the P4 and P40 sizes) in order to make a precise assessment in determining the suitability of a particular aggregate based on its MBV.
3. Research remedial techniques. More research is needed (Steps 1–7, guidelines for mitigation, Chapter 7) using problematic stockpiled materials to verify the effectiveness of different surfactants and other effective chemicals. It is recommended to follow the work under Steps 5, 6, and 7 in the field lab before applying the surfactant in the batch plant for large scale production to make sure that surfactant is providing the expected beneficial effects. It is also recommended to explore the possibility of adding dispersant with the water during washing (if applicable) in the aggregate producing plant. The presence of dispersant with washing water may be useful to remove clay minerals effectively. No investigation has been conducted in this aspect.
4. The relationship between pure clay content and MBV (Figure 3.12 in Chapter 3) is only based on two pure clay types (kaolinite and bentonite) and can be used for rough estimation of clay content at the best. Although these two clays are the dominant clay types in the soil throughout Texas, calibration curves representing the types and amount of different clay minerals present in aggregate fines in a particular region/state must be generated in order to obtain a more accurate estimation of clay content. The expansive clay content vs. MBV relation that are generated based on pit run/screening materials (Figures 4.14 and 4.15 in Chapter 4) may be used to roughly estimate expansive clay (e.g., smectite) content from measured MBV.

Further Research in HMA

The following are the areas of further research for HMA:

1. Fine tune the MBV limit.
 - a. Test an array of field sands using Hamburg and other tests.
2. Validate pass–fail recommendations based on sand equivalent/linear bar shrinkage and MMB tests.
3. Consider a specification requirement for field sands based on MBV.
4. Optimize the “design” of the anti–strip for HMA. Evaluate the effects of different types and quantities of liquid anti–stripping additives and/or lime.

Proposed Implementation Plan

It is recommended to implement the MMB as a user friendly field technique through the following activities.

PCC

1. Establish repeatability (within the Lab) and reproducibility (between the labs) of the MMB test.

- Provide equipment to five labs (cost ~ \$1500.00/ each) within TxDOT. Two can be given to TxDOT (Austin) and three can be given to three district labs.
 - Provide necessary training and workshops to the representative operator for all the labs.
 - Select some stockpiled materials (both bad and good actors, minimum five materials) and conduct MMB testing
 - Repeat six replicas per sample within the lab.
 - Reproduce between the labs. COV percent will be determined based on the average MBV of each lab (total five labs).
 - Develop a precision and bias statement.
2. Field Validation – possibility of constructing field test section using aggregate with (i) low MBV but high total fine contents, (ii) medium MBV with low/high total fine contents, and (iii) high MBV and low/high fine contents – needs to be explored in order to validate the performance under field conditions.
 3. Guidelines that are developed in Chapter 7 for controlled use of aggregate fines with varying clay contamination will be refined and updated based on more refined threshold MB values and total permissible fine contents through further research (mentioned above).
 4. Specification recommendation based on MBV – shadow specification will be prepared based on the final guidelines (Step 3) and TxDOT will decide if it wants to incorporate the shadow specification in the construction specification.

HMA

1. Select three to four districts and evaluate field sands with standard tests and MBV tests. Work with districts on upcoming hot mix projects to optimize the design of the anti-stripping additive.
2. Include districts such as Fort Worth that do not require the Hamburg test yet rely on the boil test.

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APPENDIX A

WEB SURVEY OF TXDOT DISTRICTS TO ASSESS PROBLEMS ASSOCIATED WITH CLAY IN AGGREGATE FINES

Following is a brief discussion of the results obtained by the survey TTI researchers submitted to the 25 TxDOT districts for assessing the problems the districts are experiencing with clays/fines in aggregate sources. We asked 11 questions related to testing and performance of aggregate in hot mix, seal coats, and PCC (Appendix A). We had a total of 17 respondents to the survey.

Question one asked if the districts had problems with clay coatings or clay in the aggregate. Twelve of the 17 respondents reported no difficulty with clay in aggregate or clay coatings on crushed aggregate used in seal coats, hot mix, and Portland cement concrete: three respondents reported problems coatings on crushed aggregate, and two reported problems with clay in the aggregate.

Question two asked if the districts had difficulty meeting the requirements for test methods listed in Table A.1 of Item 341 (p. 281) which is reproduced below for your convenience (Table A.1). Sixteen respondents reported no problems and one respondent reported having problems meeting the requirements listed.

Question three asked if they are having difficulty meeting the requirements, then which requirements are they having difficulty with. There were four respondents that reported difficulty meeting the 1.5 percent maximum for deleterious materials or decant, and one respondent reported difficulty meeting the 30% maximum for magnesium sulfate soundness test. These answers do not match the answers we received for question two where only one respondent reported problems, whereas five respondents report problems in this question.

Question four asked if the districts are doing any additional testing to detect clay problems. Two respondents stated that they used plasticity index testing to detect clays. The other respondents reported no additional testing to those listed in Table 1.1 above.

Question five asked if there were other tests not listed in the previous questions that the districts are doing to detect clay in aggregate. There were zero districts that reported any test methods other than ones we listed previously.

Question six asked if the problem can be related to contamination by the contractor. Nine of the respondents reported that contamination by the contractor is the problem while eight report that the problem is not contamination by the contractor.

Question seven asked if the problem was due to variations in the aggregate itself. Five respondents reported that the problem was due to variations in the aggregate and 12 stated that they had no problems due to aggregate variability.

Question eight asked if they had any information on the type of coating on the aggregate. The answers could be divided into four groups: 1) natural clay from the ground mixing with the sand during stockpiling; 2) fines generated from crushing; 3) clay balls generated when loader

operator picks up clay from ground beneath the stockpile; and 4) clay or shale seams in the rock quarry that are mixed with the good rock during quarrying. There was no information about the mineralogy of the fines.

Table A.1. In Item 341 (p. 281) of TxDOT Specifications of Tests Used to Detect Clay in Aggregates.

Property	Test Method	Requirement
Coarse Aggregate		
SAC	AQMP	As shown on plans
Deleterious Material, %, max	Tex-217-F, Part I	1.5
Decantation, %, max	Tex-217-F, Part II	1.5
Micro-Deval abrasion, %, max	Tex-461-A	Note 1
Los Angeles abrasion, %, max	Tex-410-A	40
Magnesium sulfate soundness, 5 cycles, %, max	Tex-411-A	30
Coarse aggregate angularity, 2 crushed faces, %, min	Tex 460-A, Part I	85 Note 2
Flat and elongated particles @ 5:1, %, max	Tex-280-F	10
Fine Aggregate		
Linear shrinkage, %, Max	Tex-107-E	3
Combined Aggregate³		
Sand equivalent, %, Min	Tex-203-F	45

1. Not used for acceptance purposes. Used by the engineer as an indicator of the need for further investigation.

2. Only applies to crushed gravel.

3. Aggregates, without mineral filler, RAP, or additives, combined as used in the job-mix formula (JMF).

Question nine asked what was the source (quarries) of the problematic aggregate? The following quarries were listed: 1) Martin Marietta, North Troy Quarry; 2) Arnold Crushed Stone, Blum Quarry; 3) Cemex South Quarry; 4) Superior Crushed Stone Quarry; and 5) any limestone quarry along IH–35 corridor.

Question ten asked for locations of problems due to aggregate for the researchers to visit in the future. The only location we received was US 287 in Navarro County. Other responses we received were the projects with problems that had already been covered by seal coats or overlays.

Question eleven asked what remedial measures they use to avoid contamination in aggregate. Answers include: 1) None; 2) have concrete plants run sprinklers on stockpiles and check decantation; 3) On a concrete pavement they had the contractor clean each hole generated by clay balls and fill each hole with epoxy; 4) removal of material from the project; 5) going over the QCP plan with the contractor at the pre–placement meeting; 6) turning over the stockpiles on a regular basis; 7) checking decant and sending in samples prior to delivery onto the project; and 8) educating loader operators to keep the blades off the natural ground.

Results from this survey tell the researchers that most districts (12 responses) are not aware of durability issues with aggregate used in seal coats, hot mix, or Portland cement concrete. Eight districts did not take the survey so we can only assume that they are not aware of

any problems due to clay in the aggregate. The question the researchers ask is how do the districts know that there is not a problem with durability if they do not do any durability testing with the finished product (concrete, asphalt, or seal coat)? There were five districts that reported problems with either clay balls or coatings on the aggregate.

APPENDIX B

IDENTIFICATION OF CLAY MINERALS BY XRD AND QUANTIFICATION BY NEWMOD

The X-ray diffraction method is the best method to identify and quantify the clay minerals in aggregate fines with reasonably good accuracy, but this method is cumbersome and requires advanced training to operate. Quantitative XRD was used as an advance research tool to quantify clay minerals in aggregate fines in this study. It was established in Task 2 that clay minerals cannot be detected by XRD in a powder mixture with pure quartz below the detection limit (e.g., < 5 percent). A combined pretreatment procedure which involves chemical pretreatment, size fractionation, and reduction of clay suspension volume was employed in order to concentrate the clay minerals above the detection limit. Below is a detailed explanation of the steps necessary to fractionate the different grain sizes in order to characterize the clay minerals of an aggregate fine sample.

METHODS

Pretreatments to Enrich Clay Fraction

In the chemical pretreatment process, carbonate minerals (calcite and dolomite), iron and manganese oxides, and organic matter are dissolved and removed from the samples, which helps to liberate clay minerals occur inside the larger non-clay particles (sand and silt-sized particles). Any time chemical pretreatments are used, there is a risk of altering or destroying parts of the soil or rock not intended by the treatments. However, without the pretreatments, the data are very limited because the clay mineral fraction (the most important of the minerals as far as reactivity is concerned) is generally in concentrations too low to be detected by conventional XRD analysis.

A portion of the minus No. 10 sieve fraction is weighed out and placed into 250 ml Nalgene centrifuge bottles (Figure B-3). The amount of material (passing No. 200 sieve) needed will vary because some soils and rocks have a higher concentration of clay than others. Only 1 g of clay is needed for the full analysis, so select enough of a sample to yield 1 g of coarse clay and 1 g of fine clay. The researchers typically start with 100 g of soil passing No. 10 sieve. For the calcareous materials (e.g., limestone fines with clay impurity), the -2 mm materials were ground to < 105 μm (- 140 mesh) in order to increase the reaction rate of carbonate dissolution.

The first step is removal of carbonates which is necessary to effectively separate the silt and clay by centrifugation in the later steps. Carbonates also decrease the efficiency of hydrogen peroxide treatment (described next). To remove the carbonates a 1N Na acetate solution buffered to pH 5.0 with acetic acid is added to the 250 mL centrifuge bottles and placed in a hot water bath to speed up carbonate removal (Figure B-1). During carbonate removal, bubbles will appear in the solution from evolution of CO_2 gas as the carbonate is dissolved. A sign that the reaction is complete is a lack of bubbles in the sample.



Figure B–1. The Bottles with Sample and 1N Na Acetate Solution Are Placed in Water Bath for Carbonate Removal.

After the reaction has subsided, centrifuge the sample at 1500 to 2000 rpm for 10 to 15 minutes. Pour off the clear supernatant and add more of the Na acetate solution to the sample and react as before, until there is no reaction (carbonate bubbles) when the Na acetate is added to the sample which indicates that the carbonate removal is complete. Police down the sides of the centrifuge bottle and wash two more times with pH 5, 1N Na acetate.

For aggregates with less carbonate minerals, this treatment is brief, lasting several days at most. In carbonate–rich materials (e.g., crushed limestone), however, complete dissolution of carbonate minerals may require long period of time (e.g., 1–2 months). Reaction rate was accelerated further by heating solution and sample to 90°C in a water bath. For samples with higher quantities of carbonate minerals and those containing less reactive minerals such as dolomite, concentrated acetic acid was added to the pH 5 buffer in a ratio approximately 1 part acetic acid to 10 parts pH 5 buffer solution. The use of buffer solution and monitoring solution pH are applied to prevent alteration of the clay minerals present. None of the treatments' buffer solutions were observed to have pH below 4. A pH 3 environment is considered as the threshold for decomposition of clay minerals. Buffer solutions were replaced every 2–3 days.

The second step is to remove the organic matter because it tends to aggregate mineral grains, making it difficult for mineralogical analyses requiring sample dispersion. The procedure follows Jackson (1969) where 30 percent H₂O₂ is buffered by a pH 5, 1N Na acetate solution. Following the completion of carbonate and soluble salt removal, 5 to 10 mL of 30 percent H₂O₂ are added along with equal quantities of pH 5 1N Na acetate to remove organic matter by oxidation. Pyrite and Manganese oxides are also removed in this step. The 250 mL centrifuge bottles are placed inside beakers because violent reactions can occur in this step, and the sample can all boil out onto the counter top unless the sample is placed inside a beaker to catch all of the material that boils over (Figure B–2).



Figure B–2. Removal of Organic Matter Often Results in a Violent Reaction.

The removal of organic matter is complete when the sample loses its dark color and/or the effervescence has dramatically decreased. After organic matter has all been destroyed add about 10 ml of 30 percent H_2O_2 and place the centrifuge bottle in the water bath (Figure B–1) at a temperature slightly less than 100°C to ensure that the reaction is complete. Vigorous effervescence indicates that organic removal is not complete, but some bubbling will occur because the H_2O_2 is decomposing to H_2O plus O_2 .

After organic matter is removed, the sample should be washed one time with 200 mL of pH 5 1N Na acetate followed by one wash with 200 mL of 1N NaCl.

The next step, removal of free iron oxides, is often deleted from pretreatments because it is not problematic in most soils or samples. However, Oxisols and some Ultisols are difficult to disperse unless free iron oxides are removed (Kunze and Dixon 1986). A sodium citrate–bicarbonate–dithionite solution treatment is conducted to chelate, buffer, and reduce the ferric iron to a soluble ferrous form which is then washed out. After the sample has been treated to remove organics and carbonates, add approximately 40 ml of 0.3M of Na citrate solution and 5 mL of 0.5M Na bicarbonate solution. Heat to 80°C in a water bath (Figure B–1) and add 1 g of sodium dithionite. Stir the solution constantly for 1 minute and periodically for 15 minutes. Add 10 ml of saturated NaCl solution to flocculate the suspension. Acetone can be added in a 10 mL aliquot if suspension does not flocculate. Centrifuge for 10 to 15 minutes at 1600 to 2200 rpm and pour off supernatant. Perform the above treatment one or two more times if necessary.

Dispersion and Fractionation

As stated previously, data are limited unless the samples are separated into different size fractions. Fractionation achieves two objectives; 1) it concentrates mineral phases, and 2) it improves the preferred orientation of layer silicates (Dixon and White 1999).

In order to separate the aggregate fines into the different size fractions, the sample must first be dispersed which is usually accomplished by raising the pH to about 10 for most soils. After carbonate and organic removal, the pH of the sample stay at about 5 and will not allow most samples to disperse. A pH 10 sodium carbonate (Na_2CO_3) solution is added to aid the dispersion. Following the procedure of Jackson (1969), wash the sample several times with the pH 10 water (Na_2CO_3). Centrifuge for 10 to 15 minutes at 1600 to 2200 rpm and pour off the supernatant (Figure B–3). When the sample does not yield a clear supernatant, then the sample is considered dispersed.



Figure B–3. Centrifuge Used to Aggregate the Sample prior to Decanting Supernatant.

Following dispersion is fractionation. Depending upon your discipline (engineer, geologist, or soil scientist), obtain an appropriate sieve (#200, #230, or #325) to separate the sand from the silt and clay fractions. Using a setup like the one illustrated in Figure B–4, wet sieve the sample with pH 10 water and collect the clay and silt fractions in a 4 L Nalgene beaker. The sand fraction will be retained on the sieve, transferred to a beaker, and placed in an ultrasonic cleaner to further remove clay particles that adhere to sand grains. The supernatant will become clouded as a result of the ultrasonic cleaner. The sand fraction is then returned to the sieve and washed again to remove the disaggregated clay particles. After the sand has been cleaned with

the ultrasonic cleaner for a couple of times, wash the sand fraction with distilled water into a pre-weighed beaker and place in an oven to dry. Once the water is removed from the sand fraction, weigh the beaker to obtain the amount of sand in the soil sample.



Figure B–4. Ringstand, Funnel, and Sieve Assembly Used for Sand Fractionation.

Following the wet sieving, the silt and clay fractions are contained in the 4 L Nalgene beaker. The silt and clay fractions are poured into 750 mL centrifuge bottles and placed in an IEC Centra GP8R centrifuge (Figure B–5) and run for 2.5 minutes at 1000 rpm. The supernatant is decanted into a large plastic beaker without pouring any of the silt fraction into the beaker. Refill the centrifuge bottles containing the silt with pH 10 water and repeat the procedure until the supernatant is relatively clear. Wash the silt an additional time with distilled water and pour into a weighed beaker and dry at 60°C, overnight, in the oven (Figure 6).

