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A COMPARISON OF LIQUID BINDERS FOR LIMESTONE PELLETIZING

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1. ABSTRACT

The Limestone pelletizing process is typically operated with a water/solids binder mix as the binding agent. The binding agent is required to bond the dust particles and allow handling of the pellets until they are applied to the soil without degradation or breakdown.

The purpose of this study is to give some direct comparisons of usage rates and physical properties for 11 binders used in a controlled test environment for 2 grades of limestone fines. Some of the common binders used in the production of limestone pellets are Lignosulfonates, Brewex, and Molasses. This study was performed using different types of these binders (plus blends which may be candidates for use). During the testing the binders were not identified by name or supplier and all results were tabulated before revealing the type and source of binder.

Results of this study can be used to compare binder properties for selection of a binder to meet requirements of individual limestone pelletizing operations. Results also include properties of the finished pellets with respect to tested binders for pelletizing, drying, sizing, abrasiveness, hardness, and strength.

2. BACKGROUND

The Limestone pelletizing process produces a dry chemical product available to the general public in granular form for application on soil. Limestone pellets are typically sold in 40# bags or in bulk to large users. Like any fertilizer product, limestone has the following properties:

- Non-hazardous (for environmental concerns)
- Chemical Reactivity with water (for breakdown into the soil)
- Soil additive (for pH control and improved plant growth)

For optimum utilization of the limestone into the soil, the particle sizing should be as small as possible. Fine particles, however, are difficult to handle and distribute and are not user friendly. While ground lime does have the above properties, a “dust-free” property is attractive to the end-user for spreading and handling reasons. Agglomeration of fine limestone particles enables the limestone to be applied in pellet form which will quickly breakdown for assimilation into the soil.

The mineral (rock) source and grinding specification are two important parameters in the pelletizing process and can certainly affect the final product. After grinding, the pelletizing process is further defined by 3 common equipment categories (in order of material flow):

Pelletizing (with binder application)
Drying (with heat)
Screening

The type of binder affects the operation of each of the above processes and associated equipment design as well as other process (handling) systems such as recycling and dust collection. Most pellet production plants, however, may not be familiar with binders until they begin operations. (Published data comparing binder properties that would allow the best selection for a particular plant or material is not readily accessible). Also, many binder suppliers may or may not have data comparisons for their binder in relation to both types of limestone. The processing facility or plant must consider all logistic parameters for binder usage (cost, handling, and supply reliability) as well as usage rate and physical properties of the binder (odor, corrosion, abrasion, and other binder properties). Cost, handling, and supply reliability are location dependent and must be reviewed and selected by the plant or processor; they are not addressed in this study.

To properly compare binders, a binder test should be run multiple times varying the binder dilution rate and application rate each time and testing pellets after the run to optimize pellet characteristics. Performing this test sequence would be cumbersome and time consuming, thus preventing data in this paper from being easily presented. <u>This study tested each binder at approximately the same dry solids percentage in the finished pellet to allow comparisons to other binders under the same conditions.</u>

3. DESCRIPTION OF BINDERS

Binders and their properties have been previously described in detail in various articles including previous Mars Mineral papers (see reference list). Below is a brief description of general binder types:

Lignosulfonate – A cellulose-based organic component of trees that comes as a by-product of the paper making industry. It is generated by a chemical pulping process and is a non-toxic fluid with levels of dissolved and/or suspended solids. Lignins from the sulfite pulping process are called Lignosulfonates and will dissolve in water. They are used for their binding, dispersing, and emulsifying properties. Since the source of lignin is trees, their physical properties will vary by the type of trees processed (i.e. hardwood, softwood, etc.).

Brewex – An organic modified starch brewery by-product containing glucose, maltose, and maltodextrin. It is an evaporative product derived from beer production residuals containing the above carbohydrates, protein, and water.

Molasses – An organic by-product of cane or beet sugar refining. It is a residual heavy syrup left after the crystallization process. Cane molasses is derived as a by-product from fermentation industries (which use cane molasses) or from the production of alcohol, yeast, citric acid or other fermentation products.

Blends - Blends of molasses, whey, and lignin are available and some have been included in these tests.

4. TEST SET-UP AND PROCEDURE

4.1 GENERAL

Test runs were conducted first with Dolomitic limestone using each of the 11 binders. Similar tests were then run with the Calcitic limestone dust using each of the 11 binders. The pelletizing tests were set up with the following process equipment in order of material flow (See flowsheet FIG. 1 at end of this section):

Bag dumping – 50# bags of pulverized Dolomitic and Calcitic limestone dust were hand dumped into a hopper above a screw feeder.

