CARBON DIOXIDE CAPTURE FROM FLUE GAS USING DRY REGENERABLE SORBENTS

QUARTERLY TECHNICAL PROGRESS REPORT

Reporting Period: July 1, 2002 to September 30, 2002

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1.0 EXECUTIVE SUMMARY

The objective of this project is to develop a simple and inexpensive process to separate CO_2 as an essentially pure stream from a fossil fuel combustion system using a regenerable sorbent. The sorbents being investigated in this project are primarily alkali carbonates, and particularly sodium carbonate and potassium carbonate, which are converted to bicarbonates through reaction with carbon dioxide and water vapor. Bicarbonates are regenerated to carbonates when heated, producing a nearly pure CO_2 stream after condensation of water vapor.

This quarter, electrobalance tests suggested that higher temperature calcination of trona leds to reduced carbonation activity in subsequent cycles, but that calcination in dry carbon dioxide did not result in decreased activity relative to calcination in helium. Following higher temperature calcination, sodium bicarbonate (SBC) #3 has greater activity than either coarse or fine grades of trona.

Fixed bed testing of calcined SBC #3 at 70°C confirmed that high rates of carbon dioxide absorption are possible and that the resulting product is a mixture of Wegscheider's salt and sodium carbonate. In fluidized bed testing of supported potassium carbonate, very rapid carbonation rates were observed. Activity of the support material complicated the data analysis.

A milled, spherical grade of SBC appeared to be similar in attrition and abrasion characteristics to an unmilled, less regularly shaped SBC. The calcination behavior, at 107°C, for the milled and unmilled materials was also similar.

2.0 INTRODUCTION

Fossil fuels used for power generation, transportation, and by industry are the primary source of anthropogenic CO_2 emissions to the atmosphere. Much of the CO_2 emission reduction effort will focus on large point sources, with fossil fuel fired power plants being a prime target. The CO_2 content of power plant flue gas varies from 4% to 9% (vol), depending on the type of fossil fuel used and on operating conditions. Although new power generation concepts that may result in CO_2 control with minimal economic penalty are under development, these concepts are not generally applicable to the large number of existing power plants.

This study is based on the use of a dry, regenerable sorbent to remove CO_2 from flue gases. Sorbent regeneration produces a gas stream containing only CO_2 and H_2O. The H_2O may be separated by condensation to produce a pure CO_2 stream for subsequent use or sequestration. The primary reactions, based upon the use of sodium bicarbonate (SBC) as the sorbent precursor and sodium carbonate as the reaction product are:

$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g) \qquad (1)$$

and

$$Na_2CO_3(s) + CO_2(g) + H_2O(g) \rightarrow 2NaHCO_3(s) \qquad (2)$$

Reaction (1) releases CO_2 and regenerates the sorbent, while Reaction (2) is used to capture CO_2. Several other solid products, intermediate between sodium carbonate and sodium bicarbonate, may also be produced under the anticipated reaction conditions. An intermediate compound, $Na_2CO_3 \bullet 3NaHCO_3$, known as Wegscheider's salt, forms at the reaction conditions of interest.

Analogous reactions (Reactions 3 and 4) take place within the potassium carbonate system:

$$2KHCO_3(s) \rightarrow K_2CO_3(s) + CO_2(g) + H_2O(g) \tag{3}$$

and

$$K_2CO_3(s) + CO_2(g) + H_2O(g) \rightarrow 2KHCO_3(s). \tag{4}$$

A compound salt of potassium carbonate and potassium bicarbonate is also thought to be of importance at the conditions of interest.

Trona (sodium sesquicarbonate) can also be used as a sorbent precursor. The following reactions of trona are slightly different from the direct reversible reaction of $NaHCO_3$ (reaction 1). Trona is initially calcined according to:

$$2[Na_2CO_3 \bullet NaHCO_3 \bullet 2H_2O(s)] \rightarrow 3Na_2CO_3(s) + CO_2(g) + 5H_2O(g) \tag{5}$$

Subsequent carbonation and calcination reactions proceed according to:

$$Na_2CO_3(s) + CO_2(g) + H_2O(g) \leftrightarrow 2NaHCO_3(s) \tag{6}$$

This report describes activities conducted between July 1, 2002 and September 30, 2002 by RTI and its subcontractors Louisiana State University (LSU) and Church and Dwight (C&D). Activities conducted this quarter include electrobalance (thermogravimetric analysis [TGA]) and fixed bed reactor studies at LSU and fluidized-bed reactor testing and mathematical model development at RTI. Church and Dwight prepared a jet-milled potassium carbonate sorbent and characterized a spherical Grade 4 sodium bicarbonate for reactivity and attrition resistance.

3.0 EXPERIMENTAL

3.1 Electrobalance Testing at LSU

3.1.1 Sorbents Used

Thermogravimetric analysis (TGA) testing was conducted at LSU with trona Grade T-50, trona Grade T-200, and SBC #3. Selected properties of these materials, and other sorbents used (both as-received and following calcination), were reported in previous quarterly reports (Green et al., 2001a; b).

3.1.2 Previous Experimental Results

A summary of experimental results reported in the previous quarterly reports is presented below to provide background for the new results reported in this report. Although all samples were screened initially for reactivity, most of the early detailed testing used SBC #3. More recently the study has been expanded to include Trona T-50 and Trona T-200. Because of somewhat different results, separate summaries are presented for SBC #3 and the trona samples.

3.1.2.1 SBC #3

1. Both the initial reaction rate and achievable CO_2 capacity decrease with increasing carbonation temperature.

2. The possible formation of by-products including $Na_2CO_3{\bullet}H_2O$, $Na_2CO_3{\bullet}NaHCO_3{\bullet}2H_2O$, and $Na_2CO_3{\bullet}3NaHCO_3$ (Wegscheider's salt) at carbonation conditions of potential interest was proven by thermodynamic analysis.

3. At constant temperature, the global reaction rate increases with an increase in both CO_2 and H_2O concentrations.

4. Calcination in 100% CO_2 and 80% CO_2/20% H_2O at temperatures as high as 200^{o}C did not cause a significant reduction in the sorbent activity in the subsequent carbonation cycle.

5. Five-cycle tests using SBC Grade #3 at standard carbonation and calcination conditions show a gradual loss in both reaction rate and final fractional carbonation with increasing cycle number.

6. Five-cycle test results using SBC Grade #3 at more severe calcination conditions of 200^{o}C in atmospheres of pure CO_2 and 80%CO_2/20% H_2O were not significantly different than results at less severe standard calcination conditions.

3.1.2.2 Trona T-50 and T-200

1. All trona tests that examined the effect of reaction parameters using different samples for each run have been plagued with lack of reproducibility. Multicycle tests using the same trona sample showed improved reproducibility.

2. A five-cycle test using trona T-200 at standard calcination and carbonation conditions showed no loss of either reactivity or capacity over five cycles.

3. More severe calcination conditions (higher temperature and CO_2 atmosphere) caused greater losses in reactivity and capacity for both T-50 and T-200 than for SBC #3.

3.1.3 Experimental Procedure

3.1.3.1 Base Case Reaction Conditions

Base case reaction conditions are shown in Table 1. Results from experimental tests to examine the effect of carbonation and calcination temperature and gas composition are compared to results from these base case conditions. Base case carbonation gas composition approximates the flue gas composition resulting from the combustion of natural gas using 10% excess air. Base case calcination conditions, while not practical in commercial operation, were chosen to provide minimum severity of sorbent exposure during regeneration.

Table 1. Base Case Reaction Conditions For LSU TG Experiments.

Calcination	Temperature	120°C
	Pressure	1 atm
	Gas Composition	100% He
Carbonation	Temperature	70°C
	Pressure	1 atm
	Gas Composition	8 mol% CO_2
		16 mol% H_2O
		76 mol% He
	Gas Flow Rate	600 scc/min

The following experimental procedure is used in base case tests. An initial charge of approximately 70 mg of sorbent precursor is heated from room temperature to 100°C at a rate of 5°C/min and from 100°C to the final calcination temperature of 120°C at a rate of 1°C/min under flowing He. After calcination is complete (as indicated by constant weight), the temperature is decreased at a rate of 2°C/min still under He to the 70°C carbonation temperature. The gas composition is then changed to 8 mol% CO_2, 16 mol% H_2O, balance He flowing at 600 scc/min and carbonation is continued until the reaction rate approaches zero. Appropriate changes in procedure are made when carbonation and calcination temperatures and gas compositions are altered from the base case.

3.1.3.2. Testing Conducted During This Quarter

Five new multicycle electrobalance tests, four five-cycle and one three-cycle, were completed during the quarter. These tests were designed to complete gaps in the data obtained in previous runs. Standard carbonation conditions were used in each test, while calcination temperature and/or atmosphere were varied. Calcination conditions used in the tests are summarized in Table 2.

Table 2. Conditions for Electrobalance Tests Conducted This Quarter.

Sorbent Precursor	Calcination Conditions		Number of Cycles
	Temperature, °C	Atmosphere	
T-200	120	He	5
T-200	120	CO_2	3
T-200	100	He	5
SBC #3	160	He	5
T-50	160	He	5

The first run listed in the table used standard calcination conditions and duplicated a previous run. The second run used standard calcination temperature and substituted CO_2 for He in the calcination atmosphere. Calcination in CO_2 at this temperature was extremely slow and the test was terminated after three cycles. Since previous results showed that the rate of T-200 sorbent deterioration increased with increasing calcination temperature, the 100°C calcination temperature was used in the third test to determine if improved results could be obtained at still lower temperature. The SBC #3 test and the T-50 test were designed to complete gaps in the existing database for the effect of calcination temperature on these sorbents.

3.2. Fixed Bed Testing at LSU

In previous fixed-bed tests a syringe pump was used to feed liquid water. Feed lines were heat traced to produce steam, but the low carbonation temperature made it difficult to vaporize the water and provide just the right amount of preheat energy. With too much preheat energy, the combined gas temperature exceeded the desired carbonation temperature; with too little preheat energy, vaporization was extremely slow and sometimes incomplete.

In fixed-bed tests conducted this quarter, the syringe pump was replaced by a wash bottle. N_2 and CO_2 at the desired flow rates were bubbled through the wash bottle whose temperature was controlled to 56°C so that the exit gases would contain the desired steam content (assuming equilibrium was achieved). Early tests using this feed system were plagued by leaks and produced no useful data. The pressure drop associated with flow through the packed bed and the need to maintain the temperature of the exit gases from the reactor complicates the sending of the reactor. After the leaks were eliminated, one good run was completed with SBC #3 as the sorbent precursor.

3.3 Sorbent Preparation at RTI

A sorbent material was prepared composed of 20% sodium bicarbonate on a matrix similar to that used in commercial fluidized bed catalytic cracking catalysts. A 1 kg batch of this material was prepared by spray drying a slurry of sodium carbonate and proprietary support materials. The spray dried product was then calcined in a laboratory furnace. Attrition testing by ASTM Method D5757-95 indicated that this material was extremely susceptible to attrition and the material was deemed unsuitable for carbonation testing. Preparations were made to produce another, more attrition resistant material.

3.4 Fluidized Bed Reactor Testing at RTI

One 5-cycle fluidized bed reactor test was conducted this quarter, using the supported 10% potassium carbonate sorbent produced in the previous quarter. Carbonation took place in a simulated flue gas stream of 6.8% carbon dioxide, 6.3% H_2O at initial bed temperatures of approximately 67°C. Calcination was conducted in dry nitrogen at 150°C.

3.5 Sorbent Material Development and Material Characterization Studies at Church and Dwight (C & D)

Church and Dwight prepared a jet milled potassium carbonate sorbent for testing in the coming quarter. The material as supplied has a tendency to agglomerate; however a similar material could be produced with an additional flow aid, if tests indicate that it is a promising sorbent. Attrition testing of this material at RTI, by ASTM D5757-95 was inconclusive because of the caking of the material in the attrition tester.

Church and Dwight conducted comparison testing of spherical Grade 4 sodium bicarbonate vs. a control grade 4 material. Attrition and abrasion tendency were tested using a Lab-Line Hi-Speed Fluid Bed Dryer (Model 23852), for 6 hours. Church and Dwight also conducted comparison decomposition rate testing using a DuPont Thermogravimetric Analyzer (Model 2950).

4.0 RESULTS AND DISCUSSION

4.1 Electrobalance Testing at LSU

4.1.1 Sodium Carbonate Conversion based on Wegscheider's Salt as Carbonation Product

As reported in the previous quarterly report (Green, et al., 2002b), Wegscheider's salt ($Na_2CO_3 \cdot {}_3NaHCO_3$) was identified as the primary carbonation product from a fixed-bed reactor test at LSU. Until that time, all fractional carbonation results, f(t), had been reported on the basis of $NaHCO_3$ being the primary product. The values of f(t) in this report are changed to reflect the Wegscheider's salt product. The conversion is straightforward based on the molecular weights and compositions of the sorbent precursor (sodium bicarbonate or trona), of the calcination product (sodium carbonate), and carbonation product (Wegscheider's salt). When pure sodium bicarbonate is calcined to sodium carbonate and then carbonated back to sodium bicarbonate the relationship between dimensionless weight and fractional carbonation is:

$$f(t)_{sbc} = \frac{w - 0.631}{0.369} \qquad (7)$$

When the process is the same except that Wegscheider's salt is the final product, the equation is:

$$f(t)_{ws} = \frac{w - 0.631}{0.221} \qquad (8)$$

Equation (9) is obtained by ratio of equations (7) and (8):

$$f(t)_{ws} = 1.67\, f(t)_{sbc} \qquad (9)$$

In these equations, w is the dimensionless weight, while $f(t)_{sbc}$ and $f(t)_{ws}$ are the fractional carbonations based on sodium bicarbonate and Wegscheider's salt products, respectively. While the equations relating dimensionless weight and $f(t)_{sbc}$ and $f(t)_{ws}$ for T-200 and T-50 are somewhat different, the ratio is the same. That is, Eq. (9) can be used for T-200 and T-50 as well as SBC. Results from all tests completed during this quarter and results from earlier tests that are used in this report are now based on Wegscheider's salt as the carbonation product. Thus a typical value of f(150) = 0.55 reported previously becomes f(150) = 1.67(0.55) = 0.92. As a result, most of the electrobalance runs now approach complete carbonation.