The coarse and fine clay fractions are separated the same way as the silt and clay. The coarse clay is material in the 2.0 to 0.2 μm size range and should be separated from the fine clay (below 0.2 μm) because the mineralogy of the two fractions can be drastically different. The supernatant is again poured into 750 mL centrifuge bottles and placed into the centrifuge for 16 minutes at 4000 rpm. The fine clay remains in suspension and is poured into 4 L beakers. Following the coarse clay separation, the fine clay will be dispersed in several liters of water. The object is to remove as much of the water as possible before further treatment of the fine clay. In order to concentrate the fine clay fraction, and remove the excess water, sodium chloride (NaCl) is added to the dispersed sample to collapse the diffuse double layer and allow flocculation (Figure B–7). Foil is placed on top of the beaker to keep foreign matter out of the sample. The clear supernatant is poured off and the fine clay fraction at the bottom of the beaker is placed in dialysis tubing (Figure B–8) to remove the salt that was added to flocculate the fine clay fraction.



Figure B–5. IEC Centra GP8R Centrifuge Used to Separate Silt and Clay Fractions.



Figure B–6. Oven Set at 60°C for Drying Sand, Silt, and Coarse Clay Fractions.

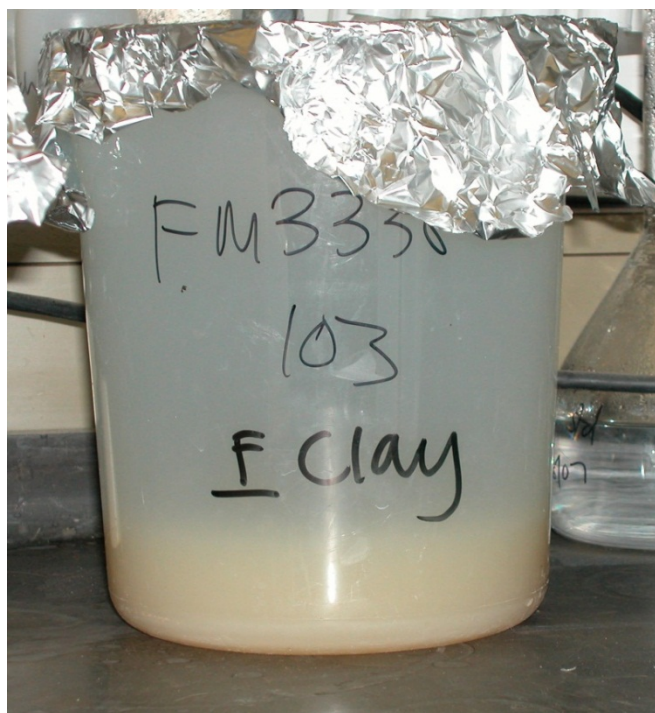


Figure B–7. Fine Clay (tan) Concentrated at Bottom of Beaker So Supernatant Can Be Removed.

Dialysis tubing is a permeable membrane that allows particles smaller than a certain size to pass through. Different types of tubing allow different sizes of particles to pass through. A beaker is filled with double distilled water, and the salt bearing, clay–water suspension is placed in the dialysis tubing (Figure B–8) and suspended in the beaker filled with distilled water. The salt ions migrate into the distilled water until the salt concentration inside the dialysis tubing is equal to the concentration in the beaker. The distilled water in the beaker is periodically changed so the salt can continue to pass through the membrane until there is essentially no salt left. When the salt is removed, the clay inside the dialysis tubing will disperse and fill the entire length of the tubing.

After the salt has been removed by dialysis, the water has to be removed from the fine clay fraction. This is accomplished by freeze drying the sample. Freeze drying is a process that removes water from the sample by sublimation (i.e., water changing from solid directly to a gaseous state). Figure B–9 is a Labconco Freezezone 4.5 benchtop freeze dryer used for removing water from the fine clay fraction. The fine clay fraction is freeze dried and not dried in an oven because the sample is easier to disperse and it preserves the structure of the clay for transmission electron microscope (TEM) analysis.

The clay–water suspension is placed directly into a cylindrical freeze dryer flask from the dialysis tubing. The clay–water suspension is frozen into an inverted cone shape by placing in a 2 liter dewar containing liquid nitrogen and continuously rotating until cracking noises are heard (Figure B–10). When it sounds like the glass is cracking, the flask of the freezing suspension is removed from the dewar and quickly rotated at about a 60° angle in the palm of a

hand covered with a cryogenic glove to allow the suspension to freeze. Be sure to freeze all of the liquid because any liquid in the flask will cause the sample to melt and not sublime.

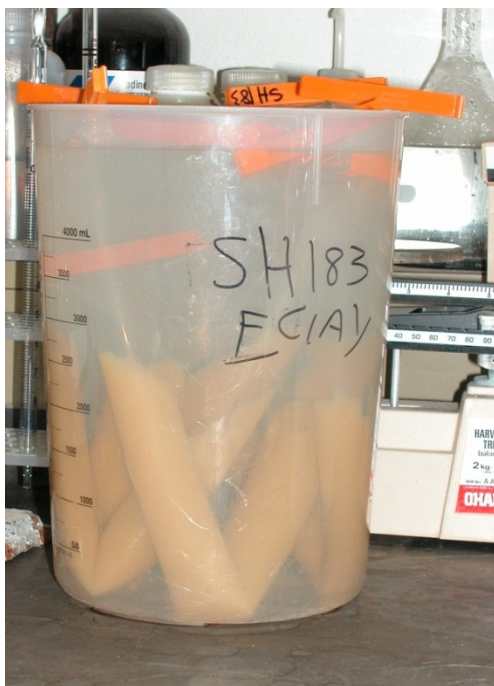


Figure B–8. Fine Clay Placed in Dialysis Tubing to Remove Salt by Osmosis.



Figure B–9. Freeze Dryer Used to Remove Water from the Fine Clay Fraction of Samples.



Figure B–10. Freezing Clay–Water Suspension Using Liquid Nitrogen.

After the clay–water suspension is completely frozen, the flask is attached to the freeze dryer, and a strong vacuum is placed on the sample to prevent melting of the frozen suspension. If the technique has been properly followed, then the outside of the flask should contain a coating of ice (Figure B–11).



Figure B–11. White Coating of Ice on the Flask, Indicative of a Successful Freezing Job.

After freeze drying is complete, weigh the fine clay fraction and place in a plastic bag labeled with the sample name and size fraction for the next step in the procedure. Compile the weights of all size fractions (sand, silt, coarse clay, and fine clay) and determine percentages of each fraction as well as percent lost due to chemical pretreatments and/or mechanical loss.

The different size fractions are now ready for XRD testing and analysis. The sand and silt sized materials can be tested by the X-ray diffractometer without any further treatment. But the coarse and fine clay fractions need further cation saturation treatment (discussed later) before XRD testing.

Preparation for XRD Testing

Sand and Silt – In order to obtain meaningful XRD data, the sand fraction needs to be pulverized in a mortar and pestle (preferably agate or aluminum oxide; Figure B–12) and passed through a #325 sieve. If one uses the #325 sieve for the silt and sand separation, then the silt fraction does not need to be pulverized because the silt particles are already smaller than the #325 sieve.



Figure B–12. Aluminum Oxide (left) and Agate Mortars and Pestles for Sand Reduction.

Once all particles in the sand fraction pass the #325 sieve the sand and silt fractions are ready to be analyzed. They are side loaded into an aluminum holder (Figure B–13) to reduce preferred orientation of minerals with strong cleavage which may lead to erroneous data resulting in misleading concentrations of those minerals in the sample.

Coarse and Fine Clay – The coarse and fine clay fractions need to be saturated with specific cations in order to obtain uniform X-ray spacings for smectite and vermiculite. The two clay fractions are saturated with potassium (K^+) which is then heat treated to help identify chlorite, hydroxyl–interlayered phyllosilicates, kaolinite, and mica. The clay fractions are also saturated with magnesium (Mg^{2+}), which is then treated with glycerol or glycol to identify the presence of smectite.

The coarse and fine clay fractions are saturated with Mg^{2+} by weighing 0.15 g of clay into a 40 mL centrifuge tube. Add about 25 mL of 1N $MgCl_2$ to the centrifuge tube and mix well. The centrifuge tube may need to be placed into an ultrasonic bath to break up clay aggregates. Centrifuge the clay suspension and decant the clear supernatant. Wash the clay with

MgCl₂ two more times. Following the three washes with MgCl₂, add 25 mL of distilled water to the sample, mix, centrifuge, and decant as before. Wash the sample with distilled water until the sample disperses (making it difficult to centrifuge): this step may require several washes. Centrifuge for a longer time and decant most of the supernatant (leave about 2 to 4 mL of distilled water in the centrifuge tube, Figure B–14) from the centrifuge tube.



Figure B–13. Aluminum Holders Used for Side Loading Sand and Silt into X–Ray Unit.

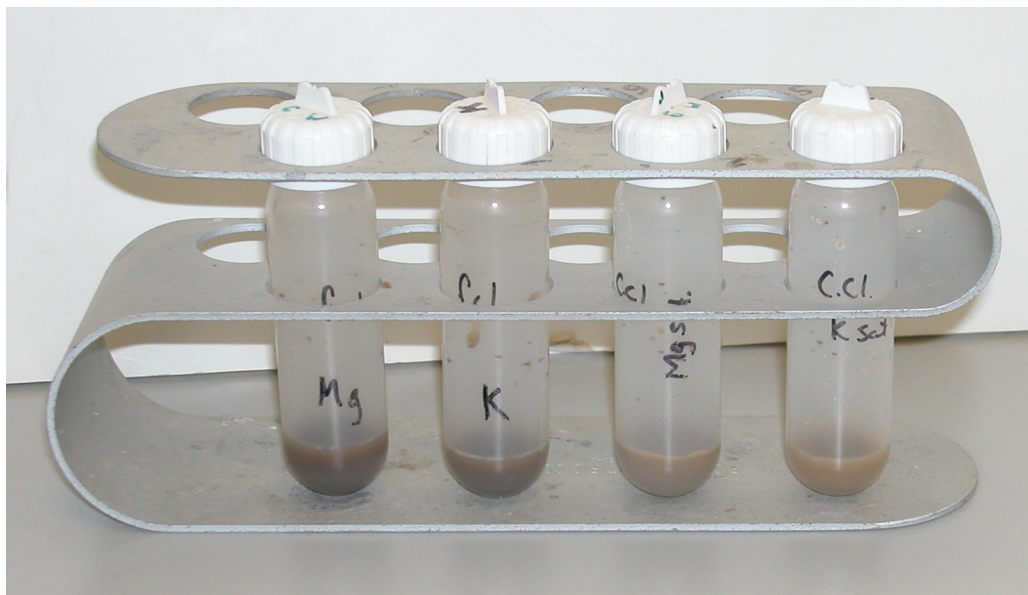


Figure B–14. Centrifuge Tubes (40 ml) with Mg²⁺ and K⁺ Saturated 2 to 4 ml Aliquots.

Follow the procedure just outlined using 1N KCl instead of MgCl₂. One should have four centrifuge tubes, following the saturations, as shown above. Be sure to label each centrifuge tube with the sample name, what clay fraction (coarse or fine), and what cation (K⁺ or Mg²⁺) the clay is saturated with.

After this step is complete, the sample is ready to be dried on slides for the X–ray unit. An aliquot of the K⁺ saturated sample is placed on a Vycor glass slide (label is etched into bottom of slide) using a disposable pipet (Figure B–15). Vycor is a very heat resistant glass that does not warp upon heat treatment.

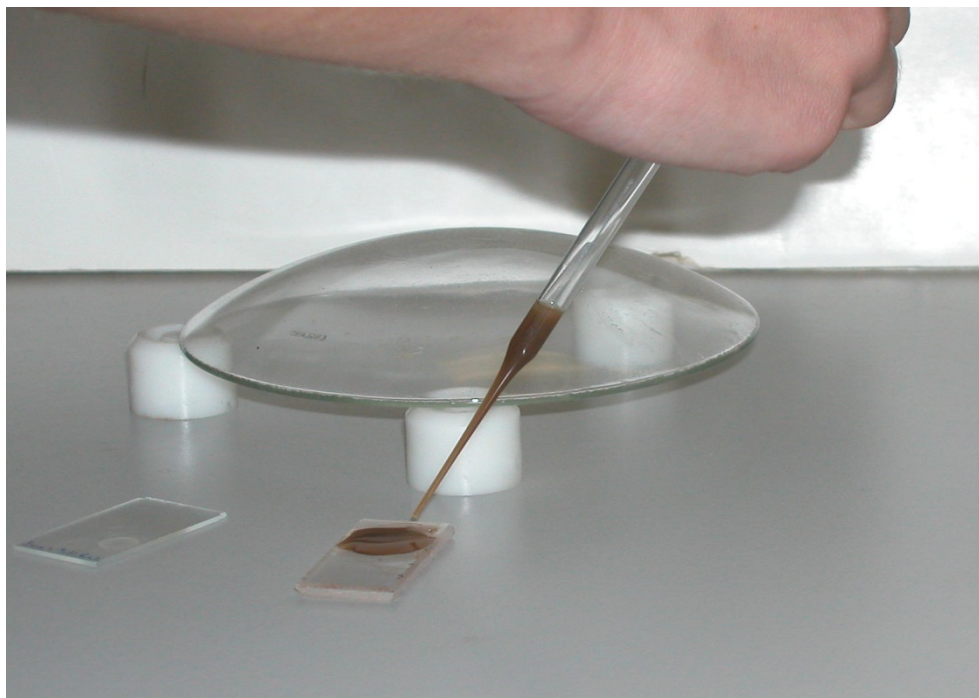


Figure B–15. Adding K^+ Saturated Clay Suspension to Vycor Slide.

Select a clean, standard petrographic microscope slide and label it with the sample name using a permanent marker. Use a new disposable pipet to place an aliquot of Mg^{2+} saturated clay suspension onto the labeled petrographic slide as described for potassium. Place the slides under a watch glass or other suitable barrier to dry without being contaminated by dust (Figure B–16).

After the samples dry onto the slides, they are ready to be X–rayed. After the Mg^{2+} saturated sample is X–rayed, the slide will be placed into a dessicator containing ethylene glycol or glycerol for 24 hours. The slide will be X–rayed again. The K^+ saturated Vycor slide will be X–rayed at room temperature ($25^{\circ}C$) and again after heat treatments of $300^{\circ}C$ and $550^{\circ}C$ in a muffle furnace.

P 1.1.2.3 X–Ray Diffraction Testing and Analysis

A Bruker D8 Advance X–ray diffractometer was used to record the diffraction patterns. Diffraction parameters included: Cu $K\alpha$ source, 35 kV and 45 mA beam energy, variable Soller and antiscatter slit length, 0.05° step size, 3 second dwell time, 30 rpm disc rotation, and SolX energy–dispersive, solid–state radiation detector. The diffractometer is semi–automated, with Bruker software capable of running 90 samples in succession via a robotic sample loader.

Step 1: Run the separated clay samples with five different treatments (as in Figures B–14–16) in the XRD machine and generate the characteristics diffraction patterns (total five patterns for each sample).

Step 2: Perform XRD analysis to identify the clay minerals present. The identification of clay minerals was performed after stacking the 5 patterns into a single figure, as shown in Figure B–17. Smectite is identifiable by layer thickness of 14 to 15 Angstroms in the magnesium saturation treatment that expands to approximately 18 Angstroms in the magnesium glycerol treatment. A perusal of Figure B–7 indicates the prominent peak at 14.6 A in the bottom pattern moves to 17.9 A in the second pattern from the bottom.

Step 3: Vermiculite, however, does not undergo peak shift in the glycerol treatment, and it is identifiable from the glycerol treatment's 14.4 A peak. However, vermiculite layer thickness collapses to 10 A upon K treatment and heating to 330 C and 550 C.

Step 4: The 14.4 A peak in the potassium 550 C treatment is attributable to clay-sized chlorite minerals. Kaolinite is identifiable from a peak in the 7 A region visible in the lower 4 patterns that disappears in the 550 C treatment.

Step 5: Illite is visible as a shoulder of the smectite peak at approximately 10 A in the magnesium and potassium treatments.

Because smectite, vermiculite, and chlorite all have peaks in the 14 Angstrom region with no saturations or magnesium treatment, all 5 treatments are necessary.

