University of Cincinnati

Date: 5/6/2011

I, Nadeesha H Koralegedara , hereby submit this original work as part of the requirements for the degree of Master of Science in Geology.

It is entitled:

**Chemical, Mineralogical and Textural Properties of the Kope Formation
Mudstones: How They Affect its Durability**

Student's name: **Nadeesha H Koralegedara**

This work and its defense approved by:

Committee chair: J Barry Maynard, PhD

Committee member: Tammie Gerke, PhD

Committee member: Warren Huff, PhD

Committee member: David Byer Nash, PhD

1448

Chemical, Mineralogical, Textural Properties of the Kope Formation Mudstones: How They Affect its Durability

A thesis submitted to the
Graduate School
of the University of Cincinnati
in partial fulfillment of the
Requirements for the degree of

Master of Science

in the Department of Geology
of the College of Arts and Sciences

05/06/2011

by

Nadeesha H. Koralegedara

Bachelor of Science (honors) Geology

University of Peradeniya, Sri Lanka

2008

Committee Members: Barry J. Maynard, Ph.D. (Chair)

Warren D. Huff, PhD.

David B. Nash, PhD.

Tammie L. Gerke, PhD.

Abstract

Slope failures are a common and longstanding problem in Cincinnati. Most are associated with the Kope Formation, a rock unit characterized by meter-scale cycles of mudstones and limestones where thick mudstone is sandwiched between two thinner limestone layers. This study evaluates chemical, mineralogical and textural properties of Kope mudstones to determine why it is less durable than other formations. A two-cycle slake durability test was performed on thirty mudstones samples belonging to three consecutive cycles of the Kope Formation from a fresh outcrop in Newport, Kentucky. Chemical and mineralogical analysis of the bulk sample and the sludge (slaked portion of the rock after second run) were determined using X-ray fluorescence and X-ray diffraction and the data were compared with the two-cycle slake durability index (ID_2). Individual chemical constituents and mineralogy do not show any significant relationship with the ID_2 of mudstones. Two main fabric types of mudstones were seen in the field - laminated and non-laminated. Detailed micro-fabric characteristics of the samples were observed using the scanning electron microscope. Laminated mudstones with turbostratic or parallel packet type fabric showed higher slake durability and lower moisture content than the non-laminated mudstones with matrix or book-house type fabric. According to the “Two-sample t-test” there is a significant difference in the ID_2 of the two types of mudstones. Laminated mudstones have a high ID_2 compared to non-laminated mudstones. Because the two mudstones types have different geotechnical properties and both types exist in many cycles of the Kope Formation, care should be taken to select core samples from both fabric types for preliminary tests in geotechnical practice. This will provide more accurate estimations of the geotechnical properties of the Kope Formation mudstones.

Acknowledgments

It is with affection and appreciation that I acknowledge my indebtedness to Dr. J. Barry Maynard, Dr. Tammie L. Gerke, Dr. Warren D. Huff, and Dr. David B. Nash for agreeing to serve on my thesis committee and for guiding and supervising me throughout this research. I would especially like to thank Dr. Maynard and Dr. Gerke for their kind help and direction during this research as well as my academic career. I extend my special gratitude to, Dr. Huff for his support on the scanning electron microscopic image analysis, Dr. Thomas Lowell for providing laboratory facilities for particle size analysis and Dr. Carlton Brett for his support in field work.

I thank Dr. Mark T. Bowers in the Department of Civil Engineering for providing engineering laboratory equipment and test procedures. I am very grateful to Dr. Tom H. Ridgway in the Department of Chemistry for allowing me to use the atomic absorption spectrometer.

I would like to express my sincere appreciation to Michael K. DeSantis , Matthew Jones and my husband, Sanjeewa Rodrigo for their kind support in sample collection and processing. A special thanks to Michael DeSantis for his nice photography. Many others, too numerous to mention individually, have given their support in various ways, and to them all I am very grateful.

Table of Contents

Abstract	ii
Acknowledgment	iv
List of Figures	viii
List of Tables	xii
Chapter 1 - Introduction	
1.1 General Introduction	1
1.2 Geology of Cincinnati	1
1.3 Kope Formation	6
1.3.1 Mudstones, Shale and Lamination	7
1.4 Previous Studies	9
1.5 Slake Durability	10
1.6 Research Objectives	11
Chapter 2 – Literature Review	
2.1 Kope Formation and its Studies	12
2.2 Slake Durability of Mudstones and its Properties	14
Chapter 3 – Methodology	
3.1 Sampling	19
3.1.1 Sampling Location	19
3.1.2 Sample Collection	24
3.2 Laboratory Procedure - Overview	26

Chapter 4 – Results and Discussion

4.1	Slake Durability	27
4.2	Chemistry	33
4.2.1	Chemical Index of Alteration (CIA)	34
4.2.2	Total Carbonate Content	35
4.2.3	Total Carbon and Total Sulphur	36
4.2.4	Exchangeable Cations	37
4.3	Mineralogy	40
4.3.1	Clay Minerals	42
4.3.2	Non-clay Minerals	44
4.3.2.1	Oxidation of Pyrite	44
4.4	Physical Properties	45
4.4.1	Grain Size	45
4.4.1.1	Total Clay Content	45
4.4.1.2	Grain Size Distribution of the Fine Fraction of Kope Formation Mudstones	46
4.4.1.3	Grain Size Distribution of Illite Based on X-Ray Diffraction Data	46
4.4.2	Moisture Content	47
4.4.3	Fabric	51
4.5	Fabric Types and Formation Mechanisms	65
4.5.1	Changes in Salinity of Water	65
4.5.2	Storm Driven Currents and Bottom Flowing Gradient Currents	66

4.5.3	Changes in Rate of Sedimentation	67
4.5.4	Degree of Bioturbation	69
4.5.5	Mechanisms Applicable for the Fabric Difference of the Kope Formation Mudstones	70
Chapter 5 – Conclusions		71
Chapter 6 – Future Studies		74
Chapter 7 - References		75
Appendices		
Appendix A	Engineering, Chemical, Mineralogical, Textural Data and X-ray Diffraction Traces	86
Appendix B	Additional Graphs Between the ID ₂ and Other Properties which do not have Significant Correlations	121
Appendix C	Particle Size Distribution of the Fine Fraction of the Kope Formation Mudstones	127
Appendix D	Detailed Procedures of the Tests Performed (Moisture Content, Two-cycle Slake Durability Test, X-ray Fluorescence Analysis, Loss on Ignition, Total Carbonate Content, Total Carbon and Total Sulphur Analysis, Atomic Absorption Spectrometric Analysis, Powder X-ray Diffraction Analysis, Total Clay Content and Particle Size Distribution of the Fine Fraction, Scanning Electron Microscopy Analysis,	129
Appendix E	Characteristics of Main Lithology Types and the Laminated and Non-laminated Mudstones in the Kope Formation	145

List of Figures

Figure 1.1	Regional geological setting of Cincinnati, Ohio	2
Figure 1.2	Stratigraphic sequence of the Upper Ordovician time in Cincinnati-Northern Kentucky – South-east Indiana (tri-state area)	5
Figure 1.3	Meter scale cycles of the Kope Formation – Fowler Creek, Cincinnati, Ohio	6
Figure 3.1	Location map of the sampling site, Newport pavilion, Kentucky	20
Figure 3.2	(a) Sampling outcrop - Newport Pavilion, Kentucky (b) Approximate positions of sampling Cycle 11, 12 and 13 in the outcrop	21
Figure 3.3	Cycles of the Kope Formation exposed in the studied outcrop, Newport Pavilion, Kentucky	22
Figure 3.4	(a) Stratigraphic profile of the three cycles studied in the Kope Formation – Newport Pavilion, Kentucky (b) Field photograph of the Cycle 11 of the Kope Formation exposed in Newport Pavilion, Kentucky	23
Figure 3.5	Mudstones sampled from Cycle 11 of the Kope Formation exposed in the studied outcrop - Newport Pavilion, Kentucky (a) laminated mudstones (b) non-laminated mudstones	25
Figure 3.6	Overview of the laboratory procedure	26
Figure 4.1	The ID ₂ of Kope Formation mudstones belonging to the three cycles (Cycle 11, 12 and 13) plotted against elevation	28

Figure 4.2	The ID ₂ of Kope Formation mudstones of Cycle 12 plotted with elevation	30
Figure 4.3	The ID ₂ of Kope Formation mudstones plotted against the chemical index of alteration [CIA = Al ₂ O ₃ / (Al ₂ O ₃ + K ₂ O+CaO*+Na ₂ O)]	34
Figure 4.4	Concentrations of water soluble Na ⁺ measured in parts per million (ppm) plotted against the ID ₂ of the Kope Formation mudstones	37
Figure 4.5	Concentrations of water soluble K ⁺ measured in parts per million (ppm) plotted against the ID ₂ of the Kope Formation mudstones	38
Figure 4.6	XRD traces of the representative samples belong to the three cycles (Cycle 11, 12 and 13) studied in the Kope Formation	41
Figure 4.7	Moisture content of mudstones belonging to the three cycles (Cycle 11, 12 and 13) of the Kope Formation plotted against elevation	48
Figure 4.8	Moisture content versus ID ₂ of the Kope Formation mudstones belong to three cycles (Cycle 11, 12 and 13)	49
Figure 4.9	The ID ₂ of Kope Formation mudstones belong to three cycles (Cycle 11, 12 and 13) plotted against elevation	51
Figure 4.10	Micro-fabric classification of rocks	53
Figure 4.11	SEM image of non-laminated mudstones of Cycle 12 of the Kope Formation (a) fabric is similar to matrix type or book house fabric (b) enlarged portion of non-laminated mudstone of Cycle 12 showing wide angles of edge-face contacts between clay flakes	55

Figure 4.12	SEM image of laminated mudstones of Cycle 12 of the Kope Formation (a) fabric is similar to the turbostratic or parallel packet fabric. Face-face contacts between clay flakes are dominant. (b) an elongated pore space of a laminated mudstone of Cycle 12	56
Figure 4.13	SEM images of laminated mudstones with laminar fabric. Both face-face contacts and face-edge contacts between clay flakes can be observed. (a) laminated mudstones sample of Cycle 11 of the Kope Formation (b) laminated mudstones sample of Cycle 13 of the Kope Formation	57
Figure 4.14	SEM image of moderately durable laminated mudstones of Cycle 12 of the Kope formation showing the arrangement of stacks of clay flakes having face-face contacts oriented at an angle to the surface	58
Figure 4.15	SEM image of pyrite framboids in non-laminated mudstones from Cycle 12 of the Kope Formation	60
Figure 4.16	Illustration of deposition of clay flakes in a sedimentary basin. (a) in saline water clay floccules deposited making in a random orientation (b) in fresh water individual clay flakes deposited making parallel orientation	66
Figure 4.17	The effect of storm driven currents on the fabric formation (a) silt grains buttress the clay floccules from collapsing and resulting in a random orientation (b) bottom flowing gradient currents disturb the parallel orientation of clay flakes	67
Figure 4.18	Illustration of the formation of preferred orientation of clay flakes in high sediment accumulating environments	68
Figure 4.19	Illustration of the formation of random orientation of clay flakes in low sediment accumulating environment	68

Figure 4.20 Illustration of the effect of degree of bioturbation on the orientation of clay flakes 69
flakes

List of Tables

Table 1.1	Mudstones and limestone composition of different rock formations around Cincinnati, Ohio	4
Table 4.1	Durability classification of weak rocks based on ID_2	29
Table 4.2	The effect of different properties of mudstones on its durability based on the reviewed literature	31
Table 4.3	The effect of different properties on the durability of Kope Formation mudstones - summary and a comparison of the present study data with reviewed literature	61

1. Introduction

1.1 General Introduction

Landslides are a common and longstanding problem in Cincinnati, Ohio and adjacent areas of Kentucky and Indiana. These slope failures damage roads, buildings and other infrastructure. Landslide remediation costs as well as the expenses to reconstruct the damaged properties are high in Cincinnati compared to other metropolitan areas (Fleming and Taylor 1980). Many of these slope failures are associated with the colluvium developed on the Kope Formation, which underlies much of the area. Several different approaches have been taken to study this problem including determination of the types of landslides, mechanisms of slope failures, mapping of landslide susceptible areas, properties of landslide materials, influence of water on slope failures etc. However, very few studies of the properties of Kope Formation mudstones have been conducted. Weathering and slaking of these mudstones produces thick soil cover, which tends to fail after a heavy rain. Therefore it is important to study the properties of the mudstones that form these soils. The present study evaluates the chemical, physical and mineralogical properties of the Kope Formation mudstones which can affect their slake durability.

1.2 Geology of Cincinnati

The exposed geology of the Cincinnati region consists of a series of bedrock formations belonging to the Upper Ordovician (445-450Ma) overlain by a thin cover of Pleistocene glacial deposits. The Cincinnati Arch, which is a broad structural uplift, is the most prominent

geological structure in the region. The Cincinnati arch is a north-south oriented, broad anticline where the oldest rocks (Upper Ordovician) are exposed along the central axis and younger rocks, up to Permian, lie on the flanks (Figure 1.1).

Figure 1.1: Regional geological setting of Cincinnati, Ohio (Coogan, 1996)

During the Ordovician period, Ohio was in the tropical latitudes and was covered by a shallow sea. Marine limestone and mudstones, formed in that period, are the geologic building blocks of the Cincinnati area. From oldest to youngest up sequence, the most prominent rock units are the Point Pleasant Formation (mostly limestones), Kope Formation (mostly mudstones), Fairview Formation (half limestones, half mudstones), Miamitown Shale and Bellevue limestone (Figure 1.2). The Kope Formation is about 74 m thick and present between the level of the Ohio River and the mid height of the hillsides (Baum and Johnson, 1996). It mainly consists of alternating mudstones and limestone beds in meter-scale cycles. The Miamitown Shale, about 0-11 m thick, lies above or within the top of the Fairview Formation (Baum and Johnson, 1996). Bellevue limestones cap the hilltops. Mudstones and limestones are the dominant rock types found in above rock formations. In addition a few siltstones are found. However the relative proportions of mudstones to limestones are varying (Table 1.1).

Many hillsides in the Cincinnati area are covered by thick colluvium. This colluvial cover derives from weathering of the Kope and Fairview Formation mudstones. An additional component may come from weathering of mudstones left from quarrying operations. Most hillsides around Cincinnati were quarried to remove limestone building blocks from the Fairview Formation. The waste mudstones were pushed over the edge of the quarry on to the hillside where they deteriorated rapidly into clay-rich soil (Agnello, 2005).

Table 1.1: Mudstones and limestone composition of different rock formations around Cincinnati, Ohio (Fleming, 1975)

Rock unit	Mudstones (%)	Limestones (%)
Point Pleasant Formation	30-50	50-70
Kope Formation	65-75	25-35
Fairview Formation	35-45	55-65
Miamitown Shale	90	10
Bellevue Limestone	0	100

SYSTEM	SERIES	STAGE	FORMATION	MEMBER	SUB MEMBER
ORDOVICIAN	CININNATIAN	MAYSVILLIAN (PART)	GRANT LAKE	Mt. AUBURN	
				CORRYVILLE	
				BELLEVUE	
			FAIRVIEW	MIAMI TOWN SHALE 0-11 m	
				FAIRMOUNT 18 m	
				Mt.HOPE 16 m	
		EDENIAN	KOPE		Wesselman
					North Bend
				McMICKEN 21 m	Taylor Mill
					Grand Avenue
				SOUTHGATE 37 m	Grand View
					Alexandria
					Snag Creek
					Pioneer Valley
				ECONOMY 16 m	Brent
					Fulton
	MOHAWKIAN	SHERMANIAN (PART)		PT.PLEASANT 6-7 m	
				BROMLEY > 7 m	

Figure 1.2: Stratigraphic sequence of the Upper Ordovician time in Cincinnati-Northern Kentucky – Southeast Indiana (modified from Brett *et al.*, 2008)

1.3 Kope Formation

The Kope Formation is a 74 m thick rock unit of 445 – 450 MA age (upper Ordovician) that extends over Southwestern Ohio, Northern Kentucky and Southeastern Indiana. According to Jennette and Pryor (1993) the Kope, Fairview and Bellevue Formations are progradational successions on a carbonate ramp and the Kope Formation is the most distal facies. According to their interpretation, the Kope Formation was deposited in a low energy environment with occasional storms. There are about 45-50 meter-scale cycles of mudstones and limestones present in the Kope Formation (Holland *et al.*, 1997) (Figure 1.3). Each cycle is defined by about 2 m thick mudstones sandwiched between bundles of thinner (25 -30 cm) skeletal limestone (Holland *et al.*, 1997).