4.1.2 Electrobalance Test Results

Figures 1 and 2 present f(25) and f(150) results of three tests using T-200 sorbent, all at a calcination temperature of 120°C. Two of the tests are duplicates in that He was the calcination atmosphere while CO_2 was used in the third test. While the excessive scatter that has plagued all trona tests is again evident in the two tests using He as the calcination atmosphere, there is no apparent difference in carbonation performance following He and CO_2 calcination.

The 100°C calcination temperature used in the third test, represented the lowest calcination temperature tested to date. Results of the five carbonation cycles are shown in Figure 3 as dimensionless sorbent weight as a function of time. The early reactivity was clearly highest in Cycle 01, but there was little difference in the early response in Cycles 02 and 05 and in any of the cycles after approximately 75 minutes.

Figures 4 and 5 compare f(25) and f(150) as a function of cycle number at three calcination temperatures of 100°C, 120°C, and 160°C for trona T-200. Helium was the calcination atmosphere in all three tests. From both figures, we see a clear reduction in activity following calcination at 160°C compared to 120°C. While there appears to be a slight improvement in performance following 100°C calcination, the data must be treated with caution given the general difficulty in obtaining reproducible results with different trona samples. However, these figures do confirm that the f(25) results in Cycles 02 through 05 and the f(150) results in all cycles are quite consistent following 100°C calcination.

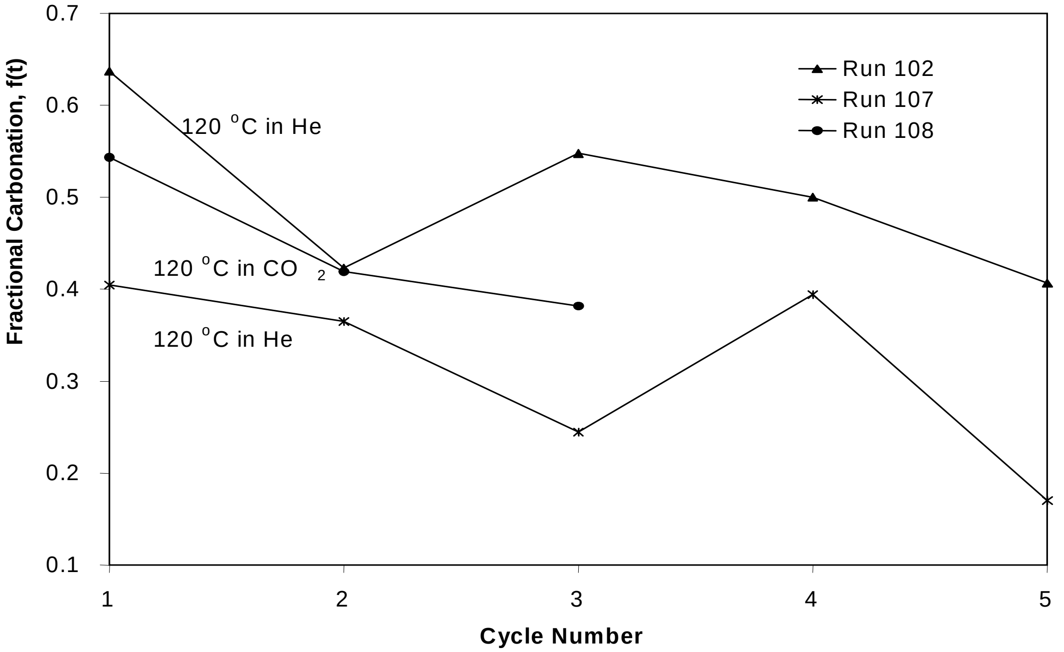


Figure 1. ***f(25)*****versus cycle number for three tests using trona T-200.**

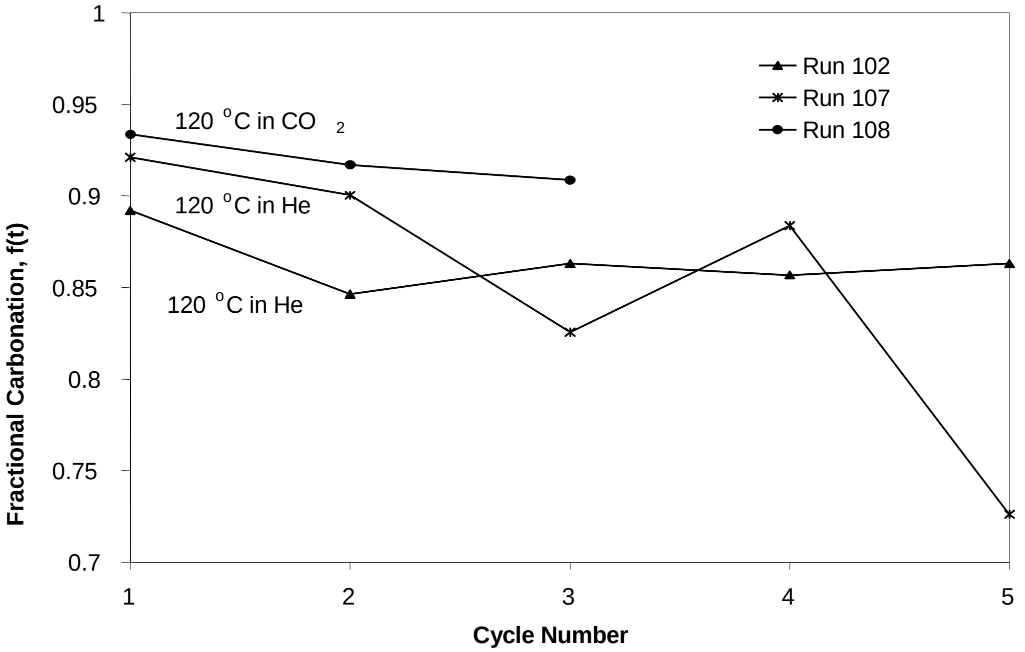


Figure 2. ***f(150)*****versus cycle number for three tests using trona T-200.**

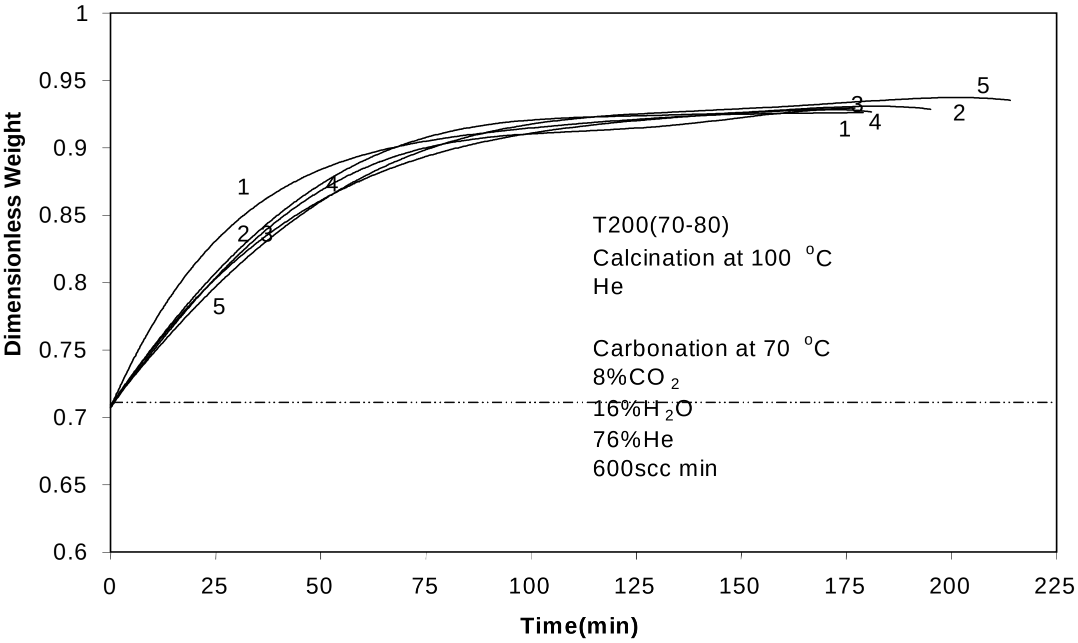


Figure 3. Dimensionless weight versus time results for five cycles using T-200 and calcination at 100°C in He.

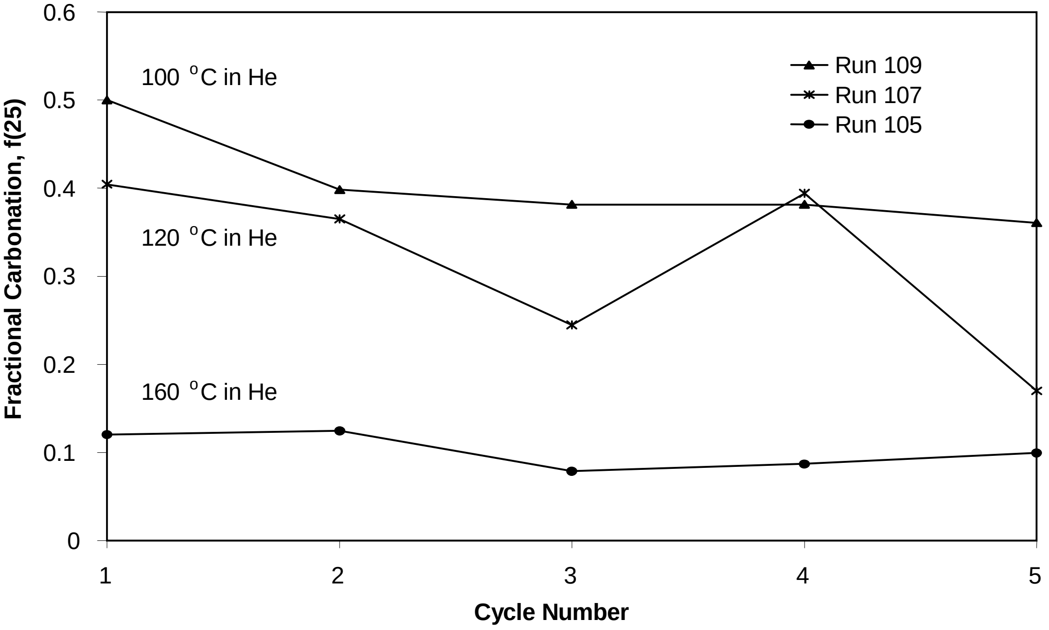


Figure 4. Trona T-200: *f(25)* versus cycle number following three calcination temperatures.

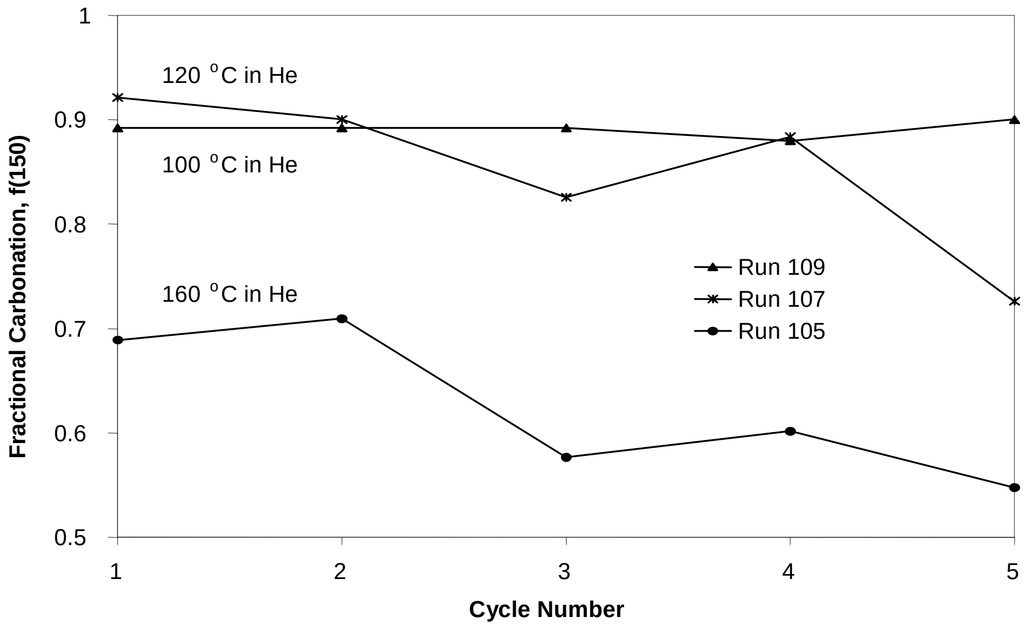


Figure 5. Trona T-200: *f(150)* versus cycle number following three calcination temperatures.

The performance of three sorbents, SBC #3, T-50, and T-200, is compared in Figures 6 and 7. Standard carbonation conditions were used in each test and calcination was carried out in He at 160°C. The performance of SBC #3 is superior to either of the trona samples, particularly in terms of f(150). Not only are the values of f(25) and f(150) generally larger for SBC #3, with the exception of the rapid decrease in f(25) for SBC #3 between Cycles 01 and 02, the slopes of the SBC #3 curves are smaller, indicating better durability. This confirms earlier results comparing these sorbents using other calcination temperatures.

