How do mud balls form in lime kilns?

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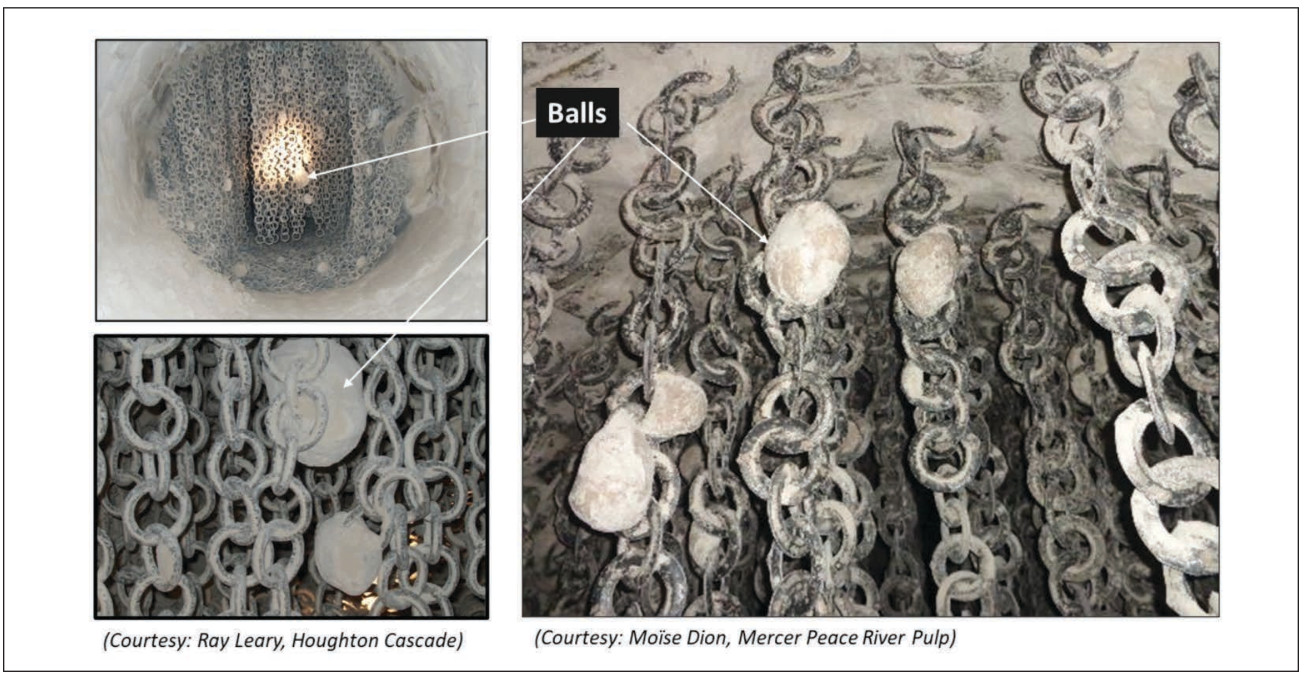
ABSTRACT: Mud ball formation in lime kilns has been a persistent problem in many kraft mills, particularly for older kilns that are equipped with chains. A systematic laboratory study was conducted to examine how mud balls are formed and the key factors that affect ball formation. The results confirm the general mill experience that high moisture and high sodium contents in lime mud are the main contributing factors to ball formation. The high moisture content allows lime mud to agglomerate and grow to form balls, while the high sodium content helps make the balls hard and retain their shape. A ball formation mechanism is proposed to explain how mud balls form and grow near the kiln feed end.

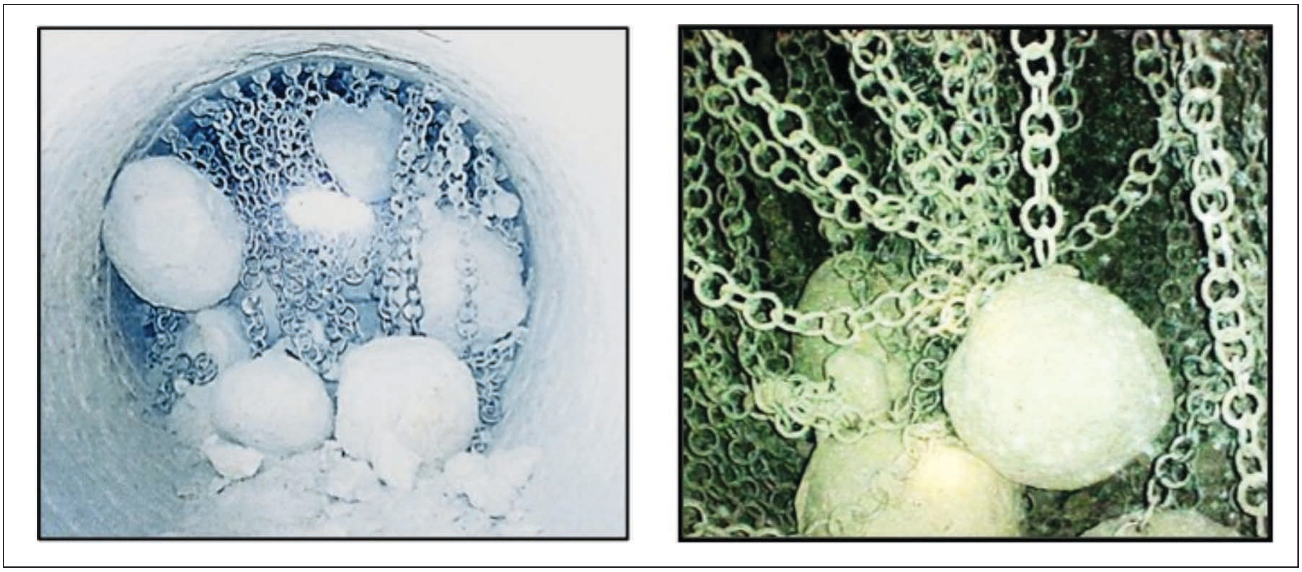
Application: Understanding the mechanism and thresholds of moisture and sodium contents required to form hard mud balls can help mills develop viable operating strategies to alleviate the problem.

