ROCK DUST SURFACE CHEMISTRY MODIFICATIONS FOR ELIMINATING CAKE FORMATION AND IMPROVING DISPERSION IN COAL DUST EXPLOSION MITIGATION APPLICATIONS

Qingqing Huang

University of Kentucky, qqhwan987@gmail.com
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Qingqing Huang, Student

Dr. Rick Honaker, Major Professor

Dr. Braden Lusk, Director of Graduate Studies
ROCK DUST SURFACE CHEMISTRY MODIFICATIONS FOR ELIMINATING CAKE FORMATION AND IMPROVING DISPERSION IN COAL DUST EXPLOSION MITIGATION APPLICATIONS

DISSEMINATION

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the College of Engineering at the University of Kentucky

By
Qingqing Huang
Lexington, Kentucky

Director: Dr. Rick Honaker, Professor of Mining Engineering
Lexington, Kentucky

2016
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ABSTRACT OF DISSERTATION

ROCK DUST SURFACE CHEMISTRY MODIFICATIONS FOR ELIMINATING CAKE FORMATION AND IMPROVING DISPERSION IN COAL DUST EXPLOSION MITIGATION APPLICATIONS

Rock dust has been historically applied to mitigate the coal dust explosion in either dry or wet form. Dry rock dust performs best in inerting the potential coal dust explosion due to the greatest dispersive properties. However, it undesirably exposes underground coal miners to respirable dust particles which imposes a severe health danger. Wet dust application is able to significantly reduce the floatable dust particles but another problem associated with caking is predominant. Caking phenomenon is usually used to describe the change of free-flowing bulk solids into agglomerated chunks. Unfortunately, the environmental conditions of an underground mine have the potential to cause caking of the rock dust, especially for wet dust application, which reduces the dispersive characteristics needed for effective explosion mitigation and is also the focus of the present study. Surface modification of rock dust to generate a hydrophobic surface is believed to alleviate the caking problem by allowing instant water drainage and eliminating the formation of water and solid bridges.

Surface modification of rock dust was evaluated in the present study with a series of potential modifying reagents including oleic acid, sodium oleate and stearic acid. The modification efficiency in terms of measured contact angle, zeta potential and dispersibility values was investigated with sodium oleate generating the best modification effect. Dispersants were investigated as well in the present work aiming to further increase the particles dispersibility in addition to the excellent hydrophobization effect generated by sodium oleate. However, dispersibility test results indicated that the adsorption of dispersant and sodium oleate was competitive. The preferential adsorption of dispersants over oleate deteriorated the surface hydrophobicity of particles and the dispersibility was decreased as a result.

As anticipated, dry rock dust always provided the best dispersibility with almost 95% of the dust remaining in suspension at a dispersion time of 30 seconds. The percentage dust dispersion values of sodium oleate treated rock dust was increased to as high as 71% in contrast to 47% of untreated wet rock dust and the explosion potential was correspondingly reduced by almost 83%. The effect of sodium oleate was further studied as a function of reagent concentration to determine the optimum application condition.
The dispersibility of rock dust particles was initially increased until the application of 0.1 wt% sodium oleate, after which it slightly decreased up to 0.5 wt% oleate. When the concentration was above 0.5 wt%, the dispersibility of dust particles substantially decreased to a value lower than the value obtained for regular wet dust. The optimum sodium oleate concentration was thus determined at approximately 0.1 by weight of rock dust particles with a corresponding contact angle of around 110 degrees.

The pivotal of rock dust modification efficiency is its long-term stability which can be corroborated by irreversible chemical adsorption rather than the short-term physical adsorption. Therefore, the fundamental adsorption mechanism of sodium oleate on rock dust surface was continuously investigated by means of using surface tension measurements, FTIR, Thermogravimetric, SEM analyses and constructing the species distribution diagram. Based on the surface tension measurements and calculated apparent surface area occupied by per oleate molecule, the monolayer adsorption of oleate on dust surface was proposed with oleate concentration falling between 0.1-0.15 wt% which guarantees the long-term surface modification efficiency. Calcium oleate started precipitating out of bulk solution and depositing on the dust surface when the oleate concentration was above 0.15 wt% which became more predominant under high oleate concentration. Super hydrophobic particles together with nucleated calcium oleate nanoparticles tend to increase particles aggregation significantly through attractive hydrophobic particle-particle interactive force, which renders the particles more agglomerated instead of dispersed.

Systematic and economic evaluation of the wet form rock dusting process in underground coal mine applications was conducted at the end to determine the safety effects, potential benefits and improvement for future implementation. Suggestions for future work were given as well to shed light on the dusting process together with rock dust surface chemistry modification.

KEYWORDS: Rock Dust, Surface Chemistry Modification, Coal Mine, Explosion Mitigation, Dispersibility

Qingqing Huang

(Author’s name)  
04/28/2016  
(Date)
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By

Qingqing Huang

Dr. Rick Honaker
Director of Thesis

Dr. Braden Lusk
Director of Graduate Studies

04/28/2016
Date
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1. **CHAPTER 1. INTRODUCTION**

1.1. **BACKGROUND**

Mine explosions have been a long-time threat to the underground coal miners and remain as the greatest hazard in coal mining industries (Cybulska, 1988). Worldwide attention has been drawn to the accumulations of the combustible dusts and gasses. In the presence of sufficient oxygen and heat, the accumulations of combustible dusts and gasses can lead to large-scale underground coal mine explosions. As a result, severe disasters accompanied by traumatic deaths and injuries would be created. To alleviate the problem, rock dusts such as limestone can serve both as a thermal inhibitor and a heat sink to inert the coal dust explosibility thereby prohibiting the occurrence of dust explosions (Dastidar et al., 2001). The dispersibility of the rock dust plays an extremely significant role in explosion mitigation. Unfortunately, the adverse environmental conditions of an underground mine are prone to cause caking of the rock dust which substantially deteriorates the dispersive characteristics needed. In addition, evaluation of the effectiveness of the applied rock dusts is a subjective and time-consuming process which requires days or a week to identify a hazard (National Institute for Occupational Safety and Health, 2011a). Therefore, it is urgent and imperative to find ways resolving the rock dust caking problems by means of efficient modification methods.

The major mechanism for the rock dust caking process is the adsorption of moisture/water causes the formation of liquid bridges at the particle-particle contact points where saturated solutions of soluble powder ingredients are formed (Bradley et al., 2000). Changes in temperature or relative humidity can result in solvent (water) evaporation and the formation of dry bridges. Therefore, the key to preventing caking phenomenon may be creating hydrophobic rock dust to repel water from the solid surface therefore preventing the formation of liquid and solid bridges. The dispersive property of rock dust could be enhanced by modification of the particle surface properties via the application of chemical additives.

The present work concentrated on developing an effective and practical surface modification process on rock dusts based on improved understanding of rock dust caking
fundamentals to prevent deterioration in the dispersive characteristic of rock dust by the application of a number of modifying reagents. Rock dust solids were treated through coating with various chemical reagents to modify the surface properties. An environmental chamber that allowed the control of humidity and temperature were used to simulate the underground mine atmosphere which helped to visualize the behavior of reagent treated samples over time. Chemical reagents including oleic acid, sodium oleate, stearic acid and a number of dispersants were tested for the performance of caking prevention. Extensive investigation was conducted which involved surface characterization of the modified rock dust surfaces, measurement of the dispersibility improvements, assessment of the explosion suppression enhancement and determination of the adsorption mechanism. The impact of dispersants in the rock dust surface modification was evaluated as well in the present work and systematic evaluation of the rock dust hydrophobization process was provided at the end of the work to shed light upon the actual application in underground coal mining industries.

1.2. OBJECTIVES

The overall objective of the present work was to develop effective modifying reagents and surface modification process to treat rock dusts. The main purpose of the study was to alleviate the caking phenomenon of rock dusts induced by moisture migration in the adverse underground mine atmosphere as a result of humidity and temperature oscillation. Meantime maintain their dispersibility to effectively quench the flame propagation during the coal dust explosion serving both as the thermal inhibitor and thermal sink. Specific objectives included:

1) Reviewing the fundamental knowledge and principles regarding rock dusting process and cake formation phenomenon.

2) Developing effective modifying reagents to prohibit or alleviate the caking process of rock dusts, maintain their dispersive characteristics and coal dust explosion inverting property.
3) Evaluating the performance of modifying reagents via laboratory experimental test designs and identifying the optimum process condition.

4) Conducting explosibility tests in the explosive chamber to evaluate the explosion mitigation performance of treated rock dust samples through determining the peak explosive pressure, the volume normalized rate of pressure rise and weight loss of the dust admixture after an explosion detonation attempt.

5) Providing systematic evaluation on the safety, reliability and economic feasibility of applying the treated rock dust particles in the underground coal mines as anti-explosive agents.

1.3. ORGANIZATION

The dissertation was organized into 7 chapters. The first chapter is a brief introduction. The second chapter is a comprehensive review of the rock dusting process in the underground coal mine industry, its associated limitations that have been brought into focus, the fundamentals of rock dust caking process and surface chemistry modification of rock dust solids.

The third chapter introduces the experimental setup, sample characterization, preparation, test procedures and measurement techniques both in the university laboratory and Georgetown explosive research lab. The corresponding test results, observations and discussions are provided in the subsequent fourth chapter. A fundamental evaluation of the modifying reagent (sodium oleate) adsorption on rock dust particles as well as safety evaluation and comparative economic analysis was conducted in the fifth chapter.

The main conclusions of the dissertation are recapitulated in the sixth chapter. Suggestions for future study are attached to the last chapter, which is also the seventh chapter.
2. CHAPTER 2. LITERATURE REVIEW AND THEORETICAL PRINCIPLES

2.1. GENERAL REVIEW OF ROCK DUSTING IN MINING INDUSTRY

Underground coal mine explosions have been a threat to miners for as long as coal has been mined and continuously remains as the severest hazard in coal mining industries (Cybulsk, 1988). During mining operation, methane can be easily accumulated at the work face which is ready to be ignited by as small ignition energy as machine sparks creating a subsequent gas explosion. The pressure wave resulting from the gas explosion is able to disperse the loose coal dust deposited on the floor, roof and ribs as it travels out from the face and acts as an ignition source for coal dust (Dastidar et al., 2001). A coal dust explosion is thereby created which generates sufficient air pressure and associated air turbulence further increasing the violence of the explosion (Harris et al., 2010). Highly advanced and mechanized underground coal mine production has gradually generated finer coal dust which is more explosive (Cashdollar et al., 2010; Harris et al., 2010). Rock dusting has been used for about 100 years by applying the inerting rock dust (typically limestone or dolomite) to increase the total incombustible content of admixtures and effectively quench the flame propagation and coal dust explosion by acting as a thermal inhibitor or heat sink (Cashdollar et al., 2010; Man and Teacoach, 2009; Amoytte et al., 1995; Rice, 1914).

Rock dust used for dusting purpose is normally pulverized calcite, dolomite, gypsum, anhydrite, shale, adobe, or other inert materials with preferred light color. One hundred percent of the dust particles should pass through a 20-mesh sieve while 70 percent or more pass through a 200-mesh sieve. In particular, when wetted and dried, the particles shall not agglomerate to form a cake that cannot be dispersed into separate particles by a light blast of air; and does not contain more than 5 percent combustible matter or more than a total of 4 percent free and combined silica (SiO₂) (US Mine Safety and Health Administration, 2016a). Rock dusting plays an extremely significant role in alleviating or abating the risk of fires and explosions in underground coal mines.

The Code of Federal Regulations (CFR) requires that all areas of a coal mine that can be safely traveled must be kept adequately rock dusted to within 40 feet of all working faces.
As long as the rock dusting is sufficiently applied and maintained, the risk of widespread underground coal mine explosions can be effectively mitigated. In addition, the total incombustible content of dusts in all entries should be maintained to no less than 80 percent by weight. When methane is present, the Emergency Temporary Standard (ETS) requires an additional 0.4 percent of incombustible material for every 0.1 percent of methane (US Mine Safety and Health Administration, 2016a).

The following points should be kept in mind in order to make rock dusting function properly: a) The fineness of the dust; b) The quantity of the dust; c) The quality of the dust, i.e., the rock dust particles should not cake when stored in the mine and will preserve its buoyant nature (McDonald, 1938).

According to an early summary paper by Greenwald (1938a), rock dust may be distributed by air current, by hand and by machine. Distribution by air current is usually not satisfactory due to the carrying limitations of the current. A crew of men can also do the work by carrying a bag of rock dust and spreading the material by hand onto the mine roof, ribs and floors. The commonly utilized way is through mechanization. In this manner, rock dust is mechanically fed and discharged through fixed openings or flexible pipes. The dust is forced through hose lines by high-pressure machines with a blower which allows applications in trackless entries or other places that the machine cannot enter. The most common mechanical types of rock dust applicators currently in use include high pressure bulk, Bantam, Slinger, Trickle, Wet/Slurry and Mine-wide automated dusting systems (The U.S. Mine Safety and Health Administration, 2016b).

Rock dusting can be applied either dry or wet (Snell, 1956). Experiments carried out in a US Experimental Coal Mine have shown that a mixture of 20-30 liters of water with about 45 kg dust yields good wet dust application from the standpoint of adherence. Wet stone dust should be applied at a rate of not less than 0.92 kg/m² of surface area to assure a good side-roof surface coverage. Drying rate of the stone dust depends on the air velocity and relative humidity. With normal air currents and relative humidity below 80-90%, the wet rock dust mixture can dry in about a week (Anonymous, 2013). Wet stone dusting is less effective than dry stone dusting in arresting the propagation of an explosion due to the deterioration in their dispersibility upon drying. Dry dusting can be
applied by a machine which slings dry dust onto surfaces of the mine or by hand, while wet rock dust is typically applied by mechanization due to its high fluidity. Figure 2.1 gives a general idea about the bulk rock-dusting system.

Figure 2.1. General bulk rock dusting system (Anonymous, 2013).

2.2. LIMITATIONS ASSOCIATED WITH ROCK DUSTING APPLICATIONS

2.2.1. Dry Dusting Application

The dry dust generates the best lift characteristics and dispersibility as the buoyant nature of rock dust is essential for coal dust explosion mitigation (McDonald, 1938). An example of the dry dusting process is shown in Figure 2.2. When an underground coal mine explosion occurs, rock dust must be readily dispersed so as to effectively quench the flame front of the propagation (McDonald, 1938; Greenwald, 1938a; Cybulska, 1988). However, the adverse effect of dry dusting is the airborne dust which is detrimental to coal miners’ health after being inhaled. A health surveillance program administered by the National Institute for Occupational Safety and Health (NIOSH) was
conducted among US coal miners in 2011 to detect the proportion of miners who had been diagnosed with pneumoconiosis (NIOSH, 2011b). As shown in Figure 2.3, percentage of miners examined with pneumoconiosis by tenure in coal mining indicates that followed 30 years of declines, a recent resurgence of black lung disease occurred from the beginnings of the 2000s which is unexpected. The U.S. Mine Safety and Health Administration (MSHA) issued a final rule in 2014 to lower the concentration limits for respirable coal mine dusts which imposes a severely restricted regulation on the upper limits of respirable dust coal miners can be exposed to (MHSA, 2014). In this case, if actions were taken to apply only limited quantities of rock dust given the purpose of reducing respirable particles, the productivity of the coal mine will be significantly affected as a result.

Figure 2.2. An example of the dry dusting process (MSHA, 2016a).
2.2.2. Wet Dusting Application

The problems associated with dry dusting can be overcome by the application of wet dusting. Wet dusting is normally conducted through a wet mixture of rock dust and water which is subsequently sprayed onto all the areas necessary for inerting (Snell, 1956), as shown in Figure 2.4. Wet dusting is able to greatly reduce the amount of respirable dust during the application but results in another problem pertaining to the caking of the wet rock dust which leads to a significant reduction in the dispersion characteristics necessary to be effective for mitigating dust explosions (Greenwald, 1938a; McDonald, 1938; Mozumdar and Singh, 1974). Caked rock dust cannot be dispersed by a blast of air due to the compaction and adherence among the dust particles. Thus, the inerting effect of rock dust on quenching the flame-front is no longer sufficiently maintained (Seaton et al., 1961).
Advantages and Disadvantages coupled with either dusting application method and mine operators baffle with the hazards that accompany with the chosen dusting application. Significant effort has been focused over several decades to remedy or reduce the associated problems with the two dusting applications. A common approach has been to modify the surface chemistry of the dust particle to render the surfaces hydrophobic which would cause the water to drain more readily through the applied rock dust and alleviate the cake formation.

2.3. FUNDAMENTALS OF CAKING PROCESS IN BULK SOLIDS

2.3.1. Caking Mechanism

Agglomeration commonly occurs with bulk solids such as food powders, pharmaceutical excipients, detergents, fertilizers, inorganic salts or other fine powders during storage, which is due to strong cohesive strength among powder particles and ultimately forms caked bed of solids. Caking is usually used to describe the change of bulk solids from free flowing materials into lumps bonding together by inter-particle forces (Specht, 2006). In general, inter-particle forces include the attractive dispersion force and the electrostatic force which can be attractive or repulsive depending on the conditions of the medium.
Sintering, chemical reaction, melting adhesion, binder hardening and crystallization are the well-known caking mechanisms firstly proposed by Rumpf (1958), which shed light on the study of bulk solids’ caking process.

Sintering is a process normally applied in the metallurgical area to prepare feed materials for steel-making or iron-making. The principle of sintering is the diffusion of molecules or atoms based on thermal activity to form a solid piece. The diffusion is only appreciable at the temperature above about one-half to two-thirds of the melting temperatures of materials. The chemical reaction depicts the reaction that occurs between two different materials to form one object through a chemically transformation such as the oxidization of magnetite in an atmosphere full of oxygen to form hematite. As for melting adhesion, it usually occurs between materials with low-melting points such as organic chemicals, thermoplastics and also low-melting inorganic compounds. Their melting points can be easily reached at the contact points while being deformed or bended by heat generated, thus being fused together. Furthermore, binders are also used to cement the objects together, e.g., the sawdust can be mixed with a starch paste binder and be bonded together as a briquette by pressing using simple briquette making presses. In addition, while placing materials in humid air, moisture is adsorbed into the powders and partially dissolves the water-soluble materials. Liquid bridges are formed at the contact points of the particles. Later on, due to the change in the temperature and humidity, moisture is evaporated and only solid crystal bridges are left. This is the caking mechanism, termed “crystallization” (Rumpf, 1958).

More recently, the concept “glass transition” was introduced to study most cases of amorphous food caking (Noel et al., 1990; Aguilera et al., 1995) and glass-rubber transition of polymers (Zuiderduin et al., 2003). As a result of the increase in the ambient temperature or the moisture adsorption, the glass transition temperatures $T_g$ of amorphous materials are achieved or lowered and materials enter the rubbery state which are subsequently solidified and strong solid bridges are formed due to the fluctuation of processing condition in terms of temperature and humidity (Aguilera et al., 1995).

Crystallization and glass transition are the two predominant mechanisms for the most undesired caking phenomenon (Specht, 2006). The major compositions of rock dust are
usually calcite, dolomite or aragonite, all of which are crystalline minerals. When rock dust is applied in a damp underground coal mine or wet form, saturated solution of soluble materials comprising the dust particles is formed at the contact points of particles and water bridges are thereby created. Water bridges that form between the particles due to humid conditions or the wet application process provide the medium through which the particles can agglomerate if the balance of the inter-particles forces is attractive. With or without particle agglomeration, the water bridge gradually evolves into a ‘rock bridge’, such as crystal calcite monohydrate, through water evaporation and dust particle recrystallization over time as a result of the fluctuation in the atmospheric temperature or humidity (Rumpf, 1958; Tardos et al., 1996; Purutyan et al., 2005; Farber et al., 2005; Bika et al., 2005). Normally the caking process among bulk solids is completed within multiple wetting and drying cyclic stages (Christakis et al., 2006), which is represented in Figure 2.5. This process eventually forms a caked bed of solids that is not as effective as free moving particles for suppressing dust explosions. The dispersibility of rock dust, which is crucial in dust explosion mitigation, is substantially reduced as a result of the caking effect.
CaCO₃(s) + H₂O(l) = Ca²⁺(aq) + CO₃²⁻(aq) + H₂O(l)  \[ \text{CaCO}_3 \text{H}_2\text{O}(s) \]

2.3.2. Size Effect

As previously mentioned, 30 CFR § 75.2 identifies the particle size requirements for rock dusts applied in underground mine which is 100 percent of which pass through a 20-mesh sieve and 70 percent or more of which pass through a 200-mesh sieve. Rock dust size is believed to have a profound effect on the amount of rock dust required to inert. Large-
scale test results on the relative effectiveness of rock dusts of different sizes were published by the Bureau of Mines in 1933 and reproduced by Greenwald (1938a) as shown in Figure 2.6. The distribution curve justifies the advantage of having finer grinding up to 70 percent minus 200 mesh. Work has been done by Amyotte and Mintz (1995) with respect to the effect of rock dust sizes on inerting. They proved that, for a given coal size, the inerting requirement for rock dusting decreased as the mass mean diameters of the rock dust decreased. The reason for that is the decrease in the mass mean diameter of rock dusts results in increased surface area which leads to greater heat adsorption and better inerting effect. A range of inerting levels for the same coal were generated with different sizes of rock dusts in their study. Dastidar and Pegg (1995) also conducted similar work and came up with the same trend which could be explained by promoting greater radiant heat adsorption and subsequent flame quenching.

Figure 2.6. Relative effectiveness of rock dusts as a function of different sizes (Greenwald, 1938a).

However, the particle size distribution and the average size have a major influence on the flowability and caking tendency of powders. Tests conducted by Kalman and Tardos (2005) indicate the significant influence of the average particle size and the size
distribution on caking tendency of materials. Figures 2.7 and 2.8 show shear stress values (an indicator of cake strength) after 24 hours of storage as a function of the median particle size and size distributions of the same material (chemical components). Clearly, as the particles become larger than about 75 microns and the span of the size distribution becomes narrower, the caking tendency disappears. The trend associated with decreasing particle size is understandable since water adsorption would increase due to higher particle surface area.

Figure 2.7. The caking tendency variation resulting from various average particle sizes (Kalman and Tardos, 2005).
2.3.3. Temperature Effect

As previously mentioned, the adhesion of fine powder occurs mainly through the adsorption of moisture/water onto the surface of solids particles. This in turn causes the formation of liquid bridges at the particle-particle contact points. Subsequent water evaporation as a result of the fluctuation in temperature and humidity causes the formation of dry bridges. Thus, temperature has a definite effect on the caking process of rock dust in the underground coal mine.

Studies have been conducted regarding the temperature effect on powder behavior such as powders’ stickness (Downton et al., 1982), and mechanical properties such as cohesion and compressibility of the powder (Shotton et al., 1966; York and Pilpel, 1973).

Related works have also been done to study the influence of temperature on bulk solids caking tendency. Figure 2.9 is an example showing that by varying the storage temperature of the tested solids, shear strength changed accordingly and shear strength is an indicator of the solids caking tendency. A higher shear strength value indicates that the solids are more prone to caking.
The processes of powder caking due to moisture uptakes and migration can be summarized into the following steps according to the study of Christakis (2006):

a. Wetting and moisture adsorption,
b. liquid bridging,
c. drying and moisture desorption,
d. hardening and solid bridging,
e. compacting and caking.