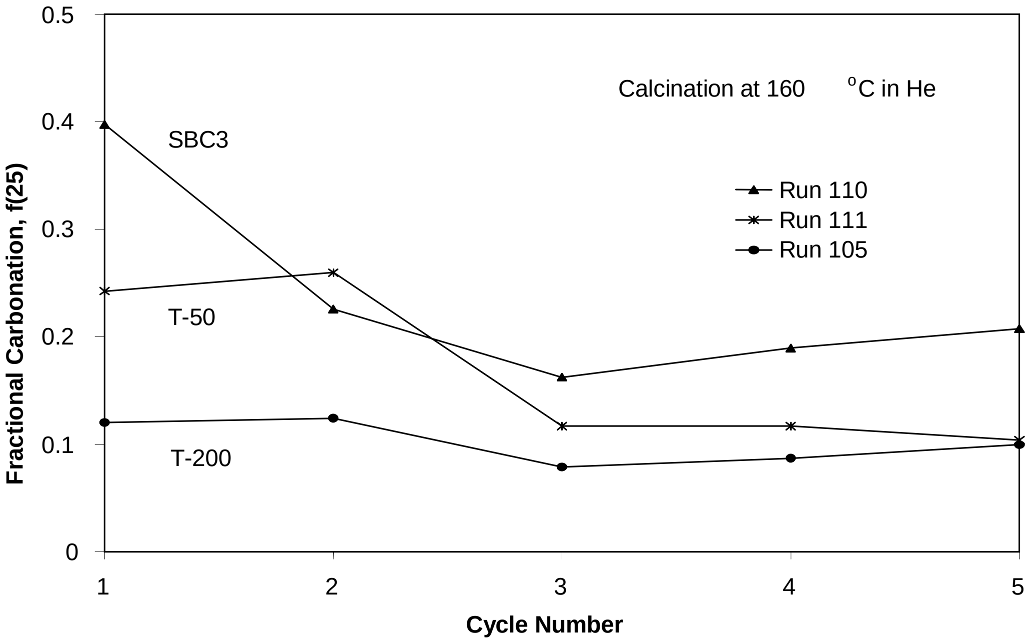


Figure 6. **Comparison of the performance of SBC #3, T-200, and T-50: *f(25)* versus cycle number following 160°C calcination in He.**

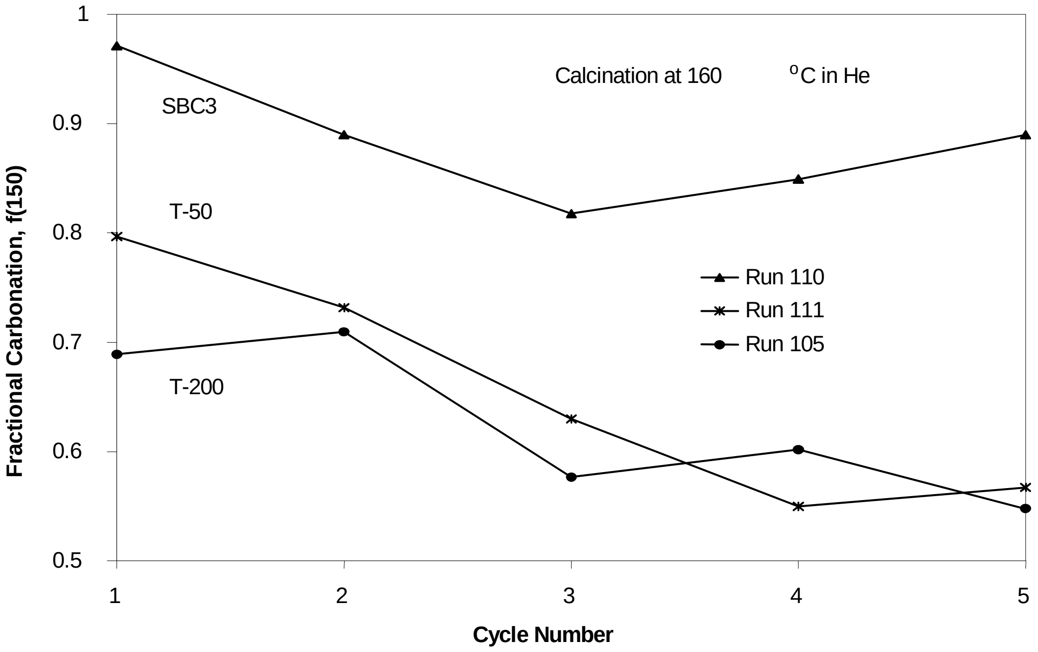


Figure 7. **Comparison of the performance of SBC #3, T-200, and T-50: *f(150)* versus cycle number following 160°C calcination in He.**

4.2 Fixed Bed Reactor Testing at LSU

Valid data were obtained from one test with SBC #3 as the sorbent precursor, this quarter. CO_2 concentration in the product gas as a function of time in both the calcination and carbonation cycles is shown in Figure 8. While standard carbonation conditions were intended, the carbonation results described below suggest that the CO_2 content of the feed gas was actually about 9.5% instead of the intended 8.0% (both wet basis).

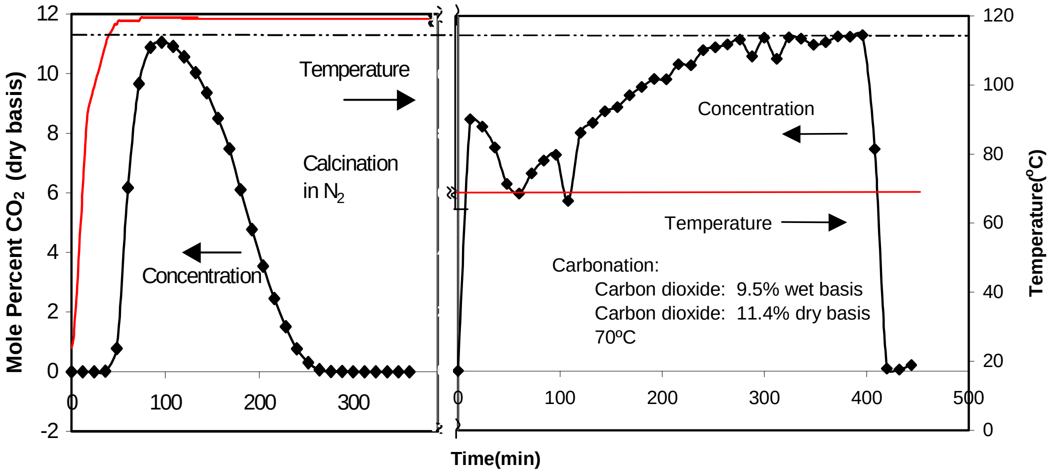


Figure 8. Fixed-bed reactor test: CO_2 concentration as a function of time during calcination and carbonation (SBC #3).

Good material balance closure was obtained during the calcination cycle. The quantity of SBC #3 used was sufficient to produce 0.152 mols of CO_2 during calcination and the area under the calcination curve corresponds to 0.154 mols of CO_2.

CO_2 concentration during the carbonation cycle was somewhat more scattered, but, after an initial maximum, remained in the range of 6% to 7.5% for just over one hour. Thereafter the CO_2 content increased steadily to about 11.4% (dry basis). The 11.4% (dry basis) in the final product corresponds to a feed composition of about 9.5% (wet basis). Product gas containing 6% CO_2 corresponds to 47% CO_2 removal while 7.5% CO_2 corresponds to 34% removal. The total area above the breakthrough curve corresponds to 0.099 mols of CO_2 removed. This suggests that the final product may be a mixture of Wegscheider's salt ($Na_2CO_3{\cdot}3NaHCO_3$) and sodium bicarbonate ($NaHCO_3$). The CO_2 capacity corresponding to complete conversion of Na_2CO_3 to $Na_2CO_3{\cdot}3NaHCO_3$ is only 0.091 mols compared to 0.152 mols for complete conversion to $NaHCO_3$. Thus the total CO_2 removal of 0.099 mols represents about 110% of theoretical based on Wegscheider's salt and about 65% of theoretical based on sodium bicarbonate product.

Two previous fixed-bed tests using the syringe pump for water feed (Green, et al., 2002a) gave percentage CO_2 removals during the early stages of carbonation of just over 50% and just under 50%, both slightly higher than achieved in this test. All three tests used approximately the same amount of SBC #3 sorbent precursor and the amount of CO_2 removed during carbonation in the previous tests was 0.094 mols and 0.103 mols, both quite near the 0.099 mols removed in the current test.

4.3 Fluidized Bed Testing at RTI

One 5-cycle fluidized bed reactor test was conducted this quarter. The sorbent tested was a 10% potassium carbonate material. Properties of this material were reported in the previous quarterly report (Green, et al. July, 2002). The reactor was loaded with 190 g of sorbent material, which contained 19 g of potassium carbonate and 171 g of support material. The carbon dioxide capacity of the sorbent, assuming complete conversion of potassium carbonate to potassium bicarbonate (and no activity due to the support material) was 6.0 g. Integration of the carbon dioxide removal data indicated that greater than 100% of the stoichiometric capacity of the potassium carbonate was used, suggesting that the support was reversibly adsorbing carbon dioxide. Carbonation cycles were extended for 3 hours, as in past tests. Useful data were obtained from three carbonation cycles; experimental problems occurred in the first and third cycles. The carbon dioxide concentration at the reactor exit, as well as the sorbent bed temperature rise suggested that the reaction was essentially complete within the first few minutes of each carbonation cycle. Data for the second, fourth and fifth cycles are shown in Figures 9 through 11.

The data suggest a rapid reaction rate. While the reactivity of the support, which makes up 90% of the sorbent material, complicates data analysis making it impossible to derive a quantitative reaction rate, the temperature rise in the sorbent bed confirms the a rapid exothermic reaction is taking place. A sorbent of this type, or one with a greater proportion of potassium bicarbonate such as the one tested in the previous quarter, may have the high reactivity and attrition resistance necessary for successful use in a transport reactor.

4.4 Preparation and Testing of Additional Sorbent Materials

Church and Dwight produced a "Spherical Grade 4 SBC" material to investigate the effect of production method on the properties of the sorbent precursor. The spherical material, with similar particle size distribution to the granular SBC #2, was prepared by milling to produce a more rounded, more free flowing particle. The extent and rate of calcination at of spherical material and the control material were tested by TGA at 107°C, and found to be very similar. These data are included as Appendix A to this report.

The spherical material and the control were tested for attrition and abrasion using a Lab-Line Hi-Speed Fluid Bed Dryer. Neither material exhibited any signs of attrition as determined by this test. These data and the experimental procedure are included as Appendix B to this report.

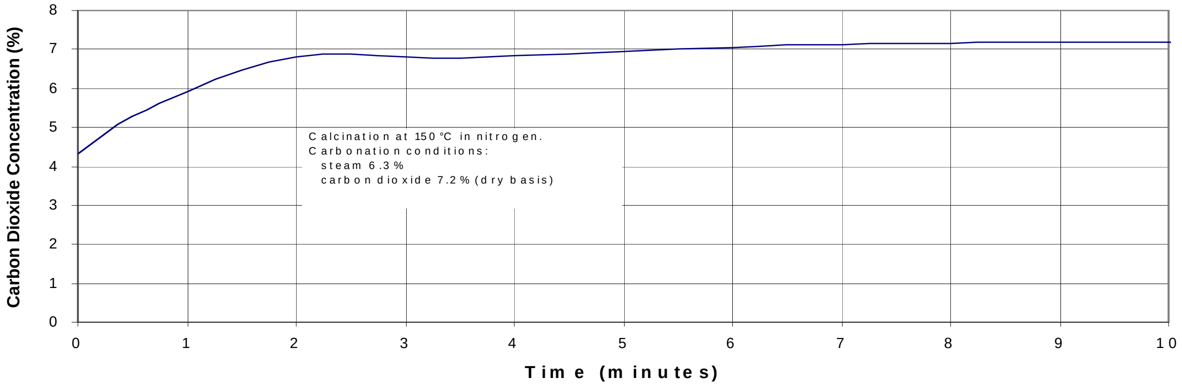


Figure 9a. Test data from carbonation cycle 2 with 10% supported potassium carbonate sorbent - CO_2 concentration in reactor exit gas.

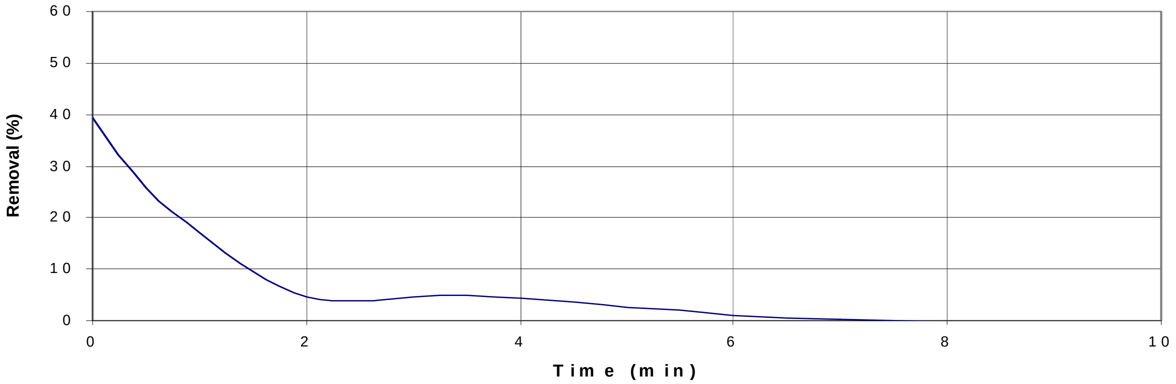


Figure 9b. Test data from carbonation cycle 2 with 10% supported potassium carbonate sorbent - CO_2 removal.

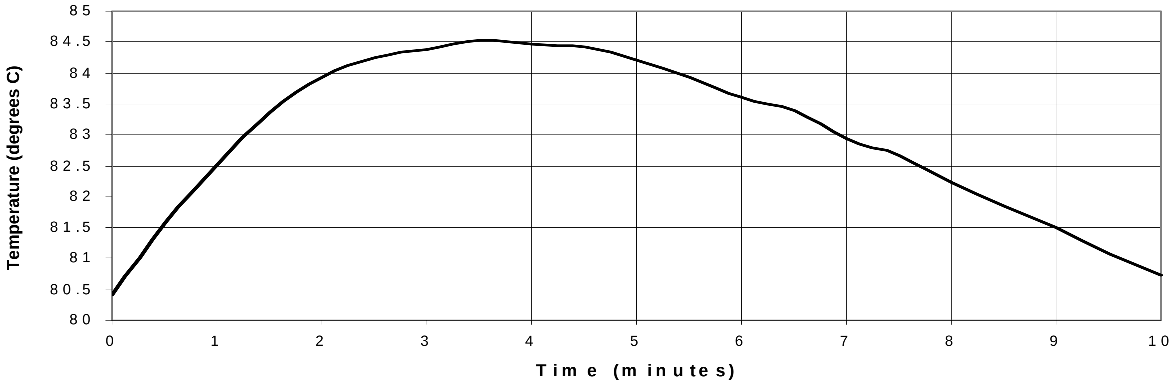


Figure 9c. Test data from carbonation cycle 2 with 10% supported potassium carbonate sorbent - average bed temperature.