Figure 1.3: Meter scale cycles of the Kope Formation – Fowler Creek, Cincinnati, Ohio. Note the landslide in top (arrow). The total height of the profile is 7 m (Photograph by Mike K. DeSantis)

Although the origin of these cycles is not resolved yet, Holland and Miller (2008) summarized three principal interpretations.

1. Variations in water depth driven by sea level fluctuations (Jennette and Pryor, 1993)
2. Changes in storm frequency and intensity

These alternate mudstones and limestones beds and the cyclic nature of the Kope Formation may reflect the frequency and the intensity of storm events at the time of deposition. The mudstones dominant beds may reflect the distal storm facies while limestones dominant beds may reflect the proximal storm facies (Holland and Miller, 2008)

3. Changes in supply of terrigenous mud

Changes in supply of terrigenous mud due to climatic changes may cause this cyclic nature of the Kope Formation (Elwood *et al.*, 2007)

1.3.1 Mudstones, Shale and Lamination

Researchers use different terminology to describe various types of fine grained argillaceous rocks. Many terms have changed with time and have multiple definitions. Therefore, the terminology used in the present study is described below. All the fine grained argillaceous sedimentary rocks found in the Kope Formation are defined as Mudstones. There are two main types of mudstones; fine grained, laminated argillaceous rocks which are defined as Shales and fine grained, non-laminated argillaceous rocks which are defined as Mudrocks (Potter *et al.*, 2005).

Both types of mudstones were found in the studied outcrop. Shales with laminations (laminated mudstones) and mudrocks with no laminations and massive or blocky appearance (non-laminated mudstones) were observed in the field. These differences reflect the different depositional environments and depositional mechanisms. Macro and micro- fabric textures of mudstones observed by various techniques such as scanning electron microscope (SEM), X-radiographs and thin section photomicrographs are used to describe different depositional mechanisms (O'Brien and Mattner, 1998).

Laminated mudstones have a preferred orientation of clay flakes with significant face-face contacts when observed under the SEM whereas non-laminated mudstones have random orientation of clay flakes with significant edge-face contacts (flocculated clay). The preferred orientation of laminated mudstones is considered to result from deposition of dispersed clay flakes. It may also be resulted by deposition of clay floccules followed by re-orientation from burial (O'Brien, 1987). Random orientation of non-laminated mudstones may result from bioturbation, storm events or abrupt changes to higher salinity environment, as in an estuary (O'Brien, 1987). According to Kohrs *et al.* (2008), the random orientation of clay flakes in the

non-laminated mudstones of the Kope Formation is unlikely to be a result of an abrupt change to a higher salinity environment but rather a result of disturbances caused by storm events and/or by the effect of bioturbation.

1.4 Previous Studies

Extensive researches have been conducted on landslides in Cincinnati, Ohio in different aspects. For example, Fleming and Taylor (1980), Fleming and Johnson (1994), Haneberg and Gokce (1994), Baum (1994) and Hough and Fleming (1974) studied different types of landslides, landslide formation mechanisms, materials associated with landslides, etc. Few researchers have studied the Kope Formation rocks with respect to landslides but many have studied the properties of colluvium associated with the landslides. As most of these slope failures are associated with the soils derived from the weathering of Kope Formation mudstones, it is important to study the properties of mudstones in the Kope Formation. In 2008, McFadden studied the physical properties of Kope Formation mudstones. According to his data, Kope Formation mudstones show a wide range of two-cycle slake durability indexes (ID_2). He pointed out the positive correlation between the unconfined compressive strength (UCS) and ID_2 of the Kope Formation mudstones. Since less durable mudstones tend to weather easily and form soil quickly, it is important to study the durability of mudstones in order to determine their contribution to these slope failures.

1.5 Slake Durability

The term durability, in Latin “durabilis”, means lasting and is used in engineering studies to describe the resistance of rocks to weathering. As there are different mechanisms by which a rock can weather when exposed to different environmental conditions, the durability of rocks can be defined in different ways, for example, abrasion-durability, frost-durability and slaking durability. Slaking, the disintegration of rock material when subjected to alternate wetting and drying conditions, is the most common way these rocks weather. Different tests have been developed to measure the slake durability of rocks. For example the jar slake test, slake index test, and slake durability test all provide information about the durability of rocks (Franklin and Chandra, 1972). The jar slake test effectively indicates the mode of slaking while the slake index test indicates both the mode of slaking and the rate of slaking (Santi and Koncagul, 1996).

The slake durability test, proposed by Franklin and Chandra in 1972, consists of alternate wetting and drying cycles. The slake durability index, given in percentage, measures the resistance of a rock to disintegration from alternate wetting and drying conditions while undergoing abrasion. Therefore it is an approach to assess the slake durability of rocks under the natural conditions they experienced in the field. Since the rotation of samples in a steel cage provides a mechanical abrasion component to the test, the procedure also gives an approximation of the resistance of rocks to abrasion under natural field conditions. Multiple cycles of wetting and drying have been used to assess the slake durability index (Santi and Koncagul, 1996, Gokceoglu *et al.*, 2000, Sri-in and Fuenkajorn, 2007 and Erguler and Ulusay, 2009). However, according to American Society of Testing and Material (ASTM) standards, the ID₂ is appropriate

for judging the slake durability of rocks for engineering applications. Therefore ID_2 is used in this study to evaluate the slake durability of Kope Formation mudstones.

1.6 Research Objectives

Many slope failures that have occurred in the Cincinnati area are associated with the soils derived from Kope Formation rocks. Mudstones, the main lithologic component of the Kope Formation, tend to break down rapidly when subjected to alternate wetting and drying cycles (slaking). The associated limestones produce little residue during weathering. Therefore mudstones are the dominant contributor in developing the soils in the Kope Formation. The slake durability determines the rate of soil formation in mudstones.

According to McFaddin (2008) and the results of the present study, there is a wide range of ID_2 in the Kope Formation mudstones. That is, the slake durability of all mudstones in the Kope Formation are not the same and it is important to know which factors affect this wide range of durability difference. Therefore, studying the effects of different properties of the Kope Formation mudstones on their slake durability is the main objective of this study.

2. Literature Review

2.1 Kope Formation and its Studies

Researchers have studied the Kope Formation mainly from two points of view.

1. Geological studies – paleontology, stratigraphy, petrology and mineralogy of rocks.
2. Engineering studies – geotechnical engineering properties of rocks.

The Kope Formation has been a classical rock unit for paleontology and stratigraphic studies. For example, Brett *et al.*, 2008, Holland *et al.*, 1997, Jennette and Pryor, 1993 and many others have done paleontological and stratigraphic research on the Kope Formation rocks. Weiss and Sweet (1964) studied different lithologies and lithological boundaries in the Kope and adjacent formations. Scotford (1965) studied the petrology and lateral and vertical variations of the mineralogical, chemical and textural parameters of the Cincinnati series shales. His data show that illite and chlorite are the dominant clays. Quartz, calcite and dolomite are the dominant non-clay minerals. Feldspars and pyrites have been found as minor minerals. According to his study, the chemical, mineralogical and textural properties of Cincinnati series shales are uniform laterally as well as vertically. Bassarab and Huff (1969) studied the clay mineralogy of the Kope and Fairview Formations. According to them illite and Fe- rich chlorite are the dominant clay minerals found in the Kope Formation. They discussed the environmental relationships of the clay mineralogy and stated that the difference in clay mineralogy is related to the environment of their source area. Haneberg and Gokce (1994) studied the clay mineralogy of the colluvium in the Delhi Pike landslide that occurred within the Kope Formation. According to

their data, there is little or no variation in clay mineralogy with depth. In the same year Fleming and Johnson (1994) studied the clay mineralogy of the material associated within the Delhi Pike landslide and found illite as the dominant clay mineral. Fleming (1975) studied the physical properties of the colluvium plus the weathered and un-weathered mudstones of the Kope Formation. By comparing the three types of materials, he observed large differences in clay fraction and Atterberg limits in the colluvium material. According to his data colluvium materials have a relatively high moisture content, a low dry density and a very low unconfined compressive strength compared to mudstones.

Although many researchers have studied the physical properties of the colluvium, very few studies have been carried out about the physical properties of mudstones in the Kope Formation. The most recent study of the physical properties of Kope Formation mudstone was conducted by McFaddin (2008). He studied two different sample preservation methods and some physical properties of mudstones including UCS, ID_2 , jar slake index, free swelling potential, swell pressure, particle size distribution, Atterberg limits and the moisture content. His work presented apparent relationships among some of the physical properties of the Kope Formation mudstones. For example, the UCS shows positive correlation with the ID_2 whereas the ID_2 shows a negative correlation with the natural moisture content of these rocks. According to his study, the ID_2 provides information about the strength as well as the slake durability of the mudstones.

2.2 Slake Durability of Mudstones and its Properties

Many researchers have studied the factors affecting the low durability of clay bearing rocks and the mechanisms which break the rocks apart when subjected to alternate wetting and drying cycles. The behavior of clay bearing rocks in water is described by Seedsman (1986). He suggested two main processes that these rocks undergo when in contact with water - swelling and slaking. The expansion of clay by absorbing water causes swelling in these rocks. The absorption of water into pore spaces creates pore-air compression which then results in slaking of clay bearing rocks. Youn and Tonon (2010) summarized four different factors that affect the slaking mechanisms of clay bearing rocks.

- 1) Air pressure entrapped in pore spaces and between clay particles
- 2) Osmotic swelling pressure of expandable clay minerals
- 3) Pre-existing fissures in rocks
- 4) Gradual removal of cementation by alternate wetting and drying

Santi and Koncagul (1996) described different modes of slaking of shale and the main cause for each type. Dispersion slaking, swelling slaking, body slaking and surface slaking are the four modes of slaking which result from the presence of Na-kaolinite, Na-montmorillonite, Ca-illite/Ca-kaolinite and Ca-montmorillonite respectively. As the Kope Formation mudstones do not contain expansive clays such as smectite in quantifiable amounts, the swelling due to the expansion of clays is unlikely for the Kope. However, pore-air pressure compression, release of residual stresses which exceeds the rock strength and the loss of cohesion of clay due to the absorption of water on to the surfaces of clay (Moon and Beattie, 1995) may be important

mechanisms applicable to the low durability of the Kope Formation mudstones. All these mechanisms show that the moisture content and porosity of a rock play significant roles in its durability. However there are many other factors affecting the durability of weak rocks like mudstones.

Taylor (1988), Dick and Shakoor (1992), Moon and Beattie (1995), Bell *et al.* (1997), Koncagul and Santi (1999), Gokceoglu *et al.* (2000), Dhakal *et al.* (2002) and Lashkaripour and Boomeri (2002) studied factors affecting the low durability of clay bearing rocks. According to those studies, the slake durability of a rock depends upon many factors such as physical and chemical properties, mineralogy, fabric (porosity, mineral alignment, micro-fractures, density) and geology (lithology, cementation and diagenetic process). Nandi and Whitelaw (2009) described the effect of calcareous minerals on the durability of calcareous shales. They showed that the presence of calcite and gypsum affect the degree of disintegration of shales upon wetting as carbonate minerals dissolve when exposed to acidic water. Lashkaripour and Boomeri (2002) studied the role of mineralogy in the durability of weak rocks. Their results indicate that the type and amount of clay minerals are the main factors influencing the slake durability index of weak rocks. Dick and Shakoor (1992), Moon and Beattie (1995), Dhakal *et al.* (2002) studied the influence of clay minerals on slake durability of weak rocks. According to Dick and Shakoor (1992) and Dhakal *et al.* (2002) smectite bearing rocks are less durable than the rocks deprived of smectite. Moon and Beattie (1995) showed that the increased kaolinite can lower the durability of mudrocks.

Dick and Shakoor (1992) categorized clay bearing rocks based on lithology and studied the correlation between the slake durability and different lithologies. Some characteristics such as grain size distribution, clay mineralogy, void ratio, micro-fracture frequency index, Atterberg limits, and laminations which they used to classify the rocks also have influence on their slake durability. They indicated that different lithologies have different properties which govern the durability of rocks. For instance, the expandable clay content governs the durability of claystones whereas the micro-fracture frequency index is mainly responsible for mudstones durability. According to them the durability of shale depends upon the degree of consolidation and its expandable clay content (terminology of Dick and Shakoor (1992) to define different lithologies are different from the terminology use in the present study). Dhakal *et al.*, 2002 stated that the mineralogical composition and textural features of the rock affect the slake durability. The presence of smectite and zeolite as alteration minerals affect the durability of rocks. High pore volumes and the wide spread of pore sizes results in low durability rocks.

The influence of textural properties or the fabric of rocks on their durability has been discussed in many studies. Gillott (1970) studied the correlation between the fabric and the engineering properties of the Leda clay in Canada. According to his study, the most important factors affecting the engineering properties of the Leda clay are the nature of inter-crystalline junctions and the effective area of the inter particle contacts. He concluded that the flocculated or deflocculated state of the sediment in the depositional environment is the main effect on the fabric of Leda clay and that these are more important for the nature of the fabric than the effect of subsequent events in the consolidation history. Lash and Blood (2004) described the origin of shale fabric by mechanical compaction of flocculated clay. The effect of bioturbation on random

fabric of grey shale with flocculated clay particles has been described by O' Brien (1987). He also described the difference between the original shale fabric and the disturbed or random fabric of shale due to bioturbation. These descriptions can be used to evaluate the depositional environments and depositional mechanisms of the Kope Formation mudstones. Huppert (1988) studied sedimentary rocks with the SEM and categorized three main types of fabrics as,

- Skeletal (discontinuous matrix, dominant inter-granular pores).
- Matrix (continuous clay matrix where large structural elements are fully immersed in matrix, large edge-face contacts of clay minerals, large pore spaces).
- Turbostratic (continuous clay matrix, face-face contacts of clay minerals, small and elongate pores).

Moon and Beattie (1995) observed the fabric of Waikato Coal Measures mudrocks under the SEM and modified the micro-structural terminology of Huppert (1988) by adding laminar fabric (transition stage in-between matrix and turbostratic fabrics) to the classification. They described the texture of rocks in two main types as,

- Continuous matrix (detrital grains are surrounded by a clay matrix).
- Discontinuous matrix (narrow clay bridges form connectors between detrital grains and assemblages of clay microaggregates).

Rocks having a continuous matrix are more durable than the rocks having a discontinuous matrix. Huppert (1988) pointed out that rocks having turbostratic fabric (continuous clay matrix, face-face contacts of clay minerals, small and elongate pores) show relatively high ID₂ whereas rocks with skeletal fabrics (discontinuous matrix, dominant inter-granular pores) show low ID₂.

Sloane and Kell (1966) and Gillott (1970) used the following terms to classify the fabric of clay.

- Random or Bookhouse fabric (random orientation of clay particles – high face to edge contacts)
- Preferred orientation or Parallel packet fabric (high face-face contacts)

3. Methodology

3.1 Sampling

3.1.1 Sampling Location

Mudstones samples were obtained from a fresh rock exposure at Newport Pavilion – Kentucky (Figure 3.1). Sampling outcrop and the positions of the three sampling cycles in the outcrop are shown in Figure 3.2. The outcrop was excavated by Maxim Constructions. The slope excavation was completed by mid summer 2008. The maximum height of the cut of the slope was 75 feet. The outcrop is Northeast facing. About 12 cycles of the Kope Formation belonging to Upper Ordovician (445–450 Ma) are exposed in the outcrop (Figure 3.3.). Each cycle in the outcrop is defined by the corresponding main limestones bed number (Figure 3.4).