Feeding – Dumped material was processed through a volumetric screw feeder designed to accurately feed material to the Pin Mixer.

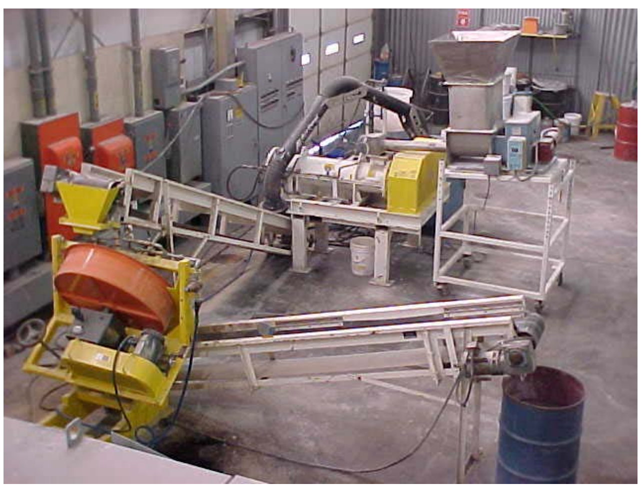

Photo 1 – System Set-up

Photo 2 – Feeding and Binder Tank

Pelletizing – Pelletizing was performed in 2 steps. The material is initially processed through a Mars Mineral Pin Mixer where the majority of the binder is applied. (The Pin Mixer sprays binder on the material, thoroughly wetting the particles, and partially agglomerates the material to prepare it for final pelletizing.) The conditioned material dropped onto a belt conveyor and transferred to a Mars Mineral Disc Pelletizer. (The Disc Pelletizer compacts the material through tumble growth agglomeration.) Finished pellets discharged onto a belt conveyor and into a storage drum. Wet pellets were screened during each test run to determine when sampling could be done. The acceptable size is considered to be passing through 4 mesh but retained on 20 mesh.

Pin Mixer - MM model 12D54L Pin Mixer	Disc Pelletizer - MM model P30 Disc Pelletizer
Pin size – 5/8" dia	Pan diameter – 3'
Pin clearance (off liner) – 3/16"	Pan depth – 8"
Motor – 40 HP	Motor – 1 HP
Rotor speed range – 560-1120 rpm	Pan speed range – 12.5-37 rpm
Liner – Natural rubber	Angle range (from horizontal) – 40-60 degrees

Binder application – Each binder tested was batch mixed with water to give a similar application rate in lbs. of solids applied per lb. of dry lime processed. (All tests were set up to add binder solids at 2% by wet pellet weight and assuming 8% moisture content in pellets. The binder spray was increased or decreased until proper size pellets were seen discharging from the Disc Pelletizer). The solution components were weighed to make a 10 gallon batch and dumped in a 30 gallon polyethylene tank. The solution was pumped through a centrifugal pump with a recirculation loop back into the tank (to ensure sufficient mixing and to provide sufficient pressure (40 psi) for the pelletizer sprays).

Samples from pelletizing (off the Disc Pelletizer discharge belt conveyor) were dried, screened, and tested below.

Photo 3 – Disc Pelletizer

Photo 4 – Pellet Discharge

Drying - Pellet samples were placed in a vibrating fluid bed with hot air blown through the bed of pellets to heat the product, evaporate the water, and set the binder. Partially dried samples were pulled from the pellet bed at 15, 30, 45, 60, and 75 seconds, and moisture content was measured to determine a drying curve for the product.

Dryer – Carrier Batch Vibrating Fluid Bed System set up with vertical stroke drive, 5 HP supply blower, 30 kw electric heater, and exhaust fan with cyclone. Bed depth set by sample size on a 1 sq. ft. deck with insertion thermocouples for air, product, and exhaust temperatures. Set-up parameters were for 25# (wet) batch, 300 cfm air flow, 3/16” stroke, and 520-540 deg.F drying air temperature.

Photo 5 - Batch Fluid Bed Dryer

Photo 6 – Dryer Samples

4.2 DEFINITIONS OF SAMPLE TESTS

Bulk Density – Weight of material per cubic foot volume. Measured with scale and graduated cylinder (1000 ml sample).