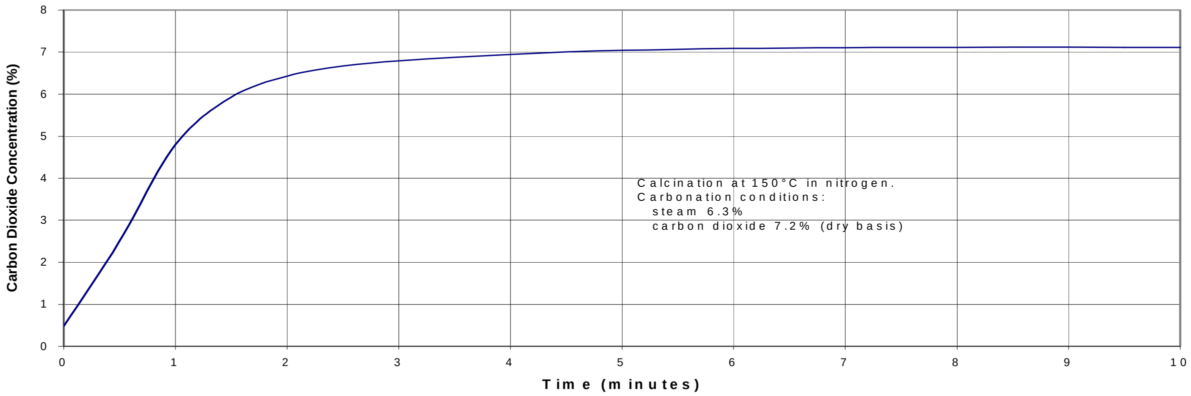


Figure 10a. Test data from carbonation cycle 4 with 10% supported potassium carbonate sorbent - CO_2 concentration in reactor exit gas.

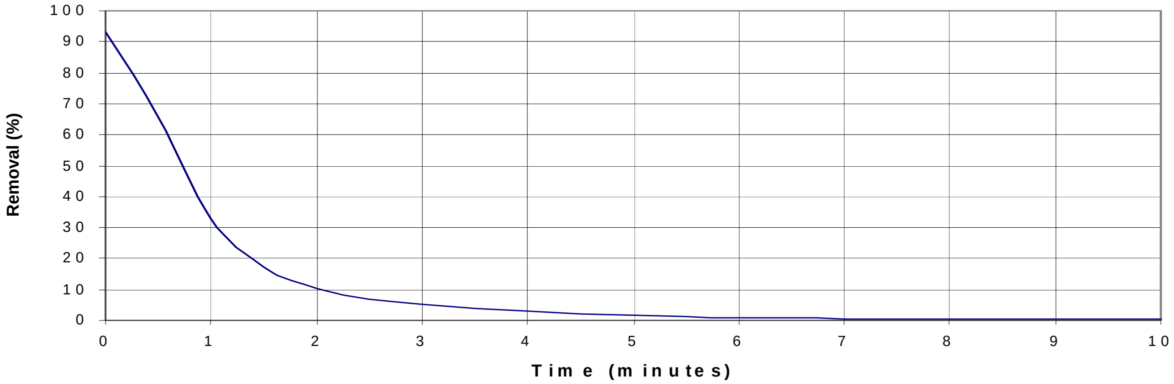


Figure 10b. Test data from carbonation cycle 4 with 10% supported potassium carbonate sorbent - CO_2 removal.

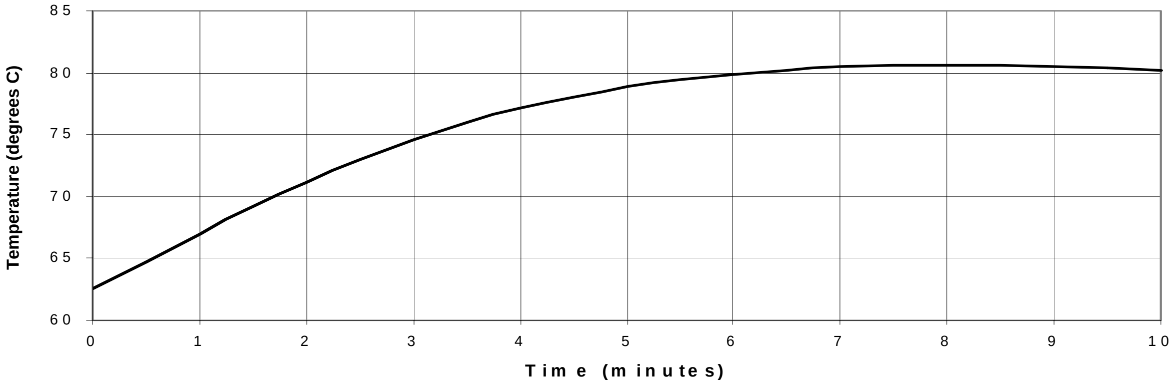


Figure 10c. Test data from carbonation cycle 4 with 10% supported potassium carbonate sorbent - average bed temperature.

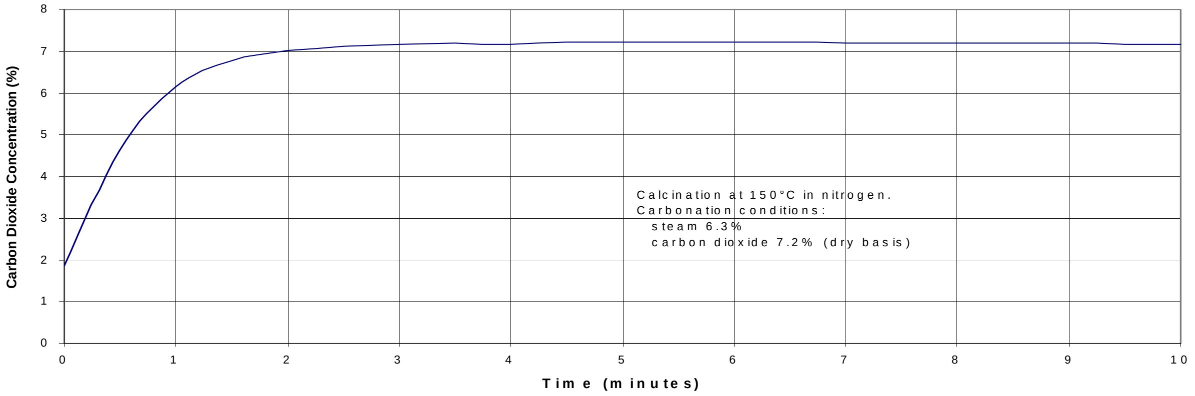


Figure 11a. Test data from carbonation cycle 5 with 10% supported potassium carbonate sorbent - CO_2 concentration in reactor exit gas.

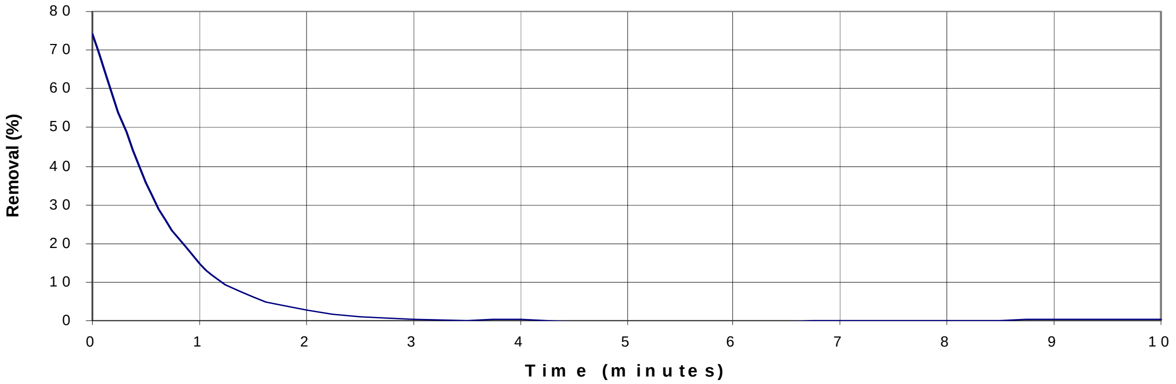


Figure 11b. Test data from carbonation cycle 5 with 10% supported potassium carbonate sorbent - CO_2 removal.

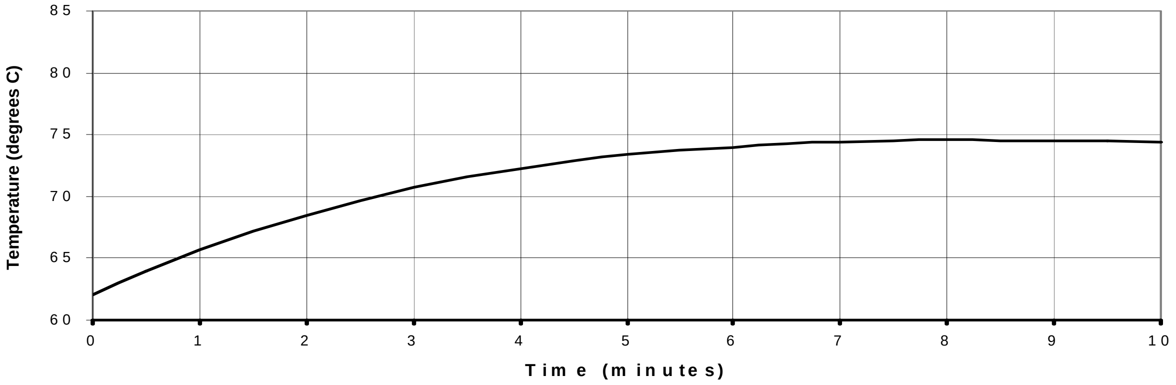


Figure 11c. Test data from carbonation cycle 5 with 10% supported potassium carbonate sorbent - average bed temperature.

4.5 Mathematical Modeling

RTI continued its efforts to develop mathematical models of a fast-fluidized bed carbonizer. This model includes the pertinent heat and material balances in the gas and solid phases. The gas and the solid particles are assumed to pass through the fast fluidized bed in plug flow. The relative velocity of the gas and solids is assumed to be the terminal velocity of individual particles in the gas phase. The rate of reaction of sodium carbonate to Wegscheider's salt is based on carbonization rates observed in the RTI and LSU TGA experiments, extrapolating the rates and geometry of the TGA to those anticipated for the fast fluidized bed. The kinetic model basically assumes that a reaction front at which sodium carbonate is converted to Wegscheider's salt moves from the external surface towards the interior of the particle. At this front, the temperature of the solid is given by the equilibrium temperature of the carbonate-Wegscheider's salt reaction, evaluated at the bulk gas partial pressure of CO_2 and water vapor. The rate of carbonization under this model is proportional to the difference between the equilibrium temperature and the bulk gas temperature. It is also proportional to a function of the fraction remaining in the solid particle, which, at conversions up to about 60%, can be represented by 1 minus the conversion. At higher temperatures, this representation gives carbonation rates lower than observed but eliminates the need to experimentally evaluate a kinetic parameter. Thus for a given length of fast fluidized bed, the model should conservatively predict the extent of sodium carbonate carbonation.

RTI is presently in the process of solving the equations describing the fast fluidized bed model. This model will be extended to simulate the RTI fluidized bed reactor experiments, which are semi-batch experiments, and thus more difficult to analyze than the steady state fast fluidized bed.

4.6 Other Project Activities

In August, RTI and Church and Dwight attended a project review meeting at DOE/NETL in Morgantown, WV. In September, RTI presented a paper, with co-authors from LSU at the Pittsburgh Coal Conference in Pittsburgh, PA.

5.0 CONCLUSIONS AND FUTURE WORK

Calcination of T-200 trona in dry carbon dioxide at 120°C takes place very slowly but does not does not result in decreased carbonation activity relative to calcination in helium at this temperature. Calcination of T-200 trona at 160°C (in helium) leads to reduced carbonation activity relative to lower temperature calcination in helium.

Following calcination in helium at 160°C, calcined SBC #3 has significantly greater carbonation activity than either grade of calcined trona.

In fixed bed testing of SBC #3, stoichiometric quantities of carbon dioxide were recovered in the initial calcination phase. During the initial stages of carbonation of the resulting sodium carbonate, between 34% and 47% of the carbon dioxide present in simulated flue gas was removed. Material balance calculations indicated that the final product, at 70°C was a combination of Wegscheider's salt and sodium bicarbonate.

Very rapid carbonation rates were observed with a 10% supported potassium carbonate sorbent in fluidized bed tests. The reaction appeared to reach completion within the first few minutes of the test, although activity of the support material make it impossible to determine the extent of reaction of the potassium carbonate. The heat of reaction produced a rapid temperature rise in the sorbent bed.

Milled spherical sodium bicarbonate appeared to be similar in properties to that of a control material of similar mesh size but less regular particle shape.

In the next quarter, LSU will conduct 5-cycle TGA testing on an SBC material other than SBC #3, for comparison purposes. Multicycle tests to evaluate the fate of SO_2 and its effect on sorbent capacity and activity will also be conducted. RTI will modify a 1-inch diameter quartz reactor and conduct fluid bed tests to confirm the fate of HCl and SO_2 in simulated flue gases. ASPEN simulations will be refined to extrapolate the reaction rates derived from TGA experiments to the conditions expected in a transport reactor.

6.0 REFERENCES

ASTM, International, Method D5757-95: Standard Test Method for Determination of Attrition and Abrasion of Powdered Catalysts by Air Jets. 1995

Green, D.A., Turk, B.S., Gupta, R., and Lopez Ortiz, A., Carbon Dioxide Capture From Flue Gas Using Dry Regenerable Sorbents, Quarterly Technical Progress Report, Research Triangle Institute, January 2001(a).