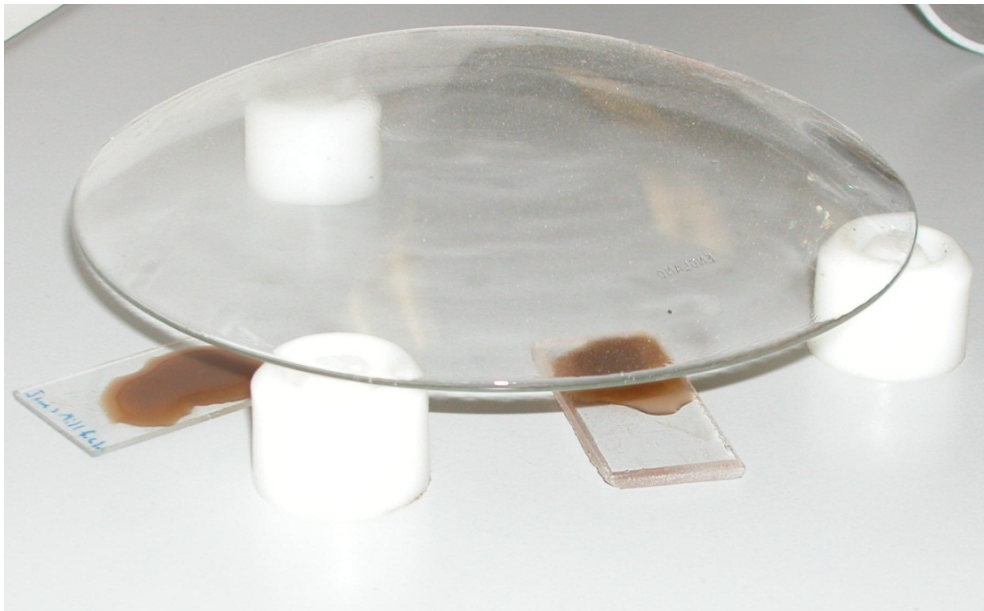


Figure B–16. Magnesium (left) and Potassium (right) Saturated Samples Drying.

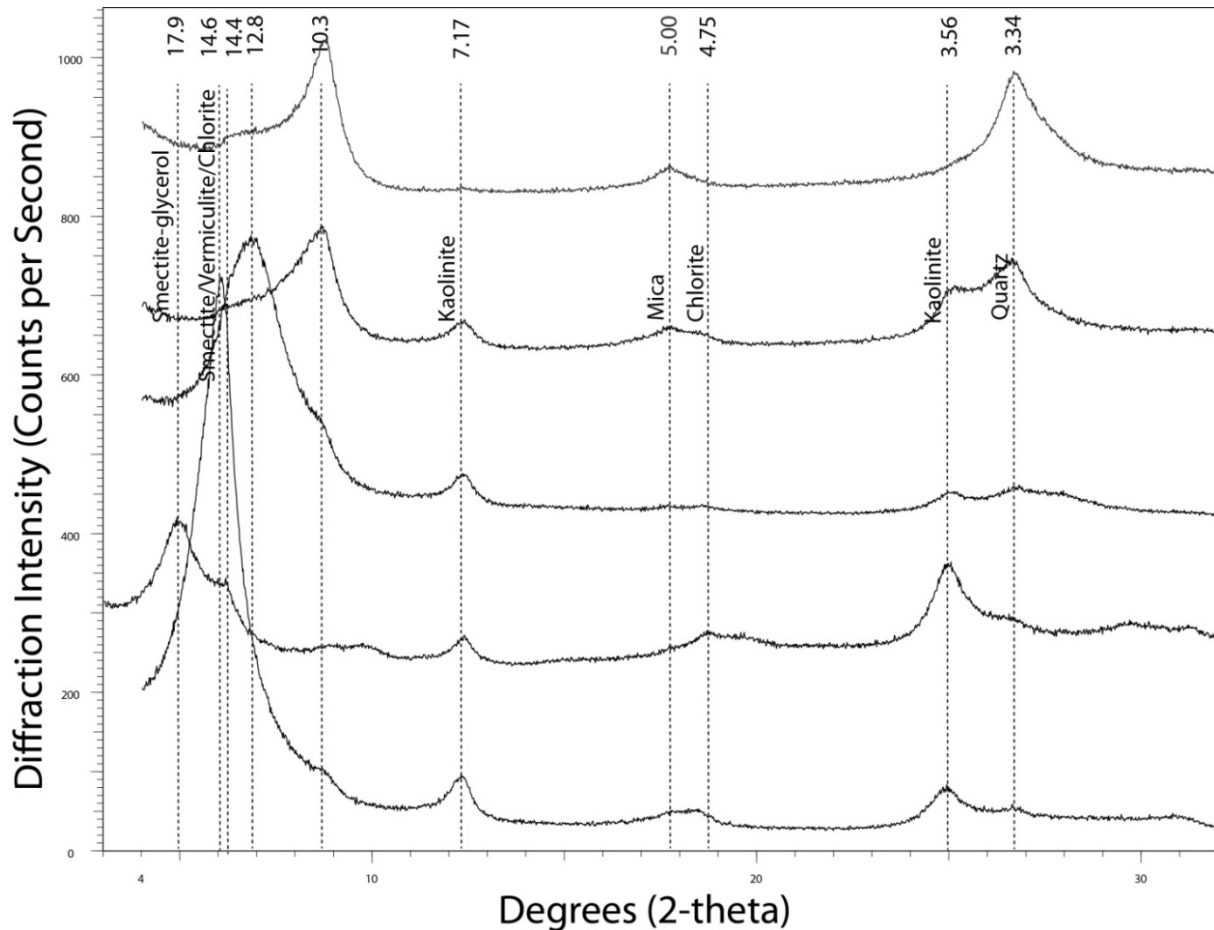


Figure B–17. Clay Minerals Identified from XRD Pattern of Jones Mill Fine Clay Fraction.

Quantification of Clay Minerals Using NEWMOD Clay Mineral Modeling Software

NEWMOD is a self-contained software program that allows users to simulate x-ray diffraction peaks of individual clay minerals (Figure B–18). NEWMOD has been the benchmark of clay mineral analysis and quantification for 25 years. One major limitation is that NEWMOD does not model non-clay, crystalline minerals such as quartz and calcite.

A least-squares refinement approach was utilized to attain the best match between simulated X-ray diffraction patterns and measured diffraction patterns recorded for each aggregate’s clay fraction. Although five patterns are recorded in order to identify all clay minerals in the clay fraction, only one pattern is used and required to produce models in NEWMOD. Raw XRD data for each clay fraction’s magnesium or magnesium–glycerol treatment was imported into a Microsoft Excel spreadsheet. If a significant quantity of vermiculite was identified in the aggregate, the magnesium–glycerol XRD pattern was modeled because the smectite peak shift allows smectite and vermiculite peaks to be distinguished and modeled in NEWMOD (Moore and Reynolds 1989). Each primary (001) peak evident in the diffraction patterns was modeled in NEWMOD and fitted by manipulating peak intensity manually in Microsoft Excel. Once parameters were set in NEWMOD for the lab’s Bruker D8

XRD, layer thickness, or d-spacing, and average number of layers per clay particle were the major variables manipulated in the program (Deng et al. 2010).

Optimal pattern fitting required the creation and importing of many simulated patterns from NEWMOD into Excel. After the 001 peaks were fitted for all clay minerals in the sample, relative mineral quantities in the clay fractions and in the overall -2 mm fractions were calculated. The presence of non-clay crystalline phase such as quartz, feldspar in very less quantity in the clay fractions was identified in some samples. As NEWMOD does not provide models for non-clay highly crystalline minerals, these highly-crystalline minerals were not accounted for in these calculations. Aggregates with intense quartz peaks in clay fractions may overestimate clay mineral quantities slightly. The greatest possibility of quartz in the clay fractions came from the carbonate-rich aggregates that were ground to -140 mesh prior to pretreatment.

Separation of clay fractions, identification of clay minerals after saturation with cations, and quantification by NEWMOD simulation is a time-consuming but established and reliable method for clay mineral identification and quantification. Without the separation of clay fractions (< 2 μm) and fixing of layer thickness with magnesium and potassium cationic solutions, correct identification of clay minerals is not possible using current methods.

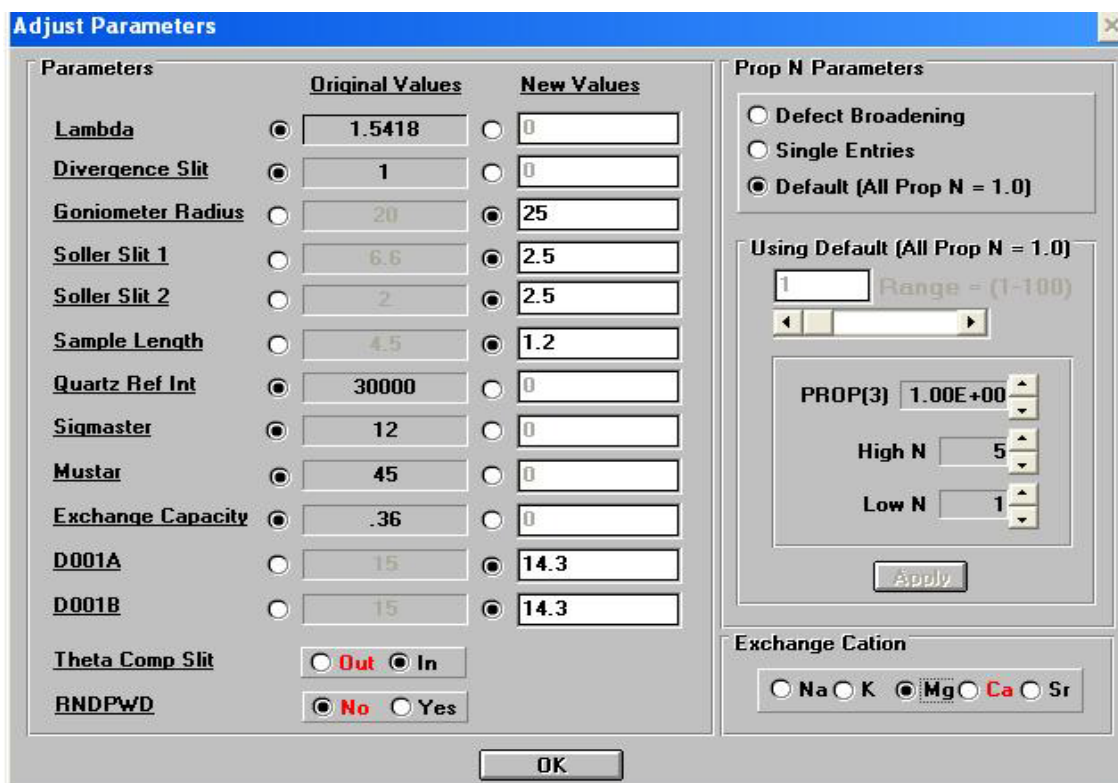


Figure B–18. NEWMOD Graphical Interface with Manipulable Parameters.

APPENDIX C
A NEW RAPID METHOD TO DETERMINE METHYLENE BLUE
VALUES OF AGGREGATE FINES FOR CONSTRUCTION MATERIALS
IN THE LABORATORY AND FIELD

*A NEW RAPID METHOD TO DETERMINE METHYLENE BLUE VALUES OF
AGGREGATE FINES FOR CONSTRUCTION MATERIALS IN THE LABORATORY
AND FIELD*

TxDOT DESIGNATION: TEX—XXX—E

Test Procedure for

**A NEW RAPID METHOD TO DETERMINE METHYLENE
BLUE VALUES OF AGGREGATE FINES FOR
CONSTRUCTION MATERIALS IN THE LABORATORY
AND FIELD**



TxDOT Designation: Tex—XXX—E

Date: October 2012

1. SCOPE

- 1.1 This test method intends to provide a rapid test to determine the amount of methylene blue adsorbed by a sample of aggregate fines for both the laboratory and field. The result is reported as a methylene blue value (MBV). The MBV is a function of the amount and activity of clay minerals present in an aggregate fine sample.
- 1.2 This test method differentiates between (i) clay and non—clay minerals and (ii) swelling and non—swelling clay minerals, in fines containing clay size particles (i.e., $< 2 \mu\text{m}$)
- 1.3 In general, a high methylene blue value is undesirable for construction applications as it is an indicator of poor aggregate performance in asphalt, concrete and other construction applications (e.g., flexible base materials).

2. DEFINITION

- 2.1 *Aggregate fines* – Aggregate passing the 4.75 mm (No. 4) sieve.

Note 1 – Aggregate fine containing up to 100% passing the 425 μm (No. 40) or 75 μm (No. 200) sieve can also be measured in this test, including limestone filler and other mineral filler.

Note 2 – The fine materials of the above sizes collected from different construction materials (e.g., coarse and fine aggregates used in portland cement concrete and hot mix asphalt, soil and flexible base materials) can be tested by this method.

2.2 The unit of MBV is milligrams of methylene blue per gram of dry sample of fine materials of the above size(s).

2.3 *Threshold MBV* – A maximum MBV may be specified to limit the permissible quantity and activity of clay in an aggregate fine sample.

3. **APPARATUS**

3.1 *4.75 mm (No. 4) sieve* with 4.75 mm openings conforming to ASTM E11.

3.2 *Mass balance* capable of measuring to the nearest 0.1 g.

3.3 *Micropipette* capable of measuring to the nearest 1 μL .

3.4 *Colorimeter* capable of reading absorbance of a sample at 610 nm \pm 1 nm at operating conditions of at least 0 to 50°C. The colorimeter shall also be able to read absorbance between zero and the absorbance associated with a 0.144% wt concentration of methylene blue solution. A Hach DR 850 colorimeter has been found to be suitable for this test. This colorimeter accommodates 16 mm diameter vials and is capable of reading absorbance between 0 and 2 A.

3.5 *Disposable items including per test:* two plastic 45-mL test tubes, one plastic 1 mL vial, one 3 mL syringe with Luer-Lok adapter, one 0.2 μm syringe filter, one colorimeter glass cuvette, one micropipette tip and three transfer pipettes.

3.6 *Additional disposable items for confirming methylene blue starting concentration:* plastic 45 mL test tube, plastic 1 mL vial, colorimeter glass cuvette, micropipette tip, and two transfer pipettes.

3.7 *Additional disposable items for calibrating colorimeter :* plastic 45 mL test tube, plastic 1 mL vial, colorimeter glass cuvette, micropipette tip, and two transfer pipettes.

3.8 *Weigh dish* – is a pour boat to hold a minimum of 20 grams of sample.

3.9 *Eyedropper* with a capacity of 7.50 mL.

3.10 *Disposable Latex Gloves* – strong enough to protect hands.

3.11 *Blow drier* to dry sample in the field.

4. **REAGENTS AND MATERIALS**

4.1 Methylene blue ($C_{16}H_{18}N_3SCl$) test solution at a weight concentration of 0.5 percent trihydrate methylene blue. Methylene blue is commercially available in both anhydrous and trihydrate form.

4.2 Purity of reagent – Reagent grade chemicals shall be used in all tests. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without compromising the accuracy of the results.

4.3 *Purity of water* – unless otherwise indicated, references to water shall be understood to mean potable water.

5. **SAMPLE PREPARATION**

5.1 Sampling of aggregate fine should be done in accordance to TEX–XXX–E (Practice D75).

5.2 Thoroughly mix the sample and reduce it as necessary using the applicable procedures in TEX–XXX–E (Practice C702).

5.3 If it appears necessary, dampen the material to avoid segregation or loss of fines during sample preparation.

5.4 Obtain at least 30 g of material passing the 4.75 mm sieve in the following manner:

5.4.1 Separate the sample on the 4.75 mm (No. 4) sieve by means of a lateral and vertical motion of the sieve, accompanied by a jarring action so as to keep the sample moving continuously over the surface of the sieve. Continue the sieving until not more than 1 weight percent of the residue passes the sieve during 1 min. Perform the sieving operation either by hand or by a mechanical apparatus. When thoroughness of mechanical sieving is being determined, test by the hand method described above using a single layer of material on the sieve.

5.4.2 Break down any lumps of material in the coarse fraction to pass the 4.75 mm (No. 4) sieve. Use a mortar and rubber–covered pestle or any other means that will not cause appreciable degradation of the aggregate.

- 5.4.3 Remove any coatings of fines adhering to the coarse aggregate. These fines may be removed by surface—drying the coarse aggregate, then rubbing between the hands over a flat pan.
- 5.4.4 Add the material passing the sieve obtained in 5.4.2 and 5.4.3 to the separated fine portion of the sample.
- 5.5 Dry the test specimen to constant weight at $110 \pm 5^\circ\text{C}$ and cool to room temperature before testing.
- 5.6 To obtain additional test specimens, repeat the procedures in 10.4 through 10.5.