In kraft pulp mills, rotary lime kilns are used to calcine lime mud ($CaCO_3$) into lime (CaO) for reuse in the causticizing plant. As the lime mud enters the kiln from the feed end and moves slowly toward the front end, it is heated, dried, calcined, and discharged from the kiln as lime. One of the persistent problems in lime kiln operation is the formation of mud balls near the kiln feed end, particularly for older units that are equipped with chains for drying the lime mud. Balls are typically round or in a slightly elongated shape, 2 in. to 6 in. (5 cm to 15 cm) in diameter. They mix and move along with lime mud on the kiln floor and eventually are discharged from the kiln along with lime. Some balls, however, may get stuck and "baked" onto the chain rings (**Fig. 1**). These balls are relatively small and do not normally pose any operational problem unless there are many of them formed on the chains, or until they have grown to a much larger size, 12 in. to 24 in. (30 cm to 60 cm), which severely obstructs the flue gas passage, as shown in **Fig. 2**.

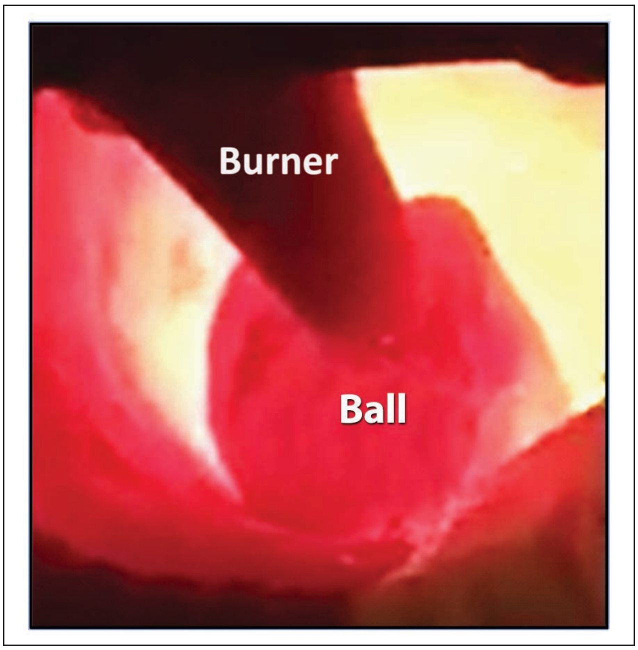
As balls grip tightly onto and cover the chains, they prevent the chains from absorbing heat from the flue gas and the kiln wall, thus lowering the chain drying efficiency. If the lime mud is still wet after it emerges from the chain section, it may adhere to the kiln wall to form mud rings [1-3], which can lead to a costly unscheduled kiln shutdown for ring removal. Furthermore, since wet mud after the chain section takes a longer time to process than dry mud,



1. Balls formed on chains in lime kilns equipped with round chains (left) and diamond chains (right).



2. Large ball formation in the chain section of two different lime kilns.



3. A large ball strikes and extinguishes the burner flame.

the resulting reburned lime is likely not well-calcined, with a higher residual $CaCO_3$ content [4].

Once emerged from the chain section, the balls, due to their larger size and heavier mass, roll through the kiln much more quickly than lime nodules. As such, they exit the kiln without being calcined. This can substantially increase the overall residual $CaCO_3$ content of the reburned lime [3]. In severe cases, large balls can roll quickly, strike, and extinguish the burner flame at the kiln front end (**Fig. 3**). And if large enough, balls can abruptly plug the kiln opening at locations that have already been significantly narrowed by ring deposits, as shown in **Fig. 4**. These cases inevitably result in unscheduled kiln shutdowns for ball/ring removal and substantial production losses.

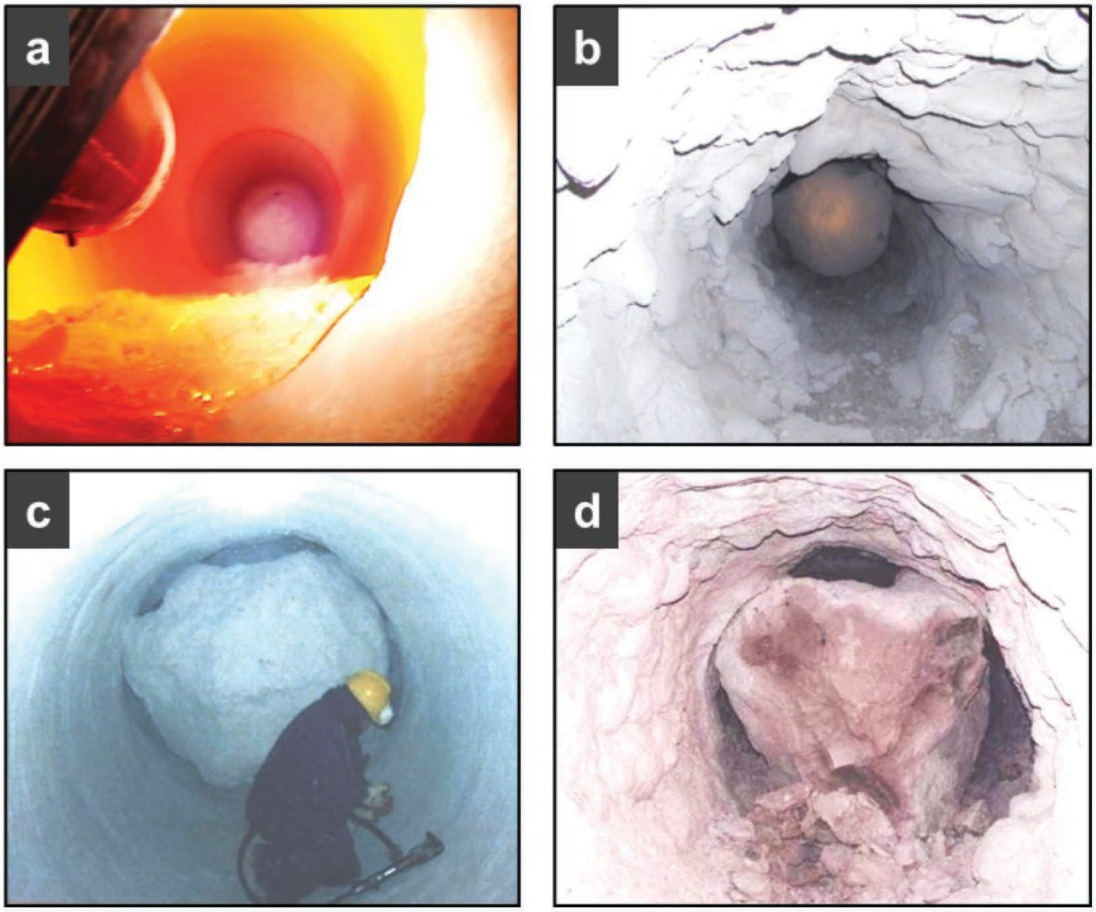
Mud balls are generally white/brighter on the surface and gray/darker on the inside. They are not as hard as ring deposits, and the composition is similar to that of the lime mud, containing over 85 wt% $CaCO_3$.