Green, D.A., Turk, B.S., Gupta, R., Lopez Ortiz, A., Harrison, D.P., and Liang, Y., Carbon Dioxide Capture From Flue Gas Using Dry Regenerable Sorbents, Quarterly Technical Progress Report, Research Triangle Institute, May 2001(b).

Green, D.A., Turk, B.S., Gupta, R., McMichael, Harrison, D.P., and Liang, Y., Carbon Dioxide Capture From Flue Gas Using Dry Regenerable Sorbents, Quarterly Technical Progress Report, Research Triangle Institute, April 2002(a).

Green, D.A., Turk, B.S., Portzer, J. W., Gupta, R., McMichael, Harrison, D.P., and Liang, Y., Carbon Dioxide Capture From Flue Gas Using Dry Regenerable Sorbents, Quarterly Technical Progress Report, Research Triangle Institute, July 2002(b).

Appendix A

Determination of Calcination Rate of Spherical Sodium Bicarbonate

LABORATORY REPORT

Date: July 12, 2002 **Author:** Chris Stairiker

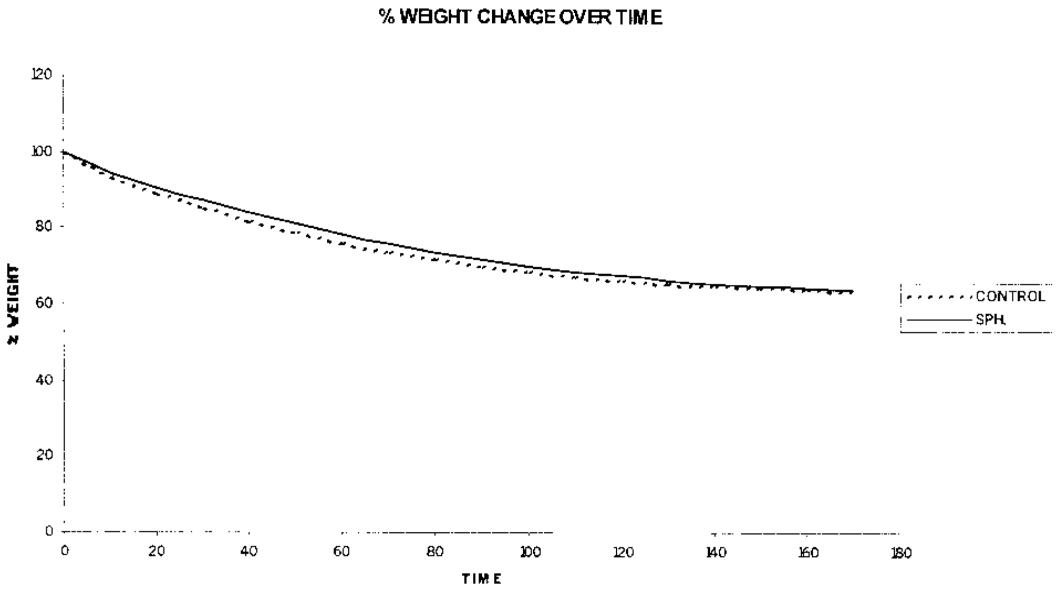
Title: TGA 2950 analysis for Grade 4 Lot # 2070 F sodium bicarbonate and spherical sodium bicarbonate #2033-39

Laboratory Notebook Number: A-2878-3-5

Objective: Compare the decomposition reaction of spherical sodium bicarbonate to untreated bicarbonate using the TGA. The control was Grade 4 with a mean particle size of 90 microns. The experimental sample, spherical sodium bicarbonate, is a milled product and compared with the control has a reduced surface area, is more free flowing and rounded, with a mesh size between 100-200.

Method: Samples of the spherical sodium bicarbonate and the control were introduced to the Thermogravimetric Analyzer TGA 2950 Dupont 2100. The sample size was approximately 400 mg. The TGA was operated isothermally at 225 ^{0} F for three hours. Weight readings were obtained every 10 minutes. First the control sample, Grade 4, was run. Then the spherical sodium bicarbonate was run. The data was compared on an excel spreadsheet

Data: See attached TGA analysis, Excel spreadsheet



Conclusions:

Grade 4: After 180 minutes the weight of the Grade 4 samples dropped to 63.51% of the starting weight of 102.31 grams. The final weight of the sample was 64.98 grams.

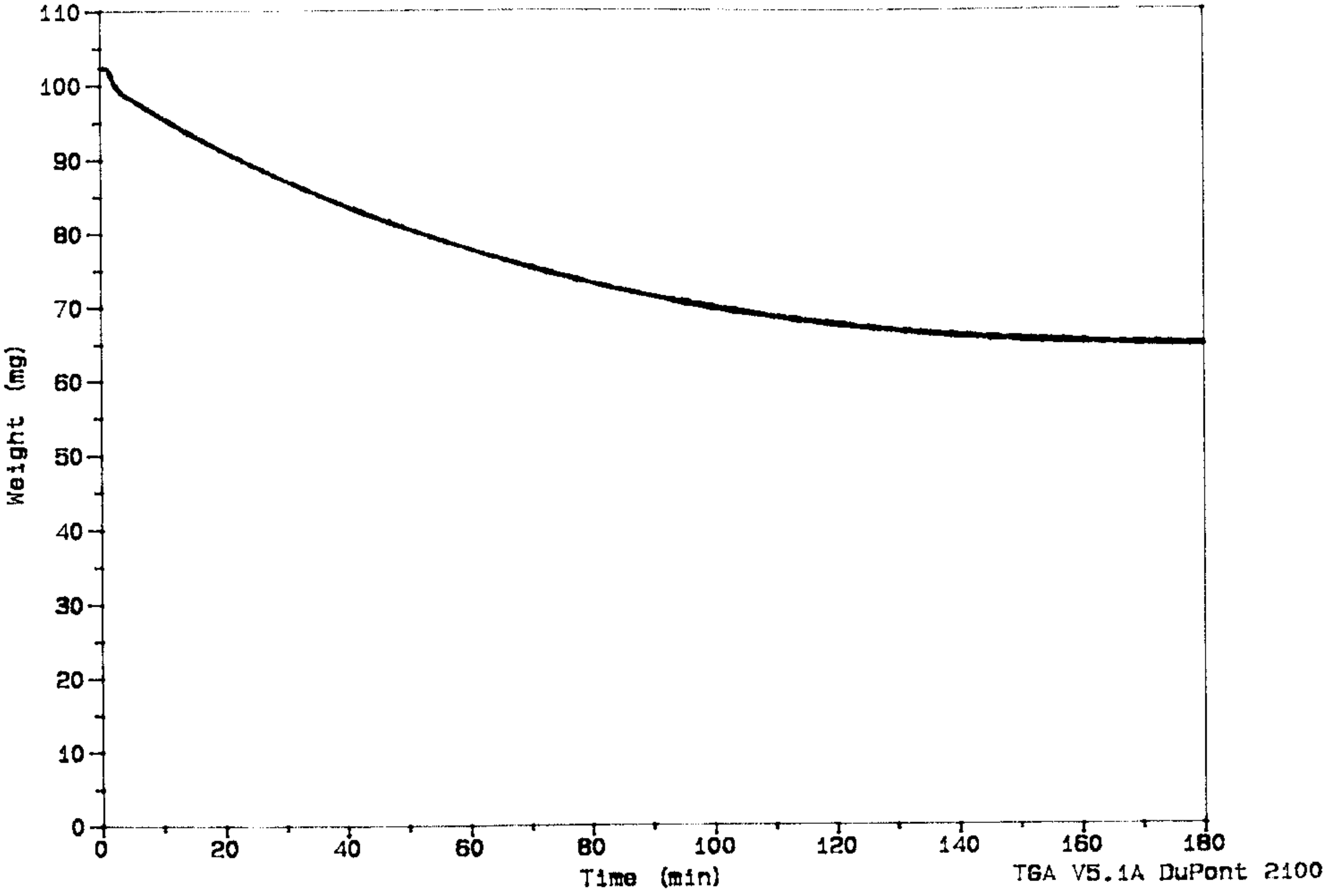
Spherical sodium bicarbonate: After 180 minutes the spherical sodium bicarbonate weight dropped to 63.83% of its starting weight of 120.4 grams. The final weight was 76.85 grams.

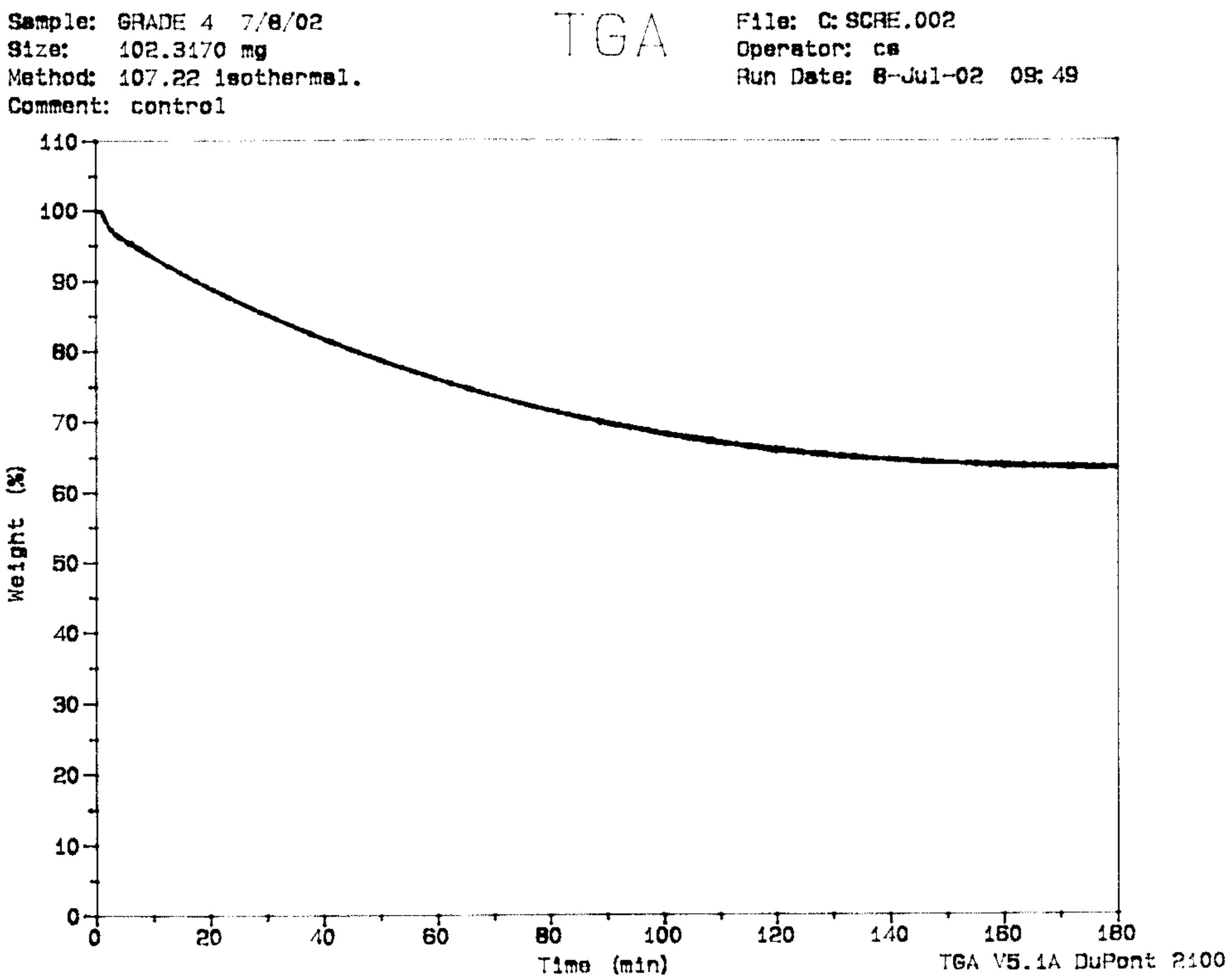
The results show very little difference in thermal properties between Grade 4 and spherical sodium bicarbonate. The small difference shown can be attributed to the difference in surface area between the control and the spherical, or more likely, the sub 200 mesh fraction seen in the control.