Drop Strength – 6 by 10 mesh pellet samples individually dropped from 18” height to determine average number of drops the pellets can withstand before breaking apart.

Compression Test - Individual 6 by 10 mesh pellets put in a 50 # crush tester to determine the average force in lbs. required to break pellet.

Attrition Test – Pellet sample screened to be 6 by 10 mesh then placed on a 20 mesh screen and agitated for 5 minutes. The fines that pass though the screen are weighed and the value recorded is the “loss” amount as a % of the starting sample weight.

Moisture Content – Wet pellet samples are put in a moisture balance which measures starting “wet” weight, evaporates off moisture, and measures finished "dry" weight during a recorded time period. The % moisture is a "wet" weight = wt. of water evaporated/wt. of wet product. (Moisture Balance – Mettler Instrument Corp., NJ model LP-16/PM480 delta range - 320 deg. F - 50 gram sample size).

Particle Size – Pellet samples passed through 4, 6, 16, 20, 30, and 40 mesh screen sizes in a mechanical shaker. Used US standard sieves on Ro-tap shaker (400 gram sample).

Abrasion Test – The purpose of this test was to obtain relative comparison of the pellet samples to determine abrasive differences caused by the binder. (Similar to ASTM Specification #G65 – Standard Test Method for Measuring Abrasion using the Dry Sand/Rubber Wheel test.) 10 # pellet samples were screened to –4 mesh and then passed between a rubber wheel and a metal specimen. The rubber wheel was rotated through a mechanical drive. The pellets were forced between the metal specimen and wheel with a counterweight. The metal specimen was weighed before and after the test run to determine mass loss from abrasion. For these tests, aluminum was used as the metal specimen material.

Solubility – A small sample of dry pellets put in a container with water to confirm their ability to break down and dissolve.

4.4 SET-UP PARAMETERS

4.4.1 Set-up Parameters for Binder Dilution

Binder # - Type	% Solids (assumed)	Density (#/gal) (assumed)	Dilution rate (%binder/ %water)	pH – raw binder (measured)	pH – diluted binder (measured)
1 – Lignin	52.0	10.5	38/62	2.0	2.2
2 – Lignin	57.4	10.9	35/65	3.7	4.2
3 – Lignin	34.8	9.8	42/58	9.5	9.5
4 – Lignin	53.4	10.6	38/62	2.9	3.1
5 – Lignin	50	9.9	40/60	6.3	6.3
6 – Lignin	54	10.4	37/63	3.1	3.6
7 – Brewex	50	10.0	40/60	4.8	5.0
8 – Molasses	60	10.5	33/67	9.5	8.7
9 – Molasses	73	11.7	27/73	5.6	5.7
10 – Mosasses/Whey	63	10.8	32/68	5.1	5.1
11 – Lignin blend	52	10.6	38/62	4.0	4.3

Note: % solids and density based upon binder vendor supplied data.

4.4.2 Set-up Parameters for Pelletizing

Target run time	30 minutes	(Adjusted as needed during test run)
Target moisture content	8%	(Adjusted as needed during test run)
Target binder application	2% solids	(Affected by % moisture applied)
Feed rate	725 lbs/hr	
Pin Mixer speed	850 rpm	
Disc angle	54 degrees	(Adjusted as needed during test run)
Disc speed	20 rpm	(Adjusted as needed during test run)

4.5 APPLICATION OF SAMPLE TESTS

Wet samples were tested for bulk density (lbs/cf), drop strength, compression strength, and attrition loss.
Wet samples were dried in a moisture balance to determine moisture content (% water of wet weight) and drying time (for comparison of drying rate).
Wet samples were dried in a fluid bed dryer to determine drying characteristics.
Dry samples were tested for bulk density (lbs/cf), drop strength, compression strength, attrition loss, sieve analysis, abrasion, and solubility.