The wetting/drying cycles are crucial to fulfilling the caking process of powder materials. The interaction between powder and ambient humidity could be quantified by conducting adsorption/desorption tests which will be further discussed in a subsequent section. Measuring the sorption isotherms at different temperature ranges provide an indication of how temperature affects the sorption process. Specht (2006) has done similar tests in terms of temperature effect on the moisture sorption of sodium carbonate monohydrate and decahydrate, which illustrate that the increase in the temperature elevates the total moisture uptakes and different hydrates are formed at certain critical relative humidity values.
However, for a given relative humidity, water sorption isotherms of foods at several temperatures usually show a decrease in the amount of adsorbed water with an increase in temperature (Iglesias and Chirife, 1982). Teunou et al. (1999) believe that flour demonstrates the behavior while tea powder demonstrates the opposite behavior. On one hand, more energy is adsorbed to liberate the moisture resulting in a decreased moisture content of the powder materials when temperature is increased; On the hand, the increase in the temperature at a constant relative humidity means higher concentration of water vapor and more moisture is taken up by powder leading to a higher moisture content. Therefore, the interplay between these two aspects should be carefully considered to determine if the equilibrium moisture content of the powder materials and the ability of powders to adsorb moisture are composition-dependent (Teunou et al., 1999).

Wetting and drying cycles which facilitate the powder caking process could be realized by conducting a temperature cycle. The temperature fluctuation is one of the important factors driving the moisture migration that propagates the caking event. Wang and Christakis (2004) applied the finite-volume method to construct a numerical model and simulated the moisture migration in an infinitely long cylindrical sugar bag in which the temperature of the exposed surface was varying periodically with time-as shown in Figure 2.10. Test results prove that moisture migration in big bags was reduced by decreasing the oscillating temperature amplitudes and oscillating temperature averages.
Oscillating temperature environment has also been created by Specht (2006) to prepare caked solids in which the temperature was varied from 25°C to 50°C and back in a 24-hour cycle. The samples were held at each temperature for approximately 7.5 hours and the temperature was increased or decreased at a rate of 2°C per minute.

Also, Ezaki and Sugiyama (1960) reported that the caking strength of NaCl varies with temperature according to the following empirical relationship

\[ \sigma \propto 10^{(0.0100 - 0.00665)t_e} \]  

where \( \sigma \) is the caking strength and \( t_e \) the temperature.

Christakis (2006) further reported that the equilibrium relative humidity could be obtained through obtaining the solution of the following quadratic derived from the sorption isotherms for granulated sugars.

\[ \frac{m_2y_2}{100} \left( \frac{T}{20} \right)^\alpha ERH^2 + m_aY_sERH + \frac{m_2y_1}{100} \left( \frac{T}{20} \right)^\alpha - K = 0 \]  

(2)
where $\gamma_1$, $\gamma_2$ and $\alpha$ are dimensionless constants specific to granular sugar, ERH the equilibrium relative humidity of air, $m_a$ the mass of air in an element, $Y_s$ the saturated absolute humidity ($\text{Kg water}/\text{Kg dry air}$), $T$ temperature of air or granular sugar ($^\circ\text{C}$). $K$ is a value that can be acquired through calculation. All these indicate that the temperature plays a significant role in controlling the moisture migration and caking process.

2.3.4. Relative Humidity Effect

As known, the interaction between the powder and ambient humidity is a determining factor as well in controlling the caking process. This kind of interaction can be quantified by conducting adsorption/desorption test, in which a small amount of dry samples are exposed to a range of relative humidity values at a constant temperature. The relative humidity is initially increased from 0 to 100% stepwise (typically 5 to 10%/step), then decreased back from 100% to 0%. The change in the weight of samples is recorded and expressed as a function of relative humidity, which is termed the adsorption/desorption isotherm. The shape of the sorption isotherm contains insightful information on the type of interaction that occurs between the powder and the vapor (Purutyan et al., 2005).

Brunauer firstly proposed five types of adsorption isotherms in 1940, as shown in Figure 2.11. For these five types of adsorption isotherms, Type I represents the well-known Langmuir adsorption, characterized by a monotonic approach to a limiting adsorption.
Type II is common for physical adsorption, multilayer can be formed while type III is relatively rare, e.g., N\textsubscript{2} is adsorbed on ice, characterized by a heat of adsorption no more than the heat of liquefaction of the adsorbate. Type IV and V are commonly for capillary condensation, level off before the saturation pressure is achieved (Adamson et al., 1997).

However, there are sorption isotherms of powder materials such as crystalline minerals that could be described by other forms rather than Brunauer’s classification. Various hydrates could be formed at different characteristic RH for crystalline materials and the interaction between the powders and relative humidity is of great significance to predict the onset of the caking event (Specht, 2006). Efforts should be continuously devoted to the investigations upon specific test materials due to the fact that Brunauer’s classification of adsorption isotherms cannot represent all the possible adsorption types and for a single material, the sorption isotherm could be unique and significant.

Studies have been conducted on the hygroscopic and crystalline materials to prove the humidity effect on powder caking process. Tardos (1996) developed a series of tests on the caking behavior of fine crystalline powders. For example, laundry detergents form crystalline bridges of sodium carbonate as the material hydrates by adsorption of moisture from the surrounding atmosphere or from other components of the powder. It was found in the study that the change in the bulk volume of the detergents, approximately by 10\%, occurs at a critical relative humidity where hydrates of sodium carbonated are formed and is associated with the powder caking. Similar behavior has been observed as well for other crystalline powders: caking of these powders could be directly related to the relative humidity where a large quantity of moisture was taken up by the crystal (Tardos, 1996).

Research has been done by Farber et al. (2005) to elucidate the properties of pharmaceutical granules produced by wet-granulation. In their work, the force exerted by drying bridges among particles and the dry bridges strength were determined by applying additional external force and following its deformation and ultimate rupture. The effect of relative humidity on bridge solidification was studied for 5\% HPC (hydroxypropyl cellulose)-5\% lactose bridges and results are shown in Figures 2.12a and b. Figure 2.12a shows the force developed during drying up to 10,000 sec while Figure 2.12b shows the
deformation and rupture of the drying bridges under tension. As seen in Figure 2.12a, the force that develops at higher humidity is smaller than that developed at lower humidity. The conclusion can also be drawn from Figure 2.12b that deformation to failure is much higher at 40% than at 20 and 30% RH, and that a brittle-to-ductile transition is indicated between 30% and 40% RH in the materials. This agrees well with the glass transition temperature of the material being a function of the relative humidity (Farber et al., 2005).

The effect of various relative humidity values on the caking process of sugar was also investigated by Christakis et al. (2006). The test work indicates that the tensile strength increased when the boundary humidity which the test sugar powder was exposed to was elevated as higher humidity resulted in an increase of moisture which sugar adsorbed during wetting. This led to an increase in the solid bridge radius during drying and the tensile strength of the caked materials increased as a result.

Teunou et al. (1999) conducted an evaluation of the influence of relative humidity on the flowability of the food powder including flour, tea and whey permeate, which shows that relative humidity has a stronger influence on the flowability of tea and whey permeate powders compared to a relative less significant effect on flour. After moisture uptakes at high humidity values, the tea powder transform into a sluggish rubbery material and whey-permeate powder was transformed into a very strong cake because of the formation of strong lactose crystal bridges between particles. However, only weak cake was formed for flour under identical conditions. The results are depicted in Figure 2.13.
Figure 2.12. Relative humidity versus bridges strength during: (a) solidification and (b) tension experiment (Farber et al., 2005).
The effects of relative humidity on the cake strength of sodium carbonate have been investigated by Specht (2006) through using the Schulze shear cell which demonstrates that more moisture is adsorbed by the particles at higher relative humidity values and the moisture uptakes lead to the increase in shear stress that in turn increases the unconfined yield strength. Also, the kinetic rate constant of the sodium carbonate decahydrate adsorption and desorption were plotted as a function of relative humidity in the study, which is reproduced in Figure 2.14. The relative humidity has a substantial influence on the desorption and adsorption rates which are the pivotal factors controlling the moisture migration and solidification process to induce the caking process.

Figure 2.13. The effect of relative humidity on particles interaction in: (a) flour (b) tea and (c) whey-permeate powder, at 20 °C (Teunou et al., 1999).
Corresponding to the oscillating environment caused by fluctuating temperature, varying relative humidity can work in a similar way to facilitate the caking process through driving moisture migration inside the bulk solids. As for the work done by Christakis (2006), the temperature was held constant while varying the relative humidity from a high level to a low one in numbers of cycles, which greatly affects the caking process.

In reality, considering one factor excluding the other one may not be feasible since the ambient temperature and relative humidity keep changing all the time and variable temperature and relative humidity are both crucial in inducing the wetting and drying cycles and moisture migration. Therefore, the combined effect of these two parameters should be kept in mind and often predominant.

2.3.5. Moisture Content Effect

Moisture content is another factor that should be taken into account. Previous studies have investigated the effect of moisture content on powder behavior and flowability such
as the angle of repose and friction coefficient (Zaallouk et al., 2009), the stickness (Downton et al., 1982), cohesion (Kemper et al., 1984) and the powder flow function (Amidon et al., 1995). Teunou (1999) indicated that the flowability of a powder first decreased with the increase in the moisture content upon a critical water content, then it increased. The rate of decrease and the critical water content depend on the powder and how it interacts with water. The flow properties of moist insoluble bulk materials are primarily determined by the moisture content and particle size distribution. Johanson and Paul (1999) showed in their work that low moistures are more likely to cause problems and high moisture may dissolve recrystallized solids and prevent strength gain. In addition, some materials include moisture in the particles or crystals, which can be a source for moisture sorption to gain strength, especially with temperature fluctuations.

Ezaki and Sugiyama (1960) pinpointed that their experimental data of $\sigma$ (caking strength of sodium chloride) yielded a maximum point with a series of moisture contents, which indicates that critical moisture content existing in sodium chloride powder provides the maximum caking strength. The results of their study are shown in Figure 2.15.

![Figure 2.15. Caking strength of NaCl versus moisture content, with a maximum value being generated (Ezaki et al. 1960).](image)

Efforts have been made by Beresnevich and Borisov (1977) to investigate self-adhesion of quarry rock dust through a specially developed device in the presence of compacting
load due to the fact that the dust in a quarry (rock mass) is often subjected to them from the wheels of tipping trucks, etc. In addition to the changes in the compacting load, moisture contents of the dusts were varied from 0 to 28% with repeated experiments in the study. The results of the investigations are reproduced in Figure 2.16. It can be clearly seen that the self-adhesion force of quarry rock dust gradually increased with moisture content upon a critical value, then sharply decreased, regardless of the compacting load. The critical moisture contents for magnetite hornfels, shales, and oxidized ores are around 20%, and for limestone is 24%, which is dependent on the rock type. Beresnevich and Borisov (1977) illustrate that this is apparently due to the maximum molecular moisture capacity of the material ($\phi_{m.m.m}$), and when the material is wetted to the value of $\phi_{m.m.m}$, the fine powders begin to acquire the properties of fluidity, converted to a gel, and self-adhesion decreases.
Figure 2.16. Self-adhesion force as a function of moisture content of rock dusts (0-50µ fraction) and compacting load: (a) limestone; (b) unoxidized magnetite hornfels; (c) oxidized ore; (d) shales; (1) without compacting load; (2,3,4) compacting load of 5,12.5, and 25 g/cm², respectively (Beresnevich and Borisov, 1977).

2.3.6. Exposure Time Effect

The caking phenomenon is a time-dependent process due to the fact the ambient environment can impose a gradual evolution on the bulk solids over time. Therefore, the caking phenomenon of bulk solids is closely dependent on the time. It must be kept in mind that the effect of relative humidity and temperature on powder flowability will also depend on the time exposure to those conditions (Teunou et al., 1999). Tanaka (1978) has concluded that the relationship between the caking strength and the moisture content should be well understood in relation to the time elapsed when the measurement is made. Kalman and Tardos (2005) found that the measured shear strength of the tested sample increases more rapidly as a function of time which indicates a higher tendency to cake induced by a long time period. Figure 2.17 including the photographs of lumps and
agglomerates after shearing is showing that caking increases with time and the caking strength is doubled after about two months, after which the process starts to be stabilized.

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![Figure 2.17. Caking tendency versus storage time during storage compression under normal pressure (Kalman and Tardos, 2005).](image)

Tardos and Farber (2007) have conducted a number of studies pertaining to the time dependence of the strength of solids and solidifying inter-particle bridges in granules of pharmaceutical powders. They illustrated the strength of the solidified bridge was generated through the crystallization process of the solids inside the saturated solution which is a strongly time-dependent evolution process. It is known for sure that moisture uptakes for materials will be substantially influenced by the time for which they are exposed to a humid environment, as shown in Figure 2.18 in the early study of Tardos (1996).
As previously mentioned, Christakis (2006) applied the wetting/drying cycles towards the granulated sugar, the tensile strength of which were dependent on the number of cycles that apparently is time-dependent as well. One example of his studies is given in Figure 2.19.

Figure 2.18. Moisture adsorption by a single granule of HZ-280 powder (Tardos et al., 1996).

Figure 2.19. The predicted and experimentally measured tensile strength of a granulated sugar sample after 32 8-h wetting/drying cycles in a tensile strength test (Christakis, 2006).
In summary, the work regarding a multitude of determining factors that influence the caking process of rock dust is very limited and rare to date. However, related research conducted on the caking events of other powder solids, as mentioned above, shed light upon how to design the experimental tests and investigate the caking phenomenon of rock dusts based on a good understanding of the fundamentals of the caking mechanism.

2.4. FUNDAMENTALS OF SURFACE CHEMISTRY MODIFICATION ON ROCK DUST

2.4.1. Surface Modification Potential

Rock dust is typically pure calcium carbonate powder which is also the most widely used filler in the plastic, rubber, paper, pigment and ink industries (Solomon and Hawthorne, 1983). The particle size distribution of the material is characterized by 100% and 70% of which is finer than 850 and 75 microns, respectively. Hydrophobization of rock dust surface through surface chemistry modification has been believed to effectively eliminate the cake formation and improve their dispersive characteristic for underground coal mine explosion mitigation (Mozumdar and Singh, 1974; Greenwald, 1938a; Spence, 2006; Vogt, 2011; Doidge and Anstine, 2014). The surface modification of calcium carbonate has been widely studied for other applications including the purification of the material using froth flotation. The following sections provide a review of research that specifically focused on methods to render the calcium carbonate surface hydrophobic.

2.4.1.1. Surface Modification of Composite filler

As aforementioned, calcium carbonate is the mostly widely used fillers for functional composite materials preparation. Investigations have been intensively conducted to convert the calcium carbonate filler from hydrophilic to hydrophobic. Fatty acid, surfactant, resin etc. are commonly used for the calcium carbonate filler modification purposes (Jeong et al., 2009). Other modifying reagents involving polystyrene (PS), polypropylene (PP), low molecular weight polyethylene (PE), monomer-styrene (Wu and Lu, 2003) and silane coupling agents (Jirui, 2010) were also applied to modify the calcium carbonate surface. In addition, investigations on mechanochemical surface
modification of calcium carbonate have also been carried out using sodium stearate (Ding et al., 2007; Ding et al., 2013), alkyl amine dimethyl phosphonic acid (Ding et al., 2008) and poly grafting (Wu and Lu, 2003) in a wet stirred mill. Modified calcium carbonate coated with organic compound by surface modification is a common way to prepare functional materials. The hydrophobicity of modified calcium carbonate is greatly improved, and their surface free energies are correspondingly decreased which result in reduced particle agglomeration, enhanced dispersion and improved powder flowability.

2.4.1.2. Surface Treatment and Wettability Alteration of Calcite/Rock

The surface of calcite is often rendered organophilic by various surface modifiers such as fatty acids, phosphates, silanes, titanates, or zirconates (Osman and Suter, 2002), which is similar to the surface treatment of ground calcium carbonate to prepare functional fillers. Osman and Suter (2002) concluded that monolayers of saturated fatty acids with long alkyl chains lead to a relatively well-ordered solid-like phase while the lower homologs (≥C10) yielded monolayers with dynamically disordered phases. For the unsaturated fatty acid-oleic acid, the monolayer of oleate acid molecules coated on the surface of calcite is subsequently polymerized generating a polymeric monolayer at relatively low temperature due to the immobilization of oleic acid by tethering them to the surface of calcite.

Wettability alteration of reservoir rock is a method of extreme significance in oil recovery and the wettability reversal of reservoir rock mineral from hydrophilic to oleophilic have been investigated fairly intensively (Karoussi and Hamouda, 2008). Adsorption of organic fatty acids (RCOOH) in the presence of a water film has also been reported to alter the water wetness of carbonate rocks towards more oleophilic (Gomari and Hamouda, 2006; Gomari et al., 2006; Karoussi and Hamouda, 2008).

2.4.1.3. The Flotation Behavior of Calcite

The interaction between fatty-acid-based collectors and salt-type minerals including calcite in the flotation process is a significant perspective from which valuable information can be generated for the purpose of modifying the surface of rock dust particles. The most extensively used collectors for these minerals are the long-chain fatty
acids and their alkaline salts, especially oleic acid and sodium oleate (Pugh and Stenius, 1985).

Studies have been made of the interaction of oleic acid and sodium oleate with calcite and their effects on the flotation of calcite (Peck, 1963; Fuerstenau and Miller, 1967; Atademir et al., 1981; Mishra, 1982; Marinakis and Shergold, 1985a; Marinakis and Shergold, 1985b; Pugh and Stenius, 1985; Rao et al., 1989; Rao and Forssberg, 1991). The series of investigations covered a number of technical areas including the electro-kinetic properties, liquid surface tension, solution chemistry, flotation behavior and adsorption mechanism. The maximum flotation response for calcite in an oleate system was achieved under conditions providing minimum interfacial tension at the air/solution interface, which occurs at high pH values by synergistic co-adsorption of acid-soap dimers, oleate monomers, dimers and neutral oleic acid molecules on the calcite surface. These associated surfactant species render the mineral hydrophobic and enhance the adhesion strength between the bubble and the calcite particles, thus increasing flotation efficiency (Pugh and Stenius, 1985). This information can be used to the benefit of preventing the caking of rock dust particles when applied to suppress coal dust explosions in damp underground mines or for the wet application of the rock dust in any coal underground operation.

2.4.2. Surface Modification for Dry Dust Applications

To enhance the effectiveness of rock dust for explosion mitigation, research programs were initiated in an attempt to resolve the caking issue. It was found that developing a waterproofing rock dust provide the means to prevent the dust from caking and thus improve dispersibility (Greenwald, 1938a). Greenwald and his co-worker (1938a; 1938b) mentioned in their studies that limestone dust treated with a water-repellent substance is difficult to wet and dries without caking even after being vigorously agitated with water; In addition, using rock dust in moisture-proof paper bags for tests of barriers unquestionably increased mine safety when rock dust was subjected to dampness (Greenwald, 1938a; Greenwald and Howarth; 1938b). These preliminary findings were the basis for subsequent research programs that investigated the technical and economic
feasibility of waterproofing rock dust particles as a promising solution to the difficulty of mine dusting field.

In 1954, McHan (1954) developed a patented calcium carbonate processing procedure that resulted in rock dust that was resistant to caking. McHan claimed a method of preparing pulverized limestone by adding a fatty acid compound selected from the group consisting of stearic, palmitic, oleic acids and their alkaline salts onto dry limestone as it is continuously fed into the continuous type pulverizer. This fatty acid group can be other higher fatty acid, either saturated or unsaturated, with a carbon atom number ranging from 10 to 22 and their derivatives such as capric, abietic, lauric, erucic, perilla oil, tall oil, linseed oil, fatty acids or alkaline metal salts. The concentration of the fatty acid and their derivative was no more than 0.3% of the dry limestone (by weight). The treated pulverized limestone product with a particle size ranging from 1 to 100 microns was particularly desirable as mine dust due to excellent dispersion characteristics. The effectiveness of the treated limestone dust for dusting purpose was decidedly improved in a damp underground coal mine application.

Several decades later, Mozumdar and Singh (1974) used stearic acid, palmitic acid and oleic acid of different quantities to waterproof rock dust. The effect of waterproofing on moisture adsorption, dispersibility, and inerting property of the rock dust was also investigated. Their tests results indicated that the dispersibility of rock dust is affected by moisture adsorption, however there is no direct relationship between moisture adsorption and dispersibility. No deterioration of waterproofing effect and the loss of flame quenching effect were detected for the fatty acid-treated rock dust particles for up to 96 hours. Mozumdar and Singh’s test results (1974) and McHan’s invention (1954) corroborate that the concept of water-repellent rock dust introduced by Greenwald and his coworkers in 1930s (1938a; 1938b) is proceeding towards the right direction.

In the 1990s, Polish researchers attempted to coat the limestone powder with stearic acid during the grinding process in stone mills; however due to the complex construction of modern mills, contamination of hydrophobization agents provided an undesirable result (Vogt, 2011; Buczek and Vogt, 2014).
A multi-stage treatment focused on rendering the surfaces hydrophobic followed by charging of the particles to improve particle dispersion was investigated to modify ultra-fine calcium carbonate powder to provide better dispersion properties (Ren et al., 2001). The method was applied by initially modifying calcium carbonate powder with modifiers including aluminic ester, sodium lauroyl sulfate and triethyl phosphate, followed by feeding the modified powder into a RLW electrostatic dispenser uniformly to charge the particle surfaces. Test results showed that powder dispersion was significantly improved through the weakening of the Van Der Waals force, capillary bridging force based on reduced surface free energy of solids, and increasing the electrostatic force caused by the same type charge-charge repulsion (Ren et al., 2001).

Spence (2004) later claimed in his invention that coating compositions containing a metallic salt of an aliphatic carboxylic acid and an effective amount of diluent for coating bulk solids are effective to reduce dust and cake formation in fertilizers and bulk solids. The metallic salt of an aliphatic carboxylic acid and the diluent can be selected from methyl and ethyl esters of fatty acid, oils, a vegetable oil including corn oil, canola oil, cottonseed oil, sunflower oil, soybean oil, linseed oil, castor oil or tall oil, glycerine, glycol, oligomers or polymers of glycerine or glycol, a petroleum hydrocarbon including white oil or refined mineral oil and their combination. This process is not specific for rock dust modification purposes. However, it sheds light upon how to resolve the caking issue of rock dust particles given a number of anti-caking reagents proposed in this invention.