Figure 3.1: Location map of the sampling site, Newport pavilion, Kentucky

(a)

(b)

Figure 3.2: a) Sampling outcrop - Newport Pavilion, Kentucky. The maximum height of the vertical cut is 23 m. Note the van which is about 3 m in height as the scale b) Approximate positions of sampling Cycle 11, 12 and 13 in the outcrop. Total thickness of the three cycles is 5.5 m

Figure 3.3: Cycles of the Kope Formation exposed in the studied outcrop, Newport Pavilion, Kentucky. Height is given in meters above mean sea level. Main limestone beds are numbered from 10 -21 (modified from Brett and Algeo, 2001)

Figure 3.4 – (a) Stratigraphic profile of the three cycles studied in the Kope Formation – Newport Pavilion, Kentucky. Height is given in meters above mean sea level. Each cycle is numbered according to the corresponding main limestone bed number (modified from Brett and Algeo, 2001) (b) Field photograph of the Cycle 11 of the Kope Formation exposed in Newport Pavilion, Kentucky. Note the geologic hammer of 2 feet high as the scale

3.1.2 Sample Collection

Twenty one mudstones samples were obtained from Cycle 12 of the Kope Formation for initial analysis (Figure 3.4). Further sampling was carried out from Cycle 13 (4 samples) and Cycle 11 (5 samples) (Figure 3.4) for total of 30 samples. Mudstones of these cycles have decimeter scale alternate laminated and non-laminated fabric. Samples weighing about 2 kg were collected within 10 cm intervals. Care was taken to select representative portions of both laminated and non-laminated mudstones from each cycle during sampling (Figure 3.5 and Appendix E). As there were no non-laminated mudstones, all the samples collected from Cycle 13 are laminated mudstones. All samples were collected from fresh surfaces obtained by clearing the colluvium and digging back 15-30 cm into the outcrop. Samples were removed using a chisel and geological hammer. Samples were removed with minimum disturbance and wrapped in two plastic bags to ensure retention of field moisture. Natural moisture content of the samples was measured within 2 hours after the collection so that the moisture lost between the sample collection and processing was minimum. Since the studied samples were obtained from a fresh, vertical exposure, they have experienced very little weathering, and effects from environmental conditions should be the same for all samples.

(a)

(b)

Figure 3.5: Mudstones sampled from Cycle 12 of the Kope Formation exposed in the studied outcrop - Newport Pavilion, Kentucky. (a) laminated mudstones – break into thin flakes parallel to the bedding plane (b) non-laminated mudstones – break irregularly into large pieces. Note the scale is in 6 cm for both images

3.2 Laboratory Procedure - Overview

All the samples were analyzed according to the procedure listed in Figure 3.6. A detailed description of each test is given in Appendix D.

Figure 3.6: Overview of all laboratory procedures

4. Results and Discussion

4.1 Slake Durability

In the present study the slake durability of Kope Formation mudstones was measured using the two cycle slake durability test. An earlier study by McFaddin (2008) included some slake durability measurements for the Kope Formation mudstones. He observed a wide range of ID_2 , from 13 to 83% with an average of 57%. He did not explore the geological reasons for this wide range of ID_2 s but studied the correlation between the ID_2 and other geotechnical properties such as unconfined compressive strength (UCS), jar slake index, free swelling potential, swell pressure, particle size distribution, Atterberg limits and the moisture content. Some of the relationships he found are - UCS increases as the ID_2 increases, both ID_2 and UCS decreases with an increase in moisture content. The present study, examined the relationship between slake durability and various geological parameters. As in McFaddin's results, present study data showed a wide range of ID_2 (Figure 4.1). All the samples were classified into different durability categories according to the classification used by Franklin and Chandra, 1972 (Table 4.1).

Figure 4.1: The ID₂ of Kope Formation mudstones belonging to the three cycles (Cycle 11, 12 and 13) plotted against elevation. Elevation is given in meters above mean sea level (AMSL). Samples were categorized according to the classification used by Franklin and Chandra, 1972 (Table 4.1). Standard deviation (SD) = 22, standard error of the mean (SE) = 4

Table 4.1: Durability classification of weak rocks based on ID₂ (Franklin and Chandra, 1972)

Two-cycle slake durability index (ID ₂)	Classification
0-25	Very low
25-50	Low
50-75	Medium
75-90	High
90-95	Very high
95-100	Extremely high

The ID₂ of Cycle 11 and 12 vary greatly, 20% - 90% within a 6 m distance. However a relatively narrow range 40% – 65% of ID₂ was observed for Cycle 13. For the whole sample set the ID₂ does not show any relationship to the elevation. Nevertheless, within Cycle 12 alone, ID₂ shows a significant positive correlation ($r^2 = 0.647$) with elevation. Samples at high elevations from AMSL have higher ID₂ than the samples at lower elevations (Figure 4.2).

Figure 4.2: The ID₂ of Kope Formation mudstones of Cycle 12 plotted with elevation. Elevation is given in meters AMSL

Only the samples from Cycle 12 show this relationship. A wide range of ID₂ was observed within Cycle 12 over 2 m distance. Based on the durability classification (Franklin and Chandra, 1972) one can classify the samples of Cycle 12 into three main groups - high-very high durable, medium durable, low-very low durable. Such distinct groupings were not observed for the samples of Cycle 13 and for Cycle 11 two distinct groups were determined - very low-low durable and medium-high durable. The above data clearly show the wide variability of ID₂ of the Kope Formation mudstones. According to the literature many factors can affect the durability of mudstones (Table 4.2). In order to find the cause for this wide range of variability of the ID₂, chemical, mineralogical, physical and textural properties of the Kope Formation mudstones were studied using Table 4.2 as a guide.

Table 4.2: The effect of different properties of mudstones on its durability based on the reviewed literature

Factor	Effect on the slake durability of rocks	References
Chemistry		
• Degree of weathering	Increase in degree of weathering decreases the durability	Dhakal <i>et al.</i> (2002)
• Total carbonate content	Increases durability. But under acidic conditions, easily dissolved, decreasing the durability	Gokceoglu <i>et al.</i> (2000)
• Total carbon and total sulphur	No effect on durability	Bell <i>et al.</i> (1997)
• Exchangeable cations	Higher the Na^+ content $\rightarrow$ low durability K^+ , Mg^{+2} , Ca^{+2} $\rightarrow$ no significant effect on durability	Bell (2000), Anderson <i>et al.</i> (2010)
Mineralogy		
• Clay minerals	Swelling clays $\rightarrow$ if present, decrease the durability Non-swelling clays $\rightarrow$ no significant effect	Dick and Shakoor (1992), Dhakal <i>et al.</i> (2002)
• Non clay minerals	Quartz $\rightarrow$ provides resistance to abrasion, but decreases the cohesion between particles	Laksharipour and Boomeri (2002)

Factor	Effect on the slake durability of rocks	References
	Feldspar → makes rocks less durable	Laksharipour and Boomeri (2002)
	Pyrite → by oxidation creates large volume changes. Decreases the durability	Pye and Miller (1990)

Physical and Textural Properties

<ul style="list-style-type: none"> Grain size 	<p>If the total clay content is higher than 50% with swelling type clay it affects the durability</p> <p>Higher clay content → lower the durability</p> <p>If total clay content is less than 50% no effect on durability</p>	<p>Moon and Beattie (1995)</p> <p>Gokceoglu <i>et al.</i> (2000),</p> <p>Lashkaripour and Boomeri (2002)</p>
<ul style="list-style-type: none"> Moisture content 	<p>Higher moisture content → low durability</p>	<p>Gurgenli (2006), Diaz-Perez <i>et al.</i> (2007), Erguler and Ulusay (2009),</p>
<ul style="list-style-type: none"> Porosity 	<p>Higher porosity → low durability</p>	<p>Koncagul and Santi (1999)</p>
<ul style="list-style-type: none"> Fabric 	<p>Discontinuous matrix results in lower durability compared to continuous matrix</p>	<p>Huppert (1988)</p> <p>Moon and Beattie (1995)</p>

4.2 Chemistry

According to the bulk chemical data (Table A-1 of Appendix A), the major constituent of all the samples is SiO_2 which ranging from 35 -54 weight percent (wt%). The second most common oxide is Al_2O_3 with 12-17 wt% followed by Fe_2O_3 which is 5-8 wt%. Overall there is no effect of bulk chemistry or sludge chemistry of these mudstones on slake durability. All studied mudstones samples are chemically similar. Although the CaO and P_2O_5 wt% shows rather wide distribution compared to the narrow distribution of other elements (Appendix A), it is not related to the fabric difference of mudstones or to the slake durability of samples. The wide range of CaO wt% and P_2O_5 wt% likely resulted from variations in fossil content, carbonate cement, organic matter content or the presence of small limestone beds within the mudstones. Similarly there is no significant variation in chemistry with respect to the elevation of the mudstones in the Kope Formation. If the samples had been weathered, there should have been a significant difference in chemistry along the vertical profile as more easily weathered elements would be leached from the top of the section relative to deeper samples.

4.2.1 Chemical Index of Alteration (CIA)

The CIA reflects the degree of chemical weathering of a rock. The CIA is calculated by the ratio between Al_2O_3 and the total of $\text{Al}_2\text{O}_3 + \text{K}_2\text{O} + \text{CaO}^* + \text{Na}_2\text{O}$ in molar proportions and expressed in percentage (Nesbitt and Young, 1982). CaO^* is the amount of CaO incorporated in the silicate fraction of the rock. Correction is made for carbonate content. The weight percent data from the XRF and the total carbonate content data of the samples were used for the calculation (Appendix A). The CIA of mudstones of the three cycles were plotted against the ID_2 (Figure 4.3).

Figure 4.3: The ID_2 of Kope Formation mudstones plotted against the chemical index of alteration [$\text{CIA} = \text{Al}_2\text{O}_3 / (\text{Al}_2\text{O}_3 + \text{K}_2\text{O} + \text{CaO}^* + \text{Na}_2\text{O})$]. Molar proportions of the oxides were used for the calculation (Nesbitt and Young, 1982)

CIA of mudstones shows a narrow range of values (44-66%) excluding the two outliers on the low side, which contain relatively higher CaO weight compared to other samples. CIA does not show any relationship to the slake durability in these samples, likely because the range of CIA values is so small. According to Nesbitt and Young (1982) more clay bearing completely weathered rocks have CIA values of 100%. Based on the data of the present study the Kope Formation mudstones show CIA values ranging from 43-64% (average 50%) indicating a low degree of chemical weathering. The narrow range of CIA suggests that all the samples have a similar degree of chemical weathering. Therefore this eliminates the effect of chemical weathering on slake durability of the studied samples.

4.2.2 Total Carbonate Content

Total carbonate content of the Kope Formation mudstones was plotted against the ID₂ (Appendix B). The total carbonate measures the amount of carbonates in individual carbonate minerals, fossils as well as in the cement, material which bind the grains together in a rock. Carbonate cement provides strength to the rock and hence increases the durability (Table 4.2). However, in acidic conditions the presence of carbonate cement makes the rocks less durable due to the dissolution of carbonates in acidic environments. According to the present study a trend of higher carbonate content was observed in samples with higher ID₂. However, this relationship is not significant ($r^2 = 0.382$) perhaps because the present study measures the total carbonate content but not the carbonate cement of the of the Kope Formation mudstones.

4.2.3 Total Carbon and Total Sulphur

The total carbon and sulphur contents of mudstones are an important control on physical properties. Floor heave induced by sulphide and sulphate bearing minerals such as pyrite, chalcopyrite, gypsum and jarosite causes low durability in many rocks especially, mudstones. Many researchers indicated the influence of sulphur bearing minerals on mudstones durability (Taylor (1988), Pye and Miller (1990), Bryant (2003), Anderson (2008), Hoover and Lehmann (2009), Song and Zhang (2009)). Carbon content plays an important role in the durability of mudstones in terms of absorbing moisture. Molinda *et al.* (2008) compared the moisture sensitivity among black and grey shales. According to their results black shales have much lower moisture content than grey shales due to the presence of high total organic carbon in grey shales. The total carbon and total sulphur contents of Kope Formation mudstones did not show any correlations with the ID₂ (Appendix B). This may be due to the quite small range of carbon and sulphur content of the Kope Formation mudstones (Appendix A). A study of Coal Measures mudstones by Bell *et al.* (1997) similarly found that there is no influence by the total carbon and total sulphur on the durability of mudstones.

4.2.4 Exchangeable Cations

Exchangeable cations in clay minerals play an important role in mudstones durability (Bell, 2000). The concentrations of exchangeable Na^+ and K^+ of the mudstones were plotted against the ID_2 (Figure 4.4 and 4.5). The concentrations of both Na^+ and K^+ show a strong negative correlation with the ID_2 .

Figure 4.4: Concentrations of water soluble Na^+ measured in parts per million (ppm) plotted against the ID_2 of the Kope Formation mudstones

Figure 4.5: Concentrations of water soluble K⁺ measured in parts per million (ppm) plotted against the ID₂ of the Kope Formation mudstones

Mudstones having low ID₂ yield higher concentrations of exchangeable Na⁺ and K⁺, whereas mudstones with high ID₂ yield low concentrations of exchangeable cations. However the corresponding relationship was not observed in the bulk chemistry data of the samples. All the studied samples have similar Na₂O and K₂O content. This implies the low durable mudstones have more exchangeable Na⁺ and K⁺ than occurs in high durability mudstones although the bulk concentrations are similar. Anderson *et al.* (2010) described the role of Na⁺

and K^+ of swelling clays when interacting with water. Na^+ saturated smectite absorb water to interlayer positions to maintain the cation equilibrium which results in large volume changes (osmotic swelling). The water absorption depends on the hydration energy of the cation. Since Na^+ has higher hydration energy than of K^+ , Na^+ bearing clays absorb more water and increase volumes more than the K^+ bearing clays. Since no pure smectites were identified in the present study it is not clear how Na^+ and K^+ are acting in this case. Note that about twice as much K^+ as Na^+ appears in the water. However, the K_2O / Na_2O ratio in the sludge and the bulk rock is about 8:1 (Appendix A). Therefore, Na^+ is much more easily leached from Kope mudstones than is K^+ .

4.3 Mineralogy

According to Dick and Shakoor (1992), Gokceoglu *et al.* (2000), Lashkaripour and Boomeri (2002) and Dhakal *et al.* (2002) mineralogy is one of the principal factors that affect the durability of rocks. Especially the presence of swelling type clay minerals decreases the durability of rock (Table 4.2). According to powder XRD analysis of the Kope Formation mudstones, illite and chlorite are the dominant clay minerals. Chlorite and kaolinite are difficult to differentiate due to the similar d-spacing of the kaolinite 001 and chlorite 002 at 7 Å and kaolinite 002 and chlorite 004 at 3.5 Å. If the both minerals are present it indicates by the doublet in 3.5 Å peak (Moore and Reynolds, 1997). Since no doublet 3.5 Å peak was observed in XRD traces of any of the Kope mudstones it is confirmed that there is no kaolinite but only chlorite present in these samples. The asymmetrical 10 Å peak of the illite has a broad shoulder (Figure 4.4) which indicates the presence of mixed layer clays (Bassarab and Huff, 1969). Relative percentages of illite and chlorite were calculated by the MacDiff software using the areas of 10 Å and 14 Å peaks of the two minerals respectively (Appendix A). All the samples have similar relative proportions of illite to chlorite. Thus, all the studied samples appear to be similar mineralogically (Figure 4.6). Calcite, quartz and feldspar were the non-clay minerals identified in these samples.

4.3.1 Clay Minerals

Dick and Shakoor (1992) stated that mixed layer illite-smectite encountered in shales accounts for their durability along with other factors such as the void ratio. Dhakal *et al.* (2002) observed smectite, a swelling clay, in their samples and concluded that the slaking behavior of argillaceous (clay bearing) rocks is largely controlled by their mineralogical properties. Gokceoglu *et al.* (2000) observed smectite in their samples. They concluded that type as well as the amount of clay affects the large scale variation in the durability of a rock. The presence of smectite decreases the durability of rocks due to its swelling nature. Although pure smectites were not observed in the Kope Formation mudstones, the presence of mixed layer clays may decrease the slake durability as stated by Dick and Shakoor (1992).