6. CALIBRATION AND STANDARDIZATION

- 6.1 *Calibration of the colorimeter for the relationship between absorbance and methylene blue concentration*—Insert a cuvette with water into the colorimeter and zero the instrument. Use the micropipette to transfer a 130 μL aliquot of the 0.5 percent methylene blue solution to a 45 mL test tube. Dilute the aliquot to a total of 45 g and gently mix the solution. Transfer solution to a cuvette. Wipe the cuvette if necessary to remove any marks. Next, insert the cuvette with the diluted methylene blue solution into the colorimeter and take a measurement to determine the absorbance. Next, rotate the glass test tube within the meter a quarter revolution and take another measurement. Repeat a total of four times and take the average of the four values; record as A_{cal} . Perform this calibration for each colorimeter at least every 6 months or whenever the light source or batteries are replaced (if applicable).
- 6.2 *Confirmation of correct initial methylene blue concentration*— Insert a cuvette filled with water into the colorimeter and zero the instrument. Use the micropipette to transfer a 130 μL aliquot of the initial methylene blue solution to a 45 mL test tube. Dilute the aliquot to a total of 45 g and gently mix the solution. Transfer solution to the cuvette. Wipe the cuvette if necessary to remove any marks. Next, insert the cuvette with the diluted initial methylene blue solution. Take a measurement to determine the absorbance of the diluted initial methylene blue solution. Next, rotate the glass test tube within the meter a quarter revolution and take another measurement. Repeat a total of four times and take the average of the four values; record as A_i . Determine the actual initial concentration prior to dilution using the following equation:

$$C_i = (0.5\%) \times \frac{A_i}{A_{\text{cal}}}$$

Repeat this entire process three times and calculate the average. Perform this check of initial concentration each day or whenever a new source or batch of methylene blue solution is used.

6.3 *Adjust initial methylene blue solution if necessary*—if the actual concentration is below 0.480 percent, discard and obtain a new solution. If the actual concentration is greater than 0.502 percent, adjust to 0.5 percent.

7. PROCEDURE

7.1 *Sample mixtures*—weigh out 20 g of fine aggregate. In the 45 mL test tube, weigh out 30 g of methylene blue solution. Add the weighed fine aggregate to the methylene blue solution, ensuring all fines are incorporated.

7.2 *Mixing*—shake sample mixture by hand for 1 minute and allow the sample to rest for 3 minutes. Shake the sample mixture again for 1 minute to complete mixing regime.

7.3 *Filtration*—remove the plunger from the 3 mL syringe and attach the syringe filter. Using a transfer pipette, add approximately 2 mL of the sample mixture to the syringe and replace the plunger. Slowly filter 0.5 to 1 mL of the sample mixture into a new 1 mL vial.

7.4 *Dilution*—using the micropipette, transfer 130 μ L of the filtered sample into a new 45 mL test tube. Dilute the filtered sample up to a total of 45 g with water. Cap the 45 mL test tube and gently shake the diluted sample for 5 seconds. Using a new transfer pipette, fill a new glass test tube approximately 2/3 full with the diluted sample and replace cap.

7.5 *Colorimeter taring*—Place a cuvette filled approximately 2/3 with water into the colorimeter and zero the instrument.

7.6 *Colorimeter measurement*—remove the glass test tube filled with water and replace with the test tube filled with the diluted sample. Take a measurement and record the absorbance. Next, rotate the glass test tube within the meter a quarter revolution and take another measurement. Repeat a total of four times and take the average of the four values; record as A_f .

7.7 *Calculation of final methylene blue concentration before dilution.*

$$C_f = (0.5\%) \times \frac{A_f}{A_{cal}}$$

7.8 *Repeat*—repeat steps 7.1 through 7.7 three times.

8. CALCULATION OR INTERPRETATION OF RESULTS

- 8.1 The MBV is a function of the initial and final methylene blue concentrations and is determined by the following equation:

$$MBV = \frac{(C_i - C_f)(30mL)}{20g} \times 1000$$

- 8.2 *Correction of MBV result* – The following equation can be used to calculate the corrected methylene blue value if the correct initial methylene blue concentration is not exactly 0.50 (section 6.2)

The following equation can be used to calculate the corrected methylene blue value if the wrong methylene blue concentration is used:

$$MBV_{corrected} = \frac{(C_{initial-actual} - C_{initial-theoretical} + \frac{MBV_{measured}(20g)}{(30ml)(1000)})(30ml)}{20g} \times 1000$$

Where: $MBV_{corrected}$ = corrected methylene blue value, mg/g

$C_{initial-theoretical}$ = theoretical concentration (0.5%)

$MBV_{measured}$ = measured methylene blue value with wrong starting solution concentration

A correction factor (C_{factor}) is determined using the following equation for each new bottle of methylene blue concentration

$$C_{factor} = MBV_{Corrected} - MBV_{measured}$$

- 8.3 *Adjustment for methylene blue values greater than or equal to 7.5 mg/g*—if the methylene blue value is greater than or equal to 7.5 mg/g, report the methylene blue value as greater than 7.5 mg/g. The test may be repeated using only 10 grams of sand. In this case, the methylene blue value should be doubled. If the methylene blue value is still greater than or equal to 15 mg/g, the methylene blue value is outside of the range of the instrument's tolerance.

NOTE 4—if the test is performed with 10 g of sand, the error in the measurement will be doubled.

9. REPORT

- 9.1 Report the average of three colorimeter results to the nearest 0.1 mg/g. A methylene blue value of 0 mg/g indicates no clay activity.

10. PRECISION AND BIAS

10.1 The precision and bias of this test method needs to be studied as a part of implementation work.

APPENDIX D
X-RAY DIFFRACTION PATTERNS AND MINERAL IDENTIFICATION
FOR THE CLAY FRACTIONS SEPARATED FROM DIFFERENT
AGGREGATE FINES

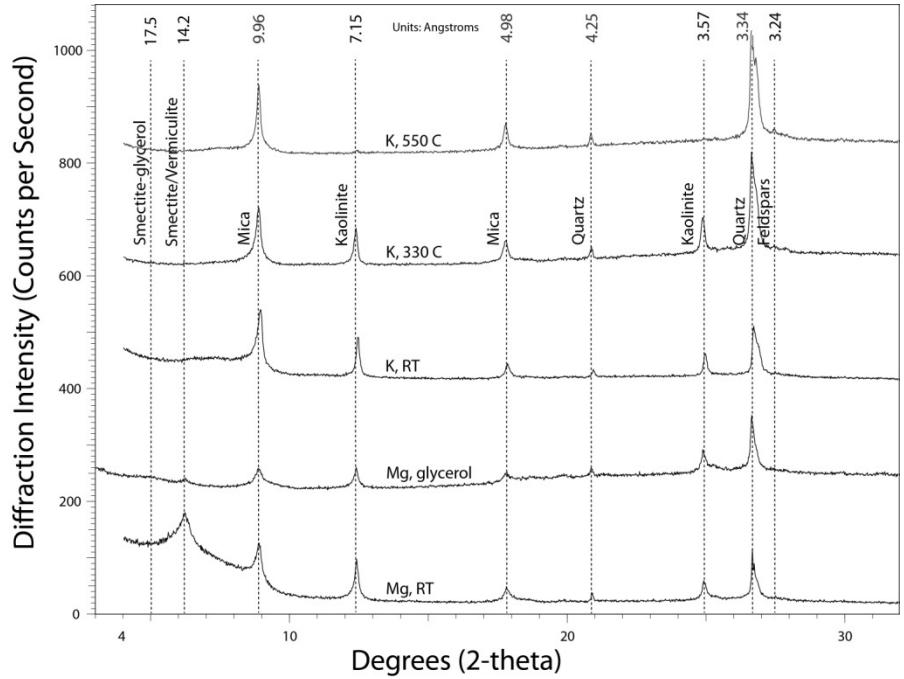


Figure D-1. Pit 365 Coarse Clay Fraction.

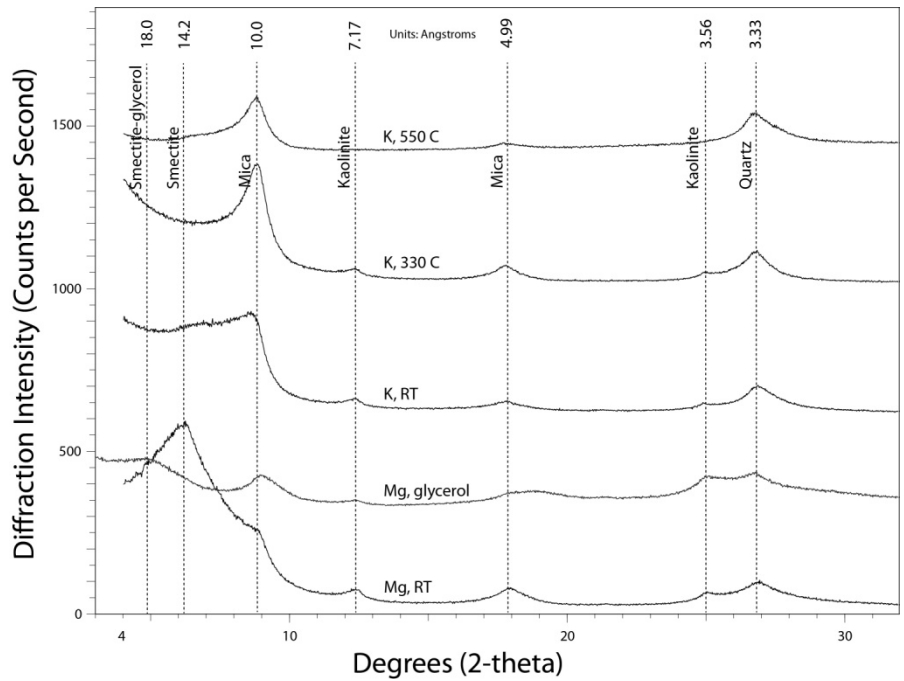


Figure D-2. Pit 365 Fine Clay Fraction.

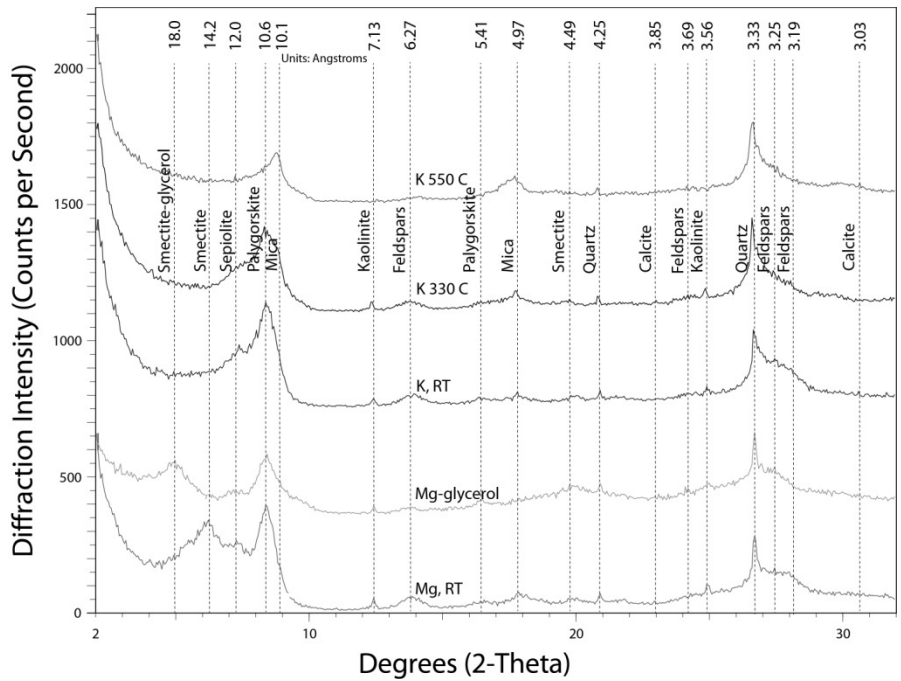


Figure D-3. Armor Total Clay Fraction.

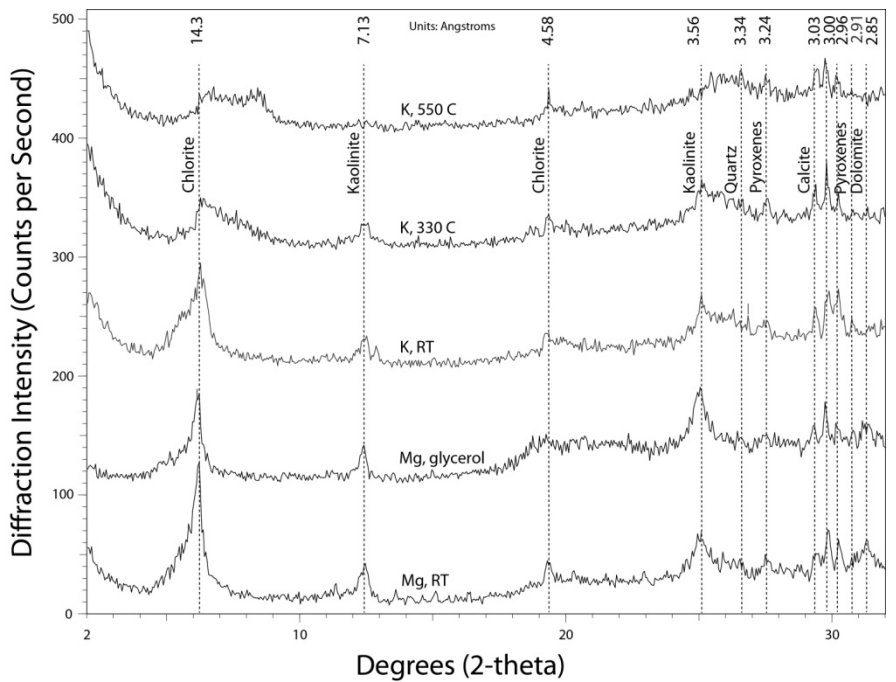


Figure D-4. Bird Hill Total Clay Fraction.

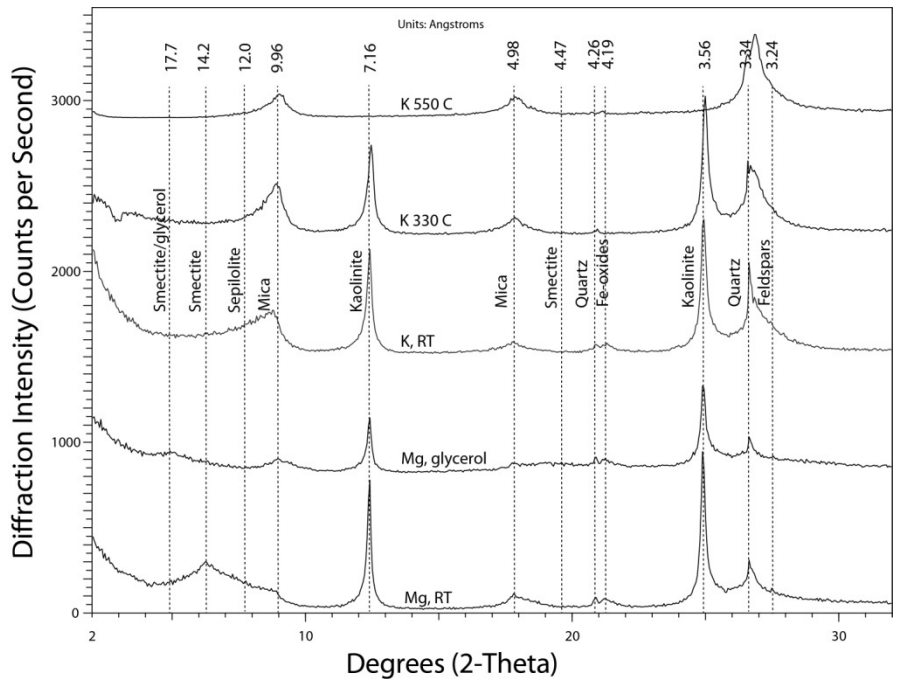


Figure D-5. Black Pit Total Clay Fraction.

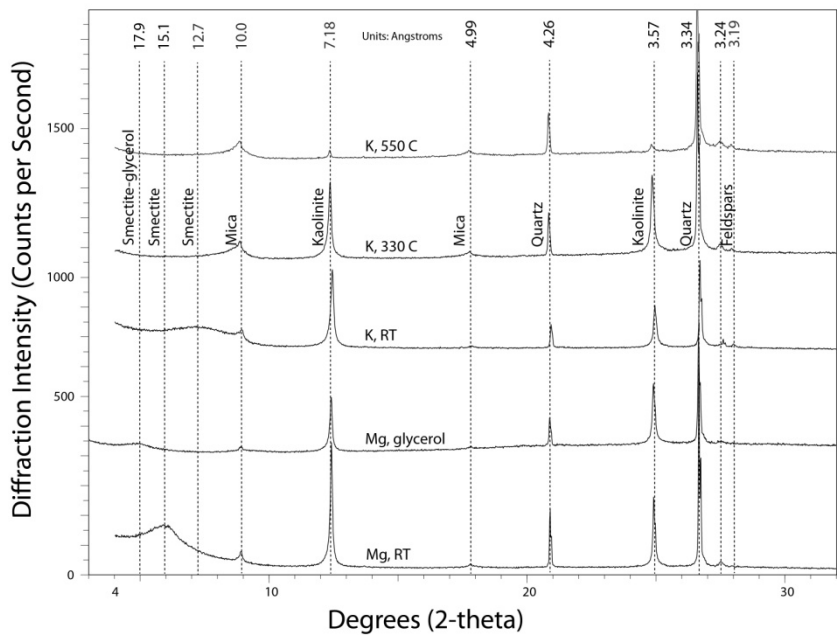


Figure D-6. Blum Coarse Clay Fraction.