Due to the aforementioned undesired contamination of the hydrophobic agent induced during the grinding process, Vogt and his co-workers (2008; 2009; 2011; 2013; 2014) continued to seek a new dust modifying method and successfully proposed two methods of limestone hydrophobization as an anti-explosive agent using stearic acid vapor and silicone solution. The hydrophobic (waterproof) limestone dust was prepared in a specially designed apparatus for well mixing and coating. The line schematic of the laboratory apparatus is reproduced in Figure 2.20 which applied high temperature ranging
from 170° C to 200° C to melt stearic acid and subsequently mixed it with rock dust countercurrent flow. The degree of hydrophobization and the preliminary estimate of the properties of the hydrophobized limestone dust were performed using the film flotation method and a Powder Characteristic Tester. The test results indicate the stearic acid vapor and silicone solution are both useful for hydrophobizing limestone dust forming a water-resistant material and the adhesive properties of particles are reduced after hydrophobization. The flow property of the modified limestone powders was also investigated using the knowledge that is normally applied in powder technology. The modified dust was beneficially enhanced based on improved dispersibility, flowability and floodability, the latter two of which are the typical characteristics of powder materials and indicate the ability of the powder to flow and its tendency to liquid-like flow, respectively. As previously mentioned, the way rock dust functions as an anti-explosive agent is by being serving as a thermal inhibitor or heat sink through heat adsorption and self-decomposition. The results of recent investigations (Buczek and Vogt, 2014) confirmed that the thermal decomposition character of the modified limestone dust was the same as regular dust which can effectively serve as an anti-explosive agent in a damp underground coal mine.
Investigations on-going simultaneously developed a method of coating calcium carbonate using stearic acid (Khanna et al., 2013; Anstine and Shurling, 2014). Calcium carbonate was treated through mixing the solids with an amount of stearic acid and an amount of water ranging from 0.1% to about 20% of the total weight of the mixture. Due to the insoluble nature of stearic acid in water solution at room temperature, high temperatures ranging from 65°C to 200°C were required for the application. Low or no detectable free stearic acid was observed using this modifying method which improves the modification.
efficiency due to the fact that most of the applied stearic acid agent is efficiently coated on the calcium carbonate particles. Afterward, the application was tested in an underground coal mine through which an anti-caking rock dust was confirmed (Anstine and Shurling, 2014; Doidge and Anstine, 2014). The concept of their research was blending untreated coarse limestone particles with fine treated (with stearic acid) hydrophobic particles so that the fine particles fill the voids between coarse particles and prevent the moisture migration. More important, the overall chemical consumption could be reduced from around 1% by weight of coarse particles to as low as 0.1% by weight of blended dust which renders the process more economically favorable. The contact angle measurements prove that with the increase in the blended portion of treated fine dust particles, the contact angle of blended particles is generally increased. Tests conducted in the dust dispersion chamber and NIOSH 20-l explosive chamber indicated that all the dust particles blended with treated fine particles were dispersible after application and aid their inerting effect in an event of a favorable coal dust explosion condition as compared to the effect of conventional caked rock dust. However, it was hard to discern any trends for the blended series tested in the study from a quantitative standpoint and the dust dispersion chamber presented its own design inadequacy which blurs the test trends.

Anstine and Shurling (2014) further proceed and expand the application with other effective modifying agents in addition to stearic acid. They claimed in their invention that rock dust comprising of untreated calcium carbonate and calcium carbonate treated with at least one fatty acid, a salt or ester with a chain length of C16 or greater could serve as a non-caking mine rock dust and render the coal dust explosively inert.

The comparison between the aforementioned investigations with respect to dry rock dust modification is summarized in Table 2.1 in chronological order. The corresponding novel contribution as well as the remaining issues is also incorporated in the table. It is not difficult to find that related study has been conducted to a limited extent and applied the similar chemistry, of which fatty acid group, especially stearic acid, is the most commonly used modifying reagents. In addition, previous investigations indicate that the concentration of modifying reagents imposes a significant effect on the modification
efficiency of rock dust and high concentration may lead to a reverse impact which calls for in-depth study. Challenges continuously remain to be solved in terms of how to make the application of the mine dusting together with dust modification operationally and economically feasible.
Table 2.1. Comparison between various dry dust modification investigations in chronological order.

<table>
<thead>
<tr>
<th>Time</th>
<th>Description</th>
<th>Chemical applied</th>
<th>Concentration</th>
<th>Novel contribution</th>
<th>Issues remain to be solved</th>
</tr>
</thead>
<tbody>
<tr>
<td>1938</td>
<td>Developed a water-repellent substance as an anti-caking agent.</td>
<td>NA</td>
<td>NA</td>
<td>Initially determined waterproofing rock dust is the pivotal point of anti-caking.</td>
<td>The operating process and test results are left blank.</td>
</tr>
<tr>
<td>1954</td>
<td>Prepared pulverized rock dust by adding chemical reagents into a continuous pulverizer.</td>
<td>Fatty acid</td>
<td>Less than 0.3% of dry dust by weight</td>
<td>Developed a complete calcium carbonate processing procedure.</td>
<td>Chemical reagents added during the grinding process cause undesired contamination.</td>
</tr>
<tr>
<td>1974</td>
<td>Investigated the effect of waterproofing on dispersibility and inerting quality of rock dust.</td>
<td>Stearic acid, palmitic acid and stearic acid</td>
<td>Less than 0.2% of dry dust by weight</td>
<td>Directly linked the waterproofing effect of rock dust with their explosion inerting quality.</td>
<td>The effect of waterproofing on the inerting quality of rock dust is not evaluated in the long-term run.</td>
</tr>
<tr>
<td>2001</td>
<td>Fed initially hydrophobized ultrafine calcium carbonate powder into a RLW electrostatic dispenser to charge the particle surfaces.</td>
<td>Aluminic ester, sodium lauroyl sulfate and triethyl phosphate</td>
<td>0.6% to 1.6% of dry powder by weight</td>
<td>Applied a RLW electrostatic dispenser to charge the particle surface given the purpose of increasing the dispersibility as a result of particle-particle repulsion.</td>
<td>It is not economically feasible in coal mining industries and only applicable to ultrafine powders.</td>
</tr>
<tr>
<td>2004</td>
<td>Developed a coating composition containing a metallic salt of an aliphatic carboxylic acid and an effective amount of diluent to reduce caking formation.</td>
<td>A general list of potential fatty acids, glycerine, glycol and their derivative products.</td>
<td>0.125 to 0.5% of the dry solids by weight</td>
<td>Generally applied to fertilizer and bulk solids.</td>
<td>No specific description was given and instructed for mine dusting field.</td>
</tr>
<tr>
<td>2008-2014</td>
<td>Proposed two methods of rock dust hydrophobization as an anti-explosive agent.</td>
<td>Stearic acid vapor and silicon solution</td>
<td>Stearic acid: 0.18% of dry dust by weight</td>
<td>Developed a self-designed apparatus to coat the rock dust and stearic acid vapor through countercurrent flow mixing.</td>
<td>Challenges are remained for scale-up and applying it in the mining industry.</td>
</tr>
<tr>
<td>2013-2014</td>
<td>Investigated the effect of hydrophobized rock dust on the inerting quality with a specially designed dust dispersion chamber and a scientifically designed NIOSH 20-1 explosive chamber.</td>
<td>Stearic acid</td>
<td>0.08% to 0.82% of overall rock dust by weight.</td>
<td>Developed a treating method by blending the untreated coarse particles together with treated fine particles given the purpose of preventing moisture migration and reducing overall chemical consumption.</td>
<td>It is hard to discern any quantitative trends due to the design inadequacy of the dust dispersion chamber. The need for the high temperature increases the operational difficulty.</td>
</tr>
</tbody>
</table>
2.4.3. Surface Modification for Wet Dust Applications

The review of existing dry dust surface modifications in the previous section shows promising results that indicate the potential of cake prevention after application in wet, underground mines. However, significant concerns exist over the application of dry dust due to the generation of respirable dust. As a result, operators have expressed significant interest in using a wet dust application. In addition, the wet application of rock dusting is easier to operate as opposed to dry application.

The aforementioned studies involving the dry applications indicate that stearic acid is the most commonly used reagent used to modify the rock dust surfaces. The process involves the setup of a hydrophobization apparatus and the application under high temperatures to melt stearic acid as illustrated in Figure 2.20. The experimental setup is relatively easy to control in the laboratory environment. However, a challenge is encountered when scaling up the process for applications in the underground coal mines. The difficulty is associated with a substantially enlarged operational scale involving the installation of boilers, heaters and compressors among other support equipment items.

As shown in Figure 2.21, simplification is achieved using the apparatus required for the wet rock dust applications. The system uses a large-volume container equipped with an industrial blender that is sufficient enough to mix the rock dust particles with modifying reagents as well as water. A high-pressure machine in connection with a nozzle sprays the prepared wet dust onto the mine floor, roof or ribs by inducing a high-velocity current. The wet application eliminates the operational difficulties associated with dry applications due to an aqueous operational environment which is simpler to operate. In addition, wet dust slurry leads to more coverage per unit weight of dust. Furthermore, the high viscosity and stickiness of the wet dust slurry render the particles more ready to stick to the mine area in contrast to the dry dust that easily falls from the mine roof and ribs resulting in a reduced buoyance and potential explosion inverting failure. In addition, it is well recognized that surface modification process is significantly more efficient in an aqueous environment compared to a dry modification process which can be attributed to the better interaction between the chemical and solid particles (Huang and Honaker,
High modification efficiency leads to a lower chemical dosage which substantially enhances the economic benefits of the wet dust application.

Figure 2.21. Simplified schematic of applying modified rock dust in wet application.

Therefore, wet dusting application needs particular attention at the moment and all the accompanying advantages make the predominant caking issue associated with wet dust upon drying extremely urgent. Several newly developed hydrophobic rock dust products have been reported recently which provide the potential to resist caking and maximize the degree of mitigating dust explosions (Perry et al., 2015). A few of the products are polymerized rock dust and foam dust developed from the addition of chemical additives to the water and rock dust admixture. These products can be applied in the same manner as wet dust while providing a level of dispersion comparable to that realized by dry dust applications without human exposure to respirable dust.

It is noticeable that studies pertaining to the modification of dust particles to facilitate wet applications are still rare to date and more attention has been drawn to the dry dust application which has recently been identified as a concern for the generation of respirable dust. Additional efforts are needed to ensure that the surface modification is technically and economically feasible including attention to the actual application process. Knowledge from the multidisciplinary areas including materials science, surface chemistry, powder technology and flotation, etc., should be fully applied to totally
understand the principles of dust caking and how to completely resolve the problem with positive impacts on the environmental health in underground coal mines.
3. CHAPTER 3. EXPERIMENTAL WORK

3.1. LABORATORY STUDIES

3.1.1. Sample Acquisition and Characterization

3.1.1.1. Rock Dust

Rock Dust used in the presented study was MineBrite G260, provided by J.M. Huber Corporation and produced in Marble Hill, Georgia. The rock dust is generally applied for mitigating coal dust explosion purpose. After receiving the rock dust from J.M. Huber, sample characterization tests were performed on the representative rock dust particles to get more detailed information.

X-ray Diffraction (XRD) and X-ray Fluorescence (XRF) are the two analytical techniques employed to determine the mineralogical and elemental compositions of the rock dust samples. XRD is a tool commonly used to identify the crystalline structure of the materials where the crystalline atoms cause a beam of incident X-rays to diffract in various directions. Based on the diffraction angles and intensities, the atom and molecular structure of a crystal can be determined. XRF is an analytical method that measures elemental content by characteristic X-rays emitted from a material after being bombarded by high energy X-rays (Huggins et al., 2016). The pure crystal structure of MineBrite G260 was confirmed by XRD analysis (D8 Discover, Bruker AXS, Germany) as shown in Figure 3.1 with x-axis and y-axis corresponding to the angles and intensity of the diffracted beams. XRD diffraction pattern of MineBrite G260 indicates the major composition of it is calcite with a relatively small amount of dolomite and even less amount of quartz.
Figure 3.1. XRD pattern of MineBrite G260 rock dust sample.

The XRF analysis (S4 Pioneer, Bruker AXS, Germany) shows the elemental composition of dust particles from a quantitative perspective and indicates that calcium carbonate accounts for more than 94% of the material followed by magnesium carbonate at 4.7% and silica at less than 1 percent. The amount of trace elements were also detected and presented in Table 3.1.

Table 3.1. XRF analysis results for the MineBrite G260.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CaCO$_3$, %</th>
<th>MgCO$_3$, %</th>
<th>Al$_2$O$_3$, %</th>
<th>SiO$_2$, %</th>
<th>Fe$_2$O$_3$, %</th>
<th>TiO$_2$, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>G260</td>
<td>94.07</td>
<td>4.69</td>
<td>0.05</td>
<td>0.52</td>
<td>0.16</td>
<td>193</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>MnO, ppm</th>
<th>K$_2$O, ppm</th>
<th>Na$_2$O, ppm</th>
<th>P$_2$O$_5$, ppm</th>
<th>SO$_3$, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>G260</td>
<td>128</td>
<td>104</td>
<td>100</td>
<td>644</td>
<td>4</td>
</tr>
</tbody>
</table>
Figure 3.2. Particle size analyzer used for particle size analysis.

CILAS 1064 Particle Size Analyzer (Figure 3.2) was employed to measure the particle size distribution of the rock dust particles by laser diffraction. The particle size analyzer with an extremely compact cast iron optical bench can integrate two sequenced laser sources positioned at 0° and 45°, to produce a diffraction pattern analyzed on a 64 channel silicon detector. Using its built-in software, the size distribution curve of the particles can be displayed over the range form 0.04 to 500 μm. The particle size analysis of rock dust particles used in the present study (Figure 3.3) found that the mean particle size was 25 μm while the 90% of the material was finer than 53 μm. Both the chemical composition and the particle size distribution satisfied federal regulations for rock dusting applications in underground coal mines. The surface area of the rock dust as determined by BET nitrogen adsorption (ASAP 2020, Micromeritics Instrument Corporation, USA) was 0.6677m²/g.
3.1.1.2. Chemicals

In the initial laboratory experimental tests, two chemical reagents including oleic acid and sodium oleate were evaluated. Oleic acid (OA) was obtained from Fisher Scientific which had a purity of more than 97%. Sodium oleate (NaOL) was supplied by TCI America which also had a purity level greater than 97%. The molecular structure of the two applied chemicals is shown in Figure 3.4, from which it can be clearly seen that sodium oleate is the sodium form of oleic acid. In addition, stearic acid (SA) provided by TCI America with a purity greater than 98% was used as well to modify the rock dust particles.
Furthermore, a series of dispersants were applied together with sodium oleate in the present work and were expected to further increase the dispersibility of initially hydrophobized dust particles. Those applied dispersants include sodium silicate (SS), sodium metaphosphate (SM) and sodium polyacrylate (SP) which are commonly used in the process industries to enhance the dispersive properties of particles. The sodium silicate solution and sodium metaphosphate powder were both purchased from Fisher Scientific, which had a purity of approximately 40% and was laboratory grade, respectively. The sodium polyacrylate was provided by Sigma Aldrich with water impurities around 8-14% by weight. Other reagents, such as sodium hydroxide and hydrochloric acid (pH regulators), were all analar grade reagents.
3.1.2. Sample Treatment

The samples were prepared based on the industrial standard mixture ratio of 2:1 (rock dust to water, by weight), which is typically used in the wet rock dusting application. The required amounts of OA and NaOL were added to 25 ml of purified water to be either totally dissolved or homogeneously dispersed in the liquid. The purified water with the conductivity less than $1 \times 10^{-6}$ S·cm$^{-1}$ was used throughout the laboratory study. After the chemical solution was ready, 50 grams of MineBrite rock dust solids were subsequently added to the solution for a 15-minute conditioning with a magnetic stirrer, which allowed sufficient time to achieve a short-term equilibrium (Pugh and Stenius, 1985). The pH of the saturated rock dust solution was around 9.4. The way the rock dust was treated with the applied chemical reagents is shown in Figure 3.4.

![Figure 3.4. Sample treatment with a magnetic stirrer.](image)

When stearic acid was applied to treat the rock dust, experimental conditions were changed according to the insoluble nature of stearic acid at room temperature. The high temperature of approximately 100 °C was initially applied to melt stearic acid in 35 ml purified water instead of 25 ml. The reason for that is because of moisture evaporation, which would eventually reduce the total water volume at the end of the process. Therefore, the initial solvent volume was accordingly increased. During the subsequent
15-minute conditioning process, a low temperature of approximately 70°C was continuously applied to avoid the precipitation of stearic acid in the rock dust saturation solution.

For the investigation of dispersants, rock dust was initially treated with 0.1% sodium oleate by weight of total dry dust to create hydrophobic particles according to the aforementioned procedure. Dispersants were then applied with the hope of further increasing the dispersibility among dust particles, which were continuously conditioned for another 5 minutes.

3.1.3. Contact Angle Measurements

Figure 3.6. Line schematic of a contact angle formed at solid-liquid-vapor interface.

Contact angle is the angle formed at liquid-solid-vapor interface as shown in Figure 3.6, measured through the liquid, which is a significant indicator of the surface hydrophobicity. Sessile drop method was employed in the present work to study the modification efficiency on the rock dust particle surface. After the surface treatment procedure, the modified rock dust samples were filtered and washed 3 to 5 times with purified water to eliminate reagent molecules that may be weakly attached to the solid surface due to physical adsorption. The samples were subsequently dried in an oven at 105°C for a period of 24 hours. A circular pellet was produced from the treated and dried
rock dust particles using a Carver Auto Pellet Laboratory Press (Model 3887) with an applied compressive pressure of $1.4 \times 10^8$ Pa for around 45 seconds. The setup for the laboratory press as well as rock dust pellets is presented in Figure 3.7. The contact angle measurements were conducted with a laboratory goniometer (Ramé-Hart Instrument Corporation, USA), which consists of a specimen stage, a variable intensity illuminator and an optical bench as shown in Figure 3.8. The measurements were taking within 10 seconds after adding one drop of deionized water on the rock dust pellet using a micro-syringe. A minimum of 10 contact angle measurements was conducted for each sample.

(a) Carver Laboratory Press.  (b) Compressed rock dust pellets.

Figure 3.7. The setup of laboratory press and compressed rock dust pellets.
3.1.4. Zeta Potential Measurements

When the particles are placed in an aqueous solution, their stability will be determined by a multitude of variables among which the particle surface charges play a significant role. This is because charged particle surfaces impose either a repulsive or attractive force among each other. The particle surface can be charged through unequal distribution of lattice-forming ions at the surface, hydrolysis of surfaces, substitution of ions in the bulk of crystalline solids, tempering of solids or adsorption of ions on the surfaces (Adamson and Gast, 1997). A charged particle that is placed in an electric field will move toward an electrode of opposite sign via electrostatic attraction. During the transport process, particles with counter ions will stay close to the solid surfaces forming a rigid layer while counter ions that are loosely attached will be dispersed into the bulk solution at a distance. This is well established by Stern Model, which is a combination of Helmholtz-Perrin and Gouy-Chapman models, as shown in Figure 3.9. As a result of the ions configuration proposed by Stern, a shear plane (Δ) exists at the solids surface at a
distance into the bulk solution. The potential at the shear plane is called the zeta potential (ζ) or electro-kinetic potential (Adamson and Gast, 1997).

![Diagram of Stern Model of double layer distribution]

Zeta potential measurements of rock dust particles were thus conducted after conditioning the dust particles with the reagent for a period of 15 minutes. The measurements were performed using a Zetaplus analyzer supplied by Brookhaven Instrument Corporation, USA, as shown in Figure 3.10. Analar grade of sodium hydroxide and hydrochloric acid were applied to adjust the solution pH from 7 to 12. Zeta potential was measured and used to evaluate the electrostatic repulsion or attraction force between rock dust particles and the modifying reagents over a range of reagent concentration and pH values.
3.1.5. Moisture Desorption Tests

After the surface treatment step, the rock dust samples were placed in an environmental chamber (Caron-6010, Caron products, USA) where the atmosphere was controlled with a temperature of 20° C and relative humidity (RH) of 80%. Moisture loss of each slurry sample was monitored and recorded as a function of time to compare the moisture desorption rates of samples treated with different modifying reagents and quantities. The tests were based on the hypothesis that hydrophobic surfaces would release moisture at a faster rate than the untreated hydrophilic surfaces since the major goal of rock dust modification is creating hydrophobic particles so as to effectively repel water and eliminate the formation of water bridges and rock bridges. The environmental chamber used in the present study is shown as followings in Figure 3.11.
3.1.6. Dispersibility Tests

On the basis of an experimental apparatus and procedure described by Mozumdar and Singh (1974), an experimental apparatus was assembled and modified to determine the dispersibility of rock dust samples. Dispersibility tests were conducted by blowing a small quantity of rock dust into a cylindrical polycarbonate tube as shown in Figure 3.12, which was 7.62-cm (3 inches) in diameter and 2.3-m (7.5 ft) in length. One gram of a rock dust sample was loaded into a brass tee located at the top of the long tube followed by sealing the brass tube using a 1.27-cm (0.5 inch) diameter pipe plug (Figure 3.13). The stainless air reservoir (Figure 3.14) was filled with air to achieve a pressure value of 165 kPa (24 psi). The small valve at the bottom was utilized to release air when the desired pressure was exceeded. A pan was placed at the bottom of the cylinder to receive the settled particles.

When valve A was opened to inject the rock dust into the vertical cylinder with the assistance of the pressurized air, time was recorded and the weight of solids collected in the pan was measured as a function of time. The pan at the bottom receiving the settled particles was continuously replaced at the end of 3, 10, 20 and 30 seconds. Therefore, the amount of solids collected in each sequential pan was the incremental weight that settled.
during a given time interval (i.e., 0-3, 3-10, 10-20 and 20-30 seconds). Each test involved the injection of five 1-gram rock dust samples into the vertical tube under identical conditions and collection of the settled solids into the pans identified by each of the aforementioned time intervals.

The incremental weights were cumulated from the starting time interval (0 – 3 seconds) to the later intervals to obtain the amount of settled (non-dispersed) solids after time \( t \). The amount of rock dust remaining dispersed within the vertical tube after time \( t \) was then determined by subtracting the cumulated settled solids weight from the total weight of the rock dust injected (i.e., 5 grams). The dust dispersion values were determined as the percentage of the total amount of rock dust injected at \( t = 0 \) that remained dispersed after time \( t \) in the vertical tube.

3.1.7. Fourier Transform Infrared Spectroscopy (FTIR) Analysis

Critical to the success of the surface modification is the long-term stability of the surface coating. The adsorption mechanism that provides long-term stability is chemisorption whereas physisorption can be reversed by changes in solution chemistry (Erbil, 2006; Webb, 2003). Fourier Transform Infrared Spectroscopy (FTIR) analysis is commonly used to detect newly formed products resulting from chemical interactions or bondages by identifying their characteristic functional groups. To identify the adsorption mechanism, the slurry suspension was centrifuged at 4000 rpm for 15 minutes to separate the chemically modified rock dusts from the physically adsorbed reagents. Afterward, the supernatant was decanted and the chemically modified rock dust was washed with purified water using 3 to 5 rinses, dried in an oven and stored for FTIR analysis. Attenuated Total-Reflectance Fourier-transform Infrared Spectroscopy (ATR-FTIR) was performed using a Varian 7000e step-scan spectrometer (Agilent Technologies, Santa Clara, CA), which enables the samples to be directly examined in either solid or liquid state without further preparation.
Figure 3.12. Experimental apparatus used to determine the dispersibility of rock dust sources.
Figure 3.13. Loading point of the apparatus used for dispersibility tests.