Swelling of clay can occur due to two mechanisms - crystalline swelling or osmotic swelling (Anderson *et al.*, 2010). Crystalline swelling can occur in any type of clay. It occurs when three or four successive layers of water molecules line up in the interlayer position as a consequence of the initial hydration of interlayer exchangeable cations in the presence of low water content, resulting in an increase in the interlayer spacing (Anderson *et al.*, 2010). But this does not cause significant volume changes in the structure. Osmotic swelling, on the other hand, occurs if the cation concentration is higher in the interlayer position than in the surrounding pore spaces. In this situation, water will absorb into inter-layer positions to dilute the higher concentrations resulting in significant volume changes. These volume changes, especially during alternate wetting and drying conditions, decrease the bonding strength and weaken the crystalline structure causing low durability in rocks (Anderson *et al.*, 2010). The osmotic

swelling that occurs in smectite group clays can cause especially large volume increases. However, argillaceous rocks that do not contain any swelling clays show large variation in slake durability. This reflects the fact that the swelling of clay is not the only factor governing the slake durability of rocks. Bell *et al.* (1997) did not observe any swelling clays in their study of British Coal Measures mudstones but still observed a range of slake durability indexes. They concluded that the mineralogy is not the only factor that governs the rock slake durability.

The small volume changes develop in illite and chlorite as a result of crystalline swelling upon wetting may have an effect on the lower slake durability of Kope mudstones as they are rich in illite and chlorite. However, as the relative proportions of illite and chlorite are similar in all the samples, the wide variability of ID₂ observed in the present study cannot be explained only with the swelling effect caused by these minerals. According to XRD data there is a very minor (unquantifiable) amount of mixed layer clays in the Kope mudstones. Therefore, osmotic swelling occurring in these mixed layer clays may have a very small contribution on the lower slake durability of the Kope Formation mudstones. Based on the above factors, one can conclude that the mineralogy is not the dominant factor that governs the slake durability of Kope Formation mudstones.

4.3.2 Non-clay Minerals

4.3.2.1 Oxidation of Pyrite

Pyrites observed in most of the Kope Formation mudstones via SEM only. Bulk chemical analysis showed that the total sulphur content of these samples are very low (<1%). Therefore, the amount of pyrite present in these rocks is low. The absence of relevant peaks of pyrite in XRD data proves the low pyrite contents of these samples. However, the presence of pyrite in mudstones can significantly affect their stability. Pye and Miller (1990) studied the effect of pyrite oxidation during the weathering of mudstones. Taylor (1988) also notes the importance of pyrite for mudstones durability.

The sulphuric acid produced from oxidation of pyrite dissolves the carbonate component of mudstones. This sulphuric acid attacks the octahedral layer of clays and enhances the ion exchange and dissolution of clay minerals. Under acid weathering conditions, chlorite can be altered to swelling chlorites and illites and can be degraded to expandable mixed –layer clays (Pye and Miller, 1990) which lower the durability. In mudstones with both pyrite and calcite, pyrite oxidation can produce gypsum which increases the volume of rock. Taylor (1988) summarized the crystalline solid expansion due to mineral alteration. Jarosite, melanterite and anhydrous ferrous sulphate formed by pyrite alteration increase volumes by 115%, 536% and 350% respectively. Gypsum formed by the alteration of calcite can increase 103% of the volume. Therefore pyrite oxidation can cause significant volume changes in rocks by the formation of minerals such as gypsum and other sulfates. Since the studied samples contain low amounts of pyrites the effect of pyrite oxidation on the slake durability of the Kope Formation mudstones is not significant.

4.4 Physical Properties

4.4.1 Grain Size

4.4.1.1 Total Clay Content

Different classification systems use different particle sizes to define the clay size fraction of a rock. According to the sedimentological classifications (Wentworth scale) particles less than 4 μm are considered as the clay fraction of a rock (Selley, 1988) whereas in engineering and engineering geological classification it is defined as the less than 2 μm fraction. According to ASTM standards particles less than 5 μm are considered as clays (Reeves *et al.*, 2006). In the present study the ASTM standard classification is used to define the clay fraction of mudstones.

Previous studies revealed that the amount of clay in a rock affects its durability. A strong negative correlation between the amount of swelling clays and the ID_2 of rocks is pointed out by Dick and Shakoor (1992), Gokceoglu *et al.* (2000) and Lashkaripour and Boomeri (2002). However, there appears to be no correlation between the ID_2 and the amount of clay when there is no swelling type clays present in a rock, as in the Kope Formation mudstones. According to Dick and Shakoor (1992), if a mudstone consists less than 50% clay size particles, the influence of clay minerals on its durability is diminished. Clay content of the studied samples ranged from 17-54%, with a median of 38% (According to Scotford (1965) the average clay content of the Kope Formation mudstones is 38%). Almost all samples have less than 50% clay, so the effect of clay on durability of the Kope mudstones is reduced compared to clay-rich mudstones. There is no statistical significant correlation between the ID_2 and the total clay percentage ($r^2 = 0.345$) of the Kope Formation mudstones.

4.4.1.2 Grain Size Distribution of the Fine Fraction of Kope Formation Mudstones

Fine fraction of a rock (particle size less than 63 μm) consists of both clay and silt sized particles. According to Wentworth's classification particles between 4 – 63 μm are classified as the silt fraction (Selley, 1988). According to the data, there is no significant difference in grain size distribution of the finer fraction of all the studied samples (Appendix C). Therefore one can assume that the effect of the finer particles of the Kope Formation mudstones on their slake durability is negligible.

4.4.1.3 Grain Size Distribution of Illite Based on X-Ray Diffraction Data

Illite is the most abundant clay mineral found in all the studied mudstones of the Kope Formation (Appendix A). Therefore the size of illite grains was measured in order to study the fabric differences of mudstones which in turn affect their slake durability. The variations of the source sediment or sediment transport mechanisms of the Kope mudstones will be reflected in the thickness variations of illite grains. Hence the mean thickness of illite grains was calculated using the MudMaster software using the XRD data of samples (Appendix A). However, there is no correlation between the mean thicknesses of illite grains and the ID_2 of mudstones (Appendix B).

4.4.2 Moisture Content

The moisture content of a rock exerts a strong effect on strength and deformability. Many researchers have studied the influence of water content on mechanical properties of rocks. Gurgunli (2006), Diaz-Perez *et al.* (2007) and Erguler and Ulusay (2009) studied the influence of initial moisture content on the strength of rocks. According to Diaz-Perez *et al.* (2007), the moisture content of a rock can affect its strength and the durability in five processes - reducing fracture energy, decreasing capillary tension, increasing pore pressure, reducing the friction between particles and deteriorating the rock chemically and mechanically. Seedsman (1986) conducted a detailed analysis about how the differences in water content influence the durability of Na and Ca bearing shales. The moisture content (Appendix A) of the Kope Formation mudstones was calculated according to both geotechnical engineering formula and geological formula.

Geotechnical Engineering Formula,

Moisture Content = (Weight of the moisture/ Weight of the dry sample) x 100

Geological Formula

Moisture Content = (Weight of the moisture/ Initial weight of the sample) x 100

The moisture content values calculated according to the geotechnical engineering formula were used in the Figures. The moisture content of the studied samples varies from about 2-10%. The variation of moisture content of the Kope Formation mudstones with the elevation is

presented in Figure 4.7 and the variation of the moisture content of mudstones with their ID₂ is plotted in Figure 4.8.

Figure 4.7: Moisture content of mudstones belonging to the three cycles (Cycle 11, 12 and 13) of the Kope Formation plotted against elevation. Elevations are given in meters AMSL

Although overall there is a trend of decreasing moisture content with increasing elevation, the correlation is not statistically significant. However, for individual cycles, the

moisture content of the samples of Cycle 12 ($r^2 = 0.601$) and 13 ($r^2 = 0.605$) are well correlated with elevation. There is no such correlation observed in mudstones of Cycle 11. These observations could be a result of the difference in the texture of samples. Mudstones of the Cycle 12 have more systematic variation in texture, high elevated samples are laminated mudstones and the low elevated ones are non-laminated mudstones, whereas Cycle 11 does not have such systematic variation of texture with elevation. However, in Cycle 13 all the collected samples are laminated mudstones and still one observed a moisture content variation with the elevation.

Figure 4.8: Moisture content versus ID₂ of the Kope Formation mudstones belong to three cycles (Cycle 11, 12 and 13)

Moisture content of the Kope Formation mudstones is strongly correlated ($r^2 = 0.80$) with the ID₂. According to the data, mudstones that have high moisture contents show low ID₂ whereas mudstones that contain low moisture contents show high ID₂. This indicates that mudstones with higher moisture contents are less durable than those with lower moisture contents. The moisture content of a rock is highly dependent upon its porosity. Seedsman (1986) pointed out that the moisture content of shales which do not contain Na-bearing swelling clays gives a measure of their initial porosity. Therefore in this study, the moisture content of the Kope Formation mudstones can be taken as a measure of the porosity as they contain very low (non quantifiable) amounts of mixed layer clays. Based on the facts discussed above, some of the Kope mudstones have significantly higher porosity than others. This is supported by SEM observations, which will be discussed in section 4.4.3.

4.4.3 Fabric

When collecting the samples, it was noted that there were two distinct fabric types present in the Kope Formation mudstones - samples readily break into thin flakes parallel to the bedding (laminated mudstones) [Figure 3.5 (a)] and samples break irregularly into blocks (non-laminated mudstones) [Figure 3.5(b)]. Subsequently it was noted that ID₂ of non-laminated mudstones was consistently lower compared to ID₂ of laminated mudstones. The ID₂ of Kope Formation mudstones plotted against elevation considering their laminated and non-laminated nature is given in Figure 4.9.

Figure 4.9: The ID₂ of Kope Formation mudstones belong to three cycles (Cycle 11, 12 and 13) plotted against elevation. Elevation is given in meters AMSL. Closed and open symbols represent laminated and non-laminated mudstones respectively. Standard deviation (SD), standard error of the mean (SE) and the mean value of both types of mudstones are given in the Figure

Most laminated mudstones belong to the medium- very high durable category whereas all non-laminated mudstones fall into the very low- medium durable category according to the classification used by Franklin and Chandra, 1972 (Table 4.1). The mean ID₂ of laminated mudstones is 71.2% whereas in non-laminated mudstones it is 38.4%. According to the “Two-sample t-test” the ID₂ of laminated and non-laminated mudstones are significantly different ($p < 0.05$) within the 95% confidence level. This reflects the effect of the laminated and non-laminated nature (fabric) of mudstones on its slake durability. Selected mudstones samples belonging to the three cycles Cycle 11, 12 and 13 of the Kope Formation were analyzed using the SEM. Micro-structural classification systems of Huppert (1988), Moon and Beattie (1995) and Sloane and Kell (1966) were used to describe the micro-structural characteristics of these samples.

Huppert (1988) proposed three main types of microfabrics; skeletal, matrix and turbostratic. Moon and Beattie (1995) modified the above classification by adding laminar fabric. The combined classification is given below in Figure 4.10. Another classification system proposed by Sloane and Kell (1966) used two main types of fabrics - random book-house and oriented parallel packet fabric. This classification is based on the arrangement of clay flakes such as face-face contacts and edge-face contacts. If significantly higher amounts of edge-face contacts between clay flakes are visible, then that type of fabric is known as book house or random orientation fabric. In 1969, Parham and Austin used the term card-house to define the same fabric. If the face – face contacts are prominent then it is named as parallel packet or an oriented fabric (Sloane and Kell, 1966). Characteristics of the fabrics described above were used in the present study to define the fabric of Kope Formation mudstones.

Figure 4.10: Micro-fabric classification of rocks (Moon & Beattie, 1995 and Huppert, 1988).

All the samples examined from the Kope Formation mudstones have a continuous matrix, that is, all the grains are completely surrounded by a clay matrix. Therefore, matrix, turbostratic and laminar are the three fabric types observed among the selected samples of the Kope Formation mudstones. Based on the SEM images of the Kope Formation mudstones a clear difference in fabric was observed. When comparing the fabrics to the ID₂, the following relationships were identified.

- Non-laminated mudstones with matrix / random / card house microfabric (Figure 4.11) have,
 - wide angles of edge-face contacts between clay flakes
 - relatively high porosity
 - surface area is more disturbed and irregular
 - low ID₂

- Laminated mudstones with turbostratic /oriented/ parallel packet microfabric (Figure 4.12) have,
 - good face-face contacts between clay flakes
 - very low porosity
 - flat and undisturbed surface area
 - high ID₂

- Laminated mudstones with laminar microfabric (Figure 4.13) have,
 - both edge-face contacts and face-face contacts between clay flakes
 - at some places clusters of stacks of clay flakes with face-face contacts are oriented at an angle to the plane making irregular surfaces (Figure 4.14)
 - moderate ID₂

(a)

(b)

Figure 4.11: SEM image of non-laminated mudstones of Cycle 12 of the Kope Formation (a) fabric is similar to matrix type (Moon and Beattie, 1995 and Huppert, 1988) or book house fabric (Sloane and Kell, 1966). The width of the image is 45 μm (b) enlarged portion of non-laminated mudstone of Cycle 12 showing wide angles of edge-face contacts between clay flakes. The width of the image is 5 μm

(a)

(b)

Figure 4.12: SEM image of laminated mudstones of Cycle 12 of the Kope Formation (a) fabric is similar to the turbostratic (Moon and Beattie, 1995 and Huppert, 1988) or parallel packet fabric (Sloane and Kell, 1966). Face-face contacts between clay flakes are dominant. The width of the image is 55 μm (b) an elongated pore space of a laminated mudstone of Cycle 12. The width of the image is 18 μm

Figure 4.13: SEM images of laminated mudstones with laminar fabric (Moon and Beattie, 1995). Both face-face contacts and face-edge contacts between clay flakes can be observed. (a) laminated mudstone of Cycle 11 of the Kope Formation. The width of the image is 50 μm (b) laminated mudstone of Cycle 13 of the Kope Formation. The width of the image is 70 μm

Figure 4.14: SEM image of moderately durable laminated mudstones of Cycle 12 of the Kope formation showing the arrangement of stacks of clay flakes having face-face contacts oriented at an angle to the surface. The width of the image is 22 μm

Parham and Austin (1969) in their study of the Decorah Shale observed that mudstones with clays oriented parallel to the bedding plane are relatively impermeable perpendicular to the bedding. However, these mudstones are permeable parallel to the bedding. In contrast, mudstones having clays with random orientation are permeable in all directions. Therefore the laminated mudstones with fairly-well oriented clay minerals (parallel packet or turbostratic fabric) are less permeable than the non-laminated mudstones with random oriented clays (book-house/ card-house or matrix type fabric). Because the permeability is high, non-laminated mudstones tend to break rapidly compared to the laminated mudstones when interacting with water. Hence laminated mudstones, having well oriented clays, are more durable than the non-

laminated mudstones with randomly oriented clays. Moon and Beattie (1995) observed a similar relationship between the fabric and the slake durability of Waikato Coal Measures mudrocks.

The slake durability of mudstones is related to the porosity difference associated with the different types of fabrics. Porosity is relatively high in non-laminated mudstones with random or book-house fabric compared to the laminated mudstones with oriented or parallel fabric. Permeability also likely depends on the fabric and significantly affects the slake durability of a rock (Marques *et al.*, 2005). The moisture content of the Kope Formation mudstones supports this idea. Therefore it would appear that the fabric is the primary control of the slake durability of the Kope Formation mudstones which are lack of swelling clays. All the above discussed factors clearly show the significance of fabric in the slake durability of the Kope Formation mudstones.

Another important feature observed among these mudstones in the SEM is the presence of pyrite crystals. However, both types of mudstones contain pyrite. These pyrite differed in size were arranged as framboids; densely packed, spherical aggregates of sub-micron sized pyrite crystals (Wilkin *et al.*, 1996). Areas around pyrite framboids is highly disturbed (Figure 4.15). The presence of pyrite is important for the stability of a rock as discussed in section 4.3.2.1. However, as the studied samples have very low amounts of pyrites, the pyrite oxidation is not significantly affecting their slake durability.

Figure 4.15: SEM image of pyrite framboids in non-laminated mudstones from Cycle 12 of the Kope Formation. Black arrows pointed the pyrite framboids. Note that areas surrounding pyrite grains are highly disturbed. The width of the image is 40 μm

The effects of different properties on the durability of mudstones were studied using Table 4.2 as a guide. In addition to the properties listed in Table 4.2, the effect of degree of lamination of mudstones on its slake durability was studied in the present study. Number of chemical, mineralogical and physical properties of the Kope Formation mudstones tested in the present study and their effects on the slake durability is given in Table 4.3. In addition conclusions of previous studies about rock durability is listed there as a comparison.