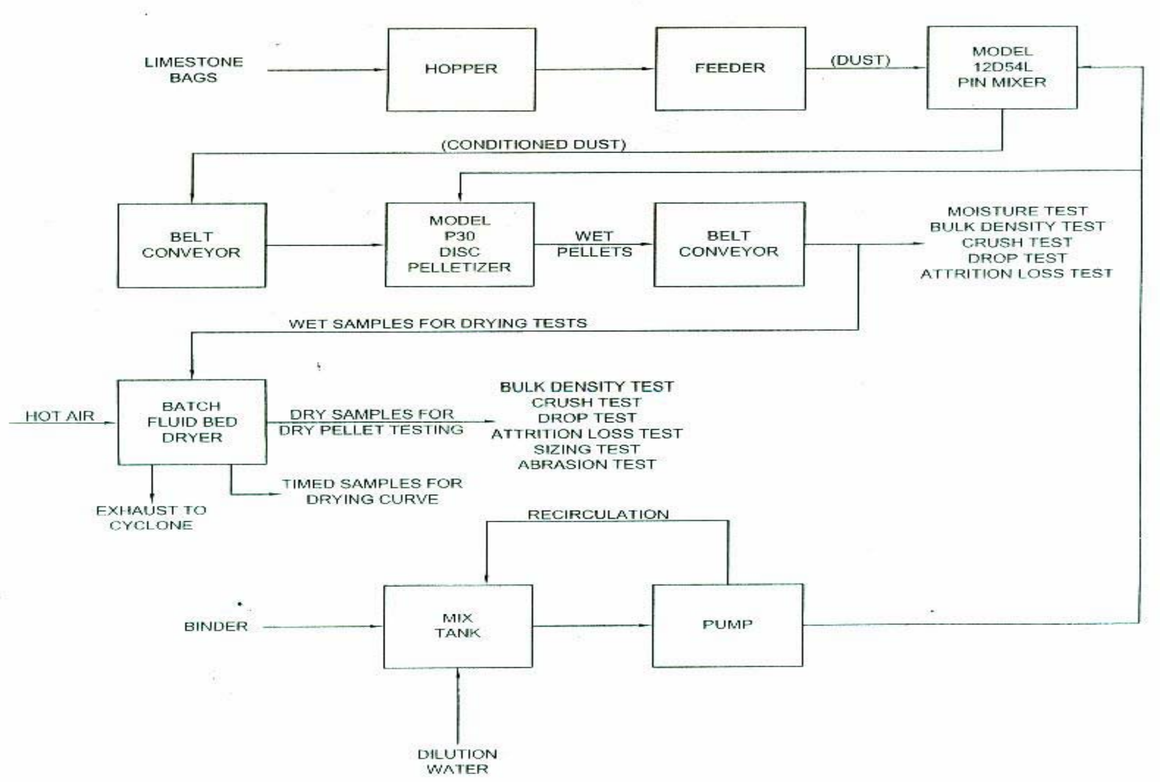

FIG. 1 LABORATORY TESTING MATERIAL FLOW SCHEMATIC

6. TEST SUMMARY

6.1. RESULTS BY TESTING PARAMETER

Listed below are conclusions as interpreted by the test run data previously shown. In general, all of these binders may be suitable for limestone pelletizing with adjustments to binder solids application rate by varying the concentration (dilution).

6.1.1. Pelletizing/Moisture/Sizing – Pelletizing was rated as either "good, fair, or poor" depending upon level of ease/difficulty and time to produce proper sized pellets.

- Using the time required to produce and maintain pellets in the required size range, the Dolomitic test runs were "easier" to pelletize.
- Calcium based Lignins produced stronger pellets for Dolomitic lime, and Sodium based Lignins produced stronger pellets for Calcitic lime.
- All Dolomitic test runs pelletized at a lower moisture content than the Calcitic test runs – a conclusion from this is that the binder dose may have to be higher for Dolomitic lime applications, in direct comparison to Calcitic lime applications, to maintain the same % solids applied to the pellets. However, satisfactory pellet strengths were achieved in most cases and the tests proved that a 2 % application rate is sufficient for some binders.
- Although the Calcitic limestone required more moisture to pelletize, and therefore more binder solids applied, it was evident that the binder applied (app. 2 %) was not sufficient for proper pellet bonding.

6.1.2. Drying – Binders were ranked for total change in moisture over the sampling times (which produced drying curves). Final moisture content is also important, but it depends upon the starting moisture which varied for each test. The pellet temperatures (when measured at the sample times) did vary for the different binders suggesting that the binder affects the specific heat of the material. The Dolomitic lime pellets seemed to have steeper drying curves than the same binders with the Calcitic lime pellets.

6.1.3. Drop Strengths - All dry samples averaged 50 + pellet drops. All green samples varied as shown on the Test Run Data. Drops were higher for most binders with the Dolomitic lime.

6.1.4. Crush Strength – Using an acceptable level of 4.0 # crush, some binders exceeded and some failed at 2 % concentration. Crush strengths were generally greater for most binders with Dolomitic lime than those of Calcitic lime.