Sample: GRADE 4 7/8/02
Size: 102.3170 mg
Method: 107.22 isothermal.
Comment: control

TGA

File: C:SCRE.002
Operator: cs
Run Date: 8-Jul-02 09:49




Sample: GRADE 4 7/8/02
Size: 102.3170 mg
Method: 107.22 isothermal.
Comment: control
TGA
File: C: SCRE.002
Operator: cs
Run Date: 8-Jul-02 09:49
Weight (%)
110
100
90
80
70
60
50
40
30
20
10
0
0
20
40
60
80
100
120
140
160
180
Time (min)
TGA V5.1A DuPont 2100

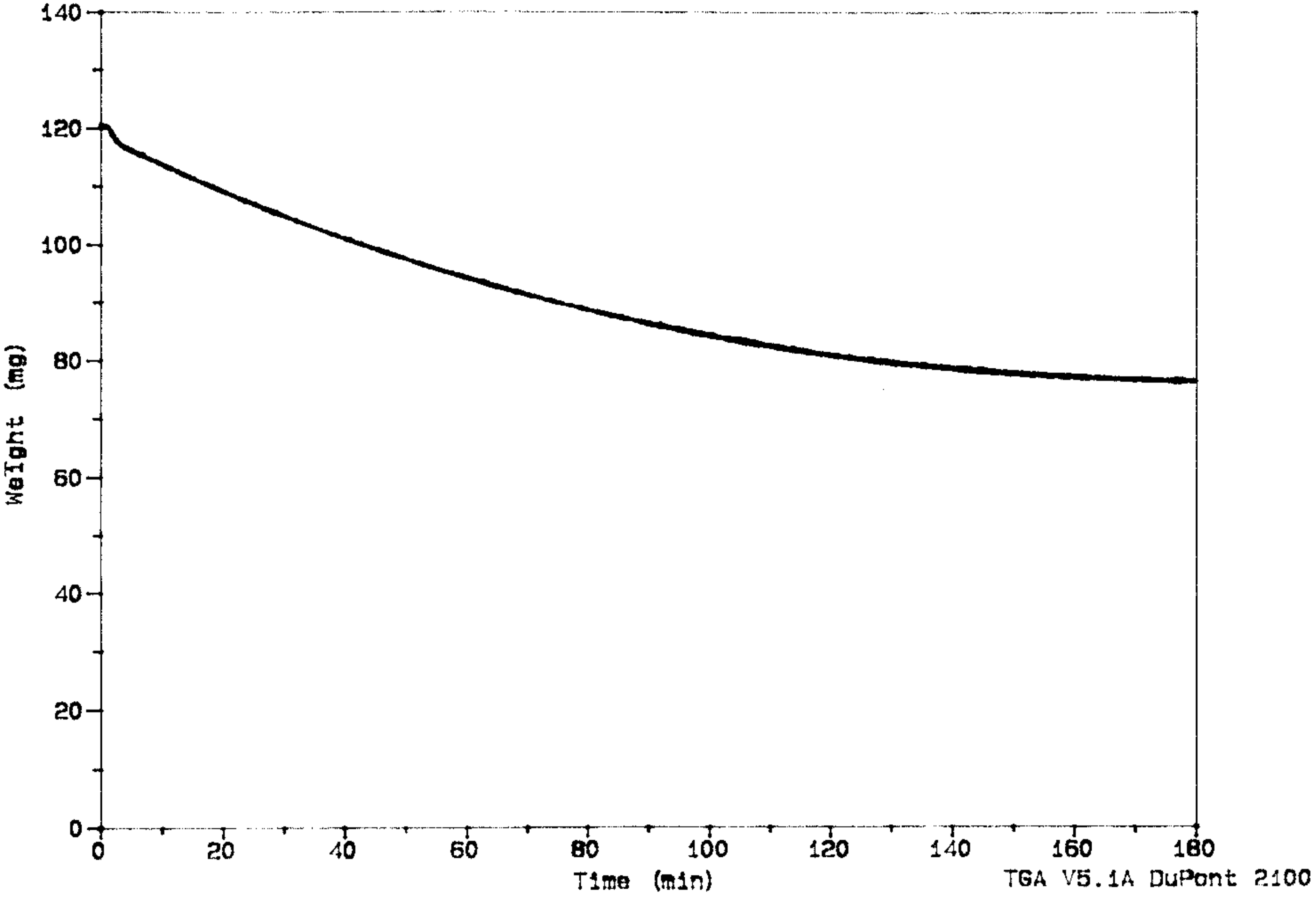
```
TGA Standard                                              10-Jul-02 09: 18  Page  1

File:  C: SCRE.002        Run Date:  8-Jul-02   09: 49
Program:  TGA V5.1A       Run Number:  157

DuPont 2100 Thermal Analysis -- TGA 1000 °C

Sample:      GRADE 4  7/8/02
Size:        102.3170 mg
Calibration Constant:  1.0000
Operator:    cs
Method:      107.22 isothermal.
Comment:     control

      Time           Weight
      min              mg
      0.00           102.3
     10.00           95.63
     20.00           91.08
     30.00           87.12
     40.00           83.63
     50.00           80.53
     60.00           77.78
     70.00           75.35
     80.00           73.22
     90.00           71.39
    100.00           69.82
    110.00           68.52
    120.00           67.46
    130.00           66.63
    140.00           66.00
    150.00           65.53
    160.00           65.20
    170.00           64.98
    180.00
```

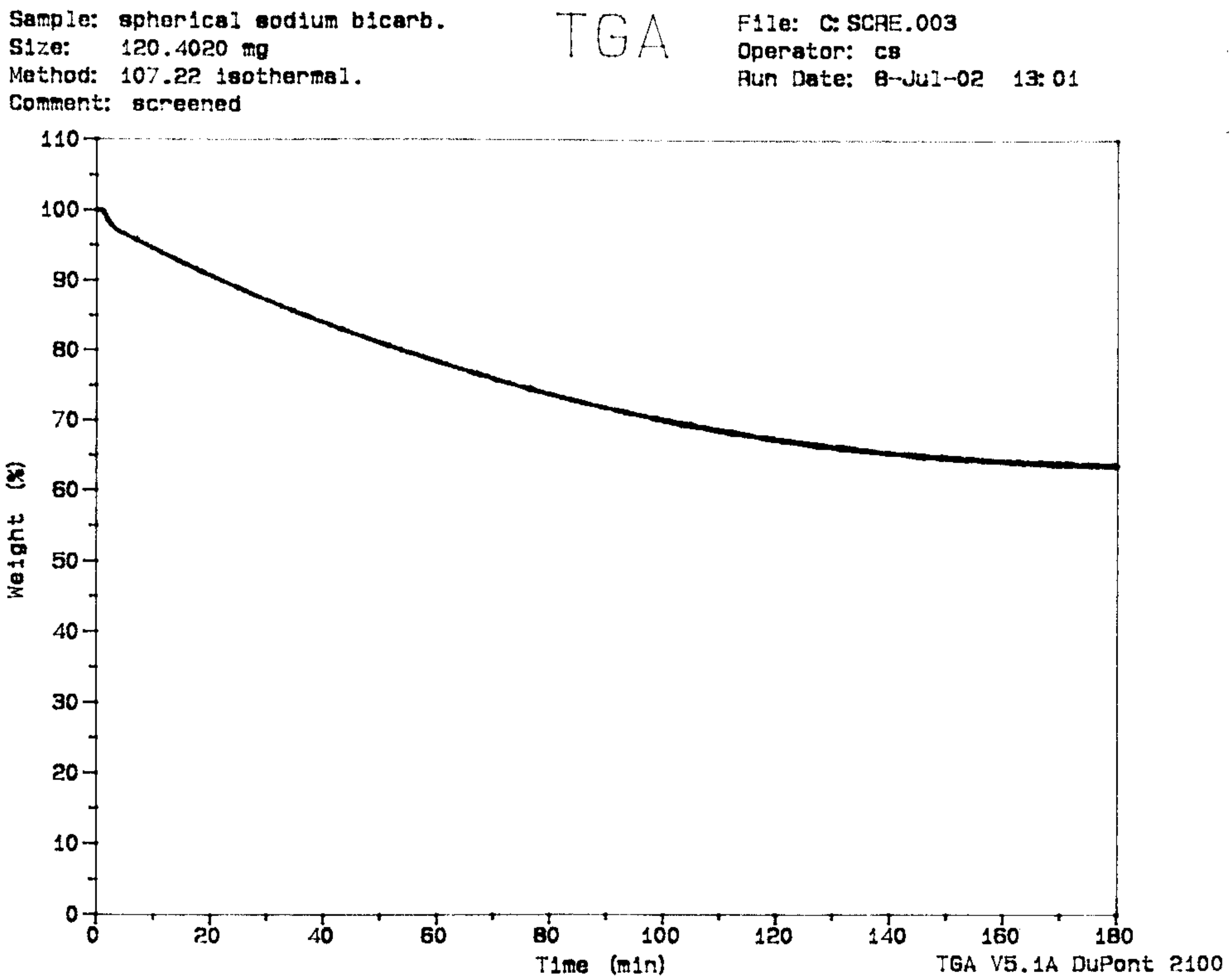
```
TGA Standard                                        8-Jul-02 15:22   Page   1

File:  C:SCRE.002          Run Date:  8-Jul-02   09:49
Program:  TGA V5.1A        Run Number:  157

DuPont 2100 Thermal Analysis --- TGA 1000 °C

Sample:       GRADE 4  7/8/02
Size:         102.3170 mg
Calibration Constant:  1.0000
Operator:     cs
Method:       107.22 isothermal.
Comment:      control

      Time              Weight
      min                 %
      0.00              100.0
     10.00              93.46
     20.00              89.02
     30.00              85.15
     40.00              81.73
     50.00              78.70
     60.00              76.01
     70.00              73.64
     80.00              71.56
     90.00              69.77
    100.00              68.24
    110.00              66.97
    120.00              65.94
    130.00              65.12
    140.00              64.50
    150.00              64.05
    160.00              63.73
    170.00              63.51
    180.00
```

Sample: spherical sodium bicarb.
Size: 120.4020 mg
Method: 107.22 isothermal.
Comment: screened

TGA

File: C:SCRE.003
Operator: cs
Run Date: 8-Jul-02 13:01





Sample: spherical sodium bicarb.
Size: 120.4020 mg
Method: 107.22 isothermal.
Comment: screened

TGA

File: C: SCRE.003
Operator: cs
Run Date: 8-Jul-02 13: 01

```
TGA Standard                                                10-Jul-02 09:13  Page  1

File:  C: SCRE.003        Run Date: 8-Jul-02   13:01
Program:  TGA V5.1A       Run Number:  158

DuPont 2100 Thermal Analysis -- TGA 1000 °C

Sample:     spherical sodium bicarb.
Size:       120.4020 mg
Calibration Constant:  1.0000
Operator:   cs
Method:     107.22 isothermal.
Comment:    screened

      Time            Weight
       min              mg
      0.00            120.4
     10.00            113.7
     20.00            109.1
     30.00            104.9
     40.00            101.0
     50.00            97.52
     60.00            94.32
     70.00            91.42
     80.00            88.79
     90.00            86.44
    100.00            84.36
    110.00            82.55
    120.00            81.00
    130.00            79.72
    140.00            78.69
    150.00            77.89
    160.00            77.28
    170.00            76.85
    180.00
```

```
TGA Standard                                          10-Jul-02 09:06   Page  1

File:  C:SCRE.003         Run Date:  8-Jul-02   13:01
Program:  TGA V5.1A       Run Number:  158

DuPont 2100 Thermal Analysis -- TGA 1000 °C

Sample:     spherical sodium bicarb.
Size:       120.4020 mg
Calibration Constant:  1.0000
Operator:   cs
Method:     107.22 isothermal.
Comment:    screened

      Time           Weight
      min              %
      0.00           100.0
     10.00           94.45
     20.00           90.59
     30.00           87.09
     40.00           83.90
     50.00           80.99
     60.00           78.34
     70.00           75.93
     80.00           73.74
     90.00           71.79
    100.00           70.07
    110.00           68.56
    120.00           67.28
    130.00           66.21
    140.00           65.36
    150.00           64.69
    160.00           64.19
    170.00           63.83
    180.00
```

Appendix B

Attrition Testing of Spherical Sodium Bicarbonate

LABORATORY REPORT

Date: September 4, 2002 **Author:** Chris Stairiker

Title: Attrition and Abrasion Tests: Grade 4 and Grade 4 Spherical

Objective: To determine whether there is any difference in the amount of handling attrition seen in spherical grade 4 sodium bicarbonate compared to grade 4 control sodium bicarbonate.

Method: Grade 4 and spherical grade 4 were run on a Lab-Line Hi-Speed Fluid Bed Dryer Model 23852 for six hours at an air pressure setting of 2. The material was collected in an air bag filter. Particle size distributions of the spherical and control were then determined using Coulter LS-200 and a Ro-Tap apparatus. The Coulter can determine mean particle size of the sample to see if it changed due to attrition or abrasion during the fluid bed dryer. Ro-Taps analysis yields the weight or percent of product retained on each size.

Data: (see below and attached sheets)

Coulters:

	Mean Particle Diameter µm / Range µm (10% - 90 %)			
	Before fluid bed dryer		After fluid bed dryer	
	Mean	Range	Mean	Range
Grade 4	133.26	77.25- 193.06	134.03	78.09- 195.66
Spherical 4	119.46	62.16- 177.76	120.5	63.27- 178.77

Ro-Taps

Grade 4				
		Cumulative weight %		% difference
USS Sieve Size	Microns	Before	After	
80	177	0.26	0.26	0.0%
100	149	0.56	0.5	10.7%
200	74	88.74	89.12	-0.4%
325	44	97.7	99.47	-1.8%
PAN		99.88	102.16	-2.3%
Spherical 4				
		Cumulative weight %		% difference
USS Sieve Size	Microns	Before	After	
80	177	0.8	0.78	2.5%
100	149	1.3	1.32	-1.5%
200	74	79.66	77.78	2.4%
325	44	95.72	95.66	0.1%
PAN		100.12	101	-0.9%

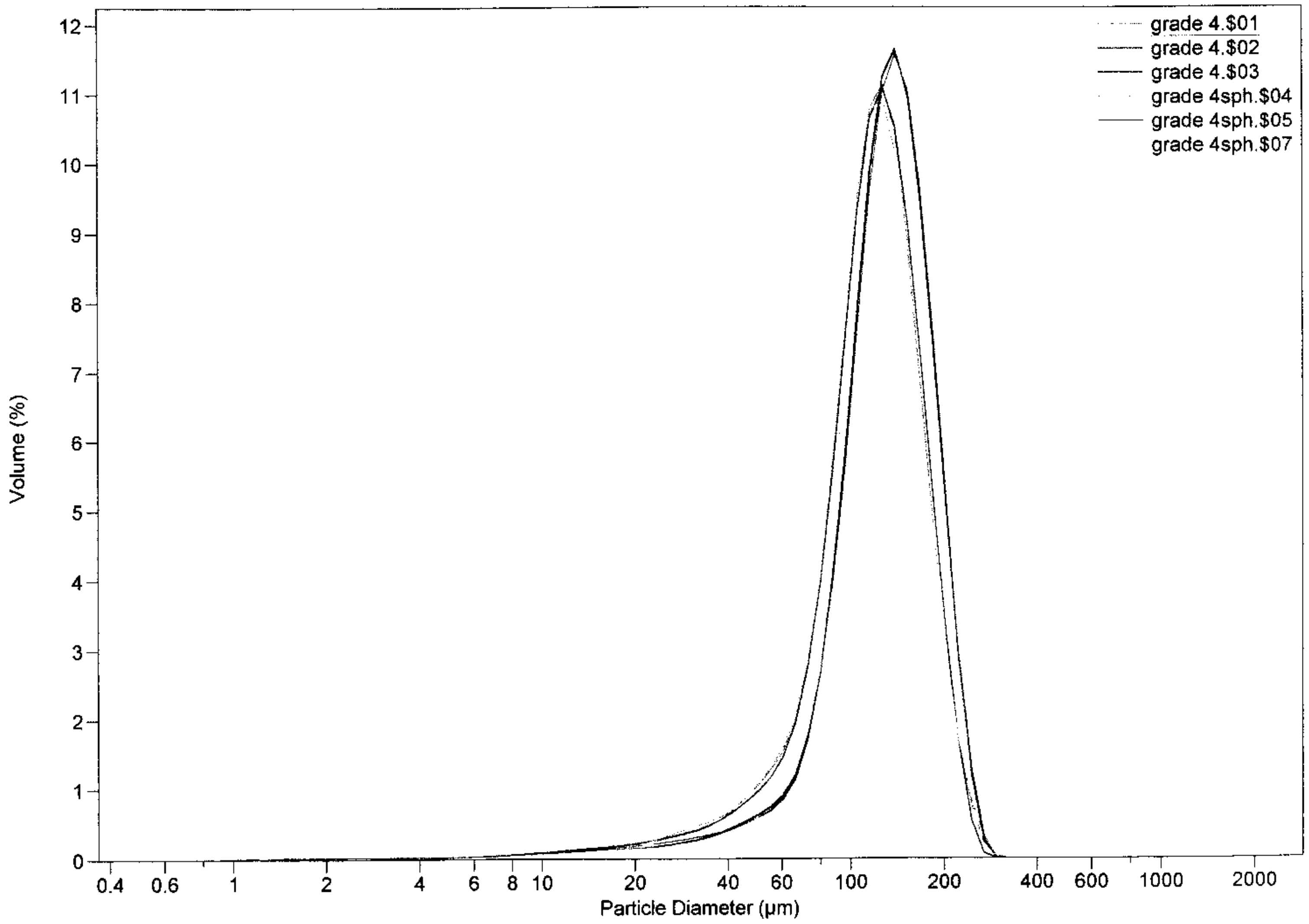
Conclusions:

There was no significant difference in particle size or cumulative weight before and after the six hours run on the fluid bed dryer. Neither the Spherical 4 nor the nonspherical Grade 4 seemed to show signs of attrition or abrasion. The small difference seen between the Coulter and Ro- tap data before and after can be attributed to normal % error in the samples.