Table 4.3: The effect of different properties on the durability of Kope Formation mudstones - summary and a comparison of the present study data with reviewed literature

Factor	Effect on the slake durability of rocks – found in literature	Observations of the present study
Chemistry		
<ul style="list-style-type: none"> Degree of weathering 	Increase in degree of weathering decreases the durability	Degree of chemical weathering is same for all samples.
<ul style="list-style-type: none"> Total carbonate content 	Carbonate cement increases durability. But under acidic conditions, easily dissolved, decreasing the durability	No significant correlation with the ID ₂ .
<ul style="list-style-type: none"> Total carbon and total sulphur 	No effect on durability	Narrow variation among samples. No correlation with the ID ₂ .

Factor	Effect on the slake durability of rocks – found in literature	Observations of the present study
<ul style="list-style-type: none"> Exchangeable cations 	<p>Higher the Na^+ content $\rightarrow$ low durability</p> <p>K^+, Mg^{2+}, Ca^{2+} $\rightarrow$ no significant effect on durability</p>	<p>Higher Na^+, K^+ $\rightarrow$ low ID_2</p>

Mineralogy

<ul style="list-style-type: none"> Clay minerals 	<p>Swelling clays $\rightarrow$ if present, decrease the durability</p> <p>Non-swelling clays $\rightarrow$ no significant effect</p>	<p>No swelling clays were observed. Relative proportions of illite and chlorite are similar in all the samples. No effect on slake durability.</p>
<ul style="list-style-type: none"> Non clay minerals 	<p>Quartz $\rightarrow$ provides resistance to abrasion, but decreases the cohesion between particles</p> <p>Feldspar $\rightarrow$ makes rocks less durable</p> <p>Pyrite $\rightarrow$ by oxidation creates large volume changes and decreases the durability</p>	<p>Present study observed constant SiO_2 wt% among all the samples. The Al_2O_3: SiO_2 ratio is similar in all the samples. No correlation to the slake durability.</p> <p>Total S content is less than 1%. Therefore very low amount of pyrite. No effect on slake durability of Kope mudstones.</p>

Factor	Effect on the slake durability of rocks – found in literature	Observations of the present study
Physical and Textural Properties		
<ul style="list-style-type: none"> Grain size 	<p>If the total clay content is higher than 50% with swelling type clay it affects the durability</p> <p>Higher clay content → lower the durability</p> <p>If total clay content is less than 50% no effect on durability</p>	<p>Average total clay content is 40%. No effect on slake durability.</p> <p>Grain size distribution of the fine fraction (<0.049 mm) is uniform and no effect on the slake durability.</p> <p>The mean grain size of illite (most abundant clay mineral of the Kope mudstones) does not vary among the studied samples.</p>
<ul style="list-style-type: none"> Moisture content 	<p>Higher moisture content → low durability</p>	<p>No effect on the slake durability.</p>
<ul style="list-style-type: none"> Porosity 	<p>Higher porosity → low durability</p>	<p>Strong negative correlation between the moisture content and ID₂. Non-laminated mudstones with higher porosity (as observed in SEM) are less durable compared to the laminated mudstones with low porosity.</p>
<ul style="list-style-type: none"> Fabric 	<p>Discontinuous matrix results in lower durability compared to continuous matrix</p>	<p>All the samples have continuous matrix, yet observed a wide range of ID₂.</p>

Factor	Effect on the slake durability of rocks – found in literature	Observations of the present study
<ul style="list-style-type: none"> Degree of lamination 	No literature was found	<p>Laminated mudstones are more durable compared to non-laminated mudstones. Laminated mudstones that have turbostratic fabric are more durable compared to the non-laminated mudstones that have matrix fabric.</p>

4.5 Fabric Types and Formation Mechanisms

Two main fabrics types observed in the Kope formation mudstones (laminated and non-laminated) may be a result of different depositional mechanisms and the degree of compaction. Four possible primary mechanisms of formation of the two fabric types are discussed below.

1. Changes in salinity of water (White, 1961)
2. Storm driven currents and bottom flowing gradient currents ((Kohrs *et al.*, 2008)
3. Changes in rate of sedimentation (Parham and Austin, 1969)
4. Degree of bioturbation (O'Brien, 1987)

4.5.1 Changes in Salinity of Water

The excess negative charge present on the surface creates an electrostatic repulsion between clay flakes. When entering to highly saline water, clay flakes tend to flocculate quickly because the large concentrations of positively charged ions present in saline water counteract the electrostatic repulsion forces between them (Potter *et al.*, 2005). These floccules then deposit making in a random orientation (Figure 4.16 a). In fresh water or if the salinity of the water is not sufficient enough to flocculate, individual flakes deposited with parallel orientation (White, 1961) (Figure 4.16 b). As the sea water-fresh water boundary moves over time, the clay flakes entering to environments such as estuaries, lagoons tend to deposit alternatively in random and parallel orientations.

Figure 4.16: Illustration of deposition of clay flakes in a sedimentary basin. (a) in saline water clay floccules deposited making in a random orientation (b) in fresh water individual clay flakes deposited making parallel orientation

4.5.2 Storm Driven Currents and Bottom Flowing Gradient Currents

Storm driven currents bring both silt and clay into sedimentary basins. The presence of silt grains prevents the collapse of clay floccules resulting in a random orientation (Kohrs *et al.*, 2008) (Figure 4.17 a). On the other hand clay floccules in less silt rich environments will be collapsed more easily and resulted parallel orientation. Kohrs *et al.* (2008) cited another mechanism for the parallel orientation of clay flakes. Clay rich sediments in diluted plumes detached from bottom flowing gradient currents start to settle when the flow velocity decreases. The rapid deposition would collapse the clay floccules resulting in a parallel orientation. However, the bottom flowing gradient currents can disrupt this parallel orientation (Figure 4.17 b).

Figure 4.17: The effect of storm driven currents on the fabric formation (a) silt grains buttress the clay floccules from collapsing and resulting in a random orientation (b) bottom flowing gradient currents disturb the parallel orientation of clay flakes

4.5.3 Changes in Rate of Sedimentation

In a high sediment accumulating environment, clay floccules settle to the sea floor and are compacted by the weight of the overlying sediments resulting in a preferred or parallel fabric (Figure 4.18). In an environment with slow sediment accumulating, the bonds between the clay flakes in adjacent clay floccules are strengthened. If the slow sediment accumulation exist for extended periods of time these bonds become stronger and prevent the collapse of floccules by overlying sediments (Figure 4.19). This results in the random orientation of clay flakes (Parham and Austin, 1969).

Figure 4.18: Illustration of the formation of preferred orientation of clay flakes in high sediment accumulating environments

Figure 4.19: Illustration of the formation of random orientation of clay flakes in low sediment accumulating environment

4.5.4 Degree of Bioturbation

Organisms living in oxic water burrow into sediments, changing the preferred orientation of clay flakes into random orientation (O'Brien, 1987) (Figure 4.20). Under an anoxic or low oxygen environment, the growth of organisms is restricted hence the effect of bioturbation is not significant. Therefore the preferred orientation of clay flakes remains undisturbed. During high rates of sediment accumulation, burrowing organisms cannot burrow into sediments hence the parallel fabric of clay flakes preserved. However, in slow sediment accumulating environments burrowing organisms have sufficient time to burrow into sediments, disrupting the preferred orientation of clay flakes.

Figure 4.20: Illustration of the effect of degree of bioturbation on the orientation of clay flakes

4.5.5 Mechanisms Applicable for the Fabric Difference of the Kope Formation Mudstones

There is no regular pattern between the two fabric types – laminated mudstones and non-laminated mudstones within the three cycles studied. Therefore, we can suggest that the fabric differences of clay flakes of laminated and non-laminated mudstones in the studied outcrop might have resulted from one or more of the mechanisms described above. However, based on the other factors such as grain size distribution and the nature of the fossils (undisturbed graptolites, crinoids) observed in the mudstones we can eliminate the effect of storm driven currents on fabric formation of Kope Formation mudstones. Therefore, the changes in rate of sedimentation and the bioturbation are the most likely explanations for the formation of the two fabric types in the Kope Formation mudstones. However, a detailed sedimentological analysis is required to confirm these hypotheses.

5. Conclusions

Based on the observations and data obtained from studying the chemical, mineralogical, physical and textural properties and the ID₂ of the Kope Formation mudstones, the following conclusions can be made.

1. Kope Formation mudstones can be categorized into two main types based on their macro-fabric - laminated and non-laminated. According to Huppert, 1988 and Moon and Beattie, 1995 classifications, laminated mudstones have turbostratic fabric whereas non-laminated mudstones have matrix fabric. The ID₂ of the laminated mudstones (71.18%) and non-laminated mudstones (38.43%) are significantly different. Non-laminated mudstones are less durable and slake rapidly compared to laminated mudstones.
2. It appears that both fabric types of Kope Formation mudstones are chemically similar. None of the chemical variables shows a good correlation with the slake durability of mudstones. Therefore, based on these data we can conclude that chemical properties of the Kope Formation mudstones do not affect their slake durability.
3. There was no mineralogical variation among the Kope Formation mudstones. Therefore, the effect of mineralogy on the slake durability of these mudstones is negligible. However, the presence of pyrite can significantly affect the durability upon chemical weathering of mudstones. The Kope Formation mudstones contain low pyrites (total sulphur content < 1%) hence the effect of pyrite oxidation on the slake durability is not significant in these rocks.

4. No swelling behavior was observed in either type of mudstones in the Kope Formation.

As the Kope Formation mudstones do not contain significant amounts of swelling clays, there is no effect of the clay component on the slake durability of mudstones.

5. The moisture content significantly affects the slake durability of the Kope Formation mudstones. According to Seedsman (1986) the moisture content of a rock which does not contain Na-bearing swelling clay gives a measure of its porosity. Hence the porosity and the moisture content of Kope Formation mudstone significantly affect its slake durability.
6. The fabric difference of laminated and non-laminated mudstones might have resulted from the degree of bioturbation, changes in rate of sedimentation or as a mixing of both events. A higher degree of bioturbation and low sedimentation rates creates random orientations of clay flakes, resulting in the high porosity in non-laminated mudstones. Laminated mudstones deposited at high sedimentation rates and under anoxic or sub-oxic conditions may not have been subjected to bioturbation and hence have well oriented clay flakes and less porosity. These same laminated mudstones are likely to have been deposited in deeper water where they received less agitation by ocean currents.
7. Considering all these factors, it is postulates that the high pore-water pressure created inside the pore spaces in mudstones rapidly fractures the rock upon contact with water (mechanical weathering). Since the porosity of the non-laminated mudstones is higher

compared to the laminated mudstones, the breakdown process upon contacting with water is more rapid in non-laminated mudstones compared to laminated mudstones.

8. The effect of above properties of the Kope Formation mudstones on their slake durability may differ according to the degree of weathering of sample. All these conclusions are valid only for fresh mudstones of the Kope Formation. For weathered mudstones the effect of mineralogy, chemistry may play a significant role on the durability other than the effect of textural properties (Taylor, 1988, Pye and Miller, 1990, Bhattarai *et al.*, 2006, Nandi and Whitelaw, 2009).

6. Future Studies

Studying the effect of rate of disintegration of mudstones on the slake durability is important. The change of slake durability with age of the core will be helpful in predicting the durability of mudstones without performing the slake durability test. This will eliminate the necessity of measuring the slake durability index of fresh core samples. If the slake durability of an old core sample is known, one can estimate the slake durability of the same sample when it was fresh. On the other hand a figure of age of the core versus slake durability will provide information about the durability of the same mudstones after a certain time that will be more important for geotechnical engineering purposes.

The vertical and lateral extent of both laminated and non-laminated mudstones and other lithologies of all the sub members of the Kope Formation should be studied. The relative proportion of each fabric type and lithology should be measured. Based on that data one can assign average values for different geotechnical properties such as slake durability, unconfined compressive strength, moisture content etc. to each sub member in the Kope Formation. The average value of each property assigned for each sub member will be more useful for geotechnical engineering purposes.

A simple quantitative assessment should be developed to differentiate the laminated and non-laminated mudstones in the field. Such a quantitative measurement will be helpful for non-geologists to identify the two mudstone types easily in the field and to compare the two mudstones types in different regions undoubtedly.

7. References

Anderson R.L., Ratcliffe I., Greenwell H.C., Williams P.A., Ciffe S., Coveney P.V., 2010.

Clay swelling-A challenge in the oil field. *Earth-Science Reviews*. 98. 201-216.

Anderson W.H., 2008. Foundation problems and pyrite oxidation in the Chattanooga Shale, Estill County, Kentucky. Report of Investigation 18. Series xii. Kentucky Geological Survey.

Agnello T., 2005. Historic rock quarries and modern landslides in Price Hill, Cincinnati. *Ohio Geology News Letter*. No.2. Ohio Department of Natural Resources, Division of Geological Survey.

Bassarab D.R., Huff W.D., 1969. Clay mineralogy of Kope and Fairview Formations (Cincinnati) in the Cincinnati area. *Journal of Sedimentary Petrology*. 39. 1014-1022.

Baum R.L., 1994. Contribution of artesian water to progressive failure of the upper part of the Delhi Pike landslide complex, Cincinnati, Ohio: U.S. Geological Survey Bulletin 2059-D. D1-D14.

Baum R.L., Johnson A.M., 1996. Overview of landslide problems, research and mitigation Cincinnati, Ohio area. U.S. Geological Survey Bulletin. 2059-A. A1-A33.

Bell F.G., 2000. Engineering Properties of Soils and Rocks (4th Ed). Blackwell Science Ltd, Oxford. 482 p.

Bell F.G., Entwisle D.C., Culshaw M.G., 1997. A geotechnical survey of some British coal measures mudstones, with particular emphasis on durability. *Engineering Geology*. 46. 115-129.

Bhattarai P., Marui H., Tiwari B., Watanabe N., Tuladhar G.R., 2006. Influence of Weathering on Physical and Mechanical Properties of Mudstone. *In*: Marui H., ed., Disaster Mitigation of Debris Flows, Slope Failures and Landslides. 2. 467- 479.

Brett, C.E. and Algeo, T.J. 2001. Stratigraphy of the Upper Ordovician Kope Formation in its type area (Northern Kentucky), including a revised nomenclature. *In*: Algeo, T.J. and Brett, C.E. eds., Sequence, cycle, & event stratigraphy of upper Ordovician & Silurian strata of the Cincinnati Arch region. Kentucky Geological Survey, Field Trip Guidebook, Series 12, Guidebook 1.

Brett C.E., Algeo T.J., McLaughlin P.I., 2008. Use of event beds and sedimentary cycles in high resolution stratigraphic correlation of lithologically repetitive successions - the Upper Ordovician Kope Formation of Northern Kentucky and Southern Ohio. *In*: Harries P.J., ed., High-Resolution Approaches in Stratigraphic Paleontology. 21. 315-350.

Bryant L., 2003. Geotechnical problem with pyritic rock and soil. Master's thesis. Virginia Polytechnic Institute and State University, Blacksburg, Virginia. 242 p.

Chen P., 1977. Table of key lines in X-ray powder diffraction patterns of minerals in clays and associated rocks. Geological Survey Occasional Paper 21. Indiana Geological Survey Report 21. 67 p.

Coogan, A. H., 1996. Ohio's surface rocks and sediments. *In*: Feldman R. M., and Hackathorn M., eds., Fossils of Ohio. Ohio Division of Geological Survey Bulletin 70, 31-50.

Dhakal G., Yoneda T., Kato M., Kaneko K., 2002. Slake durability and mineralogical properties of some pyroclastic and sedimentary rocks. *Engineering Geology*. 65. 31-45.

Diaz - Perez A., Cortés-Monroy I., Roegiers J.C., 2007. The role of water/clay interaction in the shale characterization. *Journal of Petroleum Science and Engineering*. 58. 83–98.

Dick J.C., Shakoor A., 1992. Lithological controls of mudrock durability. *Quarterly Journal of Engineering Geology and Hydrogeology*. 25. 31-46.

Eberl D.D., Srodon J., Nuesch R., 2000. Mudmaster: A program for calculating crystallite size distributions and strain from the shape of X-ray diffraction peaks. U.S. Geological Survey Open File Report. 96-171.