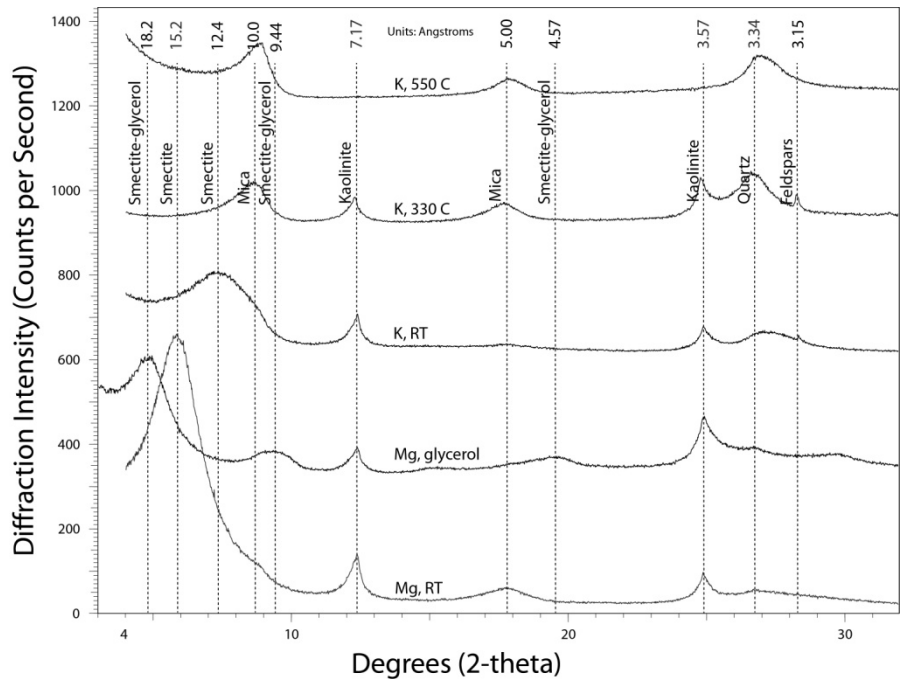


Figure D-7. Blum Fine Clay Fraction.

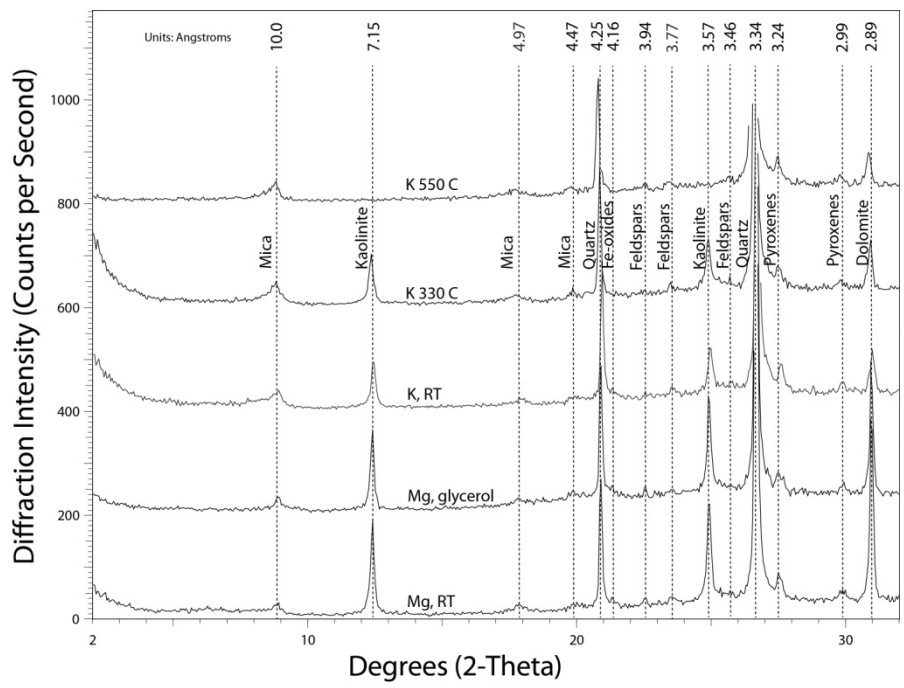


Figure D-8. Buster Smith Total Clay Fraction.

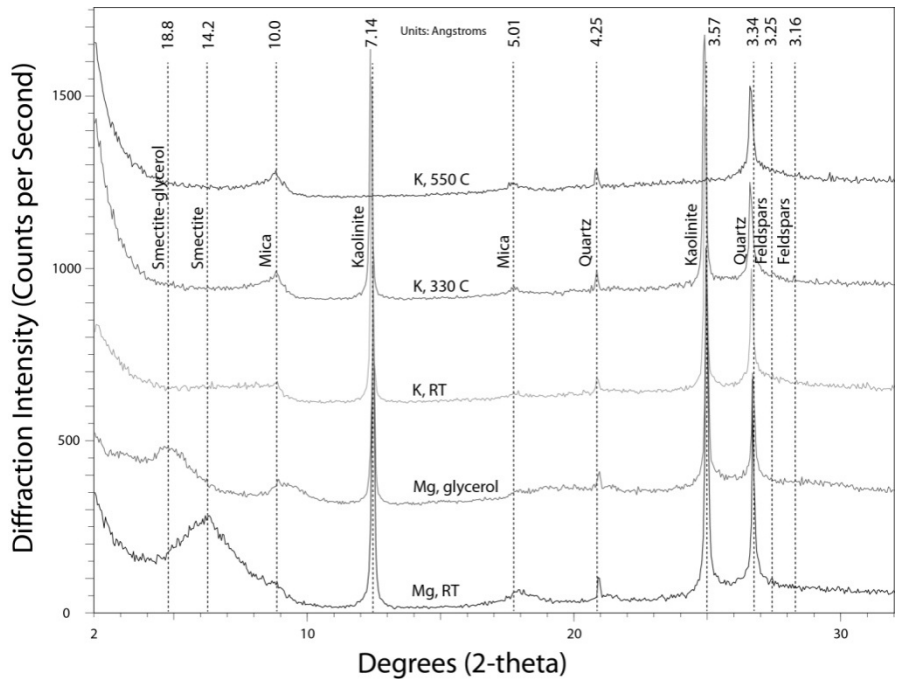


Figure D-9. Helotes Total Clay Fraction.

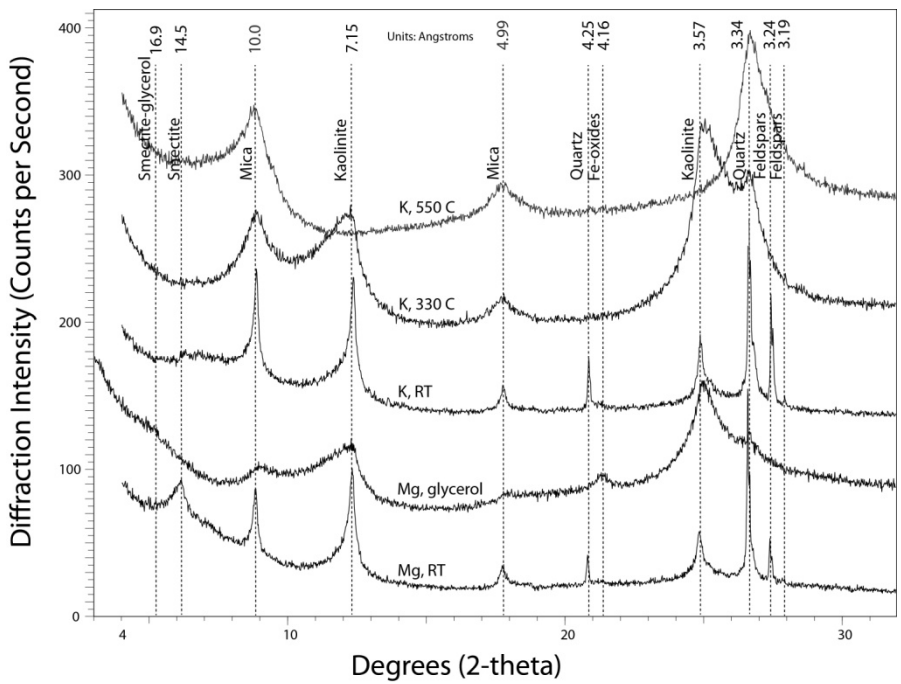


Figure D-10. Hoot Coarse Clay Fraction.

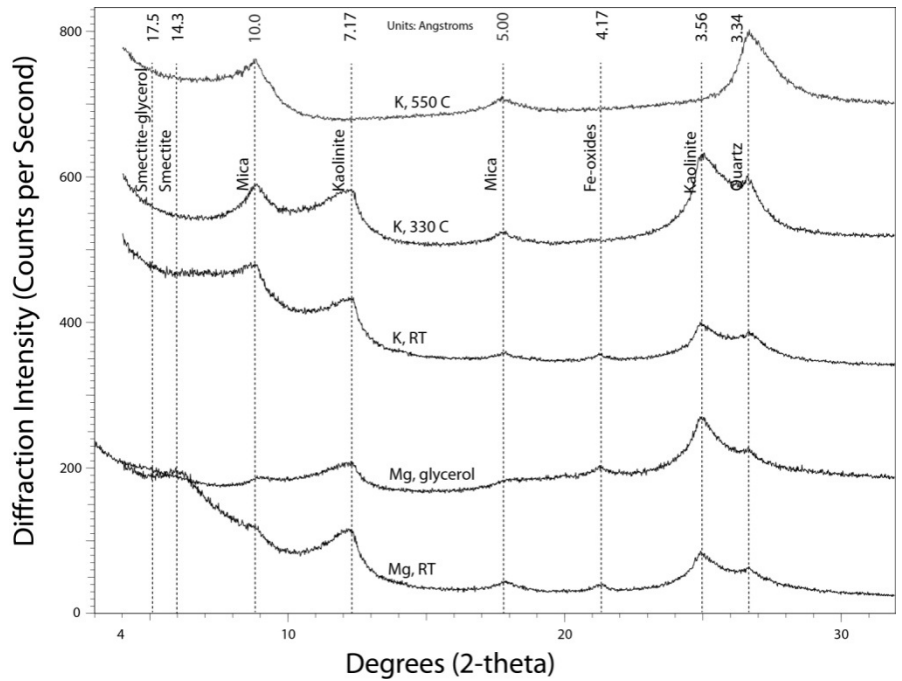


Figure D-11. Hoot Fine Clay Fraction.

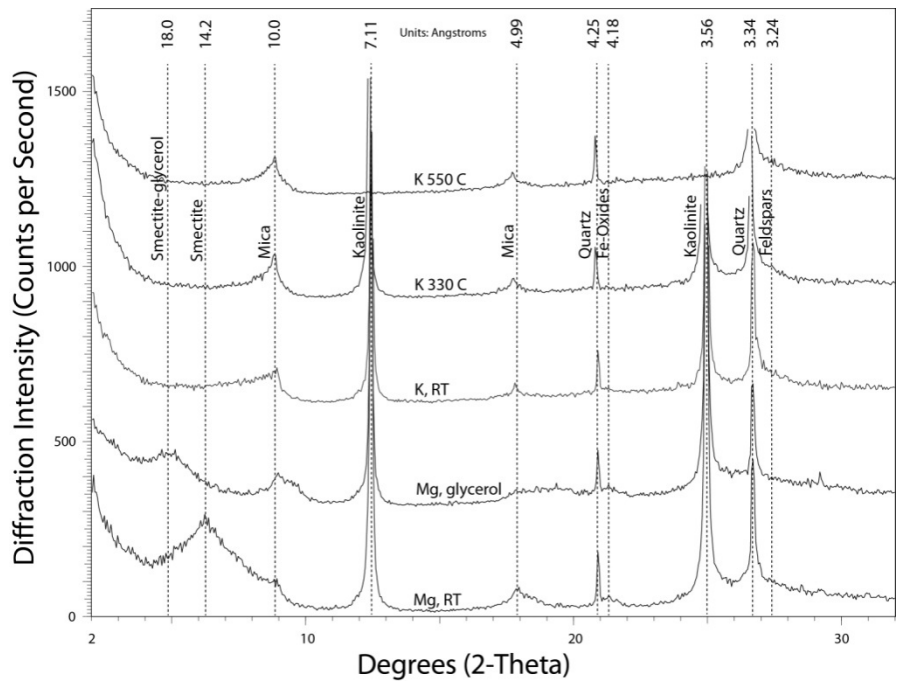


Figure D-12. Huebner Total Clay Fraction.

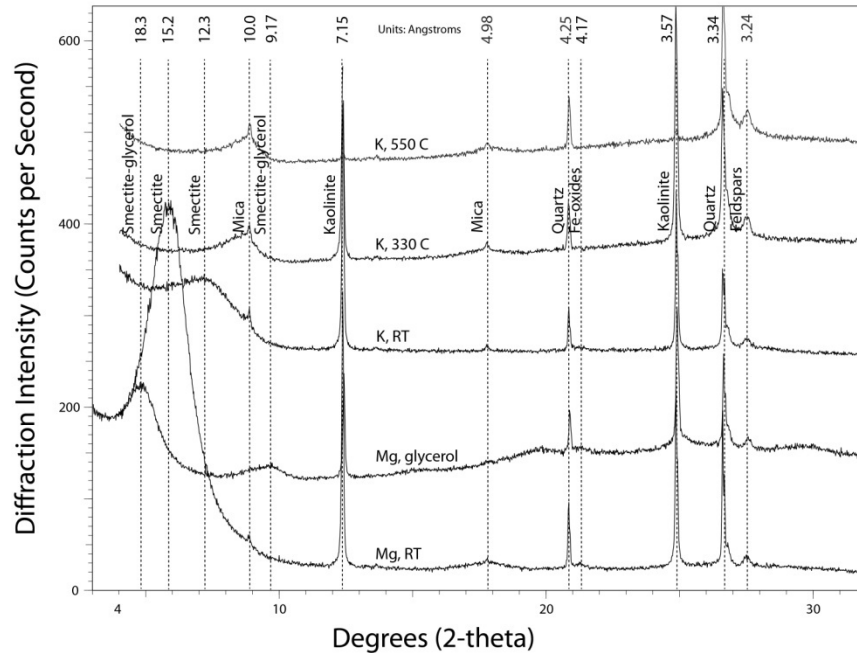


Figure D–13. Jarrell 1 Coarse Clay Fraction.

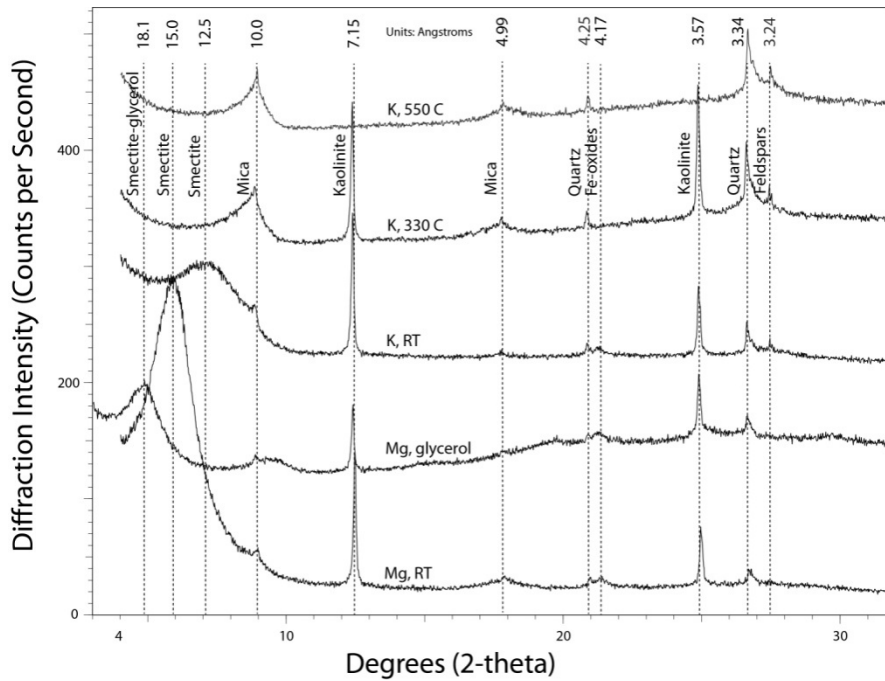


Figure D–14. Jarrell 1 Fine Clay Fraction.