LS Particle Size Analyzer

26 Jul 2002

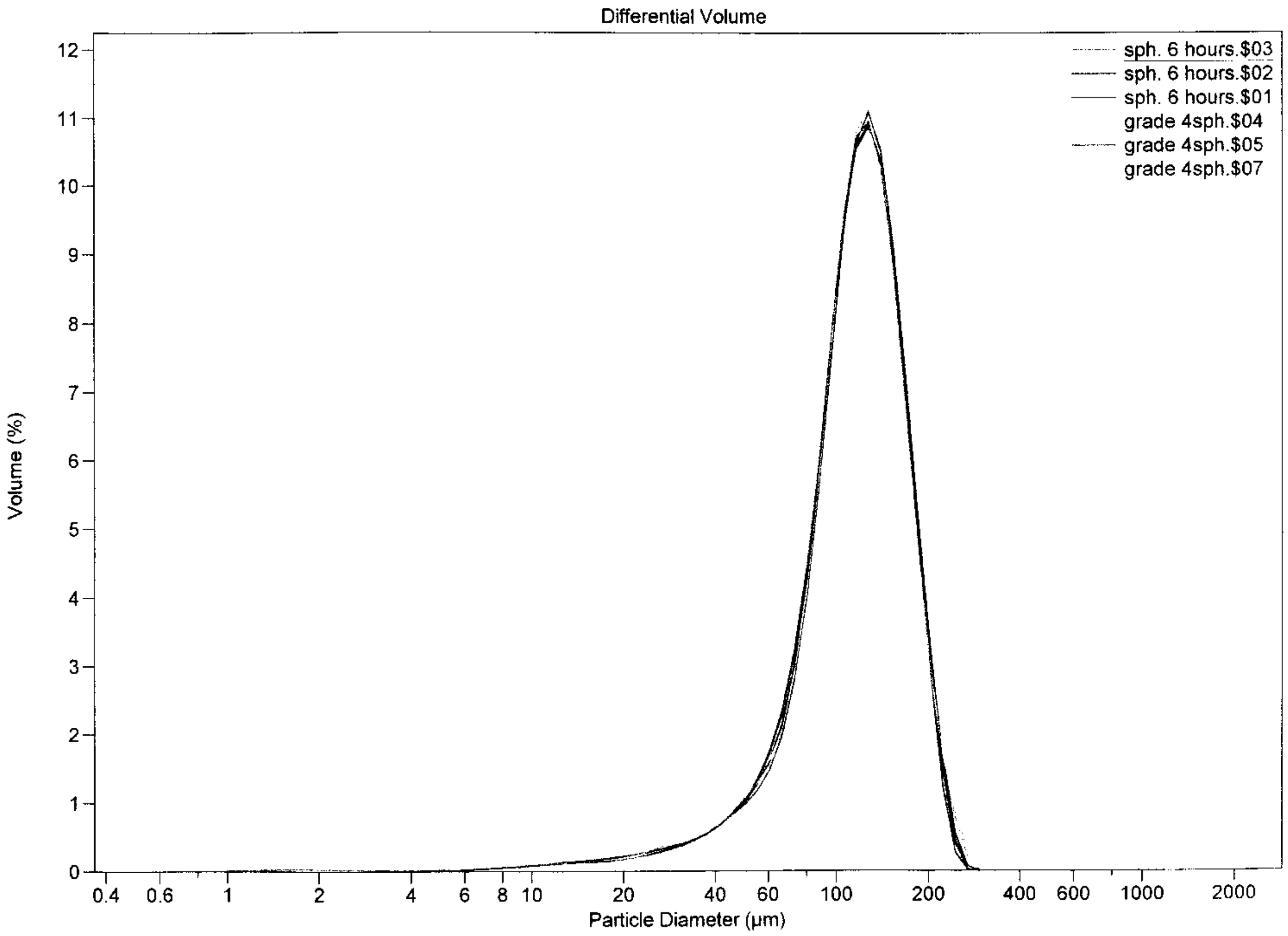
grade 4/ grade 4 spherical


Differential Volume

LS Particle Size Analyzer

8 Aug 200

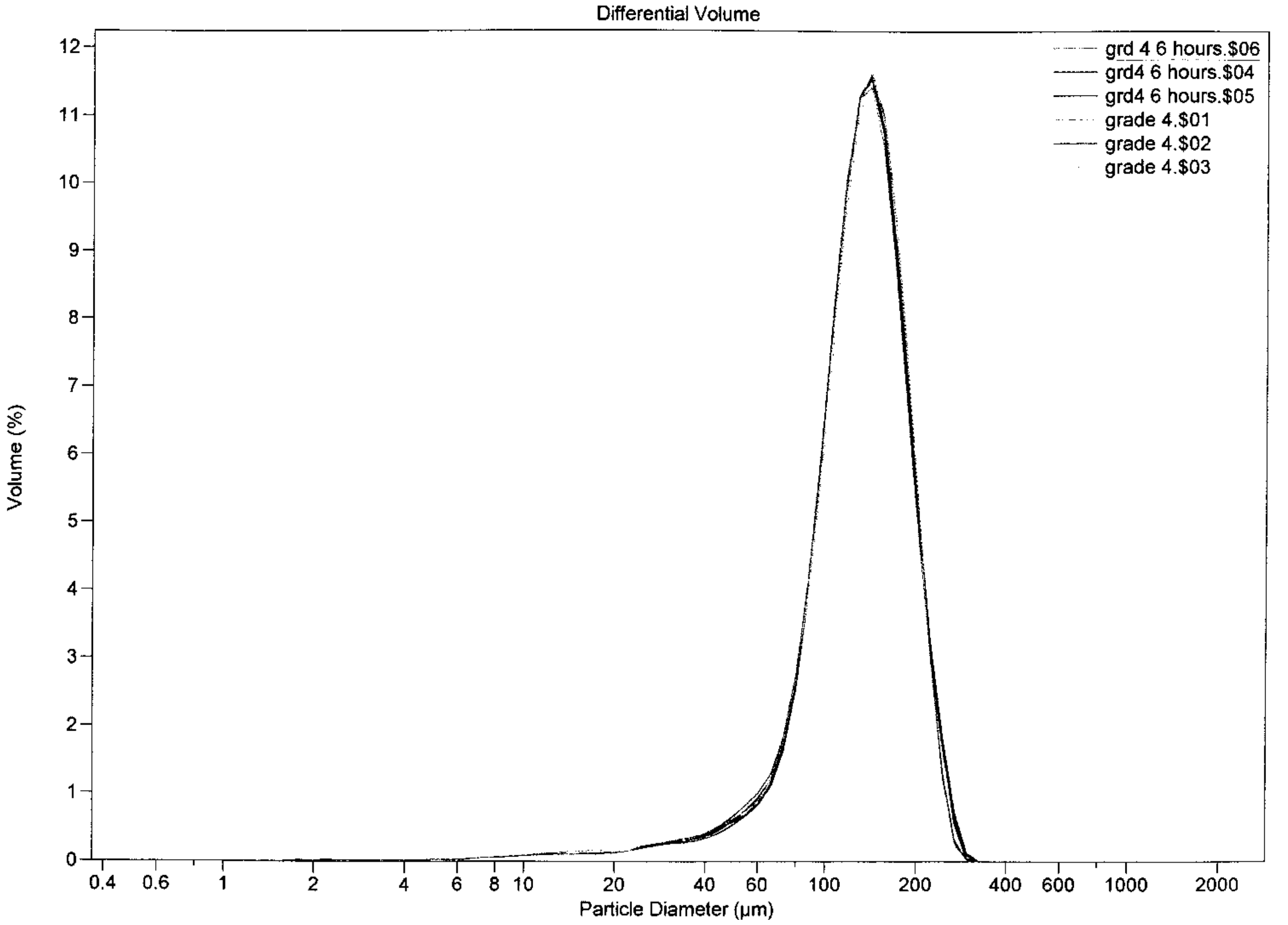
spherical grade 4, before and after (6 hours fluid bed dryer)



LS Particle Size Analyzer

8 Aug 2002

grade 4, before and after (6 hours fluid bed dryer)



Sample ID	grade 4	Initial Sample Mass:	50.0 g	Final Sample Mass	49.94			
Sieve Number	Microns	Screen weight	Sample weight	Screen & Sample	Sample weight	Average cut diameter	cumulative weight	
		(g)	(g)	Weight	(%)	(microns)	(g)	(%)
				(g)				
80	177	396.96	0.13	397.09	0.26	115	0.13	0.26
100	149	381.95	0.15	382.1	0.3	96	0.28	0.56
200	74	371.56	44.09	415.65	88.18	81	44.37	88.74
325	44	301.77	4.48	306.25	8.96	68	48.85	97.7
			0					
			0					
PAN	~3	361.52	1.09	362.61	2.18	~5	49.94	99.88

Sample ID	grade 4	Initial Sample Mass:	50.0 g	Final Sample Mass	49.94			
Sieve Number	Microns	Screen weight	Sample weight	Screen & Sample	Sample weight	Average cut diameter	cumulative weight	
		(g)	(g)	Weight	(%)	(microns)	(g)	(%)
				(g)				
80	177	397.02	0.1	397.12	0.2	115	0.1	0.2
100	149	381.94	0.08	382.02	0.16	96	0.18	0.36
200	74	371.64	44.37	416.01	88.74	81	44.55	89.1
325	44	301.76	4.39	306.15	8.78	68	48.94	97.88
			0					
			0					
PAN	~3	361.52	1	362.52	2	~5	49.94	99.88

Sample ID	grade 4 sph	Initial Sample Mass:	50.0 g	Final Sample Mass	49.95			
Sieve Number	Microns	Screen weight	Sample weight	Screen & Sample	Sample weight	Average cut diameter	cumulative weight	
		(g)	(g)	Weight	(%)	(microns)	(g)	(%)
				(g)				
80	177	396.99	0.44	397.43	0.88	115	0.44	0.88
100	149	381.93	0.3	382.23	0.6	96	0.74	1.48
200	74	371.68	38.78	410.46	77.56	81	39.52	79.04
325	44	301.83	8.15	309.98	16.3	68	47.67	95.34
			0					
			0					
PAN	~3	361.55	2.28	363.83	4.56	~5	49.95	99.9

Sample ID	grade 4 sph	Initial Sample Mass:	50.0 g	Final Sample Mass	50.06			
Sieve Number	Microns	Screen weight	Sample weight	Screen & Sample	Sample weight	Average cut diameter	cumulative weight	
		(g)	(g)	Weight	(%)	(microns)	(g)	(%)
				(g)				
80	177	396.97	0.4	397.37	0.8	115	0.4	0.8
100	149	381.97	0.25	382.22	0.5	96	0.65	1.3
200	74	371.65	39.18	410.83	78.36	81	39.83	79.66
325	44	301.8	8.03	309.83	16.06	68	47.86	95.72
			0					
			0					
PAN	~3	361.53	2.2	363.73	4.4	~5	50.06	100.12