Although the formation of mud balls in lime kilns has often been attributed to high moisture and high sodium (Na) contents in the lime mud, exactly how balls are formed and how moisture and Na contents may affect ball formation are not well understood. A systematic study was therefore conducted in the laboratory, as part of Hinton-Barber's Master of Engineering thesis project [5], to examine the effects of moisture and Na contents in lime mud on ball formation and to establish operating ranges of moisture/Na contents in which hard balls may form. In this research paper, we will first describe the experimental methods used in the study and the results obtained, and then propose a mechanism by which balls form and grow in the lime kiln and recommend strategies for alleviating ball formation.

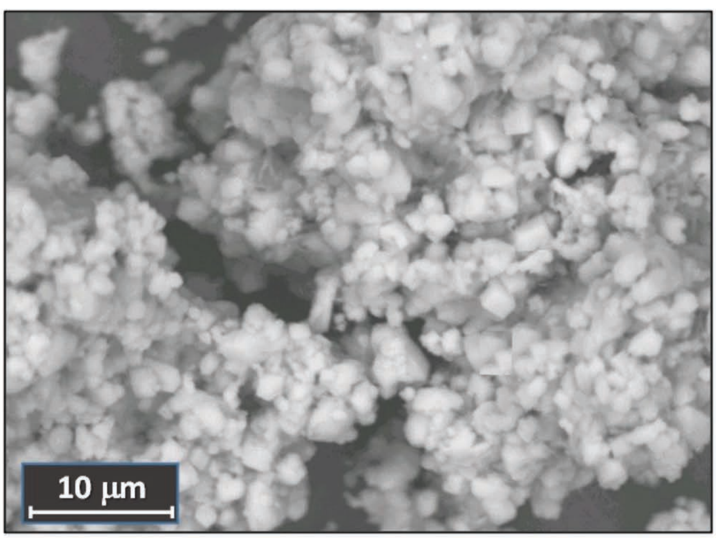
EXPERIMENTAL METHODS AND RESULTS

The lime mud sample used in this study was obtained from a kraft mill in northern Ontario, Canada. It had a relatively uniform particle size, 2 to 3 µm, and on a dry mass basis, contained 38% calcium (Ca), 1.5% magnesium (Mg), 0.7% Na, 0.6% sulfur (S), 0.2% aluminum (Al), 0.3% manganese (Mn), 0.3% iron (Fe), 0.2% silicon (Si), and 0.1% phosphorus (P) (**Fig. 5**). The elemental composition suggests that the mud was relatively pure, containing nearly 92% $CaCO_3$. This, along with the small particle size, made the mud "ideal" for use as a starting material.