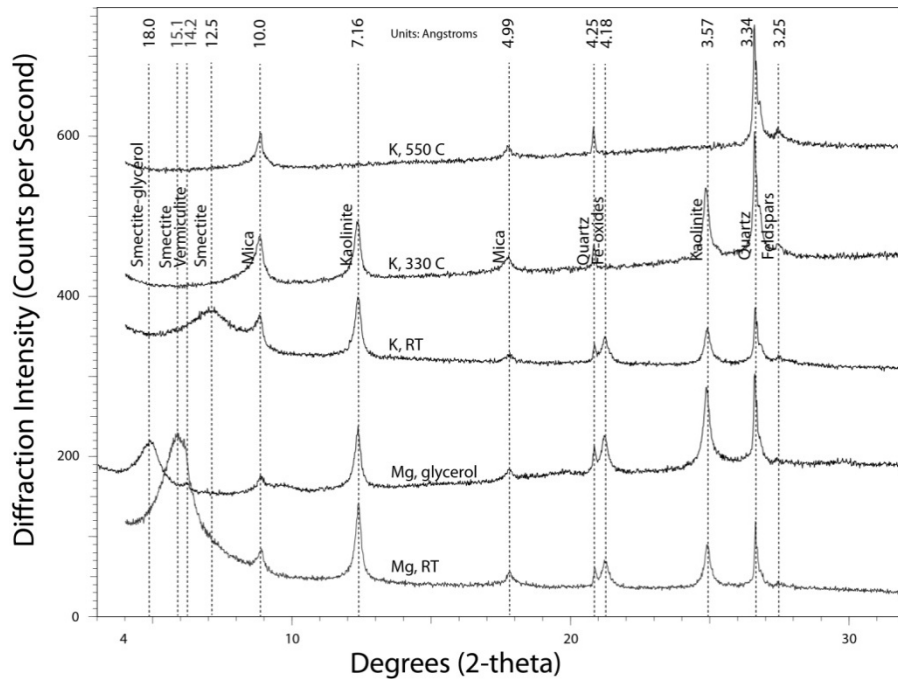


Figure D–15. Jarrell 2 Coarse Clay Fraction.

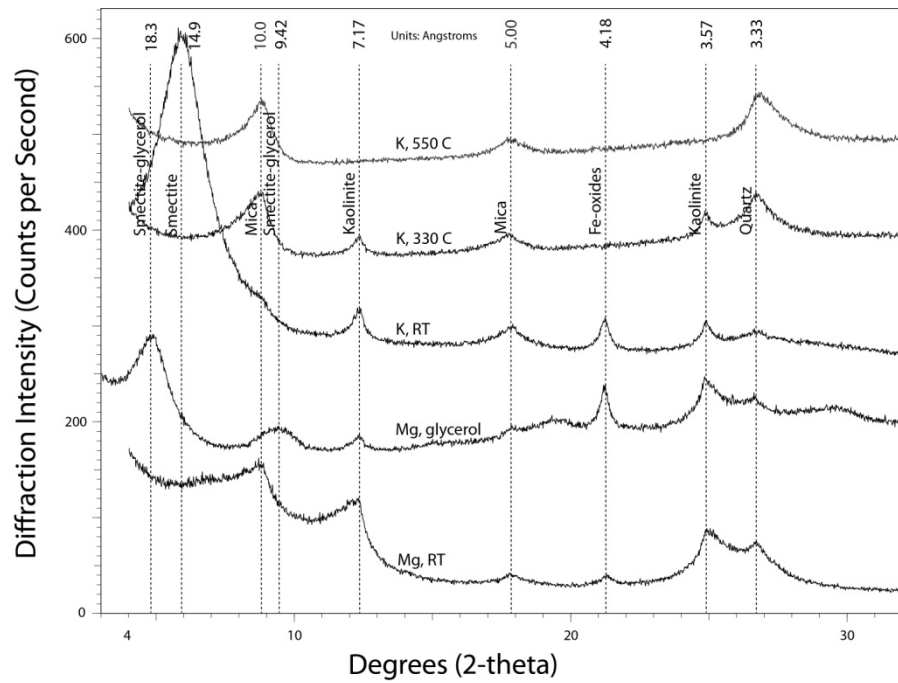


Figure D–16. Jarrell 2 Fine Clay Fraction.

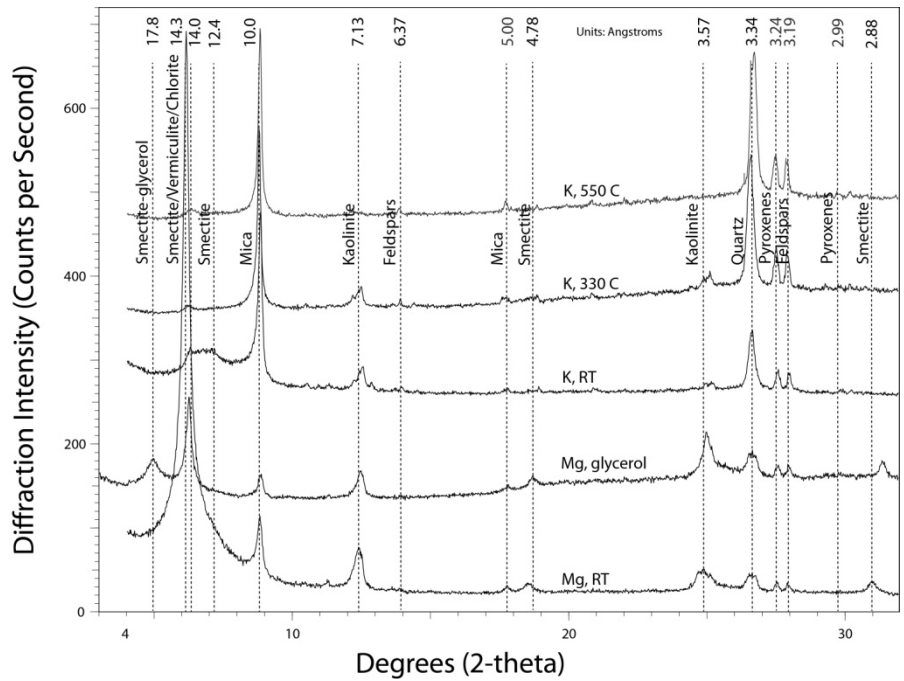


Figure D–17. Jones Mill Coarse Clay Fraction.

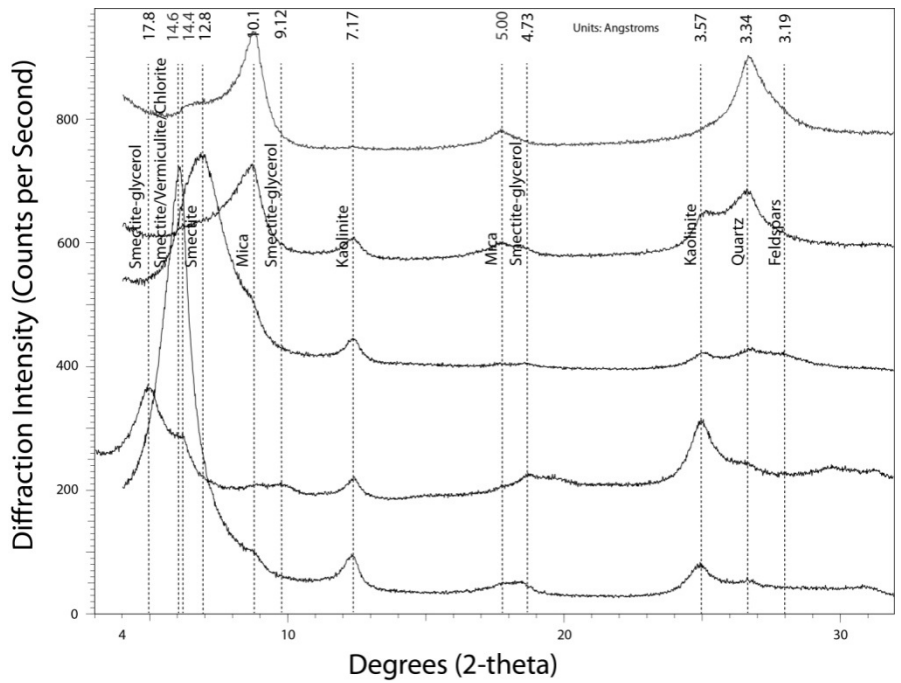


Figure D–18. Jones Mill Fine Clay Fraction.

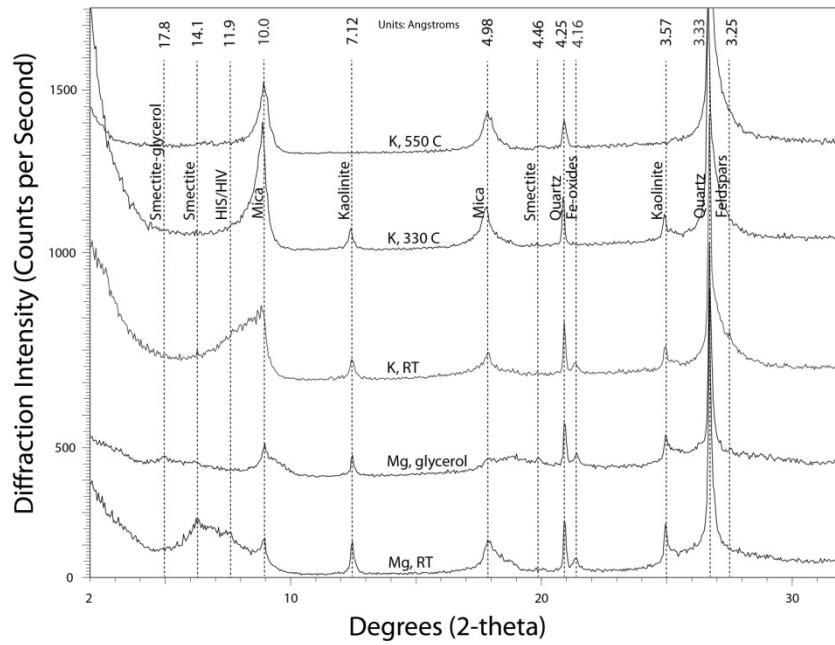


Figure D–19. Lake Bridgeport Total Clay Fraction.

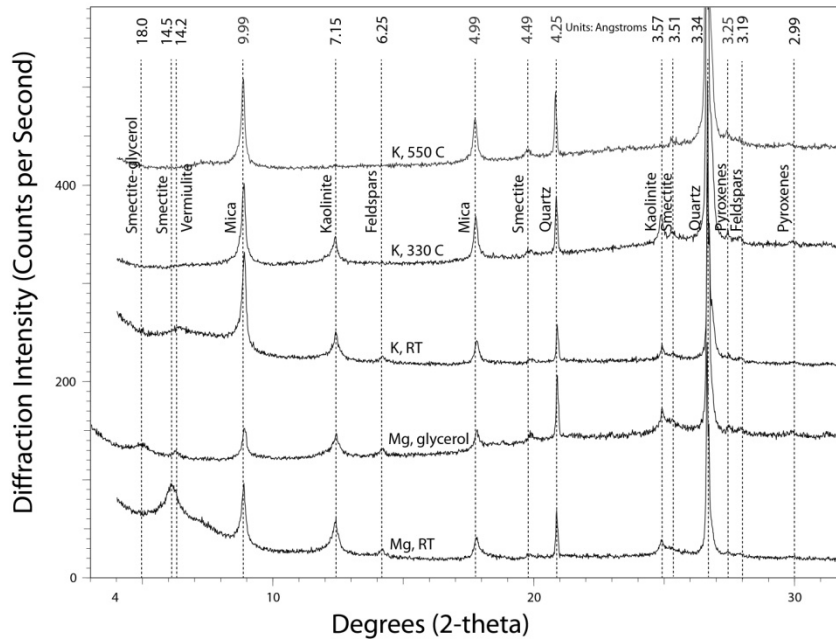


Figure D–20. Little River Coarse Clay Fraction.

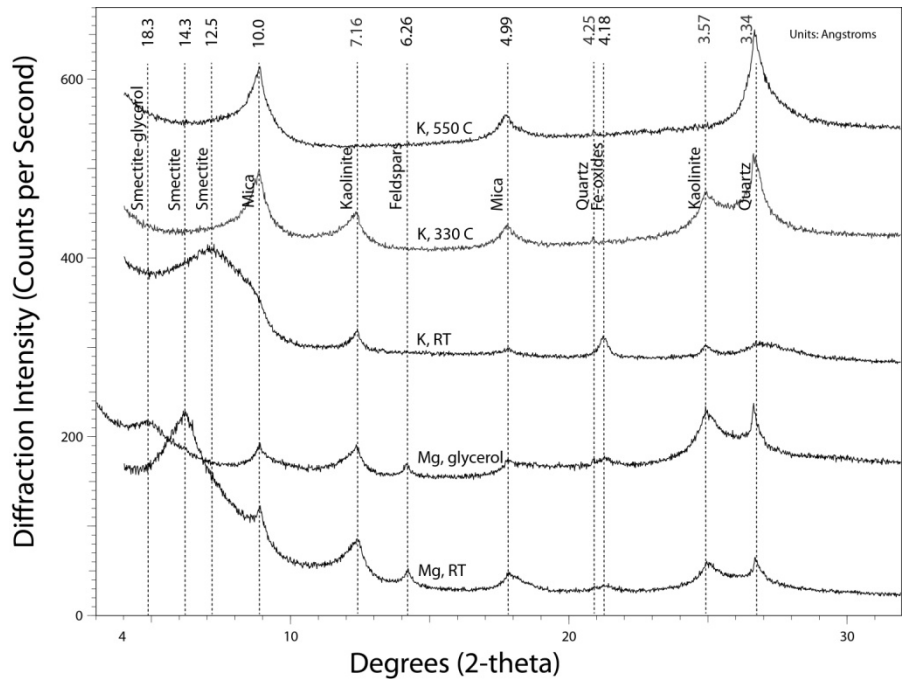


Figure D–21. Little River Fine Clay Fraction.

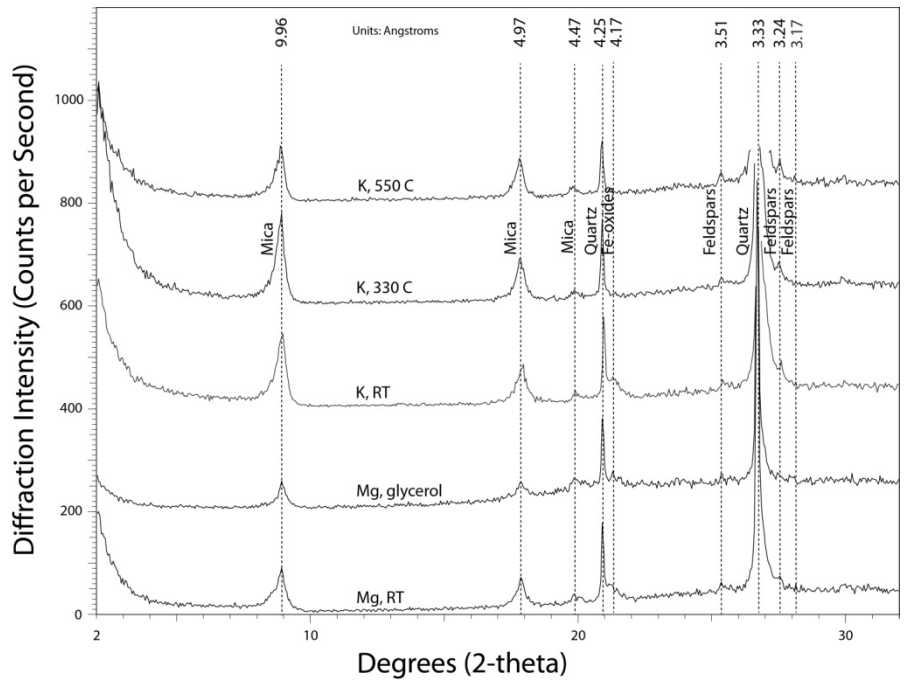


Figure D–22. McKelligon Dolomite Total Clay Fraction.