Elwood B.B., Brett C.E., Macdonald W.D., 2007. Magnetostratigraphy susceptibility of the upper Ordovician Kope Formation, northern Kentucky. *Paleogeography, Paleoclimatology, Paleoecology*. 243. 42-54.

Erguler Z.A., Ulusay R., 2009. Water induced variations in mechanical properties of clay bearing rocks. *International Journal of Rock Mechanics and Mining Sciences*. 46. 355-370.

Fleming R.W., 1975. Geologic Prospective – The Cincinnati Example. Ohio Valley Soils Seminar Proceedings. 6th. Ft. Mitchell, Kentucky.

Fleming R.W., Johnson A.M., 1994. Landslides in colluvium. Landslides of the Cincinnati, Ohio area, U.S. Geological Survey Bulletin. 2059. B1-B24.

Fleming R.W., Taylor F.A., 1980. Estimating the costs of landslide damages in the United States: U.S. Geological Survey Circular 832. 21p.

Franklin J.A., Chandra A., 1972. The slake durability test. *International Journal of Rock Mechanics and Mining Sciences*. 9. 325-341.

Gillott J. E., 1970. Fabric of Leda clay investigated by optical, electron-optical and X-ray diffraction methods. *Engineering Geology*. 4. 133-153.

Gokceoglu C., Ulusay R., Sonmez H., 2000. Factors affecting the durability of selected weak and clay bearing rocks from Turkey, with particular emphasis on the influence of the number of drying and wetting cycles. *Engineering Geology*. 57. 215-237.

Gurgenli H., 2006. Geomechanical and weathering properties of weak roof shales in coal mines. Master's thesis. West Virginia University, Morgantown, West Virginia. 99 p.

Haneberg W.C., Gokce A.O., 1994. Rapid water-level fluctuations in a thin colluvium landslide west of Cincinnati. *U.S. Geological Survey Bulletin*. 2059-C. C1-C16.

Holland S.M., Miller A.I., 2008. Biofacies and sequence stratigraphic architecture of the C1 sequence (Kope and lowermost Fairview formations), Cincinnati, Ohio area. *In*: McLaughlin P.I., Brett C.E., Holland S.M., Storrs G.W., eds., *Stratigraphic Renaissance in the Cincinnati Arch; Implication for Upper Ordovician Paleontology and Paleoecology*. Cincinnati Museum Center scientific Contributions. Number 2. 44-57.

Holland S.M., Miller A.I., Dattilo B.F., Meyer D.L., Diekmeyer S.L., 1997. Cycle anatomy and variability in the storm dominated type Cincinnati (Upper Ordovician): Coming to grips with cycle delineation and genesis. *Journal of Geology*. 105. 135-152.

Hoover S.E., Lehmann D., 2009. The expansive effects of concentrated pyritic zones within the Devonian Marcellus Shale Formation of North America. *Quarterly Journal of Engineering Geology and Hydrogeology*. 42. 157-164.

Hough J.E., Fleming R.W., 1974. Landslides-prone bedrock hillsides within the city of Cincinnati, Hamilton County, Ohio. *In* : (<http://www.cincinnati-oh.gov/transeng/pages/-7081-/>)

Huppert F., 1988. Influence of microfabric on geomechanical behavior of Tertiary fine-grained sedimentary rocks from Central North Island, New Zealand. *Bulletin of the International Association of Engineering Geology*. 38. 83-94.

Jennette D.C., Pryor W.A., 1993. Cyclic alteration of proximal and distal storm facies; Kope and Fairview formations (Upper Ordovician), Ohio and Kentucky. *Journal of Sedimentary Research*. 63. 183-203.

Kohrs R.H., Brett C.E., O'Brien N., 2008. Sedimentology of upper Ordovician mudstones from the Cincinnati arch region, Ohio/Kentucky: Toward a general model of mud event deposition. *In*: McLaughlin P.I., Brett C.E., Holland S.M., Storrs G.W., eds., *Stratigraphic Renaissance in the Cincinnati Arch; Implication for Upper Ordovician Paleontology and Paleocology*. Cincinnati Museum Center Scientific Contributions. Number 2. 44-57.

Koncagul E.C., Santi P.M., 1999. Predicting the unconfined compressive strength of the Breathitt shale using slake durability, shore hardness and rock structural properties. *International Journal of Rock Mechanics and Mining Sciences*. 36. 139-153.

Krumbein W.C., Pettijohn F.J., 1938. *Manual of Sedimentary Petrography*. Appleton-Century Company Inc. New York. 549 p.

Lash G.G., Blood D.R., 2004. Origin of shale fabric by mechanical compaction of flocculated clay: evidence from the upper Devonian Rhinestreet shale, Western New York, USA. *Journal of Sedimentary Research*. 74. 110-116.

Lashkaripour G.R., Boomeri M., 2002. The role of mineralogy on durability of weak rocks. *Pakistan Journal of Applied Sciences*. 2(6). 698-701.

Marques E.A.G., Vargas E.D.A., Antunes F.S., 2005. A study of the durability of some shales, mudrocks and siltstones from Brazil. *Journal of Geotechnical and Geological Engineering*. 23. 321-348.

McFaddin J.D., 2008. Development of correlations for unconfined compression strength and methods of field preparations and preservation of Kope shale. Master's thesis. University of Cincinnati, Cincinnati, Ohio. 106 p.

Molinda G.M., Mark C., Pappas D.M., Klemetti T.M., 2008. Overview of coal mine ground control issues in the Illinois basin. *SME Annual Meeting*. 41-48.

Moon V.G., Beattie A.G., 1995. Textural and micro-structural influences on the durability of Waikato Coal Measures mudrocks. *Quarterly Journal of Engineering Geology*. 28. 303-312.

Moore D.M., Reynolds R.C., 1997. X-ray diffraction and the identification and analysis of clay minerals. 2nd edition. Oxford University Press, Oxford, U.K. 378 p.

Nandi A., Whitelaw M., 2009. Effect of physico-chemical factors on the disintegration behavior of calcareous shale. *Environmental and Engineering Geosciences*. XV (2). 273-285.

Nesbitt H.W., Young G.M., 1982. Early Proterozoic climates and plate motions inferred from major element chemistry of lutites. *Nature*. 299. 715-717.

O'Brien N.R., 1987. The effects of bioturbation on the fabric of shale. *Journal of Sedimentary Petrology*. 57. 449-455.

O'Brien N.R., Mattner S.P., 1998. Origin of the fabric of laminated fine grained glaciolacustrine deposits. *Journal of Sedimentary Research*. 68 (5). 832-840.

Parham W.E., Austin G.S., 1969. Clay mineralogy, fabric, and industrial uses of the shale of the Decorah Formation, Southeastern Minnesota. *Report of Investigations 10*. Minnesota Geological Survey. 1-25.

Potter P.E., Maynard J.B., Depetris P.J., 2005. *Mud and Mudstones: Introduction and Overview*. Springer. Berlin Heidelberg New York. 297 p.

Pye K., Miller J.A., 1990. Chemical and biochemical weathering of pyritic mudrocks in a shale embankment. *Quarterly Journal of Engineering Geology*. 23. 365-381.

Reeves G.M., Sims I., Cripps J.C., 2006. Clay materials used in constructions. Geological Society Engineering Geology Special Publication No. 21. The Geological Society Publishing House. Bath, U.K. 513 p.

Santi P.M., Koncagul E.C., 1996. Predicting the mode, susceptibility and rate of weathering of shales. *In*: Matheson G., ed., Design with residual materials - geotechnical and construction considerations. ASCE Geotechnical Special Publication .63. 12-26.

Scotford D.M., 1965. Petrology of the Cincinnati series shales and environmental implications. Geological Society of America Bulletin. 76. 193-222.

Seedsman R., 1986. The behavior of clay shales in water. Canadian Geotechnical Journal. 23. 18-22.

Selley R.C., 1988. Applied Sedimentology. Academic Press. New York. 446p.

Sloane R.L., Kell T.R., 1966. The fabric of mechanically compacted Kaolin. Clays and Clay Minerals, Proceedings National Conference of Clays and Clay Minerals. 14. 289-296.

Song M., Zhang D., 2009. An experimental investigation into the oxidation of four pyritic shales from Western Australia. Minerals Engineering. 22. 550-559.

Sri-in T., Fuenkajorn K., 2007. Slake durability index and strength of some rocks in Thailand. *Rock Mechanics*. 145-159.

Taylor R.K., 1988. Coal Measures mudrocks: composition, classification and weathering processes. *Quarterly Journal of Engineering Geology and Hydrogeology*. 21. 85-99.

Weiss M.P., Sweet W.C., 1964. Kope Formation (Upper Ordovician): Ohio and Kentucky. *Science*. 145. 1296-1302.

White W.A., 1961. Colloid phenomena in sedimentation of argillaceous rocks. *Journal of Sedimentary Petrology*. 31. 560-570.

Wilkin R.T., Barnes H.L., Brantley S.L., 1996. The size distribution of framboidal pyrite in modern sediments: An indicator of redox conditions. *Geochimica et Cosmochimica Acta*. 60. No.20. 3897-3912.

Youn H., Tonon F., 2010. Effect of air-drying duration on the engineering properties of four clay bearing rocks in Texas. *Engineering Geology*. 115. 58-67.

Appendix A

Engineering Data

Table A-1: The two-cycle slake durability index (ID₂) of laminated mudstones (LM) and non-laminated mudstones (NLM) with the elevation measured from above mean sea level (m).

Shaded rows represent non-laminated mudstones

Cycle	Sample	Elevation – From above mean sea level (m)	Slake durability index – ID₂ (%)	
11	NP-5a	168.91	29.29	
	NP-5b	169.30	82.87	
	NP-5c	169.95	67.23	
	NP-5d	170.05	21.12	
	NP-5e	170.35	25.66	
12	NP-7a	173.68	84.32	
	NP-7b	173.64	72.22	
	NP-7c	173.60	91.90	
	NP-7d	173.55	85.72	
	NP-7e	173.50	89.23	
	NP-7f	173.43	85.22	
	NP-7g	173.34	79.65	
	NP-7h	173.28	81.18	
	NP-7i	173.20	66.72	
	NP-7j	173.10	89.15	
	NP-7k	173.02	44.94	
	NP-7l	172.92	83.25	
	NP-7m	172.82	55.31	
	NP-7n	172.76	82.04	
	NP-7p	172.57	49.48	
	NP-7q	172.42	39.31	
	NP-7r	172.22	25.47	
	NP-7s	172.17	38.57	
	NP-7u	171.97	46.55	
	NP-7v	171.77	44.02	
	NP-7aa	171.92	52.14	
13	NP-8a	174.07	45.00	
	NP-8b	173.93	66.00	
	NP-8c	173.82	56.00	
	NP-8d	173.77	61.18	
			LM	NLM
Average			71.18	38.44
Min			25.66	21.12
Max			91.90	52.14

Chemical Data

Table A-2: Weight percentages of major elements of bulk rock and sludge samples of the Kope Formation mudstones analyzed by XRF. Shaded rows represent non-laminated mudstones

Cycle	Sample	MnO ₂		TiO ₂		P ₂ O ₅		CaO		MgO	
		Bulk rock	Sludge	Bulk rock	Sludge	Bulk rock	Sludge	Bulk rock	Sludge	Bulk rock	Sludge
11	NP-5a	0.17	0.16	1.00	0.94	0.14	0.15	3.82	4.26	3.74	3.86
	NP-5b	0.19	0.18	0.98	0.98	0.16	0.14	6.61	4.67	4.70	4.04
	NP-5c	0.17	0.18	1.06	1.03	0.12	0.13	3.36	3.73	3.62	3.69
	NP-5d	0.17	0.18	1.01	1.02	0.14	0.14	3.84	3.78	3.81	3.81
	NP-5e	0.17	0.17	1.06	0.98	0.13	0.13	3.58	3.65	3.69	3.70
12	NP -7a	0.18	0.13	0.96	0.63	0.13	0.37	4.59	7.94	4.14	2.94
	NP -7b	0.19	0.11	0.89	0.83	0.30	0.38	2.13	3.90	3.22	3.11
	NP -7c	0.22	0.13	0.78	0.72	0.46	0.43	8.11	9.14	3.00	2.90
	NP -7d	0.22	0.12	0.48	0.69	0.36	0.33	17.42	7.26	2.58	2.87
	NP -7e	0.19	0.19	0.90	1.03	0.20	0.16	6.52	5.28	2.81	4.18
	NP -7f	0.19	0.18	0.88	0.99	0.20	0.15	6.93	5.40	2.80	4.23
	NP -7g	0.18	0.11	0.98	0.90	0.15	0.18	5.62	5.27	4.42	2.84
	NP -7h	0.19	0.18	0.83	0.97	0.17	0.15	6.85	5.62	2.90	4.34
	NP -7i	0.18	0.16	0.98	1.03	0.14	0.14	4.31	3.20	3.95	3.54
	NP -7j	0.20	0.18	0.88	1.00	0.17	0.16	5.72	5.27	3.06	4.24
	NP -7k	0.18	0.17	0.98	1.01	0.13	0.12	4.36	3.64	4.07	3.74
	NP -7l	0.20	0.11	0.87	0.89	0.18	0.18	6.38	6.53	2.82	2.59
	NP -7m	0.17	0.16	0.99	1.03	0.12	0.12	3.66	3.33	3.78	3.63
	NP -7n	0.18	0.10	0.90	0.93	0.17	0.17	4.65	5.92	2.97	2.71
	NP -7p	0.19	0.19	0.90	0.98	0.13	0.12	3.92	4.91	3.08	4.24
	NP -7q	0.23	0.18	0.55	0.96	0.35	0.13	11.52	4.48	2.76	4.12
	NP -7r	0.17	0.17	0.96	0.99	0.11	0.12	4.06	3.78	3.93	3.83
	NP -7s	0.19	0.19	0.88	0.93	0.15	0.14	2.82	5.65	3.22	4.55
	NP -7u	0.18	0.11	0.81	0.84	0.21	0.19	5.41	4.59	3.03	3.10
	NP -7v	0.19	0.11	0.88	0.89	0.19	0.16	3.87	3.35	3.21	3.32
	NP-7aa	0.19	0.20	0.94	0.86	0.17	0.18	6.15	7.31	4.69	5.00
13	NP-8a	0.19	0.19	0.93	0.95	0.17	0.16	4.68	4.39	4.02	3.99
	NP- 8b	0.19	0.20	0.96	0.91	0.21	0.19	5.96	5.49	4.51	4.30
	NP- 8c	0.20	0.21	0.96	0.98	0.20	0.19	5.62	5.73	4.41	4.50
	NP- 8d	0.21	0.21	0.95	0.95	0.22	0.20	5.99	5.88	4.61	4.52
	Average	0.19	0.16	0.90	0.93	0.19	0.18	5.62	5.11	3.58	3.75
	Min	0.17	0.10	0.48	0.63	0.11	0.12	2.13	3.20	2.58	2.59
	Max	0.23	0.21	1.06	1.03	0.46	0.43	17.42	9.14	4.70	5.00