Figure 3.14. Air reservoir of the apparatus used for dispersibility tests.
3.1.8. Surface Tension Measurements

Surface tension is the surface free energy per unit area or the force per unit length of a material as either solid or liquid state. Surface tension of liquid is significantly influenced by the concentration of chemical reagents or surfactants due to their surface-active nature. Therefore, surface tension measurements were conducted in the study to determine the critical micelle concentration (CMC) of reagents, the remaining concentration of reagents in the liquid or equilibrium concentration after adsorption tests and the amount of reagents being adsorbed by rock dust particles. CMC is the critical concentration above which aggregation of the long-chain electrolytes into fairly large, charge units occurs (Adamson and Gast, 1997). Surface tension study is critical to help construct the adsorption isotherm of applied reagents and determine their adsorption mechanism.

The ring method was employed to measure the apparent surface tension and the interfacial surface tension of the solutions was determined using a surface tensiometer (Fisher Tensiometer Model 20, Fisher Scientific, USA), as shown in Figure 3.15. The platinum-Iridium ring was used during the measurement at a controlled temperature of 25 °C. The tensiometer was calibrated with pure methanol solutions of various concentrations and known surface tensions. The accuracy was further checked using distilled water. Standard solutions were prepared by adding sodium oleate into distilled water to obtain the specific oleate concentration.

The rock dust suspension was placed in the environmental chamber with the aforementioned controlled atmosphere for 24 hours to ensure sufficient interaction time and subsequently centrifuged at 4000 rpm for 15 minutes to separate the chemically modified rock dusts from the physically adsorbed reagents. Afterward, the slurry was filtered and washed with distilled water using 3 to 5 rinses with filtrate being kept for surface tension measurement.
3.1.9. Thermogravimetric Analysis

Thermogravimetric analysis is a method of thermal analysis measuring changes in physical and chemical properties of materials as a function of increasing temperature or time. A laboratory thermogravimetric analyzer (SDT Q600, TA Instruments, DE) was used to monitor the weight loss of treated as well as untreated rock dust samples in the present work. The samples were centrifuged at 4000 rpm for 15 minutes, subsequently filtered and placed in an oven for 24 hours. The dry sample was then placed in an alumina pan and heated at 20 °C/min under the dry airflow (100 ml/min).

3.1.10. Scanning Electron Microscopy (SEM) Analysis

Dry rock dust samples (treated and untreated) were initially coated with gold using sputter coating to prevent charging of a sample with an electron beam. Afterward, the morphology of samples was observed in a Hitachi S-2700-Scanning Electron Microscope at 10 kV.
3.2. EXPLOSIBILITY TESTS INVESTIGATION

The University of Kentucky Explosive Research Team possesses a variety of research facilities including a high explosive shock tube and a 38-liter explosibility test chamber which are located in Georgetown, KY. The explosive tube has been used for more than a thousand tests and excellent repeatability has been indicated in terms of explosive pressure versus waveforms. It has been used for coal dust or methane explosion research since 2012. The pictures of the explosibility tube are shown in Figure 3.16 (a)-(b). The explosibility test chamber was recently built according to the US Bureau of Mines with an interior volume enlarged from the original 20-liter to 38-liter. The explosive research lab housing both the explosibility tube and chamber occupies 40,000 square feet of underground area and is able to be further expanded upon the research needs. Details regarding the sample preparation and explosibility tests procedures are described in the subsequent subsections.
Figure 3.16. The explosibility tube located in Georgetown, KY with a (a) close view and (b) remote view.

3.2.1. Sample Preparation

Aluminum trays with two different configurations were used during the sample preparation and subsequent explosibility tests. The tray was confined on three sides with a lip that is 10 mm and 20 mm in height, respectively, which can accommodate different sample sizes. According to the Title 30 of the Code of Federal Regulations Section 75.403, the minimum incombustible materials of applied rock dust should be no less than 80 wt% and should be increased by an additional 0.4 % for the presence of every 0.1% of methane. Therefore, the rock dust content was fixed at 80 wt% throughout all the explosive tests conducted in the present study. In addition, two sample configurations were prepared to determine the sample size effect on the explosibility test results, which corresponded to a total sample weight of 80 and 160 grams, respectively. The amount of
rock dust for the two sample configurations was thus 64 and 128 grams, separately, based on the predetermined 80 wt% of incombustible content.

Three inerting rock dust sources were used in the study, which were regular dry dust, wet dust and hydrophobized rock dust. The hydrophobized rock dust was selected based on the preliminary laboratory tests that generated good modification results and dispersive properties. Regular dry rock dust was simply prepared by pouring the determined amount of rock dust directly into the aluminum tray. Regular wet dust was prepared based on a typical industrial mixture ratio of 2:1 for rock dust to water. The wet dust slurry was initially agitated for around 15 minutes to ascertain a homogeneous mixture followed by being poured into the aluminum tray, which allowed the suspension to settle. The hydrophobized rock dust was prepared in the same manner as regular wet dust however with water being replaced by previously prepared surfactant solution. The samples were left to cure for either a 7-day or 14-day period after the sample preparation. It has been known from the previous literature review that there is always a huge fluctuation associated with underground coal mine atmosphere and it imposes a tremendous effect on rock dust cake formation. Therefore, investigations were initiated to monitor the temperature and relative humidity change for a period of two months from March to May at an underground coal mine in Eastern Kentucky. Two separate locations of the Eastern underground coal mine was chosen as the monitoring locations, which were termed “Station 1.2” and “Station 1.8”, separately. For each station, four sensors were used together to detect the atmosphere fluctuation with two sensors designated for temperature and the rest two for relative humidity to minimize the error and approach the true value. The monitoring results in terms of the underground coal mine temperature and relative humidity are shown in Figures 3.17-18. For one specific location, the fluctuation monitored by two sensors was almost identically for temperature and relative humidity, respectively. However, the temperature and relative humidity fluctuation at two different locations could vary differently as shown from Figures 3.17-18. In the end, the average value of 13.6°C and 68% RH was used to control the temperature and relative humidity inside the chamber, separately, in which the prepared samples for explosibility tests were subject to curing. A picture of dry dust curing in the aluminum tray is shown in Figure 3.19.
Figure 3.17. The atmosphere fluctuation at station 1.2 in terms of: (a) temperature; (b) relative humidity.
Figure 3.18. The atmosphere fluctuation at station 1.8 in terms of: (a) temperature; (b) relative humidity.
3.2.2. Flame-Extinguishing Test Method

After the samples had cured for a certain time period until they approached equilibrium with environment atmosphere and no total weight change had been observed, the flame extinguishing or quenching characteristic of the inerting rock dust were subsequent investigated. As previously described, certain amount of rock dust were initially poured into the tray of which the corresponding amount of coal dust were added on top to create the coal and rock dust mixture. Efforts were made by applying this sample configuration to simulate the float and newly produced coal dust from active mining that gradually deposits at the return airways which plays a crucial role in flame propagation. The aforementioned 38-liter laboratory explosibility test chamber that had dimensions determined by scaling of a smaller 20-liter chamber constructed and used by the U.S. Bureau of Mines (USBM) to study coal dust explosions (Cashdollar, 1996; Doidge and Anstine, 2014). Line schematics of USBM 20-liter and 38-liter explosibility test chamber used in the present study are shown in Figures 3.20-21, respectively.
Figure 3.20. Vertical cross-section of USBM 20-liter explosibility test chamber (Cashdollar, 1996).
Figure 3.21. Line schematic of the 38-liter explosibility test chamber used in the present study.
It can be seen from Figures 3.20-3.21 that in addition to the chamber volume and slight construction difference, the dust dispersion method was also modified to provide an improved representation of the explosion shock effect on dust dispersion. The 20-liter chamber used by USBM dispersed a dust mixture reservoir from the bottom of the chamber to suspend the elements within the chamber. The 38-liter chamber used in this investigation dispersed the dust from an inflow of breathable air injected over the top of the sample tray to simulate an explosion shock front impacting and forcing up settled coal and rock dust. This method was also selected to see how well the rock dust types lifted opposed to being forced into a suspension.

As aforementioned, the rock dust was placed on a tray followed by adding the coal dust to form a top layer. The tray was placed near the middle of the chamber together with a 5 kJ Sobbe igniter and a vacuum pulled to approximately 13.8kPa (2 psi). Breathable air that was provided with a concentration of 79% nitrogen and 21% oxygen was injected into the chamber to disperse the dust. A pressure reservoir with air pressure approximately 965 kPa (140 psi) to ensure proper dispersion of the sample to recreate a typical float dust mine atmosphere was applied to provide the breathable air (Cashdollar, 1989). Upon reaching atmospheric pressure (101.325 kPa), the igniter was fired with the help of an in-built software in an attempt to detonate the mixture. The software package was able to record the pressure within the chamber during all stages of the explosibility test experiment. Detailed steps regarding how to set up the explosibility tests are shown in Figure 3.22 (a)-(f).

The chamber was unsealed after the tests were completed and everything had been checked; the tray was subsequently removed with its post-explosion weight being recorded. Both the chamber and the tray were carefully cleaned using the compressed airline so as to avoid contamination for the subsequent explosive tests. Pictures of post-explosion experimental tests are displayed in Figure 3.23 (a)-(b).
Figure 3.22. Experimental setup for explosibility tests with: (a) coal and rock dust sample preparation; (b) installing the tray in the middle of the chamber; (c) installing the 5 kJ Sobbe igniter; (d) sealing the chamber; (e) filling the pressure reservoir to approximately 965 kPa; (f) the overall view after setting up the experiment.

Figure 3.23. Pictures of post-explosion tests with (a) the inside view of the chamber; (b) weighing the tray after a detonation attempt.
3.2.3. Coal Dust Explosion Tests

Explosion tests were initially conducted with pure coal dust to generate the explosibility curve of the coal dust alone. The experimental tests were repeated as a function of coal dust concentration inside the explosibility test chamber to determine the critical concentration above which the possibility and intensity of an explosion are significantly increased after a detonation attempt. A concentration greater than that critical value would be used for the subsequent rock dust inerting tests. If the concentration of the coal dust is less than the critical value, deflagration rather than detonation will occur. Deflagration is the kind of combustion or reaction in which the propagation waves travels at a velocity less than the speed of sound while detonation has a reaction wave propagates at a velocity faster than the speed of sound. As a result, there is a large pressure difference existing between deflagration and detonation. Explosion test data acquired from deflagration should not be used to determine the extinguishing characteristics of rock dust in case of underground coal mine explosion which normally is detonation.

The relative reactivity of coal dust was assessed from the peak explosive pressure and the volume normalized rate of pressure rise after the detonation attempt (Doidge and Anstine, 2014). Pressure ratio (PR) is a ratio of the peak explosive pressure to the atmospheric pressure and a value equal to or greater than 2 is indicative of a significant flame propagation or detonation. A flame propagation event is also signified when the volume normalized rate of pressure increase \( \frac{dP}{dt} \left( \frac{1}{V} \right) \) is equal to or exceeds 1.5 bar.m/s.

A total of eight coal dust concentrations were tested and each was repeated three times to minimize the experimental error. Therefore, twenty-four tests were conducted for coal dust explosion tests with concentrations varying from 200 g/m\(^3\) to 1400 g/m\(^3\) using increments of 200 g/m\(^3\).

3.2.4. Rock Dust Inerting Tests

As mentioned in the previous sample preparation section, the rock dust content was always fixed at 80 wt% with its weight varying from 64 to 128 grams for all the rock dust inerting tests. The corresponding weight of coal dust was 16 and 32 grams, respectively.
The normalized coal dust concentration based on the 38-liter chamber volume would be approximately 421 g/m³ and 842 g/m³, separately. The 421 g/m³ rock dust concentration was chosen based on the explosibility curve of pure coal dust generated and the 842 g/m³ concentration was determined based on the fact that larger sample size is more representative of the actual situation in underground coal mine applications. The rock dust inerting tests were conducted in the same way as described for the flame-extinguishing test method. Three inerting rock dusts were investigated which were regular dry, wet and hydrophobic dust.

In addition to the criteria of PR and the volume normalized rate of pressure increase \( \left( \frac{dP}{dt} V^{\frac{1}{3}} \right) \), the relative reactivity of rock dust can further be assessed from its dispersibility which was measured from the weight loss of the dust mixture not remaining in the tray after the detonation attempt (Doidge and Anstine, 2014). All those response parameters could be combined to evaluate the flame quenching characteristics of all the test rock dusts.

3.2.5. Angle of Ejection Test Method

To further compare the explosion mitigation properties of all three rock dust samples, angle of ejection tests were supplementarily conducted to measure the angle from horizontal when rock dust particle liberates from the aluminum tray after being subjected to a blasting shock wave and the following pulse. The shock tube was used to measure the angle of ejection for all three test rock dust samples. Large sample size weighing approximately 2.87 kg was chosen since it is more representative of the on-site underground coal mine applications. As a result, the curing time for the large sample size was increased to a minimum of fourteen days to make sure the equilibrium with the atmosphere was reached.

In addition to the shock tube, a velocity screen, which consists of a wood frame with plywood strips intersecting at a 30.5-cm interval, was built to assist the angle of ejection measurement. Two free field pressure sensors were installed approximately 0.4 meters to the side of the tray and 0.4 meters above the tray with each other around 0.6 meters apart. When a detonation was attempted, the two pressure sensors started recording the pressure
and speed of the blast wave and activating a high-speed camera. The high-speed camera was set up at a distance of approximately 4.5 meters to record the motion locus and ejection of dust from the tray at a rate of 250 frames per second. The angle from which the camera recorded was parallel to the shock front and the lens was set as high as the sample tray. The set-up of the velocity screen, free field pressure sensors and the sample location is shown in Figure 3.24. The explosive charge of approximately 0.57 kg C4 explosive was installed in the shock tube at a distance of around 14.3 meters from the front edge of the aluminum tray that can be seen Figure 3.25.

Figure 3.24. The experimental set-up for angle of ejection tests.

After completing the angle of ejection tests, the samples were placed in the environmental chamber in which the temperature was controlled at 40°C for a time period of 7 days to remove any excess moisture that may had been adsorbed by rock dust samples during testing. The weight difference before and after the angle of ejection tests was considered as an indicator of the dispersibility of rock dusts. In addition, the video recorded by the high-speed camera was analyzed frame by frame. The velocity screen
with known dimensions was used as the reference to measure the distance traveled by rock dust particles after being subjected to the blast wave. The angle of ejection and the lift velocity of the dust particles could be calculated based on the trigonometry, measured distances and known traveling time. The lift velocity is the velocity of rock dust particles at which they travel when the shock front impacts and forces up the dust particles.

Figure 3.25. The explosive charge installed at the shock tube.
CHAPTER 4. EXPERIMENTAL RESULTS, OBSERVATIONS AND DISCUSSIONS

4.1. LABORATORY TEST RESULTS

Previous literature review has indicated that the major mechanism for rock dust caking is the adsorption of water which forms liquid bridges between the rock dust particles where saturated solutions of soluble powder ingredients are present. Changes in temperature or relative humidity result in solvent (water) evaporation and the formation of dry bridges (Rumpf, 1958; Specht, 2006). One method to prevent caking is creating hydrophobic rock dust to repel water from the solid surface thereby preventing the formation of liquid and solid bridges. Therefore, efforts were initially devoted to laboratory experiments to successfully modify rock dusts and generate hydrophobic particles for the purpose of eliminating the formation of rock bridges and improving the corresponding dispersibility.

4.1.1. Rock Dust Treatment with Oleic Acid and Sodium Oleate

4.1.1.1. Contact Angle Measurements

OA and NaOL were initially chosen as the modifying reagents. Table 4.1 shows the contact angle measurements of the untreated and treated rock dust samples obtained over a range of reagent concentrations. Multiple measurements were conducted to obtain the average values reported in Table 4.1 and the standard deviations for all measurements were within ±4°. The contact angle value obtained for the NaOL-treated rock dust samples generally increased from 0° to 112° when the NaOL concentration was increased to a value of 0.1% by weight of dry rock dust. Strong surface hydrophobicity and thus the ability to repel water were retained even after being washed with purified water for 3 to 5 times in an attempt to eliminate weakly attached residual reagent molecules that were on the solid surfaces due to physical adsorption. A similar trend can also be observed among the OA-treated samples. However, the level of hydrophobicity was notably lower but sufficiently strong enough to repel water.
Table 4.1. Contact angle values obtained from untreated and treated rock dust samples as a function of reagent type and concentration; NaOL = sodium oleate and OA = oleic acid.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Contact Angle</th>
<th>Treatment</th>
<th>Contact Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated wet dust</td>
<td>0°</td>
<td>0.025 wt% NaOL</td>
<td>0°</td>
</tr>
<tr>
<td>0.025 wt% OA</td>
<td>0°</td>
<td>0.050 wt% NaOL</td>
<td>87°</td>
</tr>
<tr>
<td>0.050 wt% OA</td>
<td>32°</td>
<td>0.100 wt% NaOL</td>
<td>112°</td>
</tr>
<tr>
<td>0.100 wt% OA</td>
<td>83°</td>
<td>1.500 wt% NaOL</td>
<td>126°</td>
</tr>
</tbody>
</table>

It should be noticed that when 1.5 wt% NaOL was applied to modify the rock dust samples, a super-hydrophobic surface with a contact angle larger than 120° was produced which would certainly be advantageous for repelling water from the surface but would likely be economically prohibitive. At 0.1 wt% concentration, a contact angle of 112° was generated using NaOL, which could be an optimum surface treatment. The economics of reagent concentration must be balanced with the benefits gained from improved rock dust dispersibility.

4.1.1.2. Zeta Potential Measurements

The surface charge of the rock dust is an important parameter that will assist in maintaining dispersion of the particles in the presence of water, which will improve water drainage and minimize the formation of rock bridges. The zeta potential measurements of the untreated and treated rock dusts are shown in Figure 4.1. No measurements were obtained at slurry pH values less than 7 due to the fact that a significant amount of rock dust dissolves in the acidic environment. Without chemical treatment, the isoelectric point (iep) of the rock dust was determined to be around 7.6, which is in good agreement with previously reported data (Rao et al., 1989). The electrokinetic behavior of the modified rock dust shows that the particles have a net negative charge at the iep of the untreated rock dust and the negative value increases significantly with an elevation in pH. The iep of the modified rock dust samples shifts to a more acidic value relative to the untreated dust particles and the surface charge significantly increases with an elevation in pH.
reagent concentration and slurry pH value which is an important characteristic for dispersion. At a pH value of 12, the zeta potential was increased by as much as 14 mV for the reagent dosage of 0.1 wt% NaOL.

The electrophoretic curves in the presence of OA and NaOL show that the reagents have a similarly pronounced influence on the surface potential of the rock dusts in that the surfaces obtain an elevated negative charge. The trend has been reported by other investigators involving flotation studies of salt-type minerals (Mishra, 1982; Pugh and Stenius, 1985). Somasundaran and Ananthapadmanabhan (1979) indicated in their study that oleate exists as oleate ions (R\(^-\)) at high pH values, neutral molecules (RH) at low pH values and may form an ionmolecular complex (RHR\(^-\)) in the intermediate pH range. In addition, other species such as oleate dimer (R\(_2\)) may be formed after associative interactions. Therefore, the build-up of negative charge on the rock dust surface is mostly attributed to the adsorption of oleate ions (R\(^-\)), oleate dimers (R\(_2\)), ionmolecular complex (RHR\(^-\)) and their interaction with the cationic active sites on the rock dust surfaces.

Figure 4.1. Zeta potential as a function of reagent type and concentration over a range of pH values; NaOL= sodium oleate and OA= oleic acid.
4.1.1.3. Moisture Desorption Tests

The untreated and treated rock dust samples were placed in the environment chamber in which the temperature and humidity was maintained constant at 20° C and 80% RH, respectively. The weight loss (moisture desorption) of each slurry sample was recorded as a function of time. Figure 4.2 shows that the amount of moisture desorbed by the untreated and surface treated rock dust samples for a period up to nine days. Every data point is the average of two replicates. It is clear from these results that the moisture desorbed by the untreated rock dust was less than that by the surface-treated dusts. For both reagent types, the higher dosages provided greater amounts of moisture desorption which can be explained by the elevated surface hydrophobicity (Table 4.1). For the same reagent concentration, a much higher moisture desorption rate was achieved by samples treated with NaOL compared to OA. An explanation may be the higher solubility of NaOL in water which facilitates the interactions between oleate ions, associated species and rock dust particles thereby producing a more hydrophobic surface to repel and desorb water.
Figure 4.2. Moisture desorption rate comparison in an atmosphere of 20°C and 80% RH between natural rock dust and hydrophobic rock dust treated with different reagent types and reagent concentrations; NaOL= sodium oleate and OA= oleic acid.

4.1.1.4. Dispersibility Tests

Dispersibility tests were subsequently conducted in the apparatus shown in Figure 3.12 to determine the dispersive characteristic of the untreated and treated rock dusts which were obtained from the environmental chamber after nine days in an atmosphere of 20°C and 80% RH. A single data point represents a cumulative value obtained from dispersing five, one-gram samples sequentially and collecting the time increment samples from each dispersion into the same time-marked pans. Multiple tests were repeated at randomly chosen test conditions and the results indicated an experimental error defined by a standard deviation of ± 3.5 percent for the percent dust dispersion after 30 seconds which was the highest among all time intervals.
Table 4.2. Comparison of percent dust dispersion values obtained as a function of time using the dry and wet untreated rock dust samples and the treated rock dust with sodium oleate and oleic acid over a range of reagent concentrations.

<table>
<thead>
<tr>
<th>Time (seconds)</th>
<th>Percent Dust Dispersion (%)</th>
<th>Sodium Oleate Dosage (wt%)</th>
<th>Oleic Acid Dosage (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Un-treated Dry</td>
<td>Un-treated Wet</td>
<td>0.025</td>
</tr>
<tr>
<td>3</td>
<td>99.8</td>
<td>71.0</td>
<td>94.4</td>
</tr>
<tr>
<td>10</td>
<td>96.0</td>
<td>49.3</td>
<td>65.3</td>
</tr>
<tr>
<td>20</td>
<td>95.1</td>
<td>47.2</td>
<td>60.8</td>
</tr>
<tr>
<td>30</td>
<td>94.6</td>
<td>46.5</td>
<td>58.9</td>
</tr>
</tbody>
</table>

A comparison of the percent dust dispersion values obtained for the various rock dusts samples is provided in Table 4.2. As expected, the untreated dry rock dust provided the best dispersibility with 94.6% of the dust remaining in the air after 30 seconds from the time of injection. During the nine days in the environmental chamber, rock bridges formed in the wet dust sample thereby creating a cake of rock dust particles. When injected into the apparatus, 29% of the total dust settled to the bottom of the unit within 3 seconds as compared to less than 1% for the untreated dry rock dust. After 30 seconds, only 46.5% remained dispersed.

For the wet rock dust treated with NaOL, the dispersibility was significantly improved, especially during the shortest time period when explosibility issues are most critical. After 3 seconds from the time of injection, 96.1% of the rock dust treated with 0.05 wt% of the reagent remained dispersed which was significantly superior to the untreated wet dust and near the performance realized with the untreated dry dust. However, the amount of suspended dust decreased for the time periods beyond 3 seconds and reached a value of 67.7% after 30 seconds which remained a significant improvement over the values obtained with the untreated wet rock dust. Increasing the dosage to 0.1 wt% provided a
small incremental enhancement in the dust dispersibility. Given the increase in surface hydrophobicity as indicated by the contact angles listed in Table 4.1, greater dispersion improvements were anticipated. However, the higher degree of surface hydrophobicity may have created an attractive hydrophobic interaction force that exceeded the repulsive force existing between the rock dust particles thereby causing particle agglomeration and resistance of the water to desorb and drain from the small capillary-like spaces between the particles.