Various experiments were performed to examine the

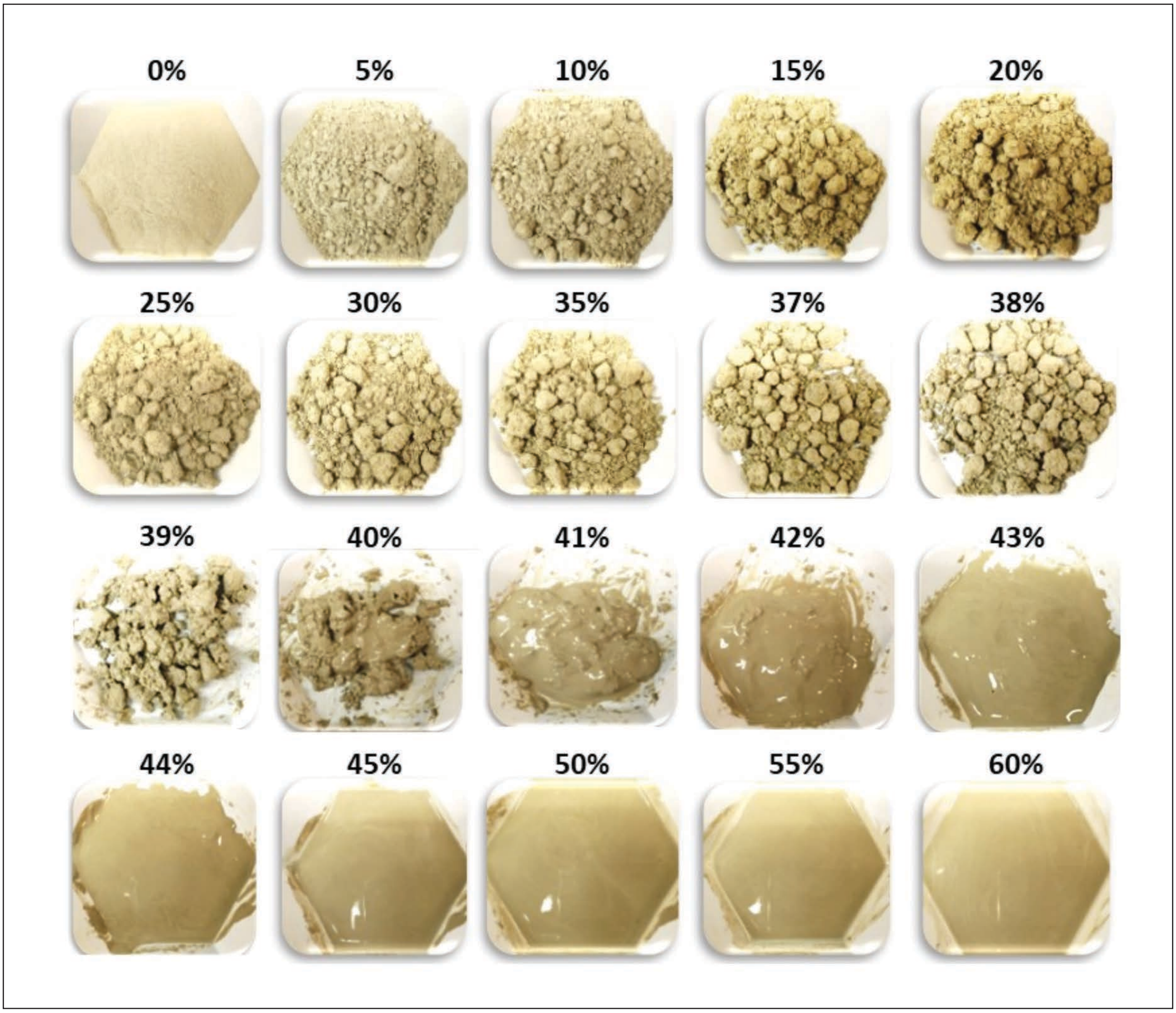


4. Clogging of the lime kiln opening by a gigantic (1.2 m to 2 m in diameter) ball at four different kraft mills.



Element	wt% ds
Calcium (Ca)	38.0
Magnesium (Mg)	1.5
Sodium (Na)	0.7
Sulfur (S)	0.6
Manganese (Mn)	0.3
Iron (Fe)	0.3
Silicon (Si)	0.2
Aluminum (Al)	0.2
Phosphorus (P)	0.1

5. Scanning electron microscope image and chemical composition of the lime mud used in this study.



6. Change in lime mud appearance with wt% moisture content.

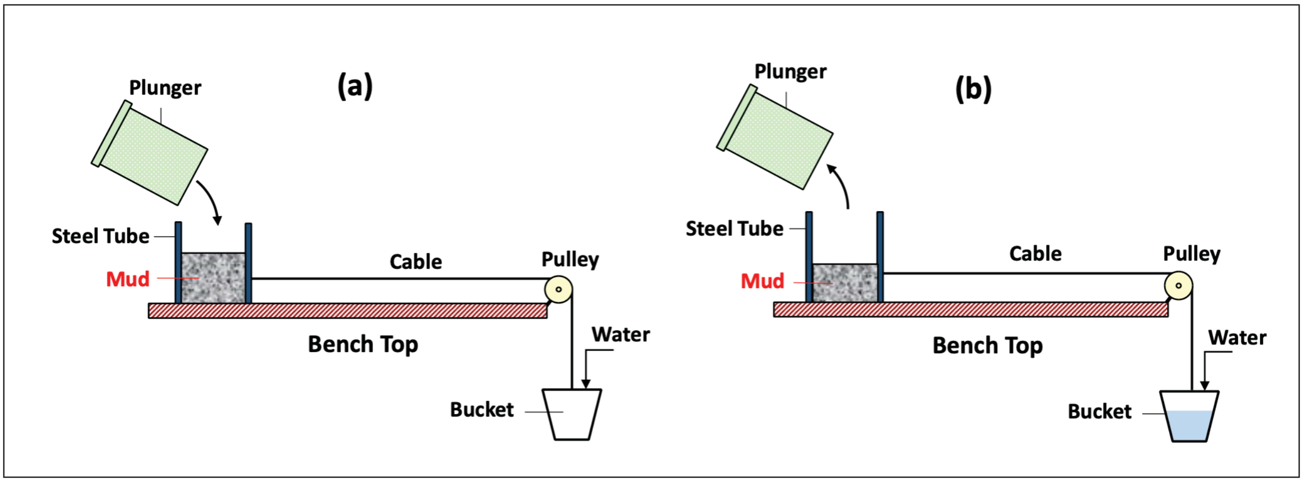
effects of moisture and Na contents on the appearance and stickiness of the mud, as well as on the strength and structural integrity of balls made from the mud.

Experiment #1 — Effect of moisture content on mud appearance

The mud was first completely dried in an electric oven at 110°C. The dried mud was stored in a sealed container until it was used. For this series of experiments, 50 g of dried mud was placed in a small plastic dish. Deionized water was added to the disk and mixed well with the mud to produce wet mud samples at different moisture contents ranging from 0% to 85%. The appearance of the wet mud was visually inspected and photographed. For each moisture content, the experiment was triplicated to improve the accuracy of the results.

Figure 6 shows photos of the samples with a moisture content up to 60% by weight. At 0% moisture, the mud looked dried and powdery as expected. At 5% moisture, some agglomeration was evident. The agglomeration became clearer at a higher moisture content up to 39%. At 40% moisture and higher, the samples were sufficiently wet that they looked shiny, indicative of free/excessive water present in the samples. Between 41% and 60% moisture, particularly > 44% moisture, the samples looked wet and fluid. At higher moisture contents, i.e., from 61% to 85%, the samples looked similar to that at 60% moisture, and thus were not shown here.

These test results suggest that lime mud starts to agglomerate at a moisture content as low as 5%. The agglomeration becomes more evident at a higher moisture content up to 39% or 40%. Above 40% moisture, the mud contains too much water so that it simply spreads out and fluidizes. This implies that in order for lime mud to agglomerate into balls, it must contain some moisture, but not more than 40%.



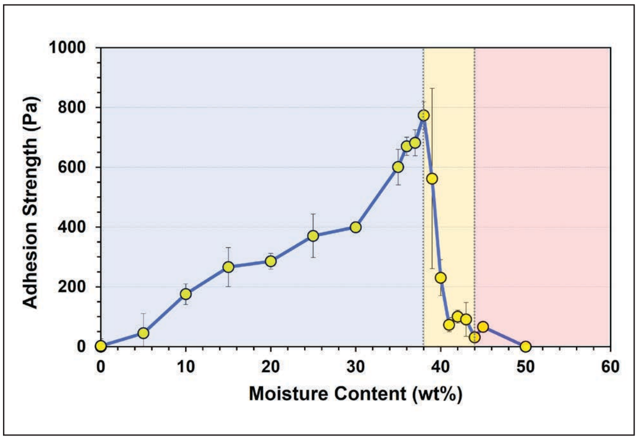
7. Adhesion strength test apparatus [6].