Table A-2 continuation

Cycle	Sample	SiO ₂		Al ₂ O ₃		Fe ₂ O ₃		K ₂ O		Na ₂ O	
		Bulk rock	Sludge	Bulk rock	Sludge	Bulk rock	Sludge	Bulk rock	Sludge	Bulk rock	Sludge
11	NP-5a	52.65	52.42	16.61	16.56	7.67	7.39	5.09	4.90	0.60	0.56
	NP-5b	50.57	52.93	13.83	15.56	6.82	7.41	4.22	4.70	0.49	0.56
	NP-5c	54.55	55.15	15.11	15.58	8.08	7.86	5.07	4.79	0.73	0.69
	NP-5d	52.91	53.75	15.30	15.70	8.00	8.12	5.04	5.03	0.64	0.65
	NP-5e	54.18	53.97	15.00	16.29	8.08	7.85	5.01	4.91	0.74	0.63
12	NP -7a	52.33	43.51	15.45	14.40	7.76	6.18	4.97	3.67	0.57	0.51
	NP -7b	50.69	50.16	17.43	16.79	7.79	7.66	4.41	4.31	0.55	0.55
	NP -7c	47.06	45.78	14.68	14.07	6.44	6.30	3.68	3.52	0.59	0.60
	NP -7d	36.92	44.53	11.77	14.48	4.91	6.58	3.09	3.68	0.46	0.55
	NP -7e	52.46	53.34	15.26	14.62	7.11	7.69	3.92	4.24	0.70	0.69
	NP -7f	52.49	52.85	15.12	14.80	6.93	7.18	3.90	4.29	0.72	0.62
	NP -7g	52.44	53.14	14.60	15.53	7.29	7.59	4.38	4.01	0.60	0.70
	NP -7h	50.51	51.78	15.52	14.88	7.32	7.45	4.04	4.39	0.61	0.58
	NP -7i	53.53	54.93	15.28	16.23	7.68	8.07	4.69	5.12	0.68	0.75
	NP -7j	51.60	52.60	16.01	15.24	7.36	7.61	4.20	4.51	0.63	0.62
	NP -7k	52.99	53.81	15.73	16.24	7.75	7.87	5.00	5.13	0.61	0.67
	NP -7l	52.57	53.35	15.58	14.93	6.88	6.91	4.03	3.89	0.68	0.78
	NP -7m	53.40	54.54	16.02	16.30	7.85	7.97	5.17	5.14	0.65	0.71
	NP -7n	52.70	53.63	16.37	15.20	7.51	7.81	4.29	3.95	0.61	0.74
	NP -7p	52.51	52.65	16.84	15.48	7.71	7.73	4.43	4.84	0.60	0.57
	NP -7q	40.72	52.93	13.47	15.92	5.69	7.91	3.50	5.03	0.47	0.59
	NP -7r	52.69	53.92	15.92	16.04	7.84	8.10	5.04	5.11	0.61	0.66
	NP -7s	51.69	50.47	17.53	15.56	7.89	7.62	4.61	4.80	0.54	0.46
	NP -7u	49.39	50.82	16.36	16.69	7.39	7.73	4.23	4.33	0.55	0.55
	NP -7v	51.15	51.54	17.14	17.49	7.87	8.00	4.46	4.61	0.56	0.52
	NP-7aa	49.14	47.23	14.58	15.05	7.57	7.08	4.60	4.17	0.42	0.28
13	NP-8a	51.79	52.78	15.36	15.69	7.43	7.67	4.61	4.69	0.52	0.57
	NP- 8b	50.83	51.23	14.21	14.78	7.28	7.31	4.30	4.32	0.51	0.50
	NP- 8c	51.28	51.43	14.13	14.21	7.63	7.82	4.31	4.32	0.53	0.56
	NP- 8d	50.38	50.63	14.57	15.14	7.41	7.35	4.40	4.37	0.49	0.43
	Average	50.94	51.73	15.36	15.52	7.36	7.53	4.42	4.49	0.59	0.59
	Min	36.92	43.51	11.77	14.07	4.91	6.18	3.09	3.52	0.42	0.28
	Max	54.55	55.15	17.53	17.49	8.08	8.12	5.17	5.14	0.74	0.78

Table A- 3: Total carbonate content, total Carbon (C) and total Sulphur (S) and loss on ignition (LOI) of the laminated mudstones (LM) and non-laminated mudstones (NLM) of the Kope Formation. Shaded rows represent non-laminated mudstones

Cycle	Sample	Total Carbonate content%		Total C%		Total S%		LOI%	
11	NP-5a	6.39		1.02		0.36		9.09	
	NP-5b	14.64		2.28		0.35		11.35	
	NP-5c	6.33		0.93		0.33		8.88	
	NP-5d	7.61		1.08		0.5		9.71	
	NP-5e	6.99		0.99		0.39		9.09	
12	NP-7a	39.08		5.90		0.48		21.29	
	NP-7b	15.05		2.34		0.54		12.83	
	NP-7c	27.74		3.70		0.46		15.31	
	NP-7d	34.72		6.26		0.89		22.19	
	NP-7e	15.56		2.25		0.67		10.30	
	NP-7f	17.50		2.29		0.56		10.23	
	NP-7g	13.87		1.90		0.61		9.46	
	NP-7h	18.27		2.70		0.80		11.48	
	NP-7i	10.30		1.21		0.68		8.97	
	NP-7j	15.28		2.25		0.48		10.54	
	NP-7k	9.65		1.19		0.39		8.66	
	NP-7l	16.55		2.26		0.38		10.19	
	NP-7m	7.09		1.02		0.47		8.78	
	NP-7n	12.70		2.10		0.48		10.09	
	NP-7p	13.53		2.07		0.52		10.09	
	NP-7q	8.93		1.19		0.59		9.25	
	NP-7r	6.11		1.09		0.66		9.09	
	NP-7s	13.02		2.14		0.40		10.91	
	NP-7u	19.55		2.94		0.76		12.86	
	NP-7v	13.40		2.52		0.71		10.87	
	NP-7aa	11.26		2.39		0.66		11.53	
13	NP-8a	3.70		1.81		0.54		10.49	
	NP-8b	11.90		2.15		0.47		11.11	
	NP-8c	15.66		2.21		0.76		10.84	
	NP-8d	13.88		2.29		0.39		10.92	
		LM	NLM	LM	NLM	LM	NLM	LM	NLM
Average		15.54	11.09	2.38	1.83	0.53	0.57	11.57	10.38
Min		3.7	6.11	0.93	1.02	0.33	0.36	8.66	9.09
Max		39.08	19.55	6.26	2.94	0.89	0.76	22.19	12.86

Table A- 4: Concentrations of three exchangeable cations (Na, K, Mg) of the laminated mudstones (LM) and non-laminated mudstones (NLM) of the Kope Formation analyzed by AAS. Shaded rows represent non-laminated mudstones

Cycle	Sample	Na (ppm)		K(ppm)		Mg (ppm)	
11	NP-5a	1.87		4.68		6.45	
	NP-5b	0.99		3.25		3.86	
	NP-5c	0.96		3.16		4.03	
	NP-5d	1.82		4.41		6.23	
	NP-5e	1.68		4.39		6.77	
12	NP-7a	0.73		2.93		6.68	
	NP-7b	1.03		3.97		7.06	
	NP-7c	0.59		2.06		3.73	
	NP-7d	1.00		2.79		5.77	
	NP-7e	0.70		2.62		3.09	
	NP-7f	0.80		3.03		3.82	
	NP-7g	1.07		3.47		3.45	
	NP-7h	0.81		3.28		3.83	
	NP-7i	1.22		4.26		4.52	
	NP-7j	0.75		2.81		3.66	
	NP-7k	1.94		4.63		5.17	
	NP-7l	1.25		3.17		2.92	
	NP-7m	1.91		4.77		5.06	
	NP-7n	0.95		3.59		4.44	
	NP-7p	1.95		3.55		7.51	
	NP-7q	1.83		4.58		7.25	
	NP-7r	1.88		5.05		9.22	
	NP-7s	1.77		5.06		10.55	
	NP-7u	1.67		4.94		12.66	
	NP-7v	1.60		5.00		10.15	
	NP-7aa	1.28		4.30		6.96	
13	NP-8a	1.15		5.41		8.32	
	NP-8b	1.01		5.13		8.11	
	NP-8c	0.97		4.61		5.33	
	NP-8d	1.05		4.67		5.64	
		LM	NLM	LM	NLM	LM	NLM
	Average	1.07	1.74	3.71	4.62	5.01	8.55
	Min	0.59	1.28	2.06	3.55	2.92	6.23
	Max	1.94	1.95	5.41	5.06	8.32	12.66

Mineralogical Data

Table A-5: Relative abundances of illite and chlorite calculated by MacDiff software, the mean thickness of illite grains calculated by MudMaster software and the total clay content of the laminated mudstones (LM) and non-laminated mudstones (NLM) of the Kope Formation.

Shaded rows represent non-laminated mudstones

Cycle	Sample	Total clay content (%)		Illite %		Chlorite %		Mean thickness of illite grains (nm)	
11	NP-5a	43.74		89.64		10.36		4.60	
	NP-5b	28.70		88.27		11.73		5.00	
	NP-5c	45.24		88.82		11.18		4.50	
	NP-5d	42.38		89.18		10.82		4.90	
	NP-5e	33.55		89.04		10.96		4.90	
12	NP -7a	30.59		90.33		9.67		4.70	
	NP -7b	32.12		90.10		9.90		4.70	
	NP -7c	32.44		91.04		8.96		4.60	
	NP -7d	17.17		88.40		11.60		4.40	
	NP -7e	47.69		92.44		7.56		4.80	
	NP -7f	35.11		89.04		10.96		4.80	
	NP -7g	50.30		88.33		11.67		4.70	
	NP -7h	22.96		87.62		12.38		4.90	
	NP -7i	43.08		85.93		14.07		5.00	
	NP -7j	29.86		87.73		12.27		4.60	
	NP -7k	49.44		86.41		13.59		4.90	
	NP -7l	31.17		90.67		9.33		5.00	
	NP -7m	46.88		86.24		13.76		4.50	
	NP -7n	40.20		91.61		8.39		4.80	
	NP -7p	40.66		92.09		7.91		4.50	
	NP -7q	33.84		89.86		10.14		5.10	
	NP -7r	43.03		86.34		13.66		4.60	
	NP -7s	32.22		86.56		13.44		4.40	
	NP -7u	33.99		87.57		12.43		4.50	
	NP -7v	53.68		86.63		13.37		4.40	
	NP-7aa	34.80		88.41		11.44		4.70	
13	NP-8a	40.45		88.56		11.20		4.60	
	NP- 8b	42.18		88.80		10.78		4.70	
	NP- 8c	32.11		89.22		12.96		4.60	
	NP- 8d	32.55		87.04		11.59		4.90	
		LM	NLM	LM	NLM	LM	NLM	LM	NLM
Average		36.37	39.82	88.84	88.48	11.17	11.51	4.74	4.63
Min		17.17	32.22	85.93	86.34	7.56	7.91	4.4	4.4
Max		50.3	53.68	92.44	92.09	14.07	13.66	5	5.1

Textural Data

Table A- 6: Moisture content of the laminated mudstones (LM) and non-laminated mudstones (NLM) of the Kope Formation Kope Formation calculated according to both civil engineering and geological formulae. Shaded rows represent non-laminated mudstones

Cycle	Sample	Moisture content			
		Civil engineering format		Geological format	
11	NP-5a	7.75		7.19	
	NP-5b	5.20		4.94	
	NP-5c	6.08		5.73	
	NP-5d	9.92		9.02	
	NP-5e	9.67		8.82	
12	NP-7a	3.61		3.49	
	NP-7b	5.48		5.19	
	NP-7c	2.80		2.72	
	NP-7d	3.21		3.11	
	NP-7e	2.70		2.63	
	NP-7f	4.11		3.95	
	NP-7g	4.11		3.95	
	NP-7h	4.15		3.99	
	NP-7i	5.28		5.02	
	NP-7j	3.92		3.77	
	NP-7k	6.01		5.67	
	NP-7l	4.39		4.21	
	NP-7m	6.27		5.90	
	NP-7n	3.85		3.71	
	NP-7p	5.15		4.90	
	NP-7q	6.36		5.98	
	NP-7r	7.34		6.84	
	NP-7s	6.53		6.13	
	NP-7u	5.89		5.56	
	NP-7v	6.43		6.04	
	NP-7aa	6.42		6.03	
13	NP-8a	5.46		5.18	
	NP-8b	5.88		5.55	
	NP-8c	5.79		5.47	
	NP-8d	7.00		6.55	
		LM	NLM	LM	NLM
Average		4.99	6.86	4.74	6.41
Min		2.7	5.15	2.63	4.9
Max		9.67	9.92	8.82	9.02

X-ray Diffraction Data

C:\DATA\NADEESHA\NHK204.RAW NP5B (CT: 8.0s, SS:0.020dg, WL: 1.5406Ao)
 C:\DATA\NADEESHA\NHK245.RAW NP5BGLY (CT: 1.0s, SS:0.020dg, WL: 1.5406Ao)

C:\DATA\NADEESHAN\HK208.RAW NPSE (CT: 8.0s, SS:0.020dg, WL: 1.5406Ao)
 C:\DATA\NADEESHAN\HK241.RAW NPSEGLY (CT: 1.0s, SS:0.020dg, WL: 1.5406Ao)

C:\DATA\NADEESHA\ARJ396.RAW NP7B (CT: 8.0s, SS:0.020dg, WL: 1.5406Ao)
 C:\DATA\NADEESHA\ARJ399.RAW NP7BGLY (CT: 8.0s, SS:0.020dg, WL: 1.5406Ao)

C:\DATA\NADEESHA\ARJ397.RAW NP7C (CT: 8.0s, SS:0.020dg, WL: 1.5406Ao)
 C:\DATA\NADEESHA\ARJ401.RAW NP7CGLY (CT: 8.0s, SS:0.020dg, WL: 1.5406Ao)

C:\DATA\NADEESHA\ARF387.RAW NP7F (CT: 8.0s, SS:0.020dg, WL: 1.5406Ao)
 C:\DATA\NADEESHA\ARF394.RAW NP7FGLY (CT: 8.0s, SS:0.020dg, WL: 1.5406Ao)

C:\DATA\NADEESHA\ARF388.RAW NP7G (CT: 8.0s, SS:0.020dg, WL: 1.5406Ao)
 C:\DATA\NADEESHA\ARF411.RAW NP7GGLY (CT: 8.0s, SS:0.020dg, WL: 1.5406Ao)

C:\DATA\NADEESHA\ARF370.RAW NP7H (CT: 8.0s, SS:0.020dg, WL: 1.5406Ao)
 C:\DATA\NADEESHA\ARF377.RAW NP7HGLY (CT: 8.0s, SS:0.020dg, WL: 1.5406Ao)

C:\DATA\NADEESHA\ARF371.RAW NP71 (CT: 8.0s, SS:0.020dg, WL: 1.5406Ao)
C:\DATA\NADEESHA\ARF378.RAW NP71GLY (CT: 8.0s, SS:0.020dg, WL: 1.5406Ao)

C:\DATA\NADEESHA\ARF372.RAW NP7J (CT: 8.0s, SS:0.020dg, WL: 1.5406Ao)
 C:\DATA\NADEESHA\ARW379.RAW NP7JGLY (CT: 8.0s, SS:0.020dg, WL: 1.5406Ao)

C:\DATA\NADEESHA\ARF373.RAW NP7K (CT: 8.0s, SS:0.020dg, WL: 1.5406Ao)
C:\DATA\NADEESHA\ARF380.RAW NP7KGLY (CT: 8.0s, SS:0.020dg, WL: 1.5406Ao)

C:\DATA\NADEESHA\ARF374.RAW NP7L (CT: 8.0s, SS:0.020dg, WL: 1.5406Ao)
 C:\DATA\NADEESHA\ARF381.RAW NP7LGLY (CT: 8.0s, SS:0.020dg, WL: 1.5406Ao)

C:\DATA\NADEESHA\ARF406.RAW NP7Q (CT: 8.0s, SS:0.020dg, WL: 1.5406Ao)
C:\DATA\NADEESHA\ARF405.RAW NP7QGLY (CT: 8.0s, SS:0.020dg, WL: 1.5406Ao)

C:\DATA\NADEESHA\ARF407.RAW NP7R (CT: 8.0s, SS:0.020dg, WL: 1.5406Ao)
 C:\DATA\NADEESHA\ARF413.RAW NP7?GLY (CT: 8.0s, SS:0.020dg, WL: 1.5406Ao)

C:\DATA\NADEESHA\AFR408.RAW NP7S (CT: 8.0s, SS:0.020dg, WL: 1.5406Ao)
C:\DATA\NADEESHA\ARF412.RAW NP7SGLY (CT: 8.0s, SS:0.020dg, WL: 1.5406Ao)

C:\DATA\NADEESHA\ARF410.RAW NP7U (CT: 8.0s, SS:0.020dg, WL: 1.5406Ao)
C:\DATA\NADEESHA\ARF415.RAW NP7UGLY (CT: 8.0s, SS:0.020dg, WL: 1.5406Ao)

C:\DATA\NADEESHA\ARF414.RAW NP7U (CT: 8.0s, SS:0.020dg, WL: 1.5406Ao)
C:\DATA\NADEESHA\ARF416.RAW NP7UGLY (CT: 8.0s, SS:0.020dg, WL: 1.5406Ao)

Appendix B

Total Carbonate Content

Graph B-2: The ID₂ of Kope Formation mudstones plotted versus the total carbonate content

Total Carbon Content

Graph B-3: The ID₂ of Kope Formation mudstones plotted versus the total carbon content

Total Sulphur Content

Graph B-4: The ID₂ of Kope Formation mudstones plotted versus the total sulphur content

Total Clay Percentage

Graph B-5: The ID₂ of Kope Formation mudstones plotted versus the total clay (< 5 μ m fraction – according to ASTM standard classification) percentage

Mean Thickness of Illite Grains

Graph B-6: The ID₂ of Kope Formation mudstones plotted versus the mean thickness of illite grains (nm) calculated by MudMaster software using XRD data

Appendix C

Particle size distribution of the representative samples from both laminated and non-laminated mudstones of the three cycles (Cycle 11, 12 and 13) of the Kope Formation are included in the figure

Appendix D

Moisture Content

Representative portions of samples were weighed (about 50 g) and placed in an oven at 105° C. Samples were re-weighed after 24 hours. There are two different ways that moisture content is expressed – Geotechnical engineering expression and the Geological and environmental engineering expression. Because slake durability is a geotechnical measurement, the engineering usage is followed in this thesis.