6.1.5. Attrition Loss – All dry Dolomitic tests had attrition losses less than 0.6 %. All dry Calcitic tests had attrition losses less than 1.7 % with the exception of binder #8. All wet Dolomitic tests had attrition losses less than 1.4 %, while all wet Calcitic tests had attrition losses much higher (this is confirmed by the fact that more fines were captured in the dryer exhaust cyclone for the Calcitic tests).

6.1.6 Pellet sizing - As noted above, it was easier for the pellets to form in the required size range for all the binders tested with the Dolomitic lime.

6.1.7. Abrasiveness – All Dolomitic lime samples were tested as well as 3 calcitic lime samples (1 with Lignin binder, 1 with Molasses binder, and 1 with Brewex binder) for comparison. The Dolomitic samples had a much higher abrasion rate on the metal specimen. No other correlations comparing binders could be made.

6.1.8. Solubility – All samples were tested, and they dissolved in water.

6.2. Ranking of Binders

The 3 "best" binders are ranked below in relation to testing parameter. Due to the minute differences in some of the measured parameters and associated inaccuracies of measurements in the tests, we have taken only the top three from the test run data.

	Testing Parameter	Best 3 – Dolomitic	Best 3 - Calcitic
6.2.1	Ease of pelletizing	6,2,11	1,7,10
	LO moisture content	6,9,5	1,11,8
6.2.2	Drying (% moisture dried)	2,4,3	7,2,8
6.2.3	HI wet drop strength	5,4,7	1,3,7
6.2.4	HI dry crush strength	5,6,8	1,3,9
6.2.5	LO wet attrition loss	4,3,2	1,11,2
6.2.6	Sizing – % 4 by 20 mesh	2,6,7	7,1,2
6.2.7	Abrasiveness	4,8,5	---

From this table we suggest that binder #6 and #2 (both Calcium based Lignins) were the best overall for the Dolomitic Test Runs. Binder #1 and binder #7 were the best overall for the Calcitic Test Runs.

Note: While we did not measure for hygroscopic (absorption of moisture into the pellet) parameters, some pellet strengths did seem to weaken after exposure to air – binders 8,9, and 10 (which are all Molasses based) had much lower crush strengths when re-tested.

6.3. SYSTEM DESIGN AND BINDER SELECTION

The pelletizing process is an operator dependent process as reflected by the fact that pellets are determined "acceptable" when their size is in the desired range. Downstream sampling after drying will determine pellet characteristics and whether or not the pellet meets strength, size, and efficiency criteria. In full scale pelletizing systems, the only control data the operator has for monitoring the pellet size range (efficiency) is to monitor product weight after screening in comparison to feed rate to determine efficiency. Off-size material must be handled through a recycle material handling system or disposed. Strength can only be tested by manual sampling (although examination of the product as discharged into bags or out of storage bin will indicate product degradation from handling). In designing pelletizing equipment and systems, Mars Mineral recommends including automation of the equipment to allow the operator to make changes in the control set-up and to reduce the number of variables in the system operation including:

- Feedrate control
- Product weight measurement
- Binder dilution and spray flow control
- Drying temperature and air flow control

This paper is not designed to examine all binders used in the agglomeration process. Certainly other dry and wet binding agents are used for various materials throughout the industry, but the ones tested here seem to be most applicable to limestone pelletizing.

The binder selection relates to long term operating costs of a limestone pelletizing system. Capital costs for purchasing binders may be compared for a site specific plant, but costing data has not been included in this study because operating costs can offset capital costs.

The following considerations are location/operation dependent:

- Location of the plant in relation to the binder source location (which affects shipping costs)
- Consumption level (gal/day) or bulk usage costs
- Environmental controls (odor, spill clean-up, corrosiveness)

The following considerations are binder dependent:

- Application rate (% binder solids to # dry pellet)
- Drying characteristics (fuel costs)
- Abrasive wear to equipment (maintenance costs)
- Pellet properties – strength, sizing, etc.