Experiment #2 — Effect of moisture content on mud stickiness

In order for lime mud particles to agglomerate to form balls, they must be sticky. In general, particle stickiness is greater in the presence of a liquid, which in this case, is the water or the moisture in the mud. In this study, the mud stickiness was measured as a function of moisture content, using the adhesion strength test apparatus similar to that used previously in our laboratory to determine the stickiness of biosludge [6]. As shown in **Fig. 7a**, the apparatus consisted of a sample steel tube (50 mm inner diameter [ID] x 150 mm height) connected to a water bucket hanging over the edge of the bench top via a cable/pulley system. The cable was tied to the steel tube at a position 1 cm from the base. An empty water bucket was hung from the other end of the cable with its top open.

The sample preparation involved placing 10 g of dried mud into the sample tube, adding an appropriate amount of water to the mud using a pipette to obtain the desired moisture content, and uniformly mixing the wet mud sample using a spatula. A 3.5 kg cylindrical plunger with a diameter slightly smaller than that of the sample tube was inserted from the top to compress the moist mud for 1 min to make it adhere to the bench top surface. After the plunger was lifted from the steel tube, water was slowly introduced into the bucket at a flow rate of 0.1 L/min (Fig. 7b). The weight of the water in the bucket pulled the sample tube on the bench top toward the pulley. As soon as the sample tube started to slip, the water flow was stopped. The difference between the amount of water required to cause the steel tube, with and without moist mud in it, to slip was used to calculate the adhesion strength of the mud sample, expressed in Pa (Pascal).

As summarized in **Fig. 8**, the adhesion strength increased almost linearly with the moisture content, reaching 760 Pa at 39% moisture. Above 39% moisture, the strength decreased drastically, down to 240 Pa at 40% moisture and below 100 Pa at 41% moisture or higher. The results are consistent with photos shown in Fig. 6, suggesting that for lime mud to be sufficiently sticky to form balls, it needs to contain a right amount of moisture, which is between 35% and 39%. Below 35%, the mud is not wet/sticky enough to form good balls, while above 39%, it is too fluid to retain a spherical shape.

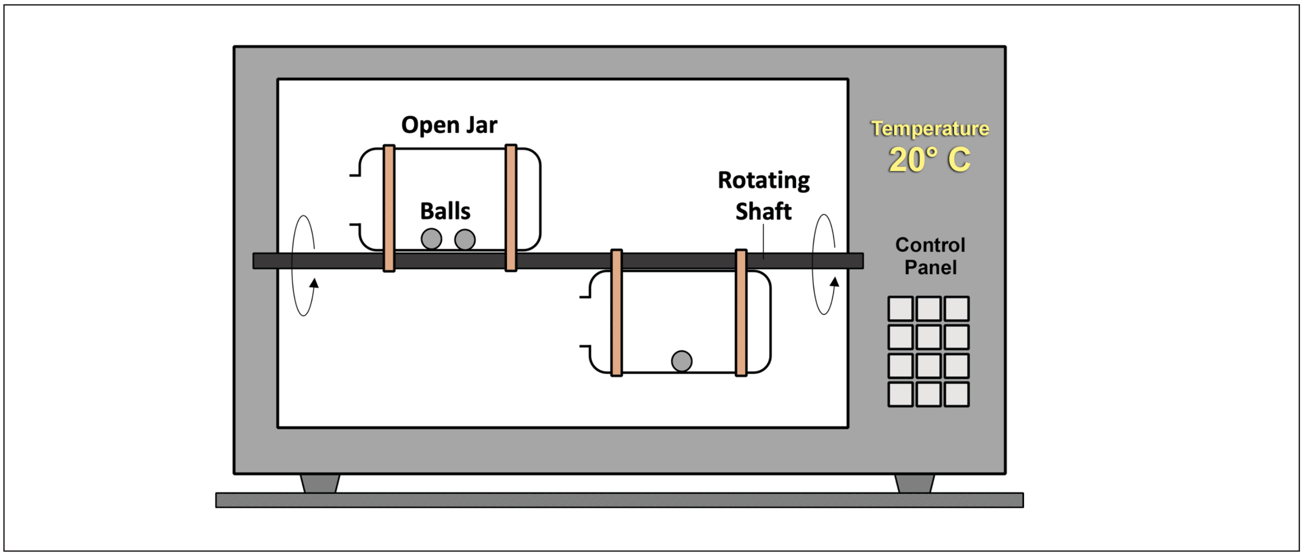


8. Effect of moisture content on adhesion strength of lime mud.

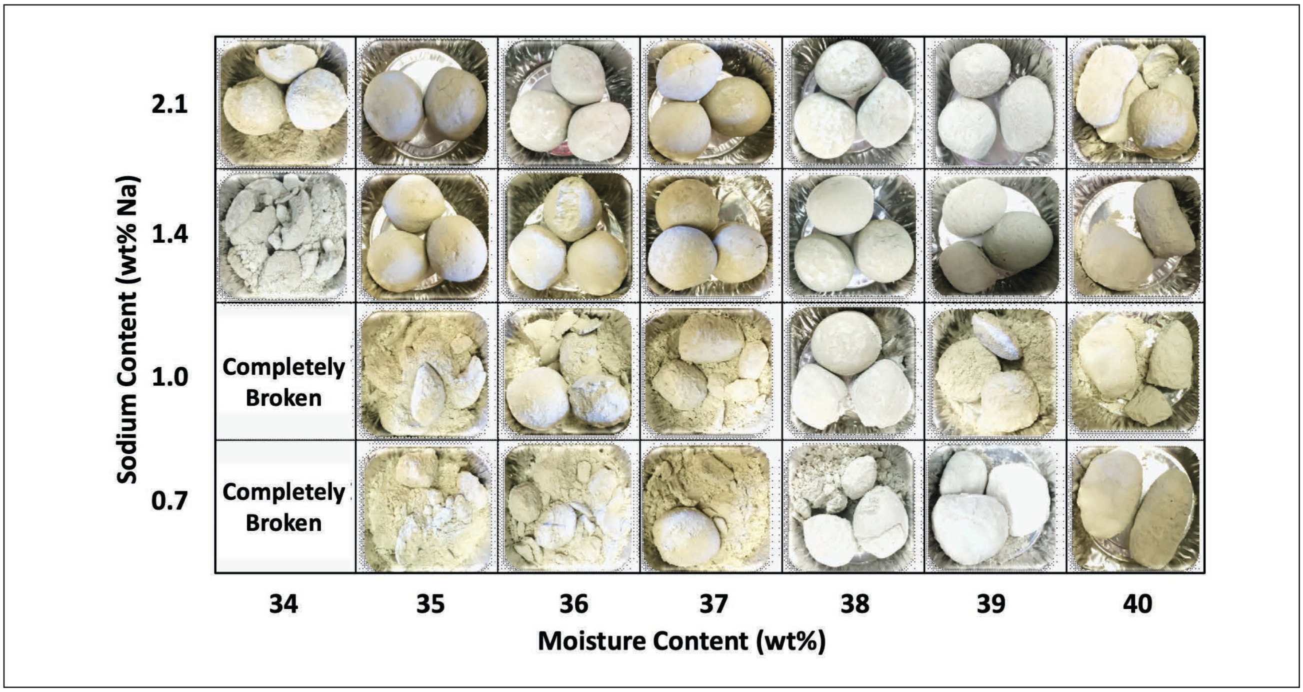
Experiment #3 — Effects of moisture and Na contents on ball stability