Treatment of the wet rock dust with OA also provided improvements in the dust dispersibility as compared to the untreated wet rock dust as indicated by the data in Table 4.2. However, the improvement is clearly inferior to the results obtained using NaOL, which is shown by the comparison in Figure 4.3. At a dosage of 0.1 wt%, the percentage of the dust remaining dispersed after 30 seconds was 55.0% whereas the dispersibility of the NaOL treated rock dust produced a value of 70.6% at the same reagent dosage. The dispersibility difference agreed well with contact angle values (Table 4.1) which indicated a higher degree of surface hydrophobicity for the rock dust treated with NaOL. The dispersibility comparison in Figure 4.3 indicates that a certain amount of caking occurred in the treated rock dust materials since the untreated dry rock dust had higher dispersibility over the time periods tested. As such, further surface modifications that lead to better water desorption and drainage may be attempted to approach the dispersibility achieved by the untreated dry rock dust.
4.1.2. Rock Dust Treatment with Stearic Acid

4.1.2.1. Contact Angle Measurements

Previous literature review has indicated that stearic acid is the most commonly used modifying reagent to treat the surface of rock dust particles. The investigation of treating rock dust using oleic acid and sodium oleate shows that they both are useful for hydrophobizing the dust surfaces and enhancing their dispersibility, especially for sodium oleate. However, the comparison between the performance of stearic acid, oleic acid and sodium oleate is unknown which requires further investigations. Therefore, the contact angle measurements were initially conducted on stearic acid treated dust surface and results are shown in Table 4.3.

It can be seen from Table 4.3 that the hydrophobization effect of stearic acid is notably less significant compared to both oleic acid and sodium oleate. When the reagent concentration was less than 0.5 wt%, there was no measured contact angle on the compressed rock dust pellets. With further increase in the reagent concentration, the
contact angle was generally elevated to the maximum value of approximately \(109^\circ\) in contrast to the maximum value of \(126^\circ\) obtained for sodium oleate treated dust particles. Less predominant hydrophobization effect of stearic acid was thus observed during the contact angle measurements.

Table 4.3. Contact angle values obtained from untreated and treated rock dust samples as a function of stearic acid concentration; SA= stearic acid.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Contact Angle</th>
<th>Treatment</th>
<th>Contact Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated wet dust</td>
<td>0(^\circ)</td>
<td>0.200 wt% SA</td>
<td>0(^\circ)</td>
</tr>
<tr>
<td>0.025 wt% SA</td>
<td>0(^\circ)</td>
<td>0.500 wt% SA</td>
<td>46(^\circ)</td>
</tr>
<tr>
<td>0.050 wt% SA</td>
<td>0(^\circ)</td>
<td>1.000 wt% SA</td>
<td>90(^\circ)</td>
</tr>
<tr>
<td>0.100 wt% SA</td>
<td>0(^\circ)</td>
<td>1.500 wt% SA</td>
<td>109(^\circ)</td>
</tr>
</tbody>
</table>

4.1.2.2. Zeta Potential Measurements

Zeta potential measurements were further conducted on SA treated rock dust particles to evaluate the surface charge characteristics and the results are shown in Figure 4.4. It can be seen that the adsorption of SA resulted in an increase in the surface charge of treated dust particles as well and the most substantial improvement of approximately \(-8\) mV occurred at the pH of around 10.7 compared to regular wet dust. There appears no significant difference among rock dust treated with 0.05 wt% and 0.1 wt% SA which may indicate there is no profound improvement in the reagent adsorption with the SA concentration varying from 0.05 wt% to 0.1 wt%. Similarly, the zeta potential values shift towards a more negative value with the increase in the pH values. While comparing the magnitude of the particle surface charge, it is not difficult to find that the build-up of negative charge on the rock dust surface is more significant for NaOL treated particles under the identical reagent concentration. For example, an increase of around \(-10\) mV was obtained for rock dust treated with 0.1 wt% NaOL compared to dusts treated with 0.1 wt% SA under the pH of approximately 12.
4.1.2.3. Moisture Desorption Tests

After the sample treatment step, dust particles treated with SA were also monitored and recorded for moisture desorption analysis for a nine-day period. The moisture desorption of SA treated rock dust as a function of exposure time in the environmental chamber with the controlled atmosphere is displayed in Figure 4.5. The moisture desorption rates among regular wet dust, dust treated with 0.025 wt% and 0.05 wt% SA are close to each other with no substantial difference observed. However, rock dust particles treated with 0.1 wt% SA generated the highest moisture desorption rate under the identical period which suggests the modified particle surfaces are more ready to repel water in contrast to the unmodified as well as other SA modified dust particles. However, the more substantial moisture desorption was always observed for NaOL modified rock dust opposed to SA modified dust particles under the same reagent concentration.
4.1.2.4. Dispersibility Tests

After the nine-day curing period and the samples were totally dry, SA treated rock dust particles were subjected to the dispersibility tests to assess the enhancement in the dispersive properties of the particles. As can be seen from Figure 4.6, significant improvement in the dispersibility of dust particles was obtained for SA treated samples. The dust percent dispersion value was increased by almost 18.7 percentage points for particles treated with 0.025 wt% SA at the end of 3 seconds after which the amount of dust remaining dispersed was decreased to a value of approximately 62% corresponding to a dispersion time of 30 seconds. Cake formation was thus indicated to some extent. However, the substantial improvement was still retained as indicated by approximately 15.5 percentage points increase in the dust percent dispersion values as opposed to regular wet dust. The elevation in the reagent concentration leads to the further increase in the dust percent dispersion values however less significant. An improvement of 6 percentage points at a dispersion time of 3 seconds was achieved for dust treated with
higher dosages (0.05 and 0.1 wt%) while approximately 3 percentage points were increased 30 seconds after an initial dispersion compared to dust treated with 0.025 wt% SA. There is almost no observed improvement between rock dust treated with 0.05 wt% and 0.1 wt% SA.

Figure 4.6. Percentage of the untreated and SA treated rock dust samples remaining dispersed after time \( t \); SA= stearic acid.

The summarized dispersibility test results for rock dust samples treated with various reagents and concentrations are shown in Figures 4.7–4.8, which are corresponding to a dispersion time of 3 seconds and 30 seconds, respectively. Generally, the increase in the reagent dosage leads to the enhancement in the dispersibility of treated particles. The percentage of dust particles remaining dispersed after 3 seconds is all above 90% for the three tested reagents as opposed to the much lower value of approximately 71% for regular wet dust. The substantial improvement observed for treated rock dust is very crucial due to the fact that the dispersibility of particles right after the coal dust mixture is ignited, maybe within microseconds, is most critical for explosion mitigation. In addition, the most significant improvement was achieved by NaOL treated rock dust samples with approximately 11.7 percentage points increase when the concentration was increased...
from 0.025 wt% to 0.1 wt% at a dispersion time of 30 seconds. NaOL treated particles generated the highest dispersibility throughout all phases of the dispersibility tests for all three investigated reagents. Previous studies have indicated that NaOL performs better than OA due to its soluble nature in aqueous solution and associated hydrolysis behavior. A superior behavior has also been observed for SA in contrast to OA which is supported by Figures 4.7-4.8. When the reagent concentration was fixed at 0.05 wt%, an improvement in the percent dust dispersion values of approximately 12.7 percentage points was obtained for SA treated samples compared to OA modified dusts at a corresponding dispersion time of 30 seconds. SA performs similarly as NaOL with NaOL producing a slightly superior performance.

![Graph](image.png)

Figure 4.7. Percentage of rock dust samples treated by various reagents and concentrations remaining dispersed 3 seconds after an initial air pulse; NaOL= sodium oleate, OA= oleic acid and SA= stearic acid.
Figure 4.8. Percentage of rock dust samples treated by various reagents and concentrations remaining dispersed 30 seconds after an initial air pulse; NaOL= sodium oleate, OA= oleic acid and SA= stearic acid.

Efforts were further made to correlate the dispersibility of treated rock dust particles and their surface hydrophobicity with the comparable contact angle values shown in Figure 4.9. It can be seen that when the concentration was below or equal to 0.025 wt%, there were no measured contact angle values for all three modifying reagents. It is also noticeable that no measured contact angle values were observed throughout SA treated dust samples until the application of 0.5 wt% SA. This may be attributed to the fact that the contact angle measurements were conducted on the compressed pellets rather than the surface of a solid chunk. The true values may not be obtained however the trend must be comparable and reliable. In addition, coating of calcium carbonate using stearic acid in aqueous medium is thought to be quite different from and less efficient than solvent or high-temperature dry coating due to its insoluble nature in water solution. The process is predominant by micelle adsorption followed by the subsequent collapse of micelles into double or multiple layers during the drying stage (Shi et al., 2010).
NaOL treated dust samples always produce the highest contact angle values and dispersibility among various reagent concentrations. For one identical reagent, the generally increased surface hydrophobicity always leads to elevated dispersive properties of particles. However, if the performance of two different modifying reagents is compared, i.e., OA and SA, it is surprising to find that OA treated particles generate noticeable larger contact angle values but much inferior dispersibility in contrast to SA treated solids under the same reagent concentration. In this case, the surface hydrophobicity of solids and the corresponding dispersibility are not perfectly correlated. Previous investigations have suggested that dispersibility is affected due to adsorption of moisture by rock dust but there is no direct relationship between moisture adsorption and dispersibility (Mozumdar and Singh, 1974; Doidge and Anstine, 2014). At this point, the relationship between the surface hydrophobicity and solids dispersibility requires fundamental investigations which may involve the chemical nature of the solids surface.

![Figure 4.9](image)

Figure 4.9. Contact angle values for rock dust treated with various reagents and concentrations; NaOL= sodium oleate, OA= oleic acid and SA= stearic acid.
4.1.3. Rock Dust Multi-Stage Treatment with Sodium Oleate and Dispersants

Dispersants are commonly applied in the process industries in a sufficient amount to prevent or effectively restrict flocculation or agglomeration of the ground calcium carbonate particles to a desired extent (Krishnan and Iwasaki, 1982; Minayoshi et al., 1991; Jones et al., 2014). They are generally water-soluble salts, which are able to supply anionic species and be adsorbed on the surface of the inorganic particles and thereby inhibit aggregation of the particles (Jones et al., 2014). Given the purpose of the present study, which is to improve the dispersive properties of rock dust (basically calcium carbonate), a series of potential dispersants including sodium silicate (SS), sodium metaphosphate (SM) and sodium polyacrylate (SP) were applied in the multi-stage treatment of rock dust samples. These dispersants are known for their low costs and commercially availability. It has been well recognized that particles hydrophobization is pivotal of eliminating the solid bridges and preventing cake formation. Therefore, sodium oleate which has been proven to be very effective in hydrophobizing the dust particles and enhancing their dispersibility was applied to initially coat the particle and generate a hydrophobic surface. Dispersants were subsequently added for another 5-minute conditioning in order to achieve a homogeneous mixture. Sample characterization tests were then conducted on the dust particles, which had been prepared through the multi-stage treatment.

4.1.3.1. Contact Angle Measurements

Contact angle measurements of rock dust treated with 0.1 wt% NaOL and various concentrations of SS are shown in Table 4.4. It is surprising to find that instead of obtaining a relatively constant contact angle value, the value was gradually decreased from 107° to 36° which was corresponding to the application of 0.05 wt% and 0.5 wt% SS, separately. The increase in the dispersant concentration leads to a general decrease in the measured contact angle values that were all below the value of 112° obtained for rock dusts modified by 0.1 wt% NaOL alone.
Table 4.4. Contact angle values obtained from rock dust treated through the multi-stage treatment with sodium oleate concentration fixed at 0.1% by weight; SS= sodium silicate.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Contact Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05 wt% SS</td>
<td>107°</td>
</tr>
<tr>
<td>0.10 wt% SS</td>
<td>94°</td>
</tr>
<tr>
<td>0.25 wt% SS</td>
<td>66°</td>
</tr>
<tr>
<td>0.50 wt% SS</td>
<td>36°</td>
</tr>
</tbody>
</table>

4.1.3.2. Zeta Potential Measurements

The effect of SS adsorption on the particle surface charge was further evaluated through zeta potential measurements. Test results from Figure 4.10 indicate that the zeta potential of particles generally shifts to a more negative value when they approach an alkaline environment. For the dust treated with 0.1 wt% and 0.5 wt% SS, the zeta potential of the solids were both noticeably increased in contrast to the regular wet dust under the same pH condition. The most significant elevation in the surface charge for rock dust treated with 0.1 wt% and 0.5 wt% SS was observed at the pH of around 12, which was corresponding to an increase of approximately -10 mv and -16 mv, respectively. The build-up of the negative charge is basically due to the adsorption of dispersant anions which is more significant for dust sample treated with 0.5 wt% SS as opposed to 0.1 wt% SS. However, the increase in the zeta potential values for dusts treated with 0.5 wt% SS is less substantial compared to the application of 0.1 wt% NaOL alone under the acid environment while a more negative value was observed for the former treatment in an alkaline solution. This finding may suggest that the adsorption between sodium oleate and the dispersant is competitive which may depend on the solution chemistry.
4.1.3.3. Dispersibility Tests

Dispersibility tests were conducted on rock dust samples treated with sodium silicate as well as sodium metaphosphate and sodium polyacrylate. Test results are shown in Figures 4.11-4.12 and Table 4.5. It can be seen from Figure 4.11 that with the increase in the sodium silicate concentration, the dispersibility of dust particles was generally decreased. At a dispersion time of 3 seconds, their dispersibility was close to the dust samples treated with 0.1 wt% NaOL alone with more than 90% of the particles remaining dispersed. However, the deterioration of the dispersibility is significant beyond 3 seconds. The percent dust dispersion values for dust treated with 0.05 wt% SS was approximately 59.2% 30 seconds after an initial air pulse, which was substantially lower than the value of 70.6% obtained for dust treated with pure NaOL. The value was further decreased to 49.1% for the application of 0.25 wt% SS. There was no improvement
observed for the application of sodium silicate. To the contrary, the deterioration in the dispersive properties of dust particles was rendered. This may be explained by the deteriorated surface hydrophobicity for particles prepared through multi-stage treatments (Table 4.4). The competitive adsorption occurs between applied sodium oleate and sodium silicate. The adsorption of sodium silicate over sodium oleate depresses the hydrophobization process of dust particles. As a result, particle surfaces are less ready to repel water adsorbed because of wet application. Liquid bridges and subsequently formed solid bridges render the bulk solids more agglomerated, which cannot be overcome by the elevated dispersion induced via adsorbed anionic species of the dispersant (Figure 4.10). The direct relationship between particles dispersibility and surface hydrophobicity was further denied based on the measured contact angle values (Table 4.4) and their corresponding dispersibility (Figure 4.11). For example, dust treated with 0.05 wt% SS generated similar dispersive performance as those treated with 0.1 wt% SS however deterioration in surface hydrophobicity was observed with a continuous increase in the SS concentration (Table 4.4).

Figure 4.11. Percentage of treated rock dust samples remaining dispersed after time \( t \); 0.1 wt% NaOL and various concentrations of SS; NaOL= sodium oleate and SS= sodium silicate.
Dispersibility tests conducted with samples treated using sodium metaphosphate and sodium polyacrylate indicate the same trend as can be seen from Table 4.5. The increase in the dispersant concentration generally deteriorated the dispersibility of particles rather than enhancing it. The percentage of dust particles remaining dispersed 30 seconds after an initial air pulse for the three investigated dispersants are summarized in Figure 4.12. When low dispersant concentration of 0.05 wt% was applied, the performance of the three dispersants was close to each other with approximately 58% dust remaining dispersed. Difference is more noticeable when the concentration was elevated. For dust treated with high concentration of SM and SP, the percentage of particles remaining dispersed was even lower than that obtained for regular wet dust. The rock dust treated with 0.5 wt% SM produced the worst scenario with only around 31.9% of the particles remaining in suspension at a dispersion time of 30 seconds which is more severe as opposed to 46.5% of regular wet dust being dispersed under the identical condition. Therefore, the application of dispersants does not induce any positive effects as expected, which may be explained by the preferential adsorption of dispersants over sodium oleate.

Table 4.5. Comparison of percent dust dispersion values obtained as a function of time for rock dust samples treated with 0.1 wt% sodium oleate and dispersants over a range of concentrations.

<table>
<thead>
<tr>
<th>Time (seconds)</th>
<th>Percent Dust Dispersion (%)</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sodium Metaphosphate Dosage (wt%)</td>
<td>Sodium Polyacrylate Dosage (wt%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>0.10</td>
<td>0.25</td>
<td>0.50</td>
<td>0.05</td>
<td>0.10</td>
<td>0.25</td>
<td>0.50</td>
</tr>
<tr>
<td>3</td>
<td>87.40</td>
<td>79.95</td>
<td>72.69</td>
<td>71.81</td>
<td>80.68</td>
<td>73.06</td>
<td>68.33</td>
<td>73.87</td>
</tr>
<tr>
<td>10</td>
<td>65.44</td>
<td>61.06</td>
<td>42.90</td>
<td>41.98</td>
<td>62.15</td>
<td>54.92</td>
<td>53.29</td>
<td>50.59</td>
</tr>
<tr>
<td>20</td>
<td>59.81</td>
<td>55.41</td>
<td>35.71</td>
<td>34.39</td>
<td>58.63</td>
<td>51.80</td>
<td>50.09</td>
<td>43.77</td>
</tr>
<tr>
<td>30</td>
<td>58.05</td>
<td>53.84</td>
<td>33.48</td>
<td>31.88</td>
<td>57.84</td>
<td>50.52</td>
<td>49.04</td>
<td>41.87</td>
</tr>
</tbody>
</table>
Figure 4.12. Percentage of treated rock dust samples remaining dispersed 30 seconds after an initial air pulse; 0.1 wt% NaOL and various concentrations of dispersants; SS = sodium silicate, SM = sodium metaphosphate and SP = sodium polyacrylate.

4.2. COAL DUST EXPLOSION TESTS

The explosibility curve of pure coal dust was initially generated with the dust concentration varying from 0 to 1400 g/m³, which was incrementally increased by 200 g/m³. The test results in terms of peak explosive pressure as a function of coal dust concentration are shown in Figure 4.13 from which it can be clearly seen that a minimum concentration of 400 g/m³ was required to achieve a PR larger than 2 and a detonation thus occurred. Based on the coal dust concentration and the chamber volume, a total amount of approximately 15.2 grams coal dust was needed to achieve the minimum dust concentration of 400 g/m³. Therefore, an amount of 16 grams coal dust was determined for the subsequent rock dust inerting tests, which equates a coal dust concentration of 421 g/m³. The other sample size of 32 grams rock dust, which equates a concentration of
842 g/m³ was used to further increase the possibility of a significant flame propagation and be more representative of the actual situations in the underground coal mine applications. When the coal dust concentration was below 400 g/m³, the chance of deflagration instead of detonation was greatly increased.

![Figure 4.13. Peak explosive pressure of pure coal dust explosion tests.](image)

### 4.3. ROCK DUST INERTING TESTS

#### 4.3.1. Regular Dry Dust

As aforementioned, two sample sizes were chosen throughout all the rock dust inerting tests, which corresponded to the coal dust concentration of 421 and 842 g/m³, respectively. Noncombustible material ratios were fixed at 80% by weight of total dust due to the regulatory requirement for such a mixture in coal mines in the United States. A total of 32 tests were conducted on the regular dry dust of which 20 tests were conducted at the low coal dust concentration while 12 were tested at the high concentration. Tests results of peak explosive pressure and the volume normalized rate of pressure increase are shown in Figure 4.14 and Table 4.6.
All the dry rock dusts tested performed well in terms of inerting coal dust flame propagation and the PR generated were all below 2 which can be corroborated from Figure 4.14 that the peak explosive pressure of all tests were below 1.57 bar. The worst scenario generating the highest peak pressure of 1.57 bar is shown in Figure 4.15. The moments when the breathable air was injected to disperse the dust mixture, the pressure gradually approached atmosphere pressure and the igniter was denoted, were all able to be observed from pressure waveforms recorded during all phases of the explosion test. The volume normalized rates of pressure increase were all below the critical value of 1.5 bar.m.s\(^{-1}\). All the tested regular dry dust successfully mitigated the potential coal dust explosion regardless of the sample configurations.
For each trial, the weight of the sample tray was weighed before and after the test, the percentage of dust mixture dispersed was calculated based on the weight difference, which is an effective indicator of the dispersibility of rock dust particles and can be used to simulate how much rock dust would be liberated from mine roofs, ribs and floor when
an underground coal mine explosion occurs. The average percentage of dust mixture being dispersed during a test was 61.4% and 51.5% for low and high coal dust concentration, respectively, which resulted in an overall average value of 57.7% for all tested dry rock dust regardless of coal dust concentration.

![Image](image_url)

Figure 4.15. Pressure waveforms recorded during all phases of a single rock dust inerting test based on regular dry rock dust (Perry et al., 2015).

It has been long known that dry rock dust always generates the best lift characteristics and dispersibility. The fact that all the tested dry rock dust successfully mitigated a potential coal dust explosion confirms the advantages of using dry dust in terms of low peak explosive pressure, low rate of pressure increase and high dispersibility. The main concern associated is the respirable dust particles it generates.

4.3.2. Regular Wet Dust

For regular wet dust, a total of 18 tests were conducted of which 12 were tested at a coal dust concentration of 421 g/m³ and the rest 6 were tested at a concentration of 842 g/m³. Two coal dust concentrations resulted in a significant difference for regular wet rock dust inerting test results. The detailed results are shown in Figure 4.16 and Table 4.7.
Figure 4.16. Peak explosive pressure for regular wet rock dust at two coal dust concentrations.

It can be clearly seen from the test results that under the low coal dust concentration, one of 12 tests failed to inert a coal dust flame propagation and the corresponding peak pressure and the rate of pressure rise was 2.92 bar and 0.61 bar.m.s\(^{-1}\), respectively. Even the rate of pressure rise was relatively low compared to the critical value of 1.5 bar.m.s\(^{-1}\), its peak explosive pressure was above two times of the atmospheric pressure, an explosion thus occurred. For high coal dust concentration, the situations were noticeably severe and 5 out 6 tests failed to inert the flame propagation. The 5 tests with regular wet dusts generated the peak pressures varying from 3.6 to 5.8 bars that the corresponding PR were all significantly greater than 2. For the worst scenario, a peak pressure of 5.5 bars and a rate of pressure increase of 5.3 bar.m.s\(^{-1}\) were generated.

In terms of percentage of dust mixture being dispersed, an overall value of 38.8% was obtained for all the tested regular wet rock dust, which is remarkably lower than 57.7% of regular dry dust. A large amount of rock dust particles remained in the sample tray after the explosibility tests, which indicates cake was formed among wet rock dust during curing and the dispersibility was greatly reduced. The dispersion value of small and large
sample size was 45.2% and 26%, separately. Caking is noticeably more predominant for large sample size and the deterioration of their explosion mitigation properties is much more tremendous.

Table 4.7. Rock dust inerting test results for all the regular wet dust.