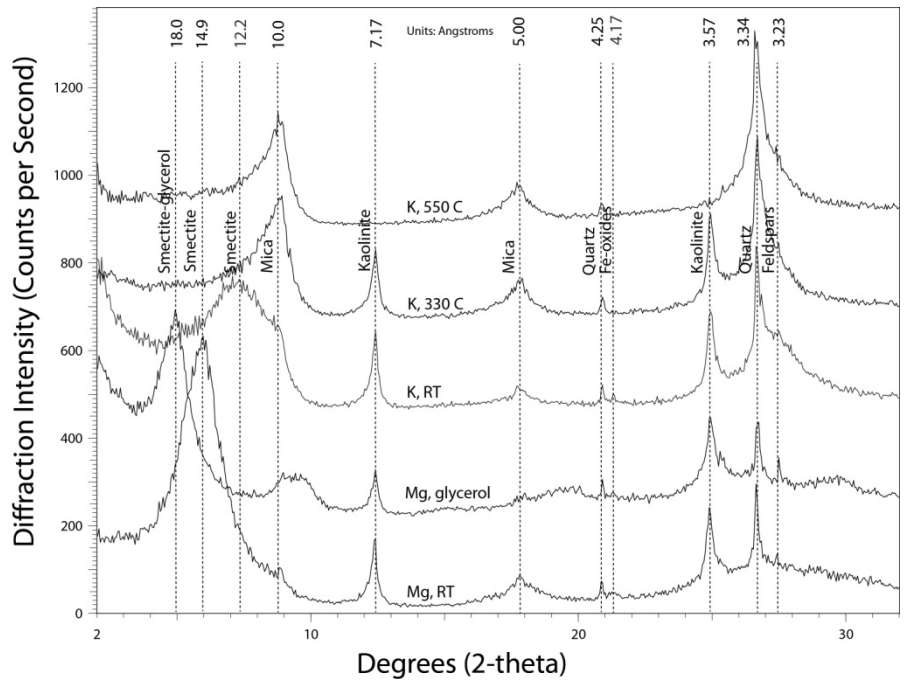


Figure D-23. Fordyce Murphy Total Clay Fraction.

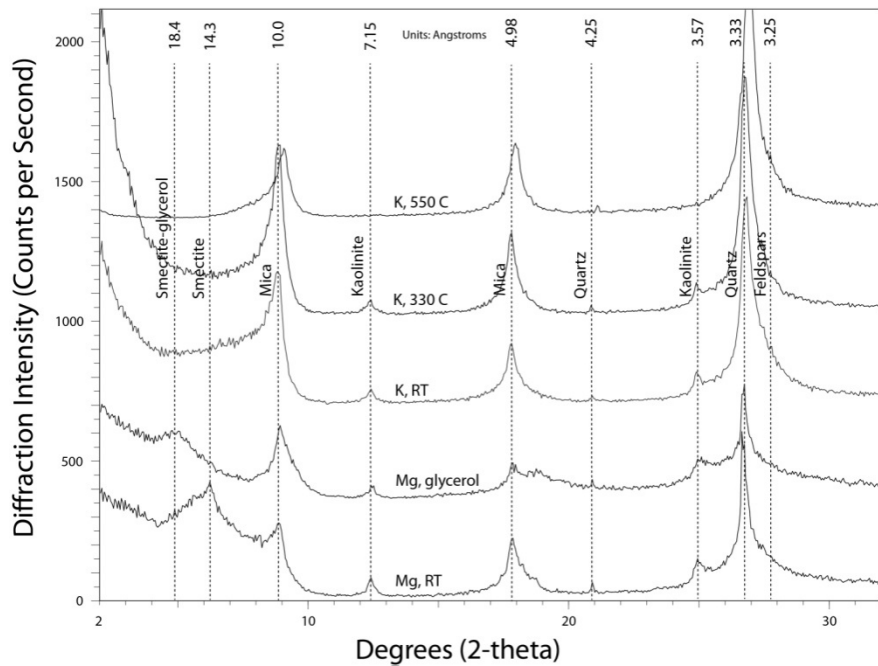


Figure D-24. South Noodle Total Clay Fraction.

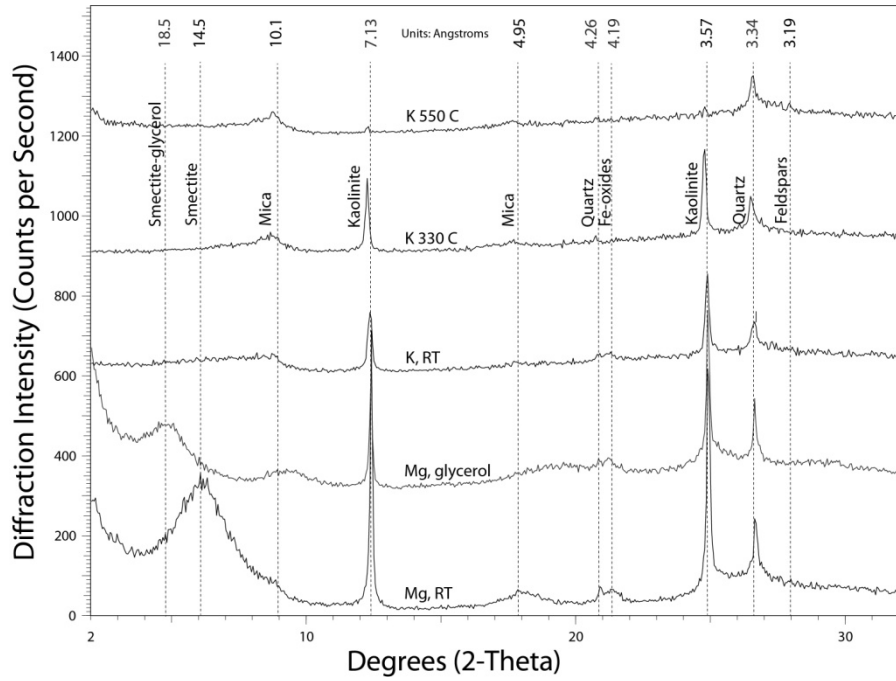


Figure D–25. Texas Crushed Stone Total Clay Fraction.

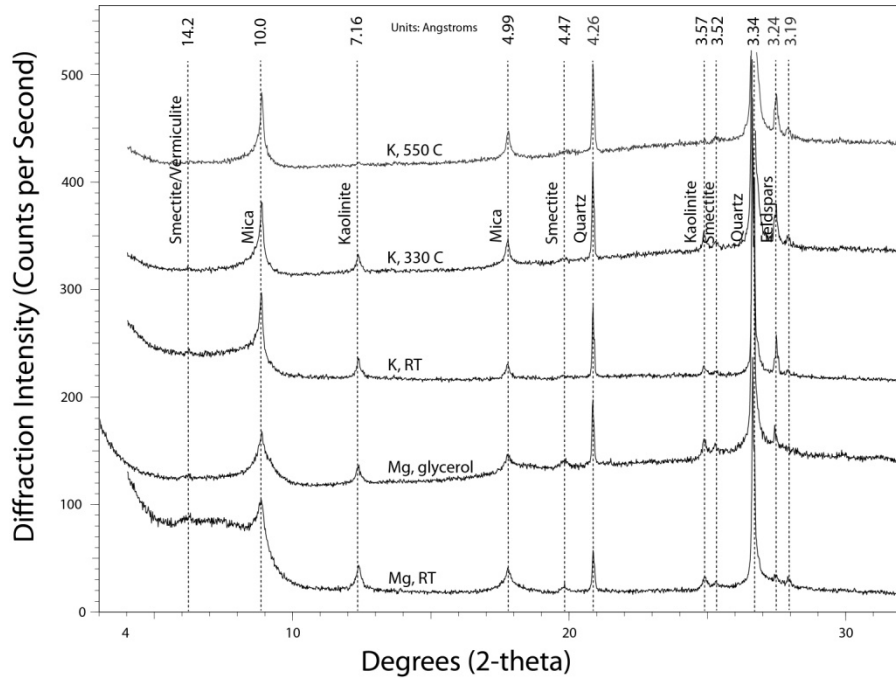


Figure D–26. Tolar Coarse Clay Fraction.

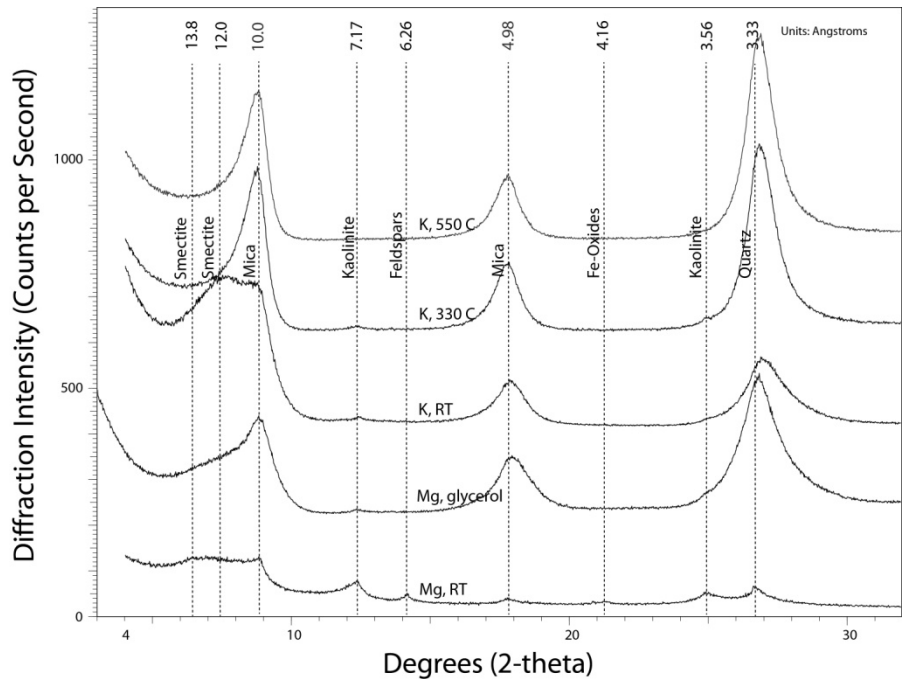


Figure D-27. Tolar Fine Clay Fraction.

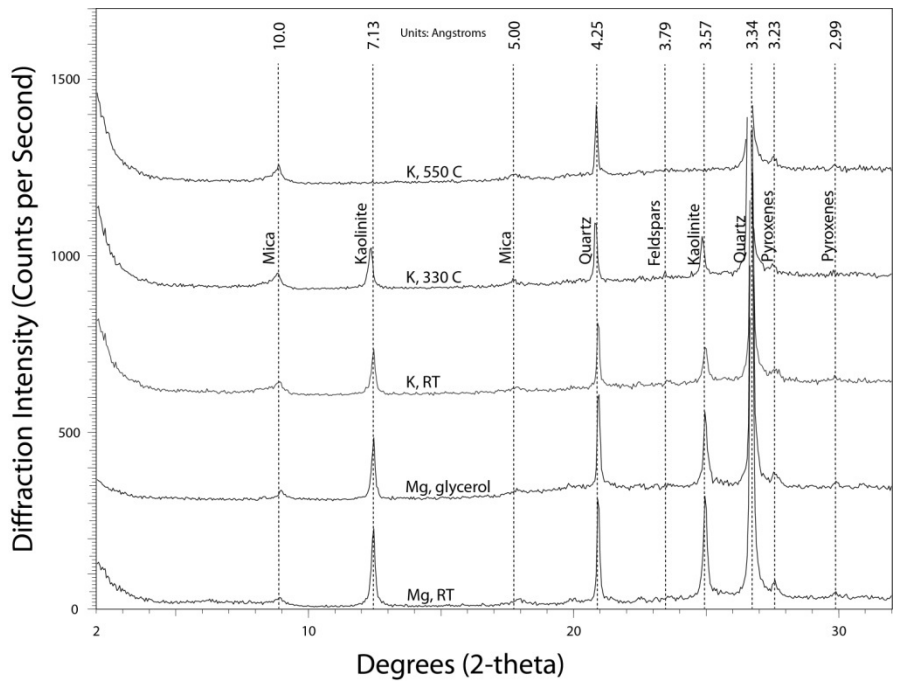


Figure D-28. North Troy Total Clay Fraction.

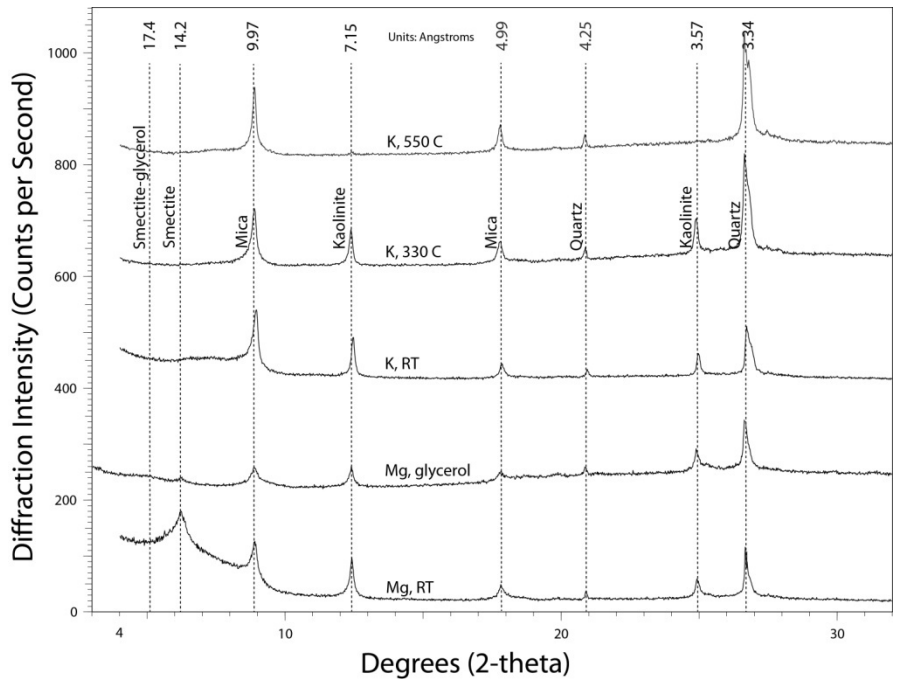


Figure D–29. Whitney Coarse Clay Fraction.

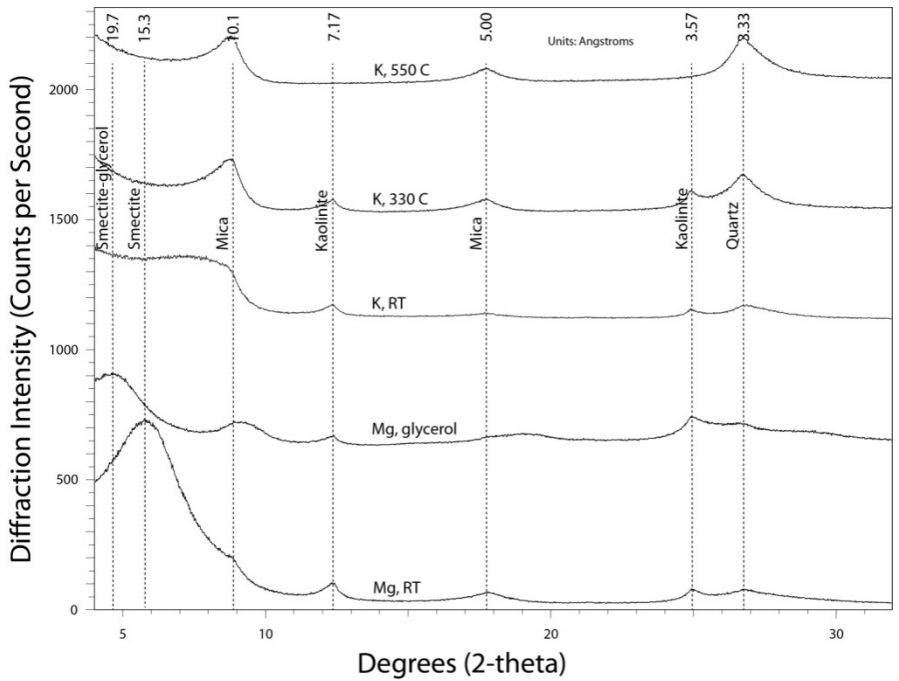


Figure D–30. Whitney Fine Clay Fraction.