Lime mud not only must be sticky enough to form balls, but the formed balls must also be rigid enough to withstand the sliding and tumbling motions of the solid bed in the kiln in order to grow larger with time. Moisture helps make mud particles sticky, as shown previously, while Na is expected to help make balls hard by gluing mud particles together.

In this study, the effects of both moisture and Na contents on ball stability were examined. The mud moisture content was varied between 30% and 40% at 1% increments, while the Na content was examined at four levels, 0.7%, 1.0%, 1.4%, and 2.1%, by uniformly mixing dried lime mud with appropriate amounts of water and white liquor obtained from the same pulp mill. Each ball was made by first molding lime mud with desired moisture and Na con-



9. Rotating convection oven.

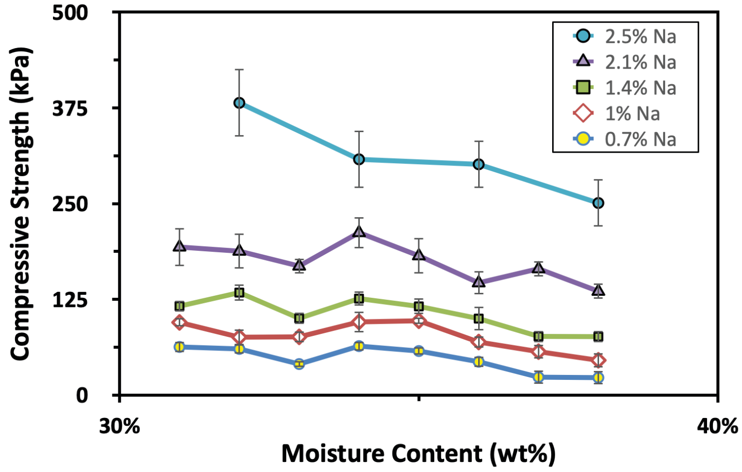


10. Effects of moisture and sodium (Na) contents on ball stability.

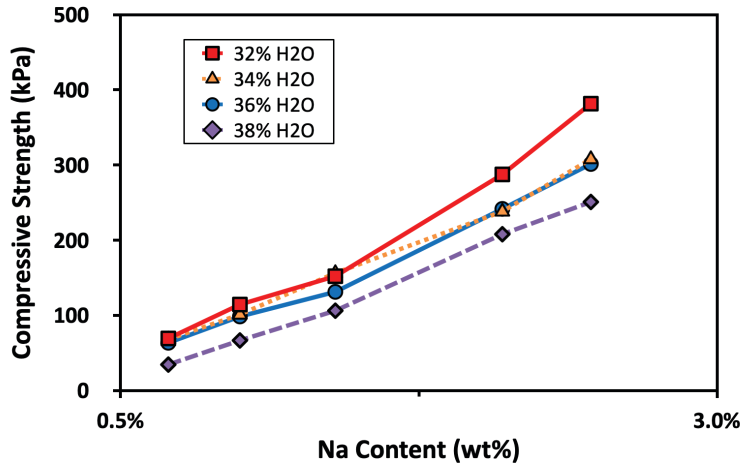
tents into two 3-cm diameter hemispheres (half-balls) and compacting them together to form a ball. A total of 44 tests (11 moisture contents x 4 Na contents) were carried out with 3 balls used per each test. The resulting balls were subsequently dried in a custom-made apparatus to determine if they were structurally strong enough to withstand the drying conditions simulated as those in the lime kiln.

As shown schematically in **Fig. 9**, the apparatus was made of a Black & Decker (Towson, MD, USA) convection oven with a rotating shaft in the middle. Two opposing glass jars were clamped tightly to the shaft. Each jar had its lid open to ensure better heat transfer from the oven to the samples, as well as to allow the water vaporized from the samples during drying to escape. Of the 3 balls used in each test, 2 were placed in one jar and 1 in the other jar to examine if there was any interference or attrition between the balls. The oven temperature was set at 200°C, the shaft was rotated slowly at 1 rpm, and the drying time was 45 min. After each test, the balls (or what was left of them) were transferred from the jars to a small aluminum tray and photographed for visual analysis.