1. Geotechnical engineering expression

$$\text{Moisture content} = [(\text{Initial weight} - \text{dry weight}) / \text{dry weight}] \times 100$$

This formula is the one generally used by geotechnical engineers for civil engineering purposes.

2. Geological and environmental engineering expression

$$\text{Moisture content} = [(\text{Initial weight} - \text{dry weight}) / \text{initial weight}] \times 100$$

This formula is the one used in geologic literature.

Slake Durability Test

The slake durability test is used to determine the slake durability index of any clay bearing weak rock. It estimates the slake durability of weak rocks quantitatively. The slake durability apparatus consists of an electric motor with two drums attached to it on either sides. Two drums are cylindrical in shape with a diameter of 140 mm and a length of 100 mm and made of 2.00 mm (No. 10) square mesh. About ten, equi-dimensional pieces of shale were selected so that the total weight becomes 450 g. (the rock pieces were free of dust and have smooth edges). Samples were kept in an oven at 110°C temperature for 10 hours until completely dried.

Figure D-1: Slake durability apparatus

The time required for a complete drying of the sample was determined by weighing one sample at different time intervals until a constant weight was observed (Table D-1 and Figure D-2). After drying completely, rock pieces were placed in the drum. Then the drum was mounted to the trough and coupled to the motor. The trough was filled by distilled water to 20 mm below the drum axis. Next the drum was rotated at 20 rpm for 10 minutes. The temperature of the water was recorded at the beginning and the end of the run. The drum was removed from the trough immediately after the run. Then the drum and the specimen were oven dried at 110° C for 10 hours until a constant weight was obtained. After that the same procedure was repeated for the second run and the final oven dried mass of the sample after the second run was obtained.

Table D.1: Weights of the tested mudstones samples at different time intervals – time required to obtain complete moisture loss by oven drying at 105° C

Time /min	Weight/g
30	1149.25
60	1144.10
90	1142.00
150	1140.35
210	1139.00
270	1139.00

Figure D.2: Weight of the samples after drying in the oven at 105° C plotted against time.

The ID₂ was calculated using the following equation.

$$ID_2 = [(W_f - C) / (B - C)] \times 100$$

ID₂ = Slake durability index (second cycle)

B = Mass of the drum+ oven dried specimen before the first cycle

W_f = Mass of the drum + oven dried specimen retained after the second cycle

C = Mass of the drum

After the second cycle of the test, the sludge portion was collected to study the mineralogy and chemistry by XRD and XRF analysis respectively. The water used for slaking samples was collected after the second run to analyze water soluble cations in mudstones.

X-Ray Fluorescence Analysis (XRF)

a) Sample Preparation – Bulk Samples

Representative portions of the original mudstones samples were crushed using a mortar and pestle [Figure D-3 (a)]. Pulverized samples were further ground in a tungsten carbide ball mill until a powder (5-10 μm size) was obtained. Propylene Glycol was used as a grinding aid [Figure D-3 (b) & (c)]. After grinding, the powder was pressed into thin pellets using a Spex 3624B X-Press 20 ton press [Figure D-3 (d)]. Prepared pellets were then stored in an oven at 55°C until analyzed.

b) Sample Preparation – Sludge

The sludge (the portion of the sample that came out of the cage after slaking) was oven dried for 24 hours at 105°C. Dried samples were then pulverized using the tungsten carbide ball mill to obtain a powder (5-10 μm size). The powder was then pressed to prepare pellets for XRF analysis using a Spex 3624B X-Press 20 ton press. Pellets were stored in an oven at 55°C until analyzed.

c) Sample Analysis

Prepared samples were analyzed using a Rigaku 3070 X-ray fluorescence spectrometer in the Department of Geology at the University of Cincinnati, Cincinnati, Ohio to measure the weight percentages (wt %) of FeO, MnO₂, CaO, K₂O, Na₂O, MgO, SiO₂, TiO₂, Al₂O₃ and P₂O₅ of samples. Corrections were made by a multiple regression matrix with coefficients established by measuring a set of United States Geological Survey (USGS) and Japan Geological Survey standards and loss on ignition data.

(a)

(b)

(c)

(d)

Figure D-3: Preparation of thin powder pellets of samples for XRF analysis. (a) samples were initially crushed using the mortar and pestle (b) samples were crushed to a powder using the tungsten carbide ball mill (c) sample container and the grinding aid (propylene glycol) (d) Powdered samples were pressed into thin pellets using a Spex 3624B X-Press

Loss on Ignition (LOI)

Loss on ignition was determined to get the total content of volatiles (CO₂, H₂O, etc.) in the samples. About 3 g of the dried, powdered sample was added to a crucible and weighed. Then the sample was ignited in the muffle furnace for 1 hour at 1000° C. After that the crucible with the baked sample in it was weighed. The LOI is calculated using the following formula:

$$\text{Loss on Ignition (LOI)} = \frac{\text{Initial weight of the sample} - \text{Weight of the baked sample}}{\text{Initial weight}} \times 100$$

Total Carbonate Content

The total carbonate content of the Kope Formation mudstones was determined by acid digestion method. About 5 g of oven dried, powdered samples of the Kope Formation mudstones were placed in a beaker and 30 ml of 10% HCl acid was added. Samples were soaked in acid for 24 hours and filtered. The non-digested portion was air dried and weighed. Total carbonate content was calculated from the weight difference.

Total Carbon and Total Sulphur Analysis

The total carbon and total sulphur content of the Kope Formation mudstones was analyzed using the Elter CS 2000 carbon sulphur determinator in the Department of Geology at the University of Cincinnati, Cincinnati, Ohio.

a) Sample Preparation

Representative portions of original samples were ground using a tungsten carbide ball mill. Powder samples were used for the carbon and sulfur analysis.

b) Sample Analysis

Devonian Black Shale (DBS -1) standard and CaCO_3 standards were used to calibrate the instrument. First 0.1 ± 0.005 g of the standard sample was added to a crucible. Then a scoop from each iron and tungsten accelerants was added. Next the crucible was ignited in the analyzer. Standards were run 5-7 times to make a calibration plot. After that 0.1 ± 0.005 g of the sample was added to a crucible. The same amounts of iron and tungsten accelerants were added to the crucible as mentioned above. Then the crucible was ignited in the analyzer. After every 5-6 samples standards were run to check the precision.

Atomic Absorption Spectrometric Analysis

The water used in the slake durability test to slake the samples were analyzed using the Perkin Elmer AAnalyst 400 flame atomic absorption spectrometer in the Department of Chemistry at the University of Cincinnati, Cincinnati, Ohio to quantify the major water soluble cations (Na, K, Ca and Mg) of mudstones. The detection limit of each element for the atomic absorption spectrometer is given in Table D-2. A hollow cathode lamp of wavelength ranging from 190 -900 nm was used in the instrument. Acetylene was used as the fuel while N₂O was used as the oxidant. The flame temperature used was 2900°C – 3100°C.

a) Sample Preparation

Water samples were centrifuged and filtered using 1.2 mm millipore filter paper to remove clay and other fine particles. The filtrate was used for the atomic absorption spectrometric analysis.

b) Standard Preparation

A multi-element standard of 100 ppm concentration was prepared using NaCl, KCl, CaCl₂ and Mg (ClO₄)₂. CsCl₂ was used to increase the atomization efficiency of the standard solution. Then the standard solutions of 0.1 ppm, 0.25 ppm, 0.5ppm, 1ppm, 2 ppm and 5 ppm concentrations were prepared from the 100 ppm standard.

c) Sample Analysis

First a calibration plot was made using the 6 standard solutions. A distilled water sample was used as the control. Three replicates were analyzed for each sample for quality assurance. In order to check the precision of data the control and the standard samples were run after every 5 samples and every 10 samples respectively.

Table D-2: Detection limits of different elements for atomic absorption spectrometer

Element	Detection Limit (mg/kg)
Na	0.0002
K	0.002
Ca	0.0001
Mg	0.002

Powder X-Ray Diffraction (XRD) Analysis

Samples were analyzed using a Siemens D-500 automated diffractometer in the Department of Geology at the University of Cincinnati, Cincinnati, Ohio.

a) Sample Preparation – Bulk Sample

Representative portions of bulk samples were crushed and pulverized using the tungsten carbide ball mill to make a fine powder. The powder was used for the powder XRD analysis.

b) Sample Preparation – Sludge Sample

The slaked portion of the samples (material that came out of the cage after the second cycle of the slake durability test - < 2 mm size portion) was ground using a mortar and pestle. The sample was thoroughly mixed with water using a Hamilton Beach mixer. The silt portion was allowed to settle first. The clay portion was separated from water by centrifuging the samples at 7000 rpm for 2 minutes and used to prepare slides by the smear method for XRD analysis.

c) Sample Analysis

Samples were analyzed using the X-ray diffractometer system, using Cu K α radiation at 30 mA and 40 kV. Sludge samples were analyzed in a 2θ range of 2° to 62° with a 0.02 step size and 8 second count time at each step. Powdered samples of the bulk rocks were packed into a 1 mm deep square shape aluminum holder and run in a 2θ range of 2° to 62° with a 0.02 step size and 1 second count time at each step.

d) Data Analysis

Mineralogical phases of the samples were identified by analyzing the XRD traces according to the values given in Chen (1977). The mean thicknesses of illite grains were calculated by the MudMaster software (Eberl *et al.*, 2000) using XRD data. The relative

abundance of clay minerals was calculated using MacDiff software based on the XRD data of the samples. All the statistical analyses were performed using MINITAB® (version 15) statistical software.

Total Clay Content and the Particle Size Distribution of the Fine Fraction of the Kope Formation Mudstones.

Total clay content of the Kope Formation mudstones was determined by pipette analysis. The particle size distribution of the fine fraction ($< 5\mu\text{m}$ fraction separated from pipette method) of the Kope mudstones was analyzed using the Beckman Coulter LS 230 particle size analyzer in the Department of Geology at the University of Cincinnati, Cincinnati, Ohio.

a) Sample Preparation

Representative portions of the bulk sample were air-dried. About 50 g of the air-dried sample was ground using mortar and pestle. Samples were crushed until the entire sample passed through a No.100 mesh (0.049 mm) sieve. Then 125 ml of 4% sodium pyrophosphate was added to the sample and left overnight to soak. After that distilled water was added into the sample container, so that the water level came up to the 10 cm level from the bottom of the container. The sample was thoroughly mixed for 2 minutes using the Hamilton Beach mixer and allowed to settle.

According to the times of settling computed using Stokes' law (given in Manual of sedimentary Petrography – Krumbein and Pettijohn, 1938), after 1 hour and 1 minute (61 minutes) the less than $5\mu\text{m}$ size fraction of the sample remains in suspension was removed using a pipette. The fraction greater than $5\mu\text{m}$ size was oven dried and weighed. The fraction less than $5\mu\text{m}$ size was used for the Coulter counter analysis to determine the particle size distribution of the fine fraction of the Kope Formation mudstones.

b) Sample Analysis

The fine fraction ($< 5\mu\text{m}$ size) of the sample was added to the sample container of the Coulter counter until the required concentration (for polarization intensity differential scattering

unit - PIDS (separate sensor to estimate clay size fraction) – 45-55%, for the laser – 8-12%) for the analysis was obtained. Sample solution was sonicated with a sonicate power of 7 to disintegrate any clay clumps that may be present. Every sample was run three times and the duration of each cycle was 60 seconds. The software in the unit automatically does statistical analysis, offset calculation, alignment check and corrections and background measurements every 30 minutes during the run.

Scanning Electron Microscopy (SEM) Analysis

Different fabric types of Kope Formation mudstones were studied by analyzing SEM images. A Philips XL 30 field emission scanning electron microscope in the advanced materials characterization center in the College of Engineering at the University of Cincinnati, Cincinnati, Ohio was used for the analysis.

a) Sample Preparation

Freshly broken, undisturbed surfaces were obtained from selected samples (both laminated and non-laminated mudstones) of the Kope mudstones. All the specimens were about 10 mm in diameter and 2 - 4 mm thickness in size in order to fit easily into the sample holder. According to Gillott (1970), the surface of the sample used for scanning electron microscopic analysis need not be perfectly flat because of the very large depth of focus in the image produced by scanning electron microscopic analysis. As most of these samples were non-conductive, the high negative charges created by the primary electron beam would produce charging of the surface of the sample, preventing observations. Therefore samples were coated with Au-Pd.

Samples were observed with 12 kv voltage and environmental mode. In the environmental mode the chamber has a gaseous environment instead of a vacuum. Since this gaseous environment is electrically conductive, it prevents the accumulation of negative charge on the surface of the specimen. The working distance was kept around 10 mm and samples were observed under high magnification from X1000 – X5000. Chemical analysis was performed on several spots of the sample by energy dispersive X-ray analysis (EDAX) to identify the mineralogy.

Appendix E

Characteristics of Major Rock Types and the Laminated and Non-laminated Mudstones in the Kope Formation

Different lithology in the Kope Formation,

1. Mudstones
2. Limestone
3. Siltstones

Mudstones

Fine grained laminated or non-laminated rocks. Consist of clay and silt size particles, but 33-65% is clay size particles. Easily break with a hammer. Feel soft with fingers due to the abundance of clay.

Siltstones

Fine grained laminated or non-laminated rocks. Hummocky laminations can be seen in some beds. Consist of clay and silt size particles, but the clay size particles are less than 33%. Silt grains are abundant and visible with hand lens. Feel gritty when chewed. Hard to break with a hammer. React with acid if carbonate minerals present.

Limestone

Fine-coarse grained rocks. Mainly consist of calcium carbonate. Rich in fossils. Readily react with acids. Hard to break with a hammer.

The three major lithology of the Kope formation can be differentiated by the above main characteristics. Once mudstones differentiated from the other two rock types following

characteristics (Figure E-1, E-2 and E-3) will be useful to distinguish the two different mudstones types – laminated and non-laminated mudstones in the Kope Formation

1. Appearance

Figure E-1: Appearance of the two types of mudstones in the outcrop. (a) laminated mudstones with flaky appearance in Cycle 13 of the Kope Formation. Note the scale is 8 cm (b) non-laminated mudstone with blocky appearance in Cycle 12 of the Kope Formation. Note the scale is 7 cm

b) Collected hand specimens,
(a)

(b)

Figure E-2: Hand specimens of the two types of mudstones. (a) laminated mudstones with flaky appearance of Cycle 12 of the Kope Formation. Note the scale is 6 cm (b) non-laminated mudstone with blocky appearance of Cycle 12 of the Kope Formation. Note the scale is 6 cm

c) In a core box,

Figure E-3: A core box with the two types of mudstones of the Kope Formation. Core drilled by HC Nutting Company from Newport Pavilion, Kentucky. Note the 30 cm ruler as the scale

Table E.1 - Characteristics of the laminated and non-laminated mudstones

	Laminated mudstones	Non-laminated mudstones
Appearance	Laminations present, fissile	Blocky or irregular
Way of breaking – with a hammer	Readily break into thin flakes parallel to the bedding plane	Break irregularly into blocks