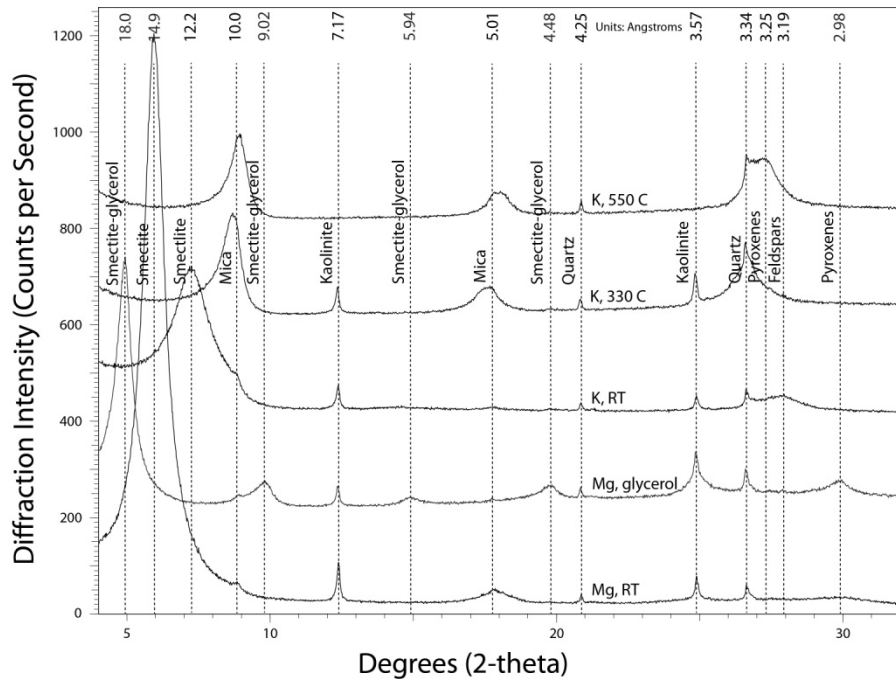


Figure D-31. Woods Coarse Clay Fraction.

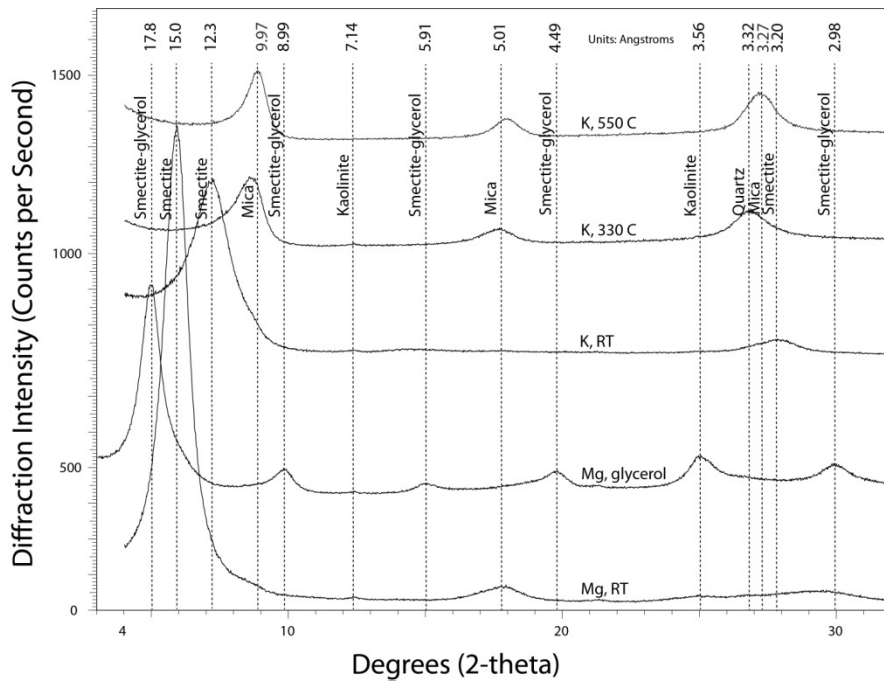


Figure D-32. Woods Fine Clay Fraction.

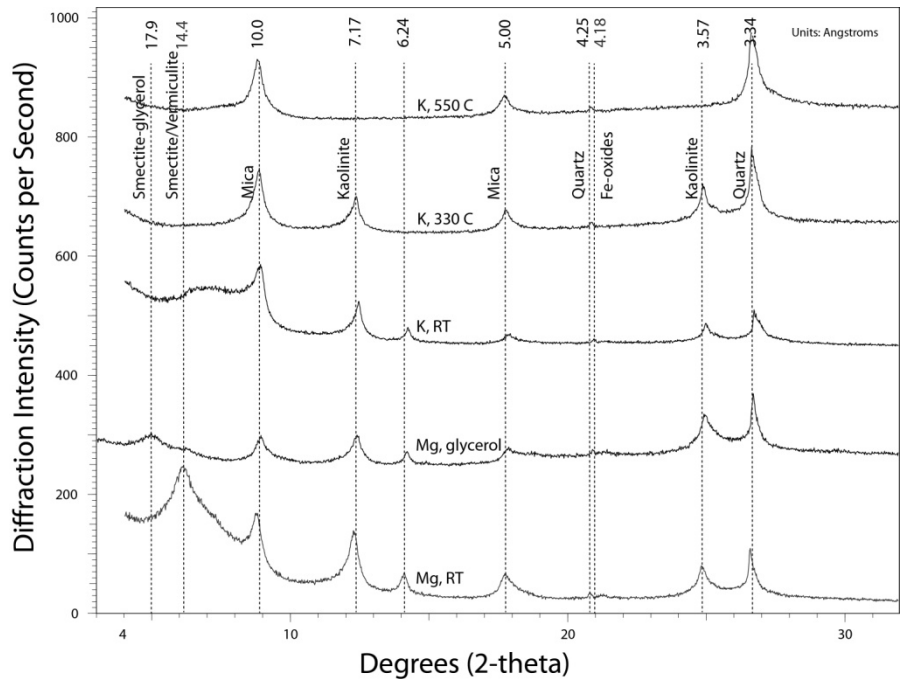


Figure D-33. Yarrington Coarse Clay Fraction.

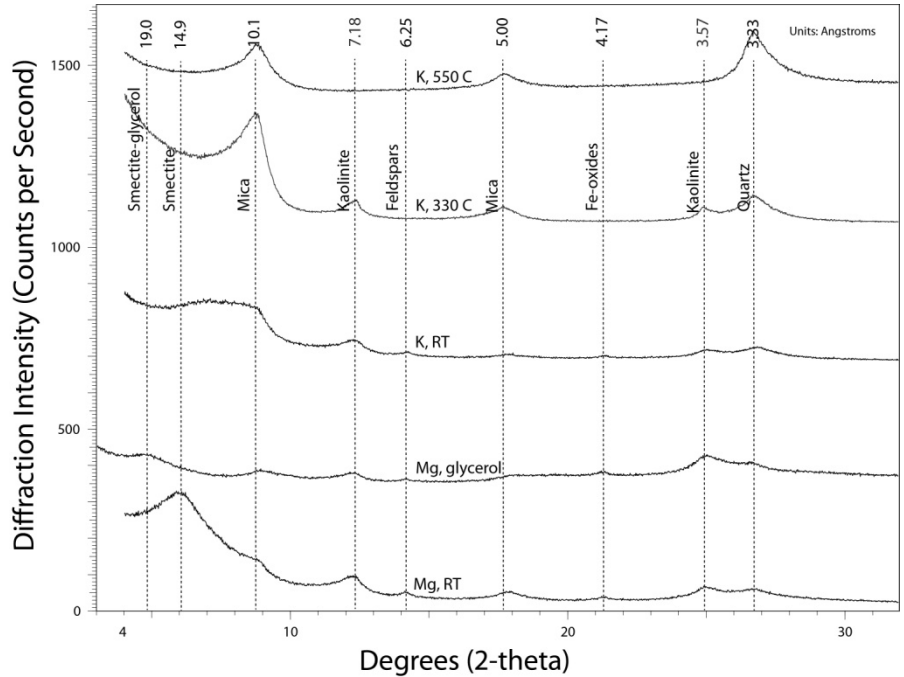


Figure D-34. Yarrington Fine Clay Fraction.

APPENDIX E

RIETVELD REFINEMENT XRD PROCEDURE FOR CLAY MINERAL QUANTIFICATION

Quantification of crystalline minerals in aggregate fines was completed from a whole-sample starting material (less than 2 mm particle diameter).

Sample Preparation for Spray-Drying

1. Grind approximately 15 g of aggregate fine with mortar and pestle until all material passed through a 60-mesh sieve (less than 250 μm).
2. 4.5 g of ground sample was weighed to 3 decimal places precision.
3. 0.5 g of zinc oxide standard was weighed out separately to 3 decimal places.
4. Sample and standard were mixed and added to a micronizing cylinder containing agate grinding elements.
5. Approximately 10 mL of 0.5% polyvinyl alcohol (PVA) in deionized water solution was added to the cylinder.
6. Sample was slurry-ground in a McCrone micronizing mill for 5–10 minutes at 3500 rpm.
7. The slurry was transferred to a 50 mL glass beaker through the pouring cap.
8. Grinding elements were rinsed with added PVA solution until the final solution was relatively clear after cleaning (approximately 20–30 mL total suspension volume). Care was taken to minimize slurry-suspension volume to be spray-dried.

Spray-Drying Procedure

1. A custom-fabricated, 90 x 44 cm aluminum spray-dryer equipped with 2, 1500 watt heating coils was heated to 130°C chamber temperature.
2. An artist's air brush was connected to a vacuum pump and to the sample slurry by PVC tubing.
3. Slurry solution was sprayed downward into the chamber through an opening in its top, at a slow rate, in a fine mist.
4. After spraying the entire suspension, heating coils were turned off and the spray dryer was allowed to cool for 15–20 minutes.
5. The spray-dryer was removed slowly from the easel pad paper on the ground, and loose spray-dried particles were slowly transferred to weighing paper. Particles adhering to paper electrostatically were freed by gently knocking against lab bench. Materials that fell to the ground without drying and dried on the paper were not collected.
6. Spray-dried materials were weighed and placed in glass vials.
7. Particle size and morphology of spray-dried specimens was observed at 6 X magnification under a light microscope and at higher magnification with scanning electron microscope (SEM).



Figure E–1. Spray–Drying Procedure for Reducing Orientation Effects during Powder Diffraction.

Rietveld Refinement Method

The Rietveld method is a full–pattern simulation that utilizes a least difference of squares statistical analysis in conjunction with models calculated from crystallographic data of real mineral samples. Online databases of crystal structures such as the International Center for Diffraction Data (ICDD) are contributed to by researchers around the world and are readily accessible online. In addition, most mineralogy labs catalog standard mineral diffraction patterns and use the crystal structure data in modeling diffraction patterns.

Quantification by the Rietveld method works by minimizing the difference between actual and modeled diffraction patterns. Researchers work to identify the minerals and select the

appropriate crystal models from a database or lab mineral reference library. The software program then runs a full pattern simulation, modeling all of a mineral's diffraction peaks (Young 1993). In modeling all peaks—even the lesser peaks in a diffraction pattern—the Rietveld approach resolves the significant issue of peak overlap that complicates quantification by other methods, such as the Reference–Intensity–Ratio method (RIR).

The major limitation of the Rietveld method is that it calculates diffraction patterns assuming 3–dimensional periodicity in mineral crystal structure. This condition, however, is only true for highly crystalline materials or minerals such as quartz and calcite. Clay mineral structure exhibits ordered arrangement of atoms in 2 dimensions along the X and Y axes, but between layers there is disordered stacking. In addition, crystallite size is much smaller in clay minerals than in more crystalline minerals, and chemical variation by isomorphic substitution is common in clay minerals as well.

The lack of 3–dimensional diffraction characteristics and variability in structure and chemical composition of clay minerals means that the development of crystal structure models for Rietveld analysis of clays is an area of ongoing research among clay researchers. Clay mineral structure is less definable due to the variable layer thickness, interstratification of clay minerals, and difference angles of layer sheet stacking.

Furthermore, in a total–sample Rietveld refinement, clay minerals may not be easily identifiable because of their lower intensities. It was determined in a previous experiment that smectite diffraction peaks were not detectable in a quartz–bentonite powder mix when bentonite was present in quantities below than 5 % mass of mixture. Definitive identification of clay minerals without fixing layer thickness of any expansive clay minerals present is further complicated by peak overlap of different phases near 14 Angstroms d–spacing.

Rietveld Procedure

1. Each spray–dried specimen was side–mounted into an XRD powder holder enclosed by a frosted–glass cover.
2. Unique diffractometer parameters for Rietveld analysis included: 3 – 80° 2 θ angle, 0.02° step size, 15 second dwell time, variable slit, and 0 rpm stage rotation.
3. Recording of X–ray diffraction patterns required approximately 18 hours per specimen.
4. Major mineral phases were identified in Bruker DIFFRAC^{plus} EVA software.
5. Appropriate crystallographic models were downloaded from the ICDD database.
6. Rietveld refinement and quantification was completed in Bruker DIFFRAC^{plus} TOPAS with downloaded crystallographic models.

Figure 2 shows the Rietveld quantification results for the crystalline minerals in an aggregate. Each colored notch at the bottom of the figure represents a simulated diffraction peak for the minerals with corresponding colors, in the upper right. The red diffraction pattern represents the actual sample, while the blue pattern is calculated. The grey pattern represents the closeness of fit, or difference between real and simulated patterns.

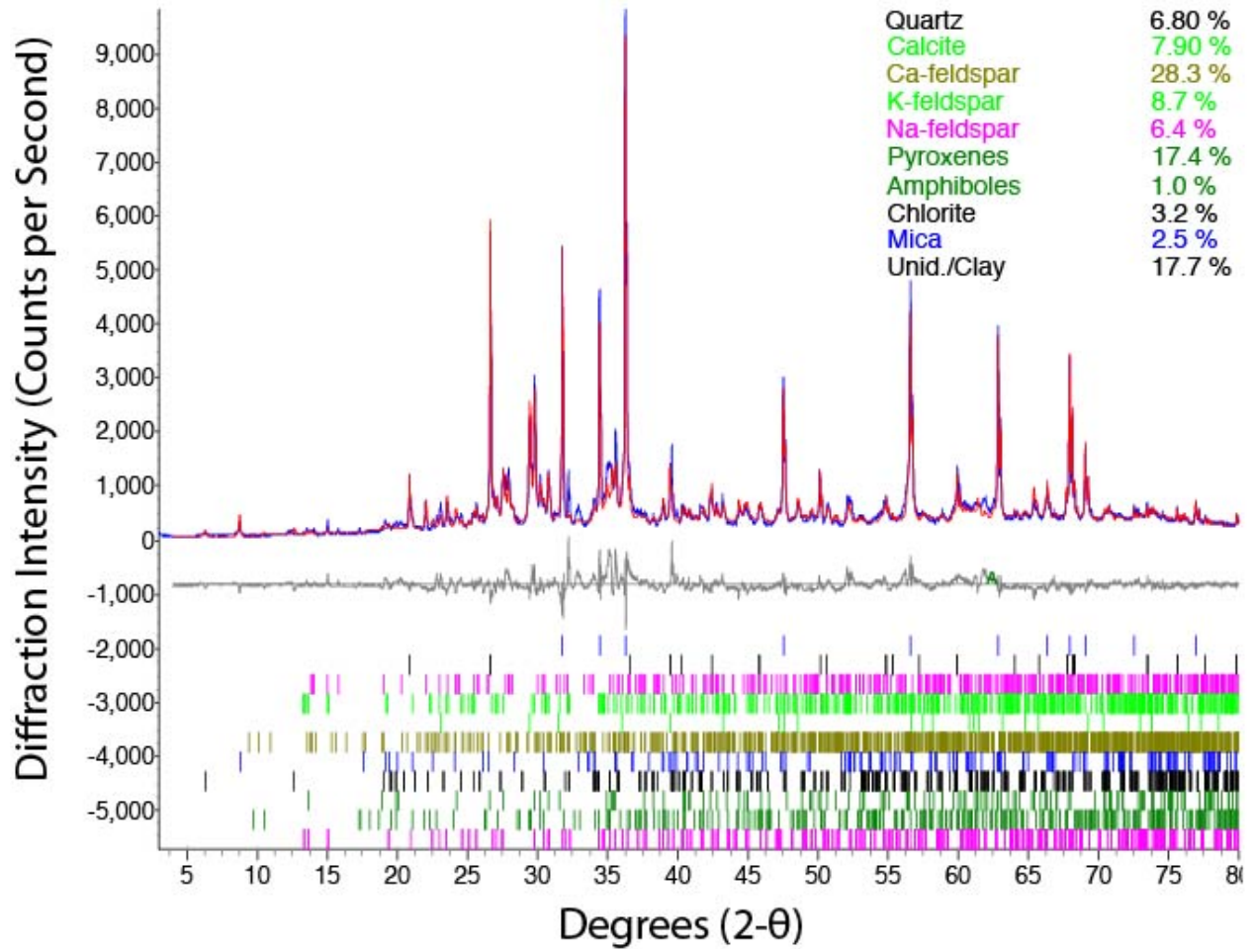


Figure E–2. Rietveld Method Quantification in Bruker DIFFRAC^{plus} TOPAS Software.