Figure 10 is a compilation of photos of the balls after the drying tests. At a moisture content between 30% and 33%, all balls completely fell apart into powder after drying, regard-



11. Effect of moisture content on pellet compressive strength at different Na contents.



12. Effect of Na content on pellet compressive strength at different moisture contents.

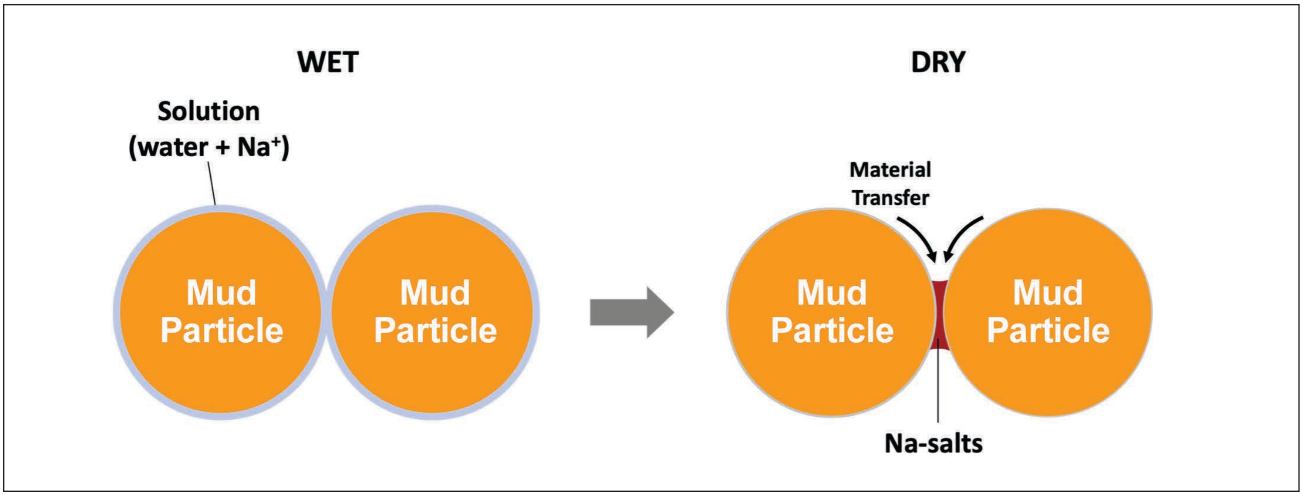
less of their Na contents. As such, no photos are shown here. At 34% moisture, only balls with high Na contents (1.4% and 2.1% Na) survived the test. At 35% moisture, balls with 0.7% and 1.0% Na crumbled after the test, while those with higher Na contents remained in good shape. In the upper right corner of Fig. 10, where both moisture and Na contents were high (i.e., > 39% moisture and > 1.4% Na), the balls remained stable, although the high moisture content may have caused them to elongate somewhat during the test.

Experiment #4 — Effects of moisture and Na contents on ball rigidity

In this series of experiments, the effects of moisture and Na contents on ball rigidity were examined by measuring the compressive strength of mud pellets prepared at different moisture and Na levels. Each pellet, 2 cm diameter x 1.25 cm height, was made by compressing 2 g of wet mud into a cylindrical steel mold. The pellet was then dried in an oven at 200°C for 45 min, and subsequently crushed using a Sintech compression tester. The test was carried out in accordance with ASTM D695 "Standard test method for compressive properties of rigid plastics," with a compression speed of 1 mm/min under a 22.7 kg (50 lb) load cell. Five pellets were used per each mud composition.

Figure 11 shows the effect of moisture content on the compressive strength in kPa of the pellet at different Na contents. At a given Na content, the compressive strength decreased with increasing moisture content, implying that high moisture content makes pellets weaker or softer. The result is not surprising, since pellets formed at higher moisture contents are more porous after drying.

Figure 12 shows exactly the same data as Fig. 11, but instead plotting the compressive strength of the pellet against Na content at different moisture levels. The results clearly show that the higher the Na content is, the greater is the strength or the harder is the pellet.



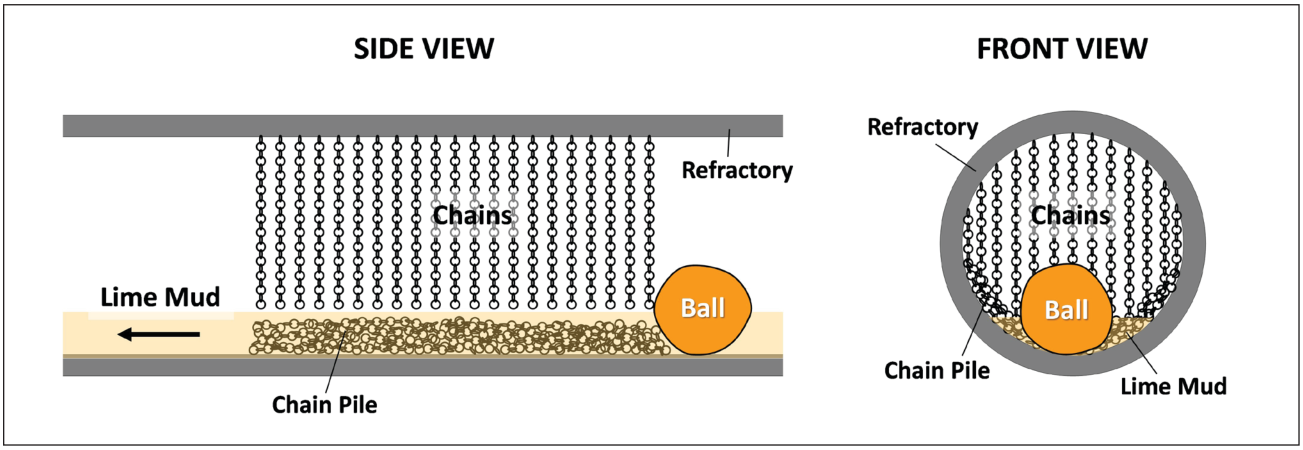
13. Role of Na in hardening of dry mud particles.

The contribution of Na in making the mud pellet hard after drying is explained in **Fig. 13**. When the mud is wet, the Na in the water is in the form of dissolved Na^+ ions. As the mud dries, Na^+ ions follow the concentrated solution and migrate toward particle-particle joints, where they eventually precipitate out as sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), sodium sulfide (Na_2S), sodium sulfate (Na_2SO_4), sodium chloride (NaCl), etc., and/or double salts of these compounds, depending on the cations available in the solution. These precipitates/crystals serve as a glue that binds mud particles together, making the pellet hard.

HOW DO MUD BALLS FORM IN LIME KILNS?

The results obtained from this work suggest that for the lime mud to be sticky to agglomerate into balls, it must contain 35% to 40% moisture. It must also contain a sufficient amount of Na for the formed balls to be structurally rigid enough to withstand the sliding/tumbling motion of the solid bed during kiln operation in order to grow larger with time. This means that for large balls to form and grow, not only must the lime mud contain sufficient moisture and Na, but also the formed balls must keep rolling in the kiln for some time.