Pelletizing System – Cost/Usage Calculation for Binder Application

Assume cost of binder @ $50/ton, density @ 10.0 #/gal, and 50 % solids in solution

($ 50/ton) x (1 ton/2000#) / (10 #/gal) = $ 0.25 /gal

Assume binder application rate @ 2 % solids/ton moisture in pellets @ 8 %

(0.02) x (2000#/ton) = 40 # dry binder solids/ton pellets
(40#/ton) / (0.50) % solids = 80 # liquid binder/ton pellets
(80#/ton) / (10.0#/gal) = 8 gal liquid binder /ton pellets

(8 gal liquid binder/ton) x ($0.25/gal) = **$2.00/ton of dry lime (binder cost)**
Dilution rate required for above = 37% binder to 63 % water

7. MATERIAL DATA

7.1 BINDER IDENTIFICATION

Binder #	Name	Description	Source
1	Norlig 12	Sodium Lignosulfonate (Hardwood)	Lignotech USA, Inc. 100 Grand Ave. Rothschild, WI 54474 715-355-3628
2	Norlig A	Calcium Lignosulfonate (Hardwood)	Lignotech USA, Inc.
3	D-1262	Developmental Sodium Lignin (Softwood)	Lignotech USA, Inc.
4	D-1736	Desugared Calcium Lignosulfonate (Hardwood)	Lignotech USA, Inc.
5	Lignin	Ammonium Lignon Sulfonate	
6	Lignin	Calcium Lignin	Westway Trading Corporation 6816 West 156th St. Oak Forest, IL 60452 708-802-8944
7	Brewex	Brewers Condensed Solubles	Developing Environmental Resources P.O. Box 194 Elkhorn, WI 53121 414-249-1750
8	Big Chief	De-Sugarized Beet Molasses	Westway Trading Corporation
9	Wes Las 79.5	79.5 Brix Cane Molasses*	Westway Trading Corporation
10	Mol-Whey 63	Cane Molasses/Condensed Whey Mix*	Westway Trading Corporation
11	Cane-Lignin Water Blend		Westway Trading Corporation

* with 1/2% sulfuric acid as preservative

7.2 BINDER PHYSICAL DATA (from vendor supplied information)

	Binder name	PH	% solids	Density (lbs/gal)	Viscosity (cps)
1	Norlig 12	2.0	52.0	10.48	75 @ 77 deg F
2	Norlig A	3.6	57.4	10.87	350 @ 77 deg. F
3	D-1262	9.2	34.8	9.81	170 @ 77 deg. F
4	D-1736	2.6	53.4	10.58	150 @ 77 deg. F
5	Lignin	5.2-6.5	50 (varies)	9.9	1500 @ 80 deg. F
6	Lignin	3-4	54	10.4	150 @ 70 deg. F
7	Brewex	3.5	50	10.0	250 @ 80 deg F
8	Big Chief		60 min	10.5	150 @ 70 deg. F
9	Wes Las 79.5	5.7	73	11.7	Up to 3500 cps
10	Mol-Whey 63		63	10.8	200 @ 70 deg. F
11	Cane Lignin Water Blend		52	10.6	300 @ 70 deg. F

7.3 DOLOMITIC LIMESTONE - Cemex (Southdown) Yardright Dolomitic pulverized limestone

	<u>Sieve Analysis</u>
Chemical – $CaCO_3$ and $MgCO_3$	1.9 % retained on 45 mesh screen
Material source – Raymond mill	7.1 % retained on 80 mesh screen
Calcium Carbonate equivalent (CCE) = 93 %	14.1 % retained on 120 mesh screen
Effective Neutralizing value (ENV) = 84 %	49.9 % retained on 200 mesh screen
Moisture content – 0.1 %	21.2 % retained on 325 mesh screen
Bulk density – 83-110 #/cf	5.8 % retained in pan

7.4 CALCITIC LIMESTONE - Cemex (Southdown) Thomasville, PA #3.5 HI-Calcitic pulverized limestone

	<u>Sieve Analysis</u>
Chemical – $CaCO_3$	1.0 % retained on 45 mesh screen
Material source – Hammermill	13.2 % retained on 80 mesh screen
Calcium Carbonate equivalent (CCE) = 98.9%	11.1 % retained on 120 mesh screen
Effective Neutralizing value (ENV) = 93.0 %	37.6 % retained on 200 mesh screen
Moisture content – 0.01 %	26.5 % retained on 325 mesh screen
Bulk density – 91-112 #/cf	10.6 % retained in pan

REFERENCES

IBA 1993 Pelletizing Limestone Fines - A Study of the Benefits of Pelletized Limestone Fines in the Commercial and Agricultural Market

IBA 1991 Of Beer, Leather, and Beets – A Study of Alternative Binders in Agitation Pelletizing

CONTRIBUTORS

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Cemex (Southdown)	For supply of Lime material
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