<table>
<thead>
<tr>
<th>Coal Dust (g)</th>
<th>Concentration (g/m³)</th>
<th>Dispersed Mixture (%)</th>
<th>Peak Pressure (bar-a)</th>
<th>Rate of Pressure Increase (bar.m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>421</td>
<td>28.64</td>
<td>1.50</td>
<td>0.20</td>
</tr>
<tr>
<td>16</td>
<td>421</td>
<td>28.02</td>
<td>1.12</td>
<td>0.07</td>
</tr>
<tr>
<td>16</td>
<td>421</td>
<td>27.00</td>
<td>1.62</td>
<td>0.24</td>
</tr>
<tr>
<td>16</td>
<td>421</td>
<td>52.02</td>
<td>1.34</td>
<td>0.22</td>
</tr>
<tr>
<td>16</td>
<td>421</td>
<td>34.94</td>
<td>1.47</td>
<td>0.21</td>
</tr>
<tr>
<td>16</td>
<td>421</td>
<td>66.58</td>
<td>1.36</td>
<td>0.20</td>
</tr>
<tr>
<td>16</td>
<td>421</td>
<td>24.95</td>
<td>2.92</td>
<td>0.61</td>
</tr>
<tr>
<td>16</td>
<td>421</td>
<td>27.57</td>
<td>1.59</td>
<td>0.64</td>
</tr>
<tr>
<td>16</td>
<td>421</td>
<td>78.94</td>
<td>1.54</td>
<td>0.57</td>
</tr>
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<td>16</td>
<td>421</td>
<td>77.06</td>
<td>1.44</td>
<td>0.47</td>
</tr>
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<td>16</td>
<td>421</td>
<td>75.44</td>
<td>1.44</td>
<td>0.50</td>
</tr>
<tr>
<td>16</td>
<td>421</td>
<td>21.63</td>
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<td>NA</td>
</tr>
<tr>
<td>32</td>
<td>842</td>
<td>22.85</td>
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<td>0.83</td>
</tr>
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<td>842</td>
<td>22.92</td>
<td>3.64</td>
<td>0.26</td>
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<td>32</td>
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<td>842</td>
<td>37.58</td>
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<tr>
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<td>842</td>
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<td>4.57</td>
<td>3.78</td>
</tr>
<tr>
<td>32</td>
<td>842</td>
<td>18.44</td>
<td>5.45</td>
<td>5.33</td>
</tr>
</tbody>
</table>

4.3.3. Hydrophobic Rock Dust

The previous laboratory test results indicate sodium oleate modified rock dust has the greatest improvement in the dispersibility of dust particles compared to regular wet dust. Therefore, rock dust treated with sodium oleate generating good hydrophobic and dispersive properties were used for the rock dust inerting tests and those rock dusts are termed “hydrophobic rock dust”.

The substantial improvement can be observed from test results with hydrophobic rock dust as opposed to regular wet dust, which is shown in Figure 4.17 and Table 4.8. For the coal dust concentration of 421 g/m³, hydrophobic rock dust performed as well as dry
rock dust. All 12 trials successfully mitigated the flame propagation with both the peak pressure and the rate of pressure increase much lower than the threshold values. The percent of dust mixture dispersed during the explosion tests was around 63.3%, which is approximately two percentages higher than the value of 61.4% for regular dry dust. The dispersibility of hydrophobic rock dust is as good as dry rock dust in small sample size which lead to an effective inerting impact on a potential coal dust explosion propagation.

![Figure 4.17. Peak explosive pressure for hydrophobic rock dust at two coal dust concentrations.](image)

However, 2 out 14 trials failed to quench the flame front under large sample size and high coal dust concentration. These two failures appeared to be more like two outliers as could be seen from Figure 4.17 that they are far away from the majority of the data points. The rest of the data points are clustered below the threshold values, which indicates precision. The detailed explosion test results are presented in Table 4.8.

The percent of dust mixture dispersed during the tests was approximately 30.5% for large hydrophobic rock dust sample size, which was lower than that of regular dry dust but higher than wet dust. Significant improvement was indicated for hydrophobic rock dust compared to regular wet dust in terms of reduced peak explosive pressure, the rate of
pressure increase and increased dispersibility. However, the two possible outliers cannot be neglected due to the fact that caking formation was not totally eliminated for hydrophobic rock dust as indicated by the reduced dispersibility in contrast to regular dry dust.

Table 4.8. Rock dust inerting test results for all the hydrophobic rock dust.

<table>
<thead>
<tr>
<th>Coal Dust (g)</th>
<th>Concentration (g/m³)</th>
<th>Dispersed Mixture (%)</th>
<th>Peak Pressure (bar-a)</th>
<th>Rate of Pressure Increase (bar.m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>421</td>
<td>66.99</td>
<td>1.40</td>
<td>0.21</td>
</tr>
<tr>
<td>16</td>
<td>421</td>
<td>61.83</td>
<td>1.19</td>
<td>0.22</td>
</tr>
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</tr>
<tr>
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</tr>
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<td>421</td>
<td>60.11</td>
<td>1.40</td>
<td>0.22</td>
</tr>
<tr>
<td>16</td>
<td>421</td>
<td>54.21</td>
<td>1.44</td>
<td>0.49</td>
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</tr>
<tr>
<td>16</td>
<td>421</td>
<td>55.34</td>
<td>1.09</td>
<td>0.22</td>
</tr>
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<td>0.23</td>
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<td>32.84</td>
<td>5.22</td>
<td>1.65</td>
</tr>
<tr>
<td>32</td>
<td>842</td>
<td>29.63</td>
<td>1.80</td>
<td>0.21</td>
</tr>
<tr>
<td>32</td>
<td>842</td>
<td>28.95</td>
<td>1.92</td>
<td>0.23</td>
</tr>
<tr>
<td>32</td>
<td>842</td>
<td>29.04</td>
<td>1.49</td>
<td>0.24</td>
</tr>
<tr>
<td>32</td>
<td>842</td>
<td>29.21</td>
<td>1.49</td>
<td>0.22</td>
</tr>
<tr>
<td>32</td>
<td>842</td>
<td>35.46</td>
<td>1.54</td>
<td>0.20</td>
</tr>
<tr>
<td>32</td>
<td>842</td>
<td>29.94</td>
<td>1.85</td>
<td>0.98</td>
</tr>
<tr>
<td>32</td>
<td>842</td>
<td>31.68</td>
<td>1.14</td>
<td>0.22</td>
</tr>
<tr>
<td>32</td>
<td>842</td>
<td>29.58</td>
<td>2.74</td>
<td>0.49</td>
</tr>
<tr>
<td>32</td>
<td>842</td>
<td>29.81</td>
<td>1.60</td>
<td>0.75</td>
</tr>
<tr>
<td>32</td>
<td>842</td>
<td>27.62</td>
<td>1.70</td>
<td>0.95</td>
</tr>
<tr>
<td>32</td>
<td>842</td>
<td>27.50</td>
<td>1.50</td>
<td>0.24</td>
</tr>
<tr>
<td>32</td>
<td>842</td>
<td>28.05</td>
<td>1.65</td>
<td>0.79</td>
</tr>
</tbody>
</table>

In the end, all the rock dust inerting test results are summarized in Table 4.9 to clearly compare the performance of the three inerting sources, which shows the explosibility test results with the rock dust content fixed at 80 wt% while the coal dust concentration was
increased from 421 g/m$^3$ to 842 g/m$^3$. In summary, when 421 g/m$^3$ coal dust was used, dry rock dust and hydrophobic dust yielded similar dispersive characteristics which were significantly improved compared to the findings obtained using wet dust on the basis of the percentage of dust mixture dispersed. The weight loss of the former two mixtures was around 16 to 18 percent higher than that of the latter one. When 842 g/m$^3$ of coal dust was used in the tests, the dispersibility of the dry dust was the highest among all samples with 51.5% of the dust mixture being dispersed. Both wet and hydrophobic dusts dispersed less than the dry rock dust. Approximately 30.5% of the hydrophobic dust mixture was dispersed compared to 26.0% of the wet dust mixture.

Irrespective of the coal dust concentration used, dry rock dust always provided superior performance in inerting the explosion while the wet, untreated dust yielded the poorest performance. Hydrophobic dust successfully reduced the explosion potential compared to regular wet dust. Under the condition of 842 g/m$^3$ coal dust, the explosion potential of the regular wet dust mixture was greatly reduced from 83.3% (5 out of 6 tests failed to inert the explosions) to 14.3% for the hydrophobic rock dust (2 of 14 tests failed to inert the explosions).

Table 4.9. Explosive test results obtained using a 38-liter chamber with different inverting rock dust sources and coal dust concentrations.

<table>
<thead>
<tr>
<th>Rock Dust (RD) Source</th>
<th>Coal Dust Concentration (g/m$^3$)</th>
<th>Dispersed Mixture (%)</th>
<th>Explosion Potential (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry 80</td>
<td>421</td>
<td>61.4</td>
<td>0 (0 out of 20 tests failed)</td>
</tr>
<tr>
<td>Wet 80</td>
<td>421</td>
<td>45.2</td>
<td>9.1 (1 out of 11 tests failed)</td>
</tr>
<tr>
<td>Hydrophobic 80</td>
<td>421</td>
<td>63.3</td>
<td>0 (0 out of 12 tests failed)</td>
</tr>
<tr>
<td>Dry 80</td>
<td>842</td>
<td>51.5</td>
<td>0 (0 out of 12 tests failed)</td>
</tr>
<tr>
<td>Wet 80</td>
<td>842</td>
<td>26.0</td>
<td>83.3 (5 out of 6 tests failed)</td>
</tr>
<tr>
<td>Hydrophobic 80</td>
<td>842</td>
<td>30.5</td>
<td>14.3 (2 out of 14 tests failed)</td>
</tr>
</tbody>
</table>

*Hydrophobic---Rock dust modified with NaOL.
4.4. ANGLE OF EJECTION TESTS

4.4.1. Regular Dry Dust

The angle of ejection tests were firstly conducted on regular dry dust with three replicate trials. The test results are shown in Table 4.10 from which it can be seen that an average angle of around 20° and lift velocity of approximately 6.8 ft/sec were achieved for dry dust. For the best trial of all three tests, a maximum value of 23° and 7.69 ft/sec was obtained for the angle of ejection and lift velocity, respectively. Figure 4.18 shows how the video recorded by the high-speed camera was analyzed for the angle of ejection results.

Table 4.10. Angle of ejection test results for the regular dry rock dust.

<table>
<thead>
<tr>
<th>Test Number</th>
<th>Angle of Ejection (degree)</th>
<th>Lift Velocity (ft/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>14.04</td>
<td>6.87</td>
</tr>
<tr>
<td>2</td>
<td>23</td>
<td>7.69</td>
</tr>
<tr>
<td>3</td>
<td>22.62</td>
<td>5.89</td>
</tr>
<tr>
<td>Average</td>
<td>19.89</td>
<td>6.82</td>
</tr>
</tbody>
</table>

Figure 4.18. Angle of ejection test for one single trial based on regular dry rock dust (Perry et al., 2015).
4.4.2. Regular Wet Dust

Angle of ejection tests were further conducted on regular wet dust with results shown in Table 4.11. An average value of 20.3° and 4.28 ft/sec was obtained for the angle of ejection and lift velocity, respectively. The angle of ejection for wet dust is close to regular dry dust however the lift velocity is lower. This is due to the moisture adsorbed among the rock dust particles, which gradually evolved into solid bridges from the initial water bridges upon drying and cake was thus formed.

Table 4.11. Angle of ejection test results for the regular wet rock dust.

<table>
<thead>
<tr>
<th>Test Number</th>
<th>Angle of Ejection (degree)</th>
<th>Lift Velocity (ft/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>14.03</td>
<td>2.86</td>
</tr>
<tr>
<td>2</td>
<td>26.57</td>
<td>5.70</td>
</tr>
<tr>
<td>Average</td>
<td>20.30</td>
<td>4.28</td>
</tr>
</tbody>
</table>

4.4.3. Hydrophobic Rock Dust

Hydrophobic rock dust generated relative consistent test results, which are shown in Table 4.12. The average lift velocity of hydrophobic rock dust was approximately 3.1 ft/sec which was lower than both regular dry and wet dust. However, the average angle of ejection was approximately 22° for hydrophobic rock dust that was higher than the former two rock dusts. In addition, the amount of dust being dispersed during the angle of ejection test was the highest for hydrophobic rock dust with approximately 631 grams out of 2.87 kg dust being dispersed compared to less amount being liberated for regular dry and wet dust. The mitigated cake formation and improved liberation characteristics could be confirmed for hydrophobic rock dust.

It is not difficult to find that the angle of ejection tests generally produced a relatively large variation among the results. This may due to the enlarged sample size compare to the rock dust inerting tests and the test condition was in the open atmosphere rather than confined explosibility test chamber that rendered the condition more difficult to control. Therefore, the rock dust inerting test would remain as the primary tool to compare the
performance of all rock dust sources with the angle of ejection test as the supplementary tool to support the findings.

Table 4.12. Angle of ejection test results for the hydrophobic rock dust.

<table>
<thead>
<tr>
<th>Test Number</th>
<th>Angle of Ejection (degree)</th>
<th>Lift Velocity (ft/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>26.56</td>
<td>3.18</td>
</tr>
<tr>
<td>2</td>
<td>20.56</td>
<td>1.98</td>
</tr>
<tr>
<td>3</td>
<td>18.43</td>
<td>4.17</td>
</tr>
<tr>
<td>Average</td>
<td>21.85</td>
<td>3.11</td>
</tr>
</tbody>
</table>

4.5. CONCLUSIONS

The study of this chapter proved the effectiveness of the use of oleic acid/sodium oleate/stearic acid to hydrophobize rock dust in an effort to ensure dispersibility when applied in wet form in underground coal mining operations. The hydrophobic rock dust allowed drainage and desorption of the water existing in a wet rock dust application. Sodium oleate was found to be a more effective reagent providing a high level of surface hydrophobicity as indicated by contact angles of 87 degrees and higher for reagent concentrations greater than 0.05% by weight of dry rock dust. Moisture desorption and dispersive characteristics were superior for the rock dust treated with sodium oleate compared to the values obtained for the oleic acid treated materials and the untreated wet rock dust. Stearic acid treated rock dust performed better than oleic acid however slightly inferior to sodium oleate which may be attributed to the less efficient coating process in aqueous solution as opposed to solvent or high-temperature coating.

Specific findings from the investigation include:

1. Surface hydrophobicity increased significantly with reagent concentration for both the oleic acid and sodium oleate. The contact angle values measured for the treated rock dust samples were elevated as high as 126°, which represents a ‘super-hydrophobic’ solid. Sodium oleate provided the highest contact angles. The hydrophobization effect is less significant for stearic acid treated rock dusts.
with no measured contact angle values when the concentration was below 0.5 wt%.

(2) Treatment of rock dust using oleic acid, sodium oleate and stearic acid result in the build-up of negative charge on the particle surface, which leads to the significant increase in the electrostatic repulsive force among dust particles. The elevation in the particle surface charge for the sodium oleate application may be attributed to the adsorption of oleate associated species such as monomers, dimers and neutral species which combine to provide the level of surface hydrophobicity and surface charge characteristics.

(3) Rock dust dispersibility tests showed that treating the rock dust with 0.025 wt% or higher with NaOL provided an amount of suspended dust equal to the dry, untreated rock dust after 3 seconds and nearly 25 percentage points higher than the results obtained using wet, untreated rock dust. Significant improvement has been indicated especially for the dispersibility during the shortest period (within microseconds) which is most crucial for explosion mitigation purpose. A substantially elevated dispersibility must be obtained within microseconds that render the modified dust particles instantly effective in inerting the potential explosion propagation. Beyond 3 seconds, NaOL concentrations of 0.025 wt% to 0.1 wt% achieved particle dispersion that was significantly higher than the values measured for the untreated wet rock dust. However, the dispersive properties were below the results obtained using the untreated dry rock dust, which indicated the presence of some degree of caking.

(4) Rock dust treated with stearic acid generated a performance similar however slightly inferior to dust particles treated with sodium oleate. The percentage of dusts remaining dispersed after 3 seconds was above 90% with 0.025 wt% or higher dosage of stearic acid, beyond which a substantial improvement in the range of 15 to 19 percentage points was obtained for all stearic acid treated dust particles in contrast to regular wet dust.

(5) Dispersants include sodium silicate, sodium metaphosphate and sodium polyacrylate were applied together with sodium oleate to modify rock dust particles. Deterioration rather than enhancement in the dispersibility was
observed after the application of dispersants. The possible explanation is the preferential adsorption of dispersants over sodium oleate which dampens the surface hydrophobicity of particles and allows the existence of liquid and solid bridges. The dust particles are rendered more agglomerated as a result.

(6) The dispersibility of dust particles is affected due to adsorption of moisture by rock dust but there is no direct relationship between moisture adsorption and dispersibility. The relationship between the surface hydrophobicity and solids dispersibility requires fundamental investigations which may involve the chemical nature of the solids surface.

(7) Explosive chamber tests confirmed the significant improvement in dispersivity from hydrophobizing the rock dust. As a result, the hydrophobic rock dust was found to significantly improve the ability to provide an inert atmosphere. When testing untreated wet rock dust, five out of six (83.3\%) trials at a coal dust concentration of 842 g/m$^3$ provided a flame propagation event. Only 2 out of 14 trials (14.3\%) using the hydrophobic rock dust resulted in an event. As such, the explosion potential was reduced using the hydrophobic dust by 82.8\% (= 100*[(83.3 – 14.3)/83]).
5. CHAPTER 5. FUNDAMENTAL EVALUATION OF SODIUM OLEATE ADSORPTION ON ROCK DUST PARTICLES

5.1. BACKGROUND

The aforementioned literature review has indicated that the key point of rock dust surface chemistry is to create hydrophobic surface that allows instant water drainage and the elimination of subsequent liquid and solid bridges. The hydrophobicity of a solid is normally indicated by the contact angle formed at the solid-liquid-vapor interfaces (Figure 3.6). The contact angle ($\theta$) is governed by Young’s Equation:

$$\cos \theta = \frac{\gamma_{SG} - \gamma_{LS}}{\gamma_{LG}}$$

where $\gamma_{SG}$, $\gamma_{LS}$ and $\gamma_{LG}$ is the solid-vapor, liquid-solid and liquid-vapor interfacial surface tension, respectively. Therefore, contact angle value is always one response parameter of interest during the present study.

For the specific rock dusting operation, moisture can be easily adsorbed among the voids between the particles due to the humid atmosphere or the wet dusting application where sufficient moisture source exists. Capillary pressure ($P_c$) is thus formed and is expressed by the Laplace Equation:

$$P_c = \Delta \rho g h = \frac{2\gamma \cos \theta}{r}$$

in which $\rho$ is the specific gravity of the liquid existing among the capillary voids, $g$ the acceleration of gravity, $\Delta h$ the capillary rise/depression, $\gamma$ the surface tension of the liquid and $r$ is the radius of the curvature formed at the capillary voids. It can be clearly seen from Equation (4) that a hydrophilic surface leads to an enhanced capillary pressure that means high external pressure is needed to drain the water from the voids. Carleton and Mackay later defined the minimum pressure required to remove the water and called it breakthrough pressure $P_b$ (Carleton and Mackay, 1988):

$$P_b = \frac{\alpha \gamma \cos \theta (1-\varepsilon)}{d_k \varepsilon}$$

110
where $\mathcal{E}$, $d_k$ and $\alpha$ is the porosity of the caked solids, Kozney mean diameter and the breakthrough pressure constant, separately. It directly shows that the minimum external pressure required to drain moisture absorbed at the contact points among particles is closely determined by the solid surface hydrophobicity which is further confirmed by the subsequent laboratory investigations as shown in Figure 5.1.

![Graph showing the relationship between breakthrough pressure and measured contact angle values on the solid surfaces](image)

**Figure 5.1.** The relationship between the breakthrough pressure and measured contact angle values on the solid surfaces (Asmatulu, 2001).

In addition, according to extended DLVO theory, the magnitude of the surface forces between two interfacial boundaries can be quantified by (Xu and Yoon, 1989; Xu and Yoon, 1990; Adamson and Gast, 1997; Yoon et al., 1997; Honaker et al., 2005):

$$F_T = F_D + F_E + F_S$$  \hspace{1cm} (6)

where $F_T$, $F_D$, $F_E$ and $F_S$ is the total interaction force, the London-Van Der Waals dispersion force, the electrostatic force and the structural interaction force, respectively.

The short-range London-Van Der Waals dispersion ($F_D$) and long-range electrostatic ($F_E$) force can be estimated using:
\[ F_D = -\frac{aA_{131}}{12H^2} \]  
(7)

and

\[ F_E = \frac{\varepsilon a\psi_d^2}{2H} \ln[1 + \exp(-\kappa H)] \]  
(8)

in which \( A_{131} \) is the Hamaker constant for two spheres of type 1 in a medium 3, \( a \) the particle radius, \( H \) the separation distance, \( \varepsilon \) the dielectric constant of the medium, \( \psi_d \) the stear potential and \( \kappa \) is the Debye reciprocal length.

In reality, zeta potential is commonly used to estimate the stear potential in colloids chemistry which has been well established by the stear model (Figure 3.9). The magnitude of particle-particle repulsion or attraction force can be estimated based on the measured zeta potential values of dust particles. It also determines whether the applied modifying reagents can be initially adsorbed on the solid surface through electrostatic attraction or rejected through repulsion.

Furthermore, structural force is an attractive and long-range force as well which was developed by Xu and Yoon (1989; 1990) and occurs while approaching two hydrophobic solid surfaces. The structural force was developed to modify the classic DLVO theory and quantified as a function of the non-dispersion component of the work of adhesion \( (W^{nd}_a) \) for water on a solid surface (Honaker et al., 2005), i.e.,

\[ F_S = \frac{aD_0C_m}{2(1+\exp[b(W^{nd}_a-K)])H} \exp\left(-\frac{H}{D_o}\right) \]  
(9)

where \( C_m, b \) and \( K \) are empirical fitting parameters and \( D_o \) is the decay length. According to the modification proposed by Xu and Yoon (1989), the non-dispersion component of the work of adhesion \( (W^{nd}_a) \) for water on a solid surface is determined by the following equation:

\[ W^{nd}_a = \gamma_w(1 + \cos\theta_w) - 2\sqrt{\gamma_S^d\gamma_w^d} \]  
(10)

in which \( \gamma_w \) is the surface tension of water, \( \cos\theta_w \) the water contact angle, \( \gamma_S^d \) the dispersion component of the surface free energy of solid and \( \gamma_w^d \) is the dispersion
component of the surface free energy of water. By substituting Equation (10) into Equation (9), the effect of the solid surface hydrophobicity on the non-dispersion component of the work of adhesion ($W_{ad}^{nd}$) and subsequent structural force can be directly related. Surface with elevated hydrophobicity results in a reduced $W_{ad}^{nd}$ and increased structural force. It also explains why attractive structural force mostly occurs among super hydrophobic surfaces.

Based on the extended DLVO theory, the dispersibility of rock dust particles originating from the particle-particle interaction force can be fundamentally investigated. A number of laboratory tests were thus designed and conducted to clarify the underlying principles behind the rock dust modification process and the resultant dispersive properties, among which, contact angle and zeta potential measurements, are the two sample characterization methods that play a crucial role in determining the particles dispersibility.