Balls are initially small, but as they roll along with the kiln rotation, they pick up more materials and grow larger. Thus, in order for balls to become massive, they must be somehow held back by a physical barrier or a step change in the kiln. Such a barrier/step change can be the inlet of a ring, a dam, or a large pile of chains, as conceptually shown in **Fig. 14**. When balls are small, they do not have sufficient inertia to roll over the barrier, so they keep rolling in front of it as the kiln rotates. If the mud bed at this location is still sufficiently moist and sticky, it will form a new coating layer on the ball surface, making the balls larger with time. As the balls become larger, they gain sufficient momentum to roll over the barrier and "escape." Once this happens, the balls, with their heavy mass and relatively round shape, can roll quickly toward the hot end of the kiln where they may strike and damage the kiln burner as shown in Fig. 4, or they may just sit on the kiln grizzly, waiting to be physically removed from the kiln hood by kiln operators.



14. A possible way for large balls to form in the lime kiln.

The previously described mud ball formation mechanism is consistent with mill experience that mud balls tend to form shortly after a precoat filter sheet drop, allowing a large amount of wet mud with a high Na content to enter the kiln at once [2]. Wet mud is sticky and can agglomerate to form balls, while the high Na content helps make balls rigid and retain their spherical shape so that they can keep growing larger with time.

The requirement of high moisture and high Na contents for ball formation means that mud balls can only form in older lime kilns that use chains to dry lime internally. For modern kilns with external lime mud driers, the lime mud fed to the kiln is almost completely dried (~ 0% moisture). Furthermore, since modern kilns are typically operated with more efficient mud washing/dewatering equipment, the Na content in the lime mud is low, making it difficult for balls to form.

Balls may also originate from pieces of ring deposits fallen from the kiln wall. Fallen ring deposits are initially in the form of curved slabs of various sizes and shapes. As they slide, tumble, and roll along with the solid bed in the kiln, they become round-edged with time. Only small pieces may end up looking like balls, while large pieces remain as slabs, as shown in **Fig. 15**.

However, the gigantic balls, such as the ones that completely block the kiln opening as shown in Fig. 4, can originate from both mud balls and fallen ring deposits. Mud balls tend to be round, with a relatively smooth surface (Figs. 4a and 4b), while fallen ring deposits tend to have an irregular shape and an irregular surface (Figs. 4c and 4d). Furthermore, since mud balls are essentially dried lime mud, they tend to have a higher $CaCO_3$ content than ring deposits. They are also not as hard as mid-kiln ring deposits that are formed via recarbonation of lime particles [1].

15. Large slabs of fallen ring deposits removed from a lime kiln.

PREVENTIVE MEASURES

This study shows that the moisture content needs to be between 35% and 40% for the lime mud to form balls. In practice, the moisture content is routinely monitored by measuring the solids content of the lime mud fed to the kiln. Since the % solids content is equal to (100% – % moisture content), in order to avoid ball formation, the mud solids content must be kept above 65% at all times.

Since the ball strength increases almost linearly with increasing Na content up to 2% Na (Fig. 12), no specific Na content range can be recommended for avoiding hard ball formation per se, other than simply that the lower the Na content the better. It is important to point out that there are three different types of Na present in the lime mud: water-soluble Na, water-insoluble Na, and guarded Na [7]. Each type is roughly about 1/3 of the total Na present in the mud. Of these types, only the water-soluble Na (the one that comes in with white liquor) can contribute to ball rigidity through the crystallization of water-soluble Na salts, as discussed previously. Since the total Na content in lime mud is typically about 1% Na or 1.4% sodium oxide (Na_2O), it is important to keep the water-soluble Na content as low as possible, preferably < 0.3% Na, through improved mud washing and dewatering.

For gigantic balls shown in Fig. 4, chances are they may originate from fallen ring deposits. As such, their preventive measures should be the same as those for ring formation. These may vary depending on the type of rings that form.

SUMMARY

A systematic study was conducted in the laboratory to examine how mud balls are formed and the key factors that affect ball formation. The results confirm the general mill experience that high moisture (low solids) and high Na contents in the lime mud fed to the kiln are the main contributing factors to ball formation. The high moisture content allows the mud to agglomerate to form balls, while the high Na content helps make the balls hard and retain their shape.

Ball formation is expected to be minimized by: i) increasing the solids content of lime mud fed to the kiln above 65%; ii) keeping the water-soluble Na content in the lime mud as low as possible through improved mud washing and dewatering; and iii) increasing the kiln feed-end temperature to help dry the mud more quickly.

A ball formation mechanism was proposed that explains how mud balls form and grow near the kiln feed end, and why the formation is limited only to older kilns employing chains to dry lime mud. Understanding the mechanism and the thresholds of moisture and Na contents required to form hard balls can help mills develop viable operating strategies to alleviate the problem. **TJ**

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About this journal

ABOUT THE AUTHORS

While mud ball formation in lime kilns is a common problem in kraft pulp mills, there has been little research done to determine the cause. This made it an interesting topic of study with the potential to help the industry understand and prevent the problem. This research complements previous research completed by our research group at the University of Toronto, particularly relating to ring formation and prevention. It differs in that it focuses on ball formation. No other research publication on this specific topic was found in our literature review.

The most difficult aspect of this research was attempting to replicate the conditions of ball formation in a lime kiln environment. We addressed this by constructing a laboratory-scale rotating drying apparatus that allowed wet mud to dry while in a rotating vessel.

As a graduate student with limited industry experience, this research provided Patrick Hinton-Barber with significant knowledge of lime kiln operation and the pulp and paper industry as a whole. The research allowed him to work with industry experts who provided him with great feedback and helped him find employment in the industry.

The most interesting/surprising aspect of our findings was to see the highly correlated linear trend between sodium content and lime mud strength. This data provided great validation of the theory that high sodium content increases the likelihood of mud ball formation.

Mills can use this information to prevent mud ball formation in lime kilns. This research provides a range of lime mud compositional parameters that mills can target during lime mud washing and drying to avoid the formation of mud balls. Possible next steps in this research would be to collect mill data to determine if the findings and recommendations of this paper are consistent and applicable to field operation.

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