### 5.2. SODIUM OLEATE CONCENTRATION STUDY

Previous study has indicated that sodium oleate has an excellent effect on hydrophobizing the rock dust particles and successfully reduces the coal dust explosion potential by almost 83% via repelling water from the modified hydrophobic surface and eliminating the formation of rock bridges which result in caking. This finding has been supported by numerous studies in mineral processing research area. Sodium oleate has been intensively used in the flotation of salt-type minerals, especially calcite (Rao and Forssberg, 1991; Mishra, 1982; Pugh and Stenius, 1985; Marinakis and Shergold, 1985a; Marinakis and Shergold, 1985b). Flotation behavior, electrokinetic properties and adsorption isotherms have been studied in detail by many researchers in an attempt to separate calcite from apatite or other minerals (Mishra, 1985; Rao et al., 1989; Rao et al., 1990). The maximum floatability was achieved by determining the optimum flotation condition to assure the adsorption of sodium oleate generates a hydrophobic calcite surface. Sodium oleate has also been applied to modify calcium carbonate powders for the purpose of preparing functional fillers in composite materials such as rubbers, textiles and plastics. After modification, the surface of calcium carbonate is converted from hydrophilic to hydrophobic. As a result, the compatibility between the carbonate filler and organic
matrix is greatly enhanced (Sheng et al., 2006; Wang et al., 2007). In addition, sodium oleate has been used as a very effective agent rendering cement-based mortars made with limestone fillers waterproof at very low dosages (Lanzón, 2011). Furthermore, findings from comminution studies show that the presence of sodium oleate improves the grinding efficiency of limestone as determined by tests conducted in a laboratory ball mill. The effectiveness of sodium oleate is attributed to its ability to prevent agglomeration and ball mill coatings of the powders (Sohoni et al., 1991)

All the aforementioned investigations support the super hydrophobization effect of sodium oleate on forming a water-repellent surface of calcium carbonate or calcium carbonate containing minerals, which agrees well with the results from rock dust modifications tests conducted to improve the health effects of the application process and the dispersion of the rock dust as needed to mitigate coal dust explosions (Huang et al., 2015). However, other studies reported enhancement in the agglomeration of calcium carbonate particles with an increase in concentration, which is not the effect desired for the underground coal dust application (Kawashima et al., 1986; Sayan, 2005; Takase, 2009). The agglomeration is easily explained by the strongly attractive hydrophobic interactions between the surfaces treated by sodium oleate. Given that the agglomeration would be detrimental to the desired dispersion effect, a detailed study was conducted to quantify the sodium oleate concentration effect on rock dust dispersion followed by a fundamental evaluation of the process.

During the fundamental study, dispersion was still measured by the percentage of the dust particles remaining in suspension 30 seconds after an air pulse was initiated in the enclosed container. Rock dust particles treated with various concentrations of sodium oleate were tested using the dispersibility test apparatus (Figure 3.12) to assess the impact on preventing the formation of rock bridges between particles and thus the overall dispersibility of the treated rock dust. Multiple tests were repeated at randomly chosen test conditions and the results indicated an experimental error defined by a standard deviation of ± 3.5 percent.

As shown in Figure 5.2, dispersibility was generally enhanced with an increase in reagent concentration until a maximum value was obtained at 0.1 wt% sodium oleate. Under the
optimum reagent concentration, dust dispersibility was 70.8% which was significantly greater than the 46.5% achieved with the untreated rock dust. For oleate concentrations ranging from 0.1 wt% to 0.5 wt%, dust dispersibility deceased slightly from the maximum value which indicated subtle variations in solution chemistry and particle-particle interactions. When the oleate concentration was further increased above 0.5 wt%, dust dispersibility sharply decreased to values lower than the value obtained for the untreated rock dust. Visual observations of the rock dust treated with high oleate concentrations (>0.5 wt%) revealed cake formation as large solid chunks that were relatively difficult to break. These findings clearly indicate that modifying rock dust to produce a hydrophobic surface has a positive impact on preventing cake formation and thus dust dispersibility at low reagent concentrations. However, high reagent concentrations have the opposite effect which is most likely due to a strong hydrophobic interaction energy between particles which induces particle agglomeration during treatment and prior to drying.

Figure 5.2. Effect of sodium oleate concentration on particle dispersibility after drying.
5.3. IN-DEPTH LABORATORY STUDIES

5.3.1. Contact Angle and Zeta Potential Measurements

Contact angle and zeta potential measurements were conducted to develop a fundamental understanding of the processes that led to the dispersion test results in Figure 5.2. The contact angle value provides an assessment of the degree of hydrophobicity generated on the surfaces of the dust particles due to the treatment with sodium oleate. Surface hydrophobicity is desired in this application to encourage water drainage from the dust particles after the wet application to the walls, floor and roof. However, particle dispersion within the wet rock dust is also required to prevent the formation of rock bridges and thus caking during the drying process. Zeta potential is an estimate of surface charge and an elevated value is desired to prevent coagulation of the rock dust particles.

Using the sessile drop technique, multiple contact angle readings were taken for each data point and the standard deviations for all the measurements were within ±4°. It can be seen from Figure 5.3 that the contact angle of treated rock dust generally increased from 0° for the untreated rock dust to 112° for rock dust treated with 0.1 wt% sodium oleate. When the concentration of sodium oleate exceeded 0.1 wt%, the contact angle continued to increase slightly until reaching a maximum value of 126° at an oleate dosage of 0.5 wt%. Further increases in the concentration resulted in no change in the observed contact angle values which indicates the maximum hydrophobicity of dust particles was achieved. By comparing Figures 5.2 and 5.3, it is clear that maximum dispersibility of the rock dust was not provided by applying reagent dosage treatments that resulted in the highest degree of surface hydrophobicity. In fact, maximum dispersion was provided by a contact angle of around 110 degrees.

According to the aforementioned extended DLVO theory for particle-particle interactions, the force among particles is dominated by the London-Van Der Waals dispersion force, the structural force and the electrostatic interaction force (Adamson and Gast, 1997; Yoon et al., 1997; Xu and Yoon, 1989; Xu and Yoon, 1990). London-Van Der Waals dispersion force is a short-range attractive force between like particles while the structural force is a long-range attractive force between hydrophobic particle surfaces.
Higher contact angle values indicate an elevated degree of hydrophobicity which leads to a stronger and longer range attractive interactive force. Dispersion forces in this study decreased with reagent adsorption due to the reduction in the non-polar component of surface free energy of the solids (Ren et al., 2001; Bargeman and Van Voorst Vader, 1972). The long-range electrostatic force is repulsive for the interactions between like particles and the strength of the force can be indicated by the zeta potential value.

The zeta potential of treated rock dust particles was measured over the range of oleate concentrations under the natural pH condition of 9.4±0.2. As shown in Figure 5.3, the treatment of the rock dust with sodium oleate elevated the zeta potential from -2.7 mV to -15.1 mV at a concentration of 0.1 wt%. The repulsive force between the treated rock dust particles was thus increased as a result of the strengthened repulsion between similarly charged particles which corresponds well with the initially elevated dispersibility as shown in Figure 5.2. A further increase in the oleate concentration resulted in an elevation in the zeta potential value which reached a high of -25 mV at a reagent concentration of 1.5 wt%. However, the conditions providing the higher zeta potential values did not prevent particle caking and thus improved dispersibility of the rock dust as indicated by the results in Figure 5.2. This is likely due, in part, to an overwhelming attractive long-range hydrophobic force that causes particle agglomeration when the particles are in the presence of water prior to the drying step. Additional studies were performed to assess other possible mechanisms including oleate adsorption on the rock dust surfaces and the impact it imposes on the surface properties of the dust particles.
5.3.2. Surface Tension Measurements

Surface tension measurements were conducted to investigate the sodium oleate adsorption on the rock dust surfaces from a perspective of the solution chemistry. Each measurement was repeated five times and the standard deviations for all the reported values were within ±0.6 dyne/cm. The surface tension values obtained over a range of sodium oleate concentrations are provided in Figure 5.4. A critical micelle concentration (CMC) of sodium oleate solution was found to be around 9×10⁻⁴ mol/l which agrees well with published values (Sayan, 2005).

Figure 5.3. Contact angle and zeta potential values obtained from untreated and treated rock dust samples as a function of oleate concentration.
The surface tension of the filtrate produced from the dewatering of the treated rock dust suspensions was measured and the values used to determine the equilibrium oleate concentration. The equilibrium value was quantified over a range of initial reagent concentrations by identifying the oleate concentration at the corresponding measured surface tension value in Figure 5.4. The amount of sodium oleate adsorbed by the rock dust particles was subsequently calculated by subtracting the equilibrium oleate concentration from the initial concentration. Both the equilibrium concentration and the amount adsorbed are shown as a function of the initial concentration in Figure 5.5. The amount of adsorbed oleate was generally elevated with an increase in the initial oleate concentration while the equilibrium concentration reached a nearly constant value for initial concentrations greater than 0.15 wt%. This finding indicates that oleate may be precipitating out of solution perhaps as a complex under the high oleate dosages. Therefore, calculations need to be further conducted to determine the species distribution.
of oleate in the water solutions and the interaction that could occur between oleate and rock dust particles at various concentrations.

Figure 5.5. The amount of adsorbed sodium oleate and equilibrium oleate concentration as a function of initial oleate concentration at pH 9.4±0.2.

5.3.3. Oleate and Calcite Species Distribution Calculations

Oleic acid is a weakly acidic insoluble compound in aqueous solution however its salt such as sodium oleate can undergo series of hydrolysis reactions and association behavior yielding complex oleate species under appropriate solution pH condition (Kulkarni et al., 1980). Ionization of oleic acid/oleate system is complicated by the formation of oleate dimers, acid soap and by the extremely low solubility of the undissociated acid (Pugh and Stenius, 1985). The equilibrium between those complex species in the oleic acid/oleate system has been summarized by Somasundaran and Ananthapadmanabhan (1979) as follows:
\[ RCOOH_l = RCOOH_{aq} \quad K_1 = 10^{-7.6} \quad (11) \]
\[ RCOOH_{aq} = RCOO^- + H^+ \quad K_2 = 10^{-4.95} \quad (12) \]
\[ 2RCOO^- = RCOO_2^{2-} \quad K_3 = 10^{4.0} \quad (13) \]
\[ RCOOH_{aq} + RCOO^- = (RCOO)_2H^- \quad K_4 = 10^{4.95} \quad (14) \]
\[ Na^+ + (RCOOH)_2H^+ = (RCOO)_2HNa \quad K_5 = 10^{9.35} \quad (15) \]

Oleate species distribution diagram as a function of pH at a room temperature of 25° was constructed on the basis of the equilibrium equations and presented here in Figure 5.5. Figure 5.6 (a)-(c) corresponds to the application of 0.025%, 0.15% and 1% oleate by weight in the wet rock dust modification, respectively. Figure 5.6 shows that in the acidic and alkaline solution, the oleate exists as either molecular acid or ionic forms while different types of species appear in the middle-range pH including the ionic monomers (RCOO^-), dimers (RCOO_2^{2-}) and ionmolecular species (RCOO_2H^-). The maximum activity of the ionmolecular complex (RCOO_2H^-) occurs in the pH range of 9 to 9.8 for all these three applications and it is also the region that precipitation of neutral oleic acid begins.

It has been proposed by Somasundaran and Ananthapadmanabhan (1979) and Pugh and Stenius (1985) that the minimum surface tension of oleic acid/oleate system observed around the intermediate pH range is caused by the presence of an ionmolecular complex. This complex is thought to be more surface active compared to their corresponding ionic monomers and dimers. The extreme surface activity of the ionmolecular complex can be explained by the increase in its molecular size and the high possibility of polar/ionic head interaction through hydrogen bonding instead of charge/charge repulsion (Somasundaran and Ananthapadmanabhan, 1979). Figure 5.6 clearly shows that the surface active ionmolecular complex exists in a significantly small quantity relative to the oleate monomers and dimers. As such, it is implausible to conclude that the ionmolecular complex is the sole driver for the surface free energy reduction and the increase in the degree of hydrophobicity. It is more conceivable that the oleate monomers, dimers, ionmolecular complex and the neutral oleic acid molecules are synergistically co-
adsorbed on the surface of the rock dust particles and contribute to the positive impacts needed to prevent cake formation.

\[
[\text{RCOO}^-]_{\text{tot}} = 1.64 \times 10^{-3} \text{ M}
\]

\[
[\text{(RCOO)}_2^2^-] = 9.85 \times 10^{-3} \text{ M}
\]
In addition, it has been known that the majority of the rock dust is calcite, which accounts for more than 94% by weight. When calcite is in contact with water, its dissolution and associated hydrolysis and complexation of dissolved species are closely pH-dependent (Rezaee et al., 2013). The equilibrium between the complex species in the calcite solution system has been summarized by previous investigations (Somasundaran and Agar; 1967; Hanna and Somasundaran, 1976) as follows:

\[
\begin{align*}
CaCO_3(s) &= Ca^{2+} + CO_3^{2-} & K_6 &= 10^{-8.4} \\
CO_3^{2-} + H^+ &= HCO_3^- & K_7 &= 10^{10.3} \\
HCO_3^- + H^+ &= H_2CO_3 & K_8 &= 10^{6.3} \\
CO_2(g) + H_2O &= H_2CO_3 & K_9 &= 10^{-1.5} \\
Ca^{2+} + HCO_3^- &= CaHCO_3^+ & K_{10} &= 10^{0.8} \\
Ca^{2+} + CO_3^{2-} &= CaCO_3(aq) & K_{11} &= 10^{3.3} \\
Ca^{2+} + H_2O &= CaOH^+ + H^+ & K_{12} &= 10^{-12.9}
\end{align*}
\]

Figure 5.6. Oleate species distribution diagram as a function of pH based on a sodium oleate concentration of (a) $1.64 \times 10^{-3}$ M; (b) $9.85 \times 10^{-3}$ M and (c) $6.57 \times 10^{-2}$ M.
\[ Ca^{2+} + 2H_2O = Ca(OH)_2 + 2H^+ \quad K_{13} = 10^{-22.8} \] (23)

In the present study, the calcite was dissolved in water in the open system rather than a closed system. Therefore, the partial pressure of atmospheric \( CO_2 \) is fixed at \( 10^{-3.5} \) atm. The activities of the calcite species can thus be calculated based on the fixed value \( PCO_2=10^{-3.5} \), which is shown in Figure 5.7. Using the calculated species activities, the total amount of carbonate and calcium can be obtained, separately, the sum up of which two leads to the total solubility of calcite as shown in Figure 5.8. According to the Beck’s theory, when a solution is in equilibrium with a solid phase, the iep of the solid corresponds to the pH of minimum solubility (Beck, 1954; Somasundaran et al., 1985). Therefore, a value of approximately 7.4 was obtained for the iep of the calcite. Previous laboratory tests indicate that the iep of the rock dust was approximately 7.6 (Figure 4.1) which is very close to the theoretic value of 7.4 in the open system. The precision and accuracy of the calculation in terms of the activities of the complex species in a rock dust saturation solution was examined.

Furthermore, it can be clearly seen from Figure 5.6 that under various concentrations of sodium oleate, the amount of oleate dimmers is presented in a gradually increased amount with an increase in the oleate concentration. When the oleate concentration was elevated from \( 1.64 \times 10^{-3} \) mol/l to \( 6.57 \times 10^{-2} \) mol/l which is corresponding to the application of 0.025 wt% and 1% wt% oleate, separately, the concentration of oleate dimmers was augmented from \( 10^{-3.16} \) mol/l to approximately \( 10^{-1.5} \) mol/l at the natural \( pH \) of around 9.4 that was substantially increased by almost 46 times. The oleate dimmers exist in a significant amount under high oleate concentrations. Moreover, the presence of calcium ions (\( Ca^{2+} \)) is also determined at an amount of approximately \( 10^{-7} \) mol/l at the \( pH \) of 9.4 from Figure 5.7. When a relatively large quantity of oleate dimmers and calcium ions exist in the rock dust saturation solution, these dimer products readily interact with calcium ions in solution (Ananthapadmanabhan and Somasundaran, 1976). Calcium oleate is produced as a result and it has been reported that the solubility product of calcium oleate is \( pK= 13.87 \) (Rao et al., 1989) and \( pK=14.13 \) (Marinakis and Shergold, 1985). When the product of the concentration of free oleate dimers and calcium ions exceeds the solubility product of calcium oleate, the complex precipitates out of solution.
which explains the relatively constant equilibrium concentration when increasing the sodium oleate concentration above 0.15 wt\% (Figure 5.5). Calcium oleate is thought to be high negatively charged in an alkaline environment (Matijević et al., 1966), which agrees well with the increase in the negative surface charge on the NaOL-treated dust particle surface at high pH values.

Figure 5.7. The ionic species distribution diagram of calcite as a function of pH (open to atmospheric carbon dioxide).
It has been suggested that the precipitation of calcium oleate starts after the formation of a monolayer on top of which calcium oleate physically deposits (Rao et al., 1989; Rao et al., 1991). The interaction between fatty acid adsorption on calcium minerals has been frequently mentioned as predominantly chemisorptions (Peck, 1964; Fuerstenau and Miller, 1967; Atademir et al., 1981; Mishra, 1982). Therefore, the adsorption mechanism involved in the oleate-rock dust aqueous solution is most likely the precipitation of calcium oleate on top of the chemically adsorbed monolayer formed because of chemical bondage between oleate associated complexes and the surface calcium cations.

5.3.4. FTIR Analysis

To provide evidence for the irreversible chemical adsorption mechanism, a study was conducted using ATR-FTIR, which initially involved an analysis of oleic acid and sodium oleate. Figures 5.9 and 5.10 are the infrared spectra of oleic acid and sodium oleate, respectively. The band appearing at 1708 cm\(^{-1}\) for oleic acid is a result of carbonyl C=O stretching, which is the characteristic of C=O associated with the carboxyl group COOH. Ionization of the carboxyl group to COO\(^{-}\) makes the band shift toward lower
wavenumbers. Intensive characteristic bands at 1558 and 1423 cm\(^{-1}\) for sodium oleate correspond to the anti-symmetrical and symmetrical vibration of the ionized carboxyl group, respectively (Peck, 1964). Bands appearing in the region 2850-3000 cm\(^{-1}\) for both oleic acid and sodium oleate are contributed to the CH\(_2\) and CH\(_3\) stretching while the transmittance in the region 1350 to 1470 cm\(^{-1}\) are associated with the CH\(_2\) and CH\(_3\) deformation. The corresponding wavenumbers for C-O stretching fall into the region of 1000-1260 cm\(^{-1}\) for both oleic acid and sodium oleate (Nakanishi et al., 1977; Silverstein and Webster, 2005). The bands at 933 cm\(^{-1}\) for oleic acid and 921 cm\(^{-1}\) for sodium oleate are caused by the OH out-of plane deformation group while the bands at 721 cm\(^{-1}\) correspond to the \((\text{CH}_2)_4\) skeletal vibrations (Peck, 1964). Two weak skeletal vibrations at 698 and 721 cm\(^{-1}\) are indicated in the infrared spectra of sodium oleate.

Figure 5.11 shows the infrared spectra of regular wet rock dust and modified rock dusts. The characteristic bands basically appear at 713 cm\(^{-1}\), 871 cm\(^{-1}\) and 1400 cm\(^{-1}\) for unmodified rock dust. This is because the vibration frequencies of rock dust corresponding to the major characteristic bands are primarily associated with the vibration energies of the CO\(_3^{2-}\) ion, which has a fairly fixed configuration (Adler et al., 1963). For rock dust modified with oleic acid, two weak characteristic bands appear at 2854 cm\(^{-1}\) and 2924 cm\(^{-1}\). Therefore, the presence of CH\(_2\) and CH\(_3\) groups is indicated on the surface of OA-modified rock dusts. Similarly, two new bands with higher intensity appear at 2850 cm\(^{-1}\) and 2920 cm\(^{-1}\) for NaOL-modified rock dusts. In addition, the intensity of characteristic band at 1400 cm\(^{-1}\) is increased and an additional “shoulder” is observed at 1570 cm\(^{-1}\). The stronger transmittance resulting from reagent adsorption indicates the presence of ionized carboxyl group in this region, which is superimposed on the existing carbonate structure. This is further proved by the appearance of the “shoulder” at 1570 cm\(^{-1}\). Despite the difficulty of interpreting the data caused by the superimposition of organic functional groups of carboxylic acid on carbonate structure, conclusions can still be drawn from the FTIR analyses that a chemical interaction between oleic acid/oleate and rock dusts exists which is important for long term stability of the surface treatment. This chemical interaction may be attributed to the monolayer adsorption of oleate on top of the rock dust particles surface formed due to the synergistically co-adsorption of oleate complex species.
Figure 5.9. Infrared spectra of oleic acid.

Figure 5.10. Infrared spectra of sodium oleate.
Figure 5.11. Infrared spectra of the untreated and treated rock dusts using sodium oleate (NaOL) and oleic acid (OA) at a concentration of 0.1 % by weight.
5.3.5. Thermogravimetric and SEM Analysis

In addition to the monolayer formation, thermogravimetric analysis was subsequently applied to confirm the precipitation of calcium oleate in the present work. The major decompositions of calcium oleate were initially detected in the temperature range of 200-600°C from Figure 5.12. The decomposition occurring below 100°C was mainly associated with the water evaporation. Figure 5.13 shows the weight loss of sodium oleate treated dust particles as a function of temperature. In general, the higher oleate concentrations led to elevated weight loss within the temperature range of 200-600°C which indicated a gradual increase in the amount of calcium oleate resulting from the chemical interaction between sodium oleate and the rock dust particles. The thermogravimetric results indicated that calcium oleate was produced due to the irreversible chemical interaction between sodium oleate and rock dust particles and the amount of calcium oleate production increased with sodium oleate concentration.

Figure 5.12. Thermogravimetric analysis of pure calcium oleate.
Figure 5.13. Thermogravimetric analysis for untreated as well as treated rock dust samples with various sodium oleate concentrations.

Direct visual observations regarding the precipitation of calcium oleate were obtained from scanning electron microscope (SEM) analyses. The micrographs of untreated and treated rock dust samples are presented in Figure 5.14. The surfaces of the untreated wet rock dust appear to have a smooth structure (Figure 5.14(a)). Figures 5.14(b)–(d) indicate that, by increasing the sodium oleate concentration, the dust particle surfaces lose their smoothness and tiny nuclei form on the particle surface in increasing quantity. These tiny nuclei were identified as calcium oleate particles which precipitated from the bulk solution and nucleated on the solid surface. When the treated samples were observed at high magnification, the nucleated calcium oleate can be clearly identified as nanoparticles as shown in Figure 5.15. These nanoparticles covered the dust surfaces and formed the typical micrograph resembling a cracked topography. It is well-known that nanoparticles tend to promote agglomerates which is a direct result of their small particle size and high degree of surface hydrophobicity (Shi et al., 2010) As such, the decrease in the
dispersibility of the dry dust above a 0.5 wt% sodium oleate dosage (Figure 5.2) could be partially explained by the presence of the precipitated calcium oleate nanoparticles.

Figure 5.14. SEM micrographs of: (a) untreated dust sample and sample treated with (b) 0.1 wt% sodium oleate; (c) 0.5 wt% sodium oleate; (d) 1.0 wt% sodium oleate.
Figure 5.15. SEM micrographs of samples treated with: (a) 0.5 wt% sodium oleate and (b) 1.0 wt% sodium oleate at high magnification.

5.4. ADSORPTION MECHANISM

As shown in Figure 5.2, dispersibility of the dry hydrophobic rock dust was maximized at a sodium oleate concentration of 0.1% by weight at which point dispersibility slightly decreased up to an oleate concentration of 0.5 wt%. Concentrations greater than 0.5 wt% resulted in a significant drop in dispersion.

To explain the observed dispersion trend with oleate concentration, the amount of absorbed sodium oleate was determined using surface tension measurements (Figure 5.5). The data was then applied to calculate the apparent surface area per molecule using the following expression:

$$\sigma = \frac{0.6677}{n \times N_A}$$  \hspace{1cm} (24)

Where \( n \) is the amount of sodium oleate adsorbed in mole/g, \( N_A \) the Avogadro constant and 0.6677 is the specific surface area of rock dust particles in m²/g. The calculated results are shown in Table 5.1.
Table 5.1. The calculated apparent surface area per oleate molecule occupied based on previous oleate adsorption data.

<table>
<thead>
<tr>
<th>Initial Oleate Concentration, wt%</th>
<th>Equilibrium Concentration, mol/l</th>
<th>Adsorbed Oleate (n), mol/g</th>
<th>Molecular Area (σ), Å²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>0.00E+00</td>
<td>0.00E+00</td>
<td>0</td>
</tr>
<tr>
<td>0.025</td>
<td>4.31E-05</td>
<td>7.56E-07</td>
<td>147</td>
</tr>
<tr>
<td>0.050</td>
<td>5.64E-05</td>
<td>1.61E-06</td>
<td>69</td>
</tr>
<tr>
<td>0.100</td>
<td>9.42E-05</td>
<td>3.24E-06</td>
<td>34</td>
</tr>
<tr>
<td>0.150</td>
<td>1.11E-04</td>
<td>4.87E-06</td>
<td>23</td>
</tr>
<tr>
<td>0.500</td>
<td>1.02E-04</td>
<td>1.64E-05</td>
<td>7</td>
</tr>
<tr>
<td>1.000</td>
<td>1.02E-04</td>
<td>3.28E-05</td>
<td>3</td>
</tr>
</tbody>
</table>

A molecular surface area of 34 Å² was calculated for a 0.1 wt% sodium oleate dosage while a value of 23 Å² was acquired with 0.15 wt% sodium oleate. The apparent surface area occupied per oleate molecule has been suggested to be in the range of 20-35 Å² depending on the degree of oleate ionization (Ananthapadmanabhan and Somasundaran, 1988; Rezaei Gomari et al., 2006). Therefore, the monolayer adsorption most likely occurs with the applied sodium oleate concentration falling between 0.10-0.15 wt%. The optimum dispersibility of the dry rock dust occurred using oleate concentrations within this range due to monolayer coverage and the resultant enhancement of particle surface hydrophobicity. With an increase in the oleate concentration above 0.15 wt%, calcium oleate is precipitated from the bulk solution and deposits on top of the hydrophobic dust particle surface which further increases the surface hydrophobicity to some degree (Somasundaran and Ananthapadmanabhan, 1979).
When the concentration of applied sodium oleate exceeded 0.5 wt%, calcium oleate continuously precipitated from the bulk rock dust solution and was more predominant which was corroborated by thermogravimetric and SEM analyses. Calcium oleate is thought to have a highly negative charge in an alkaline environment (Matijević, 1966) which is consistent with the noticeable rise in the negative zeta potential values at high oleate dosages. However, the long-range attractive hydrophobic interaction force strengthened by an increase in reagent dosage has the ability to exceed the repulsive electrostatic force thereby inducing agglomeration and reducing particle dispersion.

On the basis of the findings, the stages of sodium oleate adsorption on the rock dust surface were proposed and illustrated as in Figure 5.16. Stage (a) occurs when the oleate concentration is less than 0.1 wt% of rock dust and stage (b) of monolayer adsorption is completed by the application of 0.15 wt% oleate. Precipitation of calcium oleate gradually initiates deposition on top of the oleate monolayer at high dosages as shown in stage (c). The calcium oleate deposition is physical and generally weak.
Figure 5.16. Proposed mechanism for the adsorption of sodium oleate onto rock dust surface with various reagent concentrations: a) free monomer adsorption; b) monolayer formation; c) calcium oleate precipitation on top of the monolayer adsorption.

5.5. SAFETY EVALUATION OF APPLIED REAGENTS IN ROCK DUST MODIFICATION PROCESS

It has been widely known that oleic acid and stearic acid are fatty acids that occur naturally in a variety of animal and vegetable fats and oils with stearic acid more abundant in animal fat than vegetable fat. No hazardous healthy effects have been identified for these two fatty acids, and they are safe to be used in the rock dusting
applications. As for sodium oleate, according to the US Environmental Protection Agency, it is the salt of oleic acid, which is not identified as a reproductive or developmental toxicant to produce either adverse health effects or irritation of the respiratory tract following inhalation. Sodium oleate is readily biodegradable as well. Therefore, they are relatively safe to be used in the underground coal mine applications for rock dusting purposes.

5.6. ECONOMIC EVALUATION OF OLEATE MODIFIED ROCK DUST IN COAL DUST EXPLOSION MITIGATION APPLICATIONS

To further assess all these inerting rock dust types, a comparative economic analysis was provided among regular dry dust, wet dust and hydrophobic dust on a cost per raw coal tonnage basis. The dimensions of the typical underground coal mine entry used in this cost analysis are given in Figure 5.17 and the length, width and height are corresponding to 20, 6 and 2 meters, respectively.
Figure 5.17. The dimensions of a typical underground coal mine entry.
In addition, it has been known that the unit price for regular rock dust is approximately varying from $38 to $45 per tonnage, a large portion of which is attributed to the transportation cost (Perry et al., 2015). Therefore, an approximate cost of $40/tonnage was used in the present calculation with known loose density of 0.93 g/cm³ (J.M. Huber rock dust) and assumed typical raw coal density of 1.6 g/cm³. The hydrophobic rock dust used in the economic analysis was modified with 0.05 % sodium oleate by weight of total dry dust. The price of the sodium oleate is substantially flexible based on different chemical providers, which is further exacerbated by the fact that only a small amount was purchased for the laboratory use. The overall cost of chemicals should be significantly decreased through bulk orders. Furthermore, sodium oleate is the salt form of oleic acid, which could be simply produced by adding oleic acid into the corresponding sodium hydroxide solution at natural conditions. The price would be much lower by directly converting oleic acid into sodium oleate. Therefore, an average price of $50/500g was used in the calculation for the cost of sodium oleate. Industrial water rate of approximately 0.88 $/378.5 liters was incorporated as well for the wet rock dust application calculations (Pennsylvania American Water, 2016). Based on the aforementioned dimensions of a typical coal mine entry, the cost of various inerting rock dust sources is given in Table 5.2 as a function of the thickness of applied rock dusts.

Table 5.2. Dusting prices based on a typical underground coal mine entry.

<table>
<thead>
<tr>
<th>Thickness (mm)</th>
<th>Dry</th>
<th>Wet</th>
<th>Hydrophobic</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.254</td>
<td>0.008</td>
<td>0.008</td>
<td>0.018</td>
</tr>
<tr>
<td>1.270</td>
<td>0.039</td>
<td>0.040</td>
<td>0.090</td>
</tr>
<tr>
<td>2.540</td>
<td>0.079</td>
<td>0.081</td>
<td>0.179</td>
</tr>
<tr>
<td>5.080</td>
<td>0.157</td>
<td>0.162</td>
<td>0.359</td>
</tr>
<tr>
<td>7.620</td>
<td>0.236</td>
<td>0.243</td>
<td>0.538</td>
</tr>
<tr>
<td>10.160</td>
<td>0.315</td>
<td>0.324</td>
<td>0.717</td>
</tr>
<tr>
<td>12.700</td>
<td>0.393</td>
<td>0.405</td>
<td>0.897</td>
</tr>
</tbody>
</table>

It can be clearly seen from Table 5.2 that regular dry dust is the inerting rock dust source that cost least and regular wet dust is a little bit more expensive due to the involvement of wet application. However, the hydrophobic rock dust is the most expensive one with its
cost approximately two times as high as regular dry dust. The rock dust cost is known to be sensitive to the dimensions of the coal mine entry (Perry et al., 2015) and the actual cost of hydrophobic dust could be lower based on the individual case. In addition, if the process of modified rock dust was applied in the underground coal mine applications, the mine-scale operation will render the chemical cost much lower through substantial bulk orders. The increased rock dust cost should be definitely overcome by the significant benefits of their enhanced explosion mitigation properties.

5.7. CONCLUSIONS

This chapter provided a detailed evaluation and fundamental study of the use of sodium oleate to generate hydrophobic rock dust particles that can be applied in wet form to avoid respirable dust issues and be readily dispersed upon drying to inert potential coal dust explosions in an underground mine. An optimum sodium oleate dosage of 0.1 wt% was realized from a series of tests conducted over a wide range of sodium oleate dosages. The optimum dosage maximized the dispersion of the rock dust after drying. Contact angle measurements found that increasing the sodium oleate dosage to values greater than 0.15 wt% significantly increased the degree of surface hydrophobicity as indicated by contact angles greater than 120 degrees which would imply an improved ability to repel water and thus potentially prevent particle caking. However, the enhanced hydrophobicity likely produces a strongly attractive particle-particle interaction force that induces particle aggregation of the rock dust particles and the generation of large, hard clumpy material. In addition, sodium oleate dosages greater than 0.5 wt% were found to produce calcium oleate nanoparticles as confirmed from thermogravimetric, SEM and surface tension studies. These nanoparticles aid in the agglomeration of the rock dust particles. As such, under the solution chemistry conditions evaluated in this study, positive impacts on dispersion resulting from the treatment of the rock dust to generate a hydrophobic surface was found to be limited to the generation of a contact angle of approximately 110 degrees.

Specific findings from this investigation include:
(1) The percentage of dust particles remaining in dispersion after 30 seconds was initially elevated to a high of 70.8% at a sodium oleate concentration of 0.1 wt%. The percent of dust being dispersed was slightly decreased up to the concentration of 0.5 wt% oleate and sharply decreased to a value lower than the value obtained from the untreated wet dust when the concentration was above 0.5 wt%.

(2) Surface hydrophobicity continued to be enhanced with an increase of sodium oleate up to a concentration of 0.5 wt% which provided the highest contact angle of 126°. Further addition of sodium oleate imposed no change on the measured contact angle values. Zeta potential of treated rock dust particles shifted to a more negative value with a corresponding increase in oleate concentration which resulted in an elevated electrostatic repulsive force.

(3) ATR-FTIR studies provided evidence of chemisorption for both the oleic acid and sodium oleate at pH 9.4 which is critical for long-term effectiveness of the surface treatment. The oleate species distribution diagram showed the existence of a surface active ionmolecular complex that is likely co-adsorbed with other associated species such as monomers, dimers and neutral species which combine to provide the level of surface hydrophobicity and surface charge characteristics.

(4) Thermogravimetric analysis corroborated the precipitation of calcium oleate from bulk solution which became dominated at the high oleate concentrations. The change in the morphology of oleate treated samples was confirmed visually by SEM micrographs. High oleate concentrations led to more calcium oleate nanoparticles nucleated on top of the dust surfaces which tended to induce agglomeration and the generation of densely-packed particles upon drying.

(5) Based on oleate adsorption data derived and calculated from the surface tension measurements, a sodium oleate adsorption mechanism was proposed with an initial monolayer coverage achieved at a dosage of 0.10 wt% to 0.15 wt% sodium oleate. Higher dosages initiate calcium oleate precipitation on top of the hydrophobic rock dust surface, which becomes predominant at high oleate concentrations and enhances the hydrophobic interaction forces between particles. The overall effect from the sodium oleate treatment is improved dispersion characteristics at low dosages due to the ability to repel water followed by a
decline in dispersion at high dosages due to particle agglomeration resulting from an enhanced attractive hydrophobic particle-particle interactive force and precipitated nanoparticles.

(6) Modifying reagents applied in the present study are safe to be used in the rock dust modification process and underground coal mine applications.

(7) Comparative economic analysis indicates that hydrophobic rock dust is substantially more expensive than the two conventional dusting methods. This is majorly due to the chemical cost which can be significantly reduced through the process scale-up and bulk orders.
6. CHAPTER 6. CONCLUSIONS

Laboratory and explosibility tests with the application of surface chemistry modified rock dust have been conducted together to prove their effect on cake formation prevention and explosion mitigation when applied in underground coal mines. A systematic investigation has been conducted to characterize the modified rock dust samples, assess the dispersibility enhancement and coal dust explosion mitigation properties. Fundamental evaluations have been given as well to clarify the adsorption mechanism of applied chemical on the dust surface from a perspective of solution chemistry. Specific conclusions from the present work are:

1. The pivotal of alleviating cake formation is long believed to create hydrophobic rock dust particles which are ready to repel water, allow instant water drainage and eliminate the formation of liquid and subsequent solid bridges.

2. Surface hydrophobicity was significantly increased for dust samples treated with both oleic acid and sodium oleate. The highest contact angle was obtained as 126° for the application of sodium oleate. The increase in the surface hydrophobicity of stearic acid treated dusts was much less significant compared to sodium oleate and oleic acid.

3. Treatment of rock dust samples led to the increase in the negative surface charges for all the applications using sodium oleate, oleic acid and stearic acid. The build-up of negative charge results in an increased charge-charge repulsive force among bulk solids that is beneficial for the particles dispersibility.

4. Rock dust dispersibility tests show that sodium oleate treated rock dust performed the best in enhancing the dusts dispersibility followed by stearic acid and then oleic acid. Oleate treated dust particles provided an amount of suspended dust equal to regular dry dust 3 seconds after an initial air pulse and nearly 25 percentage points higher than the results obtained with regular wet dust. The dispersibility during the shortest period such as within microseconds is most crucial for explosion mitigation purpose. Beyond 3 seconds, the dispersibility of oleate treated dust was decreased but still significantly higher than the values measured for regular wet dust.
(5) Rock dust treated with stearic acid generated a performance that was slightly inferior to dusts treated with sodium oleate however superior to the dusts treated with oleic acid in terms of enhancing the dust dispersibility.

(6) The application of dispersants imposes a harmful rather than enhanced effect on the dispersibility of dust particles due to the preferential adsorption of dispersants over sodium oleate, which deteriorates the surface hydrophobicity of dust particles and facilitates the existence of liquid and solid bridges.

(7) Dispersibility of rock dust is affected by moisture adsorption. However, there is no perfectly direct relationship between moisture adsorption and dispersibility of dust particles that needs further investigations which may involve the chemical nature of solids surface.

(8) Tests conducted in the explosive chamber prove that the explosion potential could be reduced by almost 82.8% using the oleate treated rock dust at the concentration of 0.05% by weight of total rock dust weight, which is a significant improvement compared to regular wet dust applications.

(9) Fundamental investigations of sodium oleate adsorption on rock dust surfaces show that the maximum dispersibility of treated rock dust occurred at the application of 0.1 wt% oleate with approximately 70.8% of the dust remaining dispersed after a dispersion time of 30 seconds. The percent of dust being dispersed slightly decreased up to the application of 0.5 wt% oleate and then drastically decreased a value much lower than the values obtained for regular wet dust without treatment.

(10) The maximum surface hydrophobicity corresponding to the highest contact angle of 126° was observed at the application of 0.5 wt% oleate. Further increase in the oleate concentration imposed on change on the measured contact values. The dust surface charge gradually shifted to a more negative value with the elevation in the oleate concentration, which results in an enhanced electrostatic repulsive force.

(11) A nonreversible and long-term chemical interaction between oleate and rock dust particles has been proved by ATR-FTIR analysis and the construction of oleate species distribution diagram which can be attributed to the co-synergistic
adsorption of oleate associated species such as monomers, dimers and neutral species which combine to provide the level of surface hydrophobicity and surface charge characteristics.

(12) The precipitation of calcium oleate from bulk solution has been conformed by thermogravimetric analysis and SEM micrograph observation under high oleate concentration.

(13) Precipitated calcium oleate particles were identified as nanoparticles which tend to agglomerate and generate dense-packed particles due to their small particle sizes.

(14) Based on the surface tension measurements and calculated oleate adsorption data, a sodium oleate adsorption mechanism was proposed with an initial monolayer adsorption completed with the oleate concentration falling between 0.1 wt% to 0.15 wt% which is a long-term chemical adsorption. Higher dosages initiate the calcium oleate precipitation on top of the hydrophobic dust surface and enhance the attractive hydrophobic interaction forces among super hydrophobic solid surfaces.

(15) The overall effect from the sodium oleate treatment is improved dispersion characteristics at low dosages due to the ability to repel water followed by a decline in dispersion at high dosages due to particle agglomeration resulting from an enhanced attractive particle-particle interactive force and nanoparticles agglomeration.

(16) Economic analysis results indicate that the oleate treated rock dust is approximately twice as expensive as regular dry dust due to the associated chemical cost. However, the cost could be substantially reduced for enlarged underground coal mine applications and the benefits of enhanced explosion mitigation properties should overcome the economic costs. More important, sodium oleate, as well as oleic acid and stearic acid, is safe to be applied in the underground coal mine applications.
7. CHAPTER 7. SUGGESTIONS FOR FUTURE STUDY

The present work here has indicated the potential of applying surface chemistry modified rock dust for eliminating cake formation and improving dispersion in coal dust explosion mitigation. However, efforts should be continuously devoted to further improve the modification process. Suggestions for the future studies are given as followings:

(1) Observations during the dispersibility tests have indicated that after the initial air pulse, size distribution for the settled particles as a function of dispersion time was dependent on the dispersive properties of tested samples, e.g., dusts generated high percent dispersion values normally produced finely dispersed particles in contrast to large clumps obtained for particles generating low dispersion values. It is known that finely distributed particles with high buoyance lead to the most effective explosion mitigation properties. Therefore, sieve analysis can be conducted in future on the settled particles and correlate the specific particle size distributions with the dispersibility of rock dusts to generate a more comprehensive evaluation.

(2) Dispersibility test apparatus applied during the present study had a relatively small volume which restricted the sample size to some extent. Efforts can be made in future to scale up the dispersibility test apparatus, maybe build a dust dispersion chamber, in which enlarged sample size can be loaded to minimize the experimental error and configuration can be further designed to be more representative of the actual situation in underground coal mines.

(3) Previous studies have shown that conditioning time and solution chemistry are critically important for optimizing the positive effects of surface modification at minimum cost. The typical surface modification treatment currently occurs in a system that provides a very short residence time for conditioning with the dust particles. Therefore, the effect of conditioning time, conditioning speed, solution pH and other determining parameters on the surface modification efficiency could be fundamentally investigated to determine the optimum operational conditions.
(4) Efforts should be dedicated as well to seeking for other potential modification methods to further optimize the modification efficiency such as aforementioned polymerized rock dust and foam dust developed from the addition of chemical additives to the water and rock dust admixture. These products have been indicated as a promising alternative to dry rock dusting in terms of resisting caking and maximizing the degree of suppressing dust explosions (Perry et al., 2015).

(5) Additional efforts are needed to ensure that the surface modification is technically and economically feasible including attention to the actual application process.
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VITAE

Education

- PhD, Mining Engineering,
  September 2011-May 2016 (GPA: 4.0/4.0)
  University of Kentucky, Lexington, USA
- BS, Mineral Processing Engineering,
  September 2005-June 2009
  Central South University (CSU), Changsha, China

Professional Preparation

- PE exam passed, license pending experience

Research Expertise

- Surface chemical aspects pertinent to mineral processing, coal preparation, flotation, explosion mitigation, pyrometallurgy and hydrometallurgy for metal recovery from ores. Specific experience in characterization and performance evaluation of frothers, collectors and surfactants. Additional experience with iron ore sintering/pelletization and economic evaluation of coal fines pelletization.

Research Experience

- Working with SNF Flomin through the fellowship provided, 2012-present
  Responsible for developing, performing and interpreting flotation tests to evaluate candidate materials as well as other projects related to product development for freeze conditioning and side release agents. Theoretical mineral processing knowledge has been applied to industrial production to resolve problems such as evaluating candidate reagents, optimizing flotation performance and reducing mineral processing costs. Conducted numerous industry-oriented laboratory- and pilot-scale studies on coal preparation, iron ore and phosphate flotation.
- Working in the Department of Ferrous and Metallurgy, Central South University, 2009-2011

Investigated the effect of pyrometallurgical and hydrometallurgical processing methods on the recovery of nickel and cobalt from Indonesian laterite ores, Central South University Collaborative Project, China.

**Industrial Experience**


  Particiated in the company’s industrial development/commercialization projects focused on dry coal processing, searched for innovative ideas to increase separation efficiency and reduce operating costs. Also, prepared and hosted exhibits at professional coal conferences.

- Interned at Baosteel, Shanghai, China, 2009

- Interned at Xiangtan Iron & Steel Plant, Hunan, China, 2008

- Interned at the Xinyu Iron & Steel Plant, Jiangxi, China, 2007

**Selective Projects**

- Conducted a project entitled “Modern Rock Dust Development and Evaluation” to provide a hydrophobic rock dust greatly reducing the coal dust explosion potential through surface chemistry modification for industrial rock dusting, Kentucky Department for Energy Development and Independence, 2013-2015.

- Conducted numerous coal flotation projects to compare the flotation performances of various reagents based on different coal sources, SNF Flomin Coal, 2013-2015.

- Cooperated with University of Kentucky Center for Applied Energy Research (CAER) on conducting the systematic economic assessment for building a plant with 50 TPH throughput to pelletize, dry and briquette fine coals, Center for Advanced Separation Technology (CAST), 2012-2013.

- Conducted a series of iron ore flotation projects to develop products, SNF Flomin Coal, 2011-2012.
Assisted the phosphate flotation project for flotation optimization, the Mosaic Company, 2011-2012.

**Pedagogy Experience**

- MNG341-Mine Ventilation
- MNG580-Mineral Processing Plant Design

**Awards & Honors**

- Outstanding Graduate Student Award, University of Kentucky Department of Mining Engineering, 2016
- Selected as Henry Krumb Lecturer, Society for Mining, Metallurgy and Exploration (SME), 2015-2016
- Selected as Co-chair for the 2015 Joint Spring Meeting of the West Virginia Coal Mining Institute, the West Virginia Coal Association, and the Central Appalachian Section of SME, 05/13-05/15,2015
- G. William Kalb Scholarship award, Coal Preparation Society of America (CPSA), 2015
- Graduate Fellowship-Engineering, SNF Flomin, 2012-2016
- Outstanding Graduate Award, Central South University, 2009
- Metso Eminence Scholarship, Central South University, 2008-2009
- Outstanding Student Scholarships, Central South University, 2005-2009

**Professional Affiliations**

- Society for Mining, Metallurgy and Exploration (SME)
- Coal Preparation Society of America (CPSA)

**Publications**


**Patent**