ROTAP PARTICLE SIZE ANALYSIS

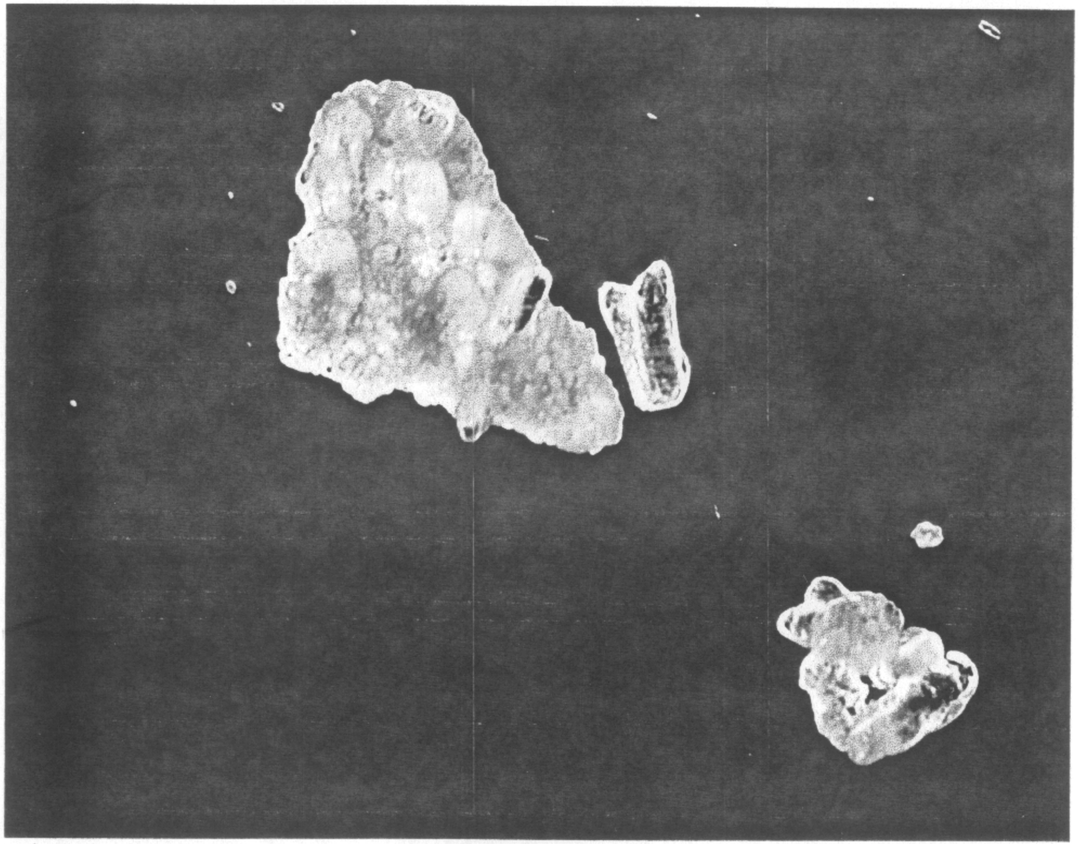
Analyzer:	Christine Stairker
Date	08/08/2002
Supplier	
Time	5.0 min
NBR#	

Sample ID	grade 4 6 h.	Initial Mass:	50.0 g	Final Sample Mass:	51.08			
Sieve Number	Microns	Screen weight	Sample weight	Screen & Sample	Sample weight	Average cut diameter	cumulative weight	
		(g)	(g)	Weight	(%)	(microns)	(g)	(%)
				(g)				
80	177	396.93	0.13	397.06	0.26	115	0.13	0.26
100	149	381.92	0.12	382.04	0.24	96	0.25	0.5
200	74	371.52	44.31	415.83	88.62	81	44.56	89.12
325	44	301.77	5.18	306.95	10.36	68	49.74	99.48
PAN	~3	335.14	1.34	336.48	2.68	~5	51.08	102.16

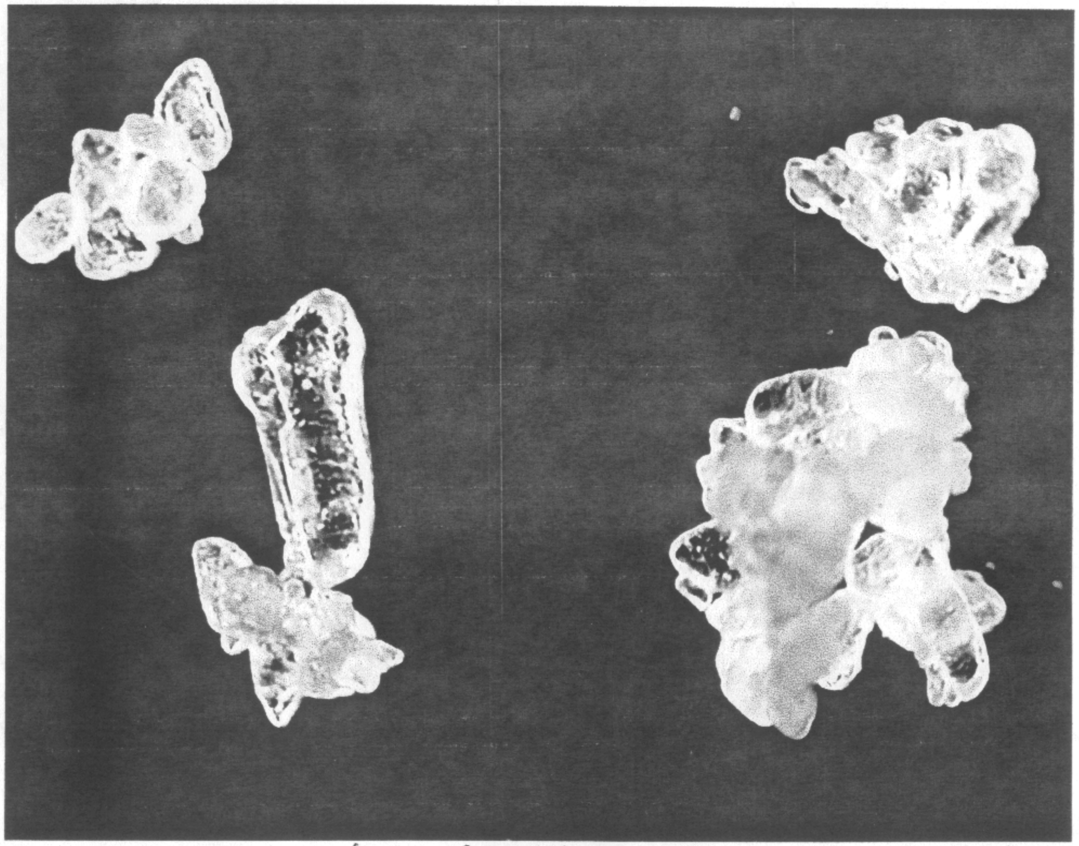
Sample ID	grade 4 6 h.	Initial Sample Mass	50.0 g	Final Sample Mass:	50.41			
Sieve Number	Microns	Screen weight	Sample weight	Screen & Sample	Sample weight	Average cut diameter	cumulative weight	
		(g)	(g)	Weight	(%)	(microns)	(g)	(%)
				(g)				
80	177	396.95	0.12	397.07	0.24	115	0.12	0.24
100	149	381.96	0.13	382.09	0.26	96	0.25	0.5
200	74	371.55	43.96	415.51	87.92	81	44.21	88.42
325	44	301.82	5.05	306.87	10.1	68	49.26	98.52
					0			
					0			
PAN	~3	335.34	1.15	336.49	2.3	~5	50.41	100.82

Sample ID	grd 4 sph 6 h	Initial Sample Mass	50.0 g	Final Sample Mass	50.5			
Sieve Number	Microns	Screen weight	Sample weight	Screen & Sample	Sample weight	Average cut diameter	cumulative weight	
		(g)	(g)	Weight	(%)	(microns)	(g)	(%)
				(g)				
80	177	397	0.39	397.39	0.78	115	0.39	0.78
100	149	381.95	0.27	382.22	0.54	96	0.66	1.32
200	74	371.81	38.23	410.04	76.46	81	38.89	77.78
325	44	301.82	8.94	310.76	17.88	68	47.83	95.66
			0					
			0					
PAN	~3	335.13	2.67	337.8	5.34	~5	50.5	101

Sample ID	grd 4 sph 6 h	Initial Sample Mass	50.0 g	Final Sample Mass	51.15			
Sieve Number	Microns	Screen weight	Sample weight	Screen & Sample	Sample weight	Average cut diameter	cumulative weight	
		(g)	(g)	Weight	(%)	(microns)	(g)	(%)
				(g)				
80	177	396.98	0.37	397.35	0.74	115	0.37	0.74
100	149	382	0.17	382.17	0.34	96	0.54	1.08
200	74	371.69	38.16	409.85	76.32	81	38.7	77.4
325	44	301.83	9.48	311.31	18.96	68	48.18	96.36
			0					
			0					
PAN	~3	335.16	2.97	338.13	5.94	~5	51.15	102.3

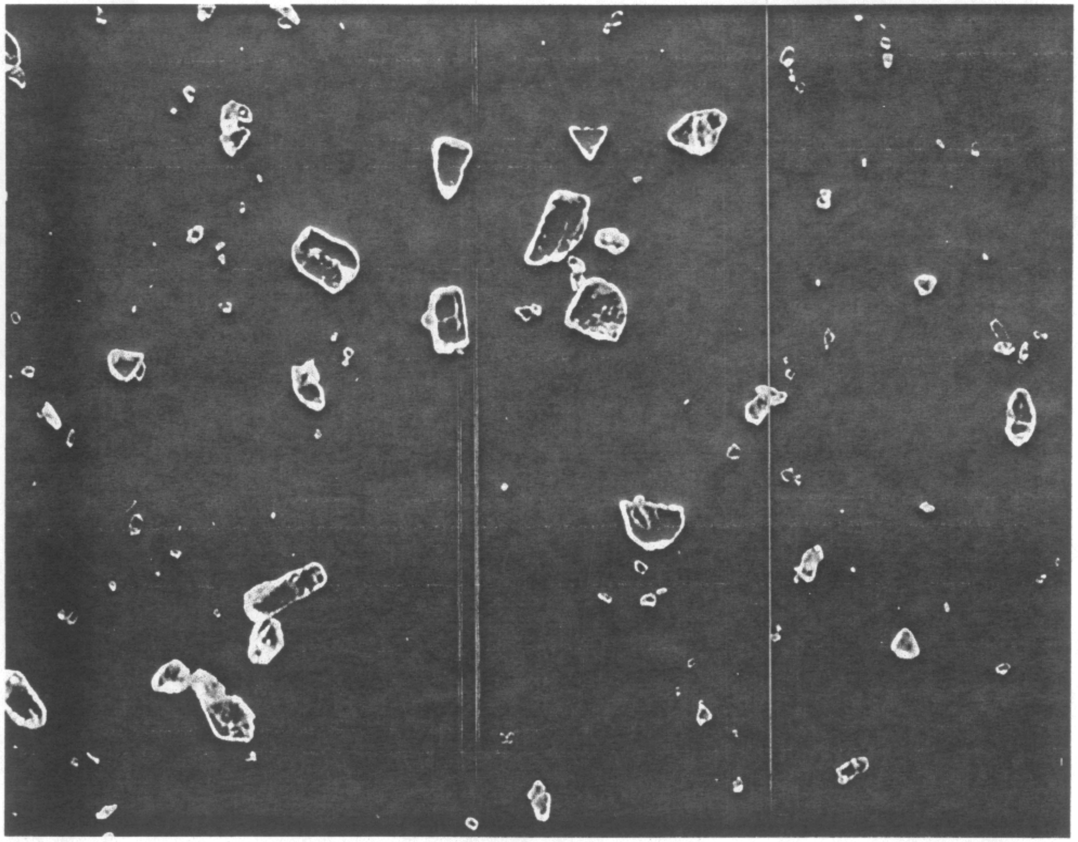


Grade 4 6hours dryer +80 mesh spherical 60X



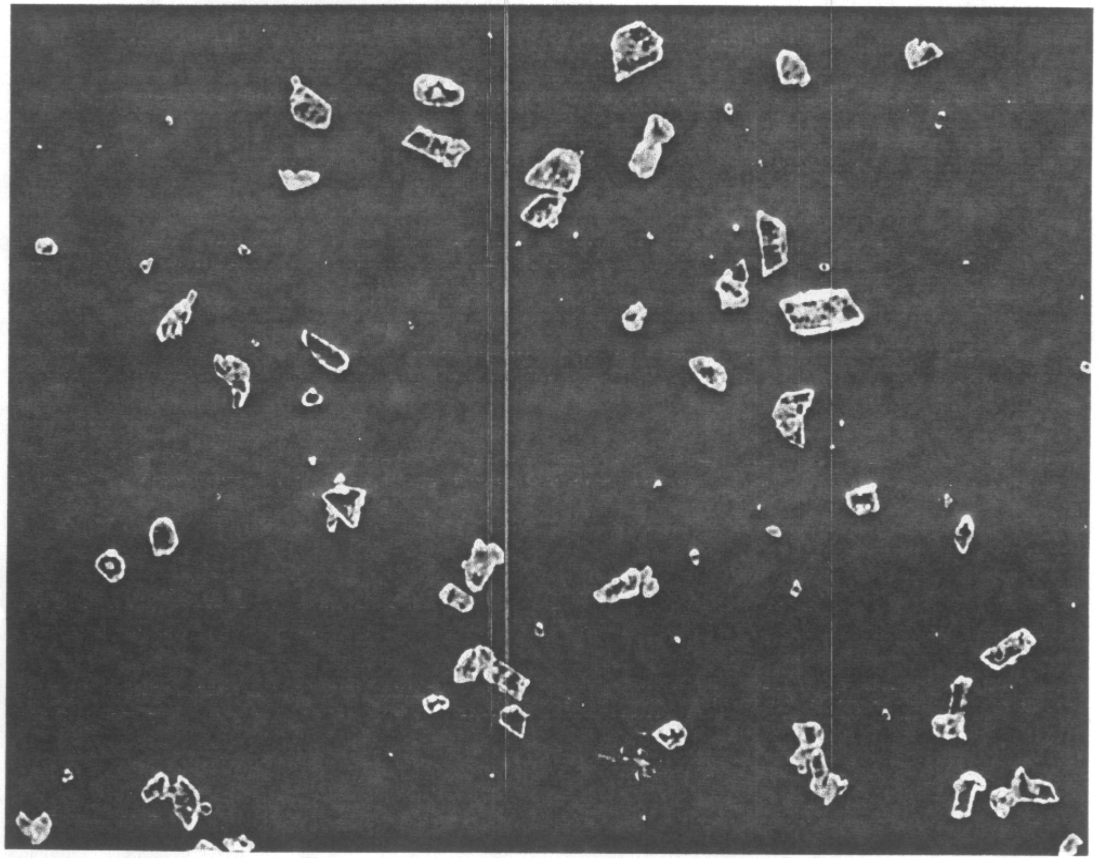
Grade 4 spherical 6 hour fluid bed dryer -on 80 mesh 60X
+80mesh

Grade 4 spherical
6 hour fluid bed dryer
NTBK #A2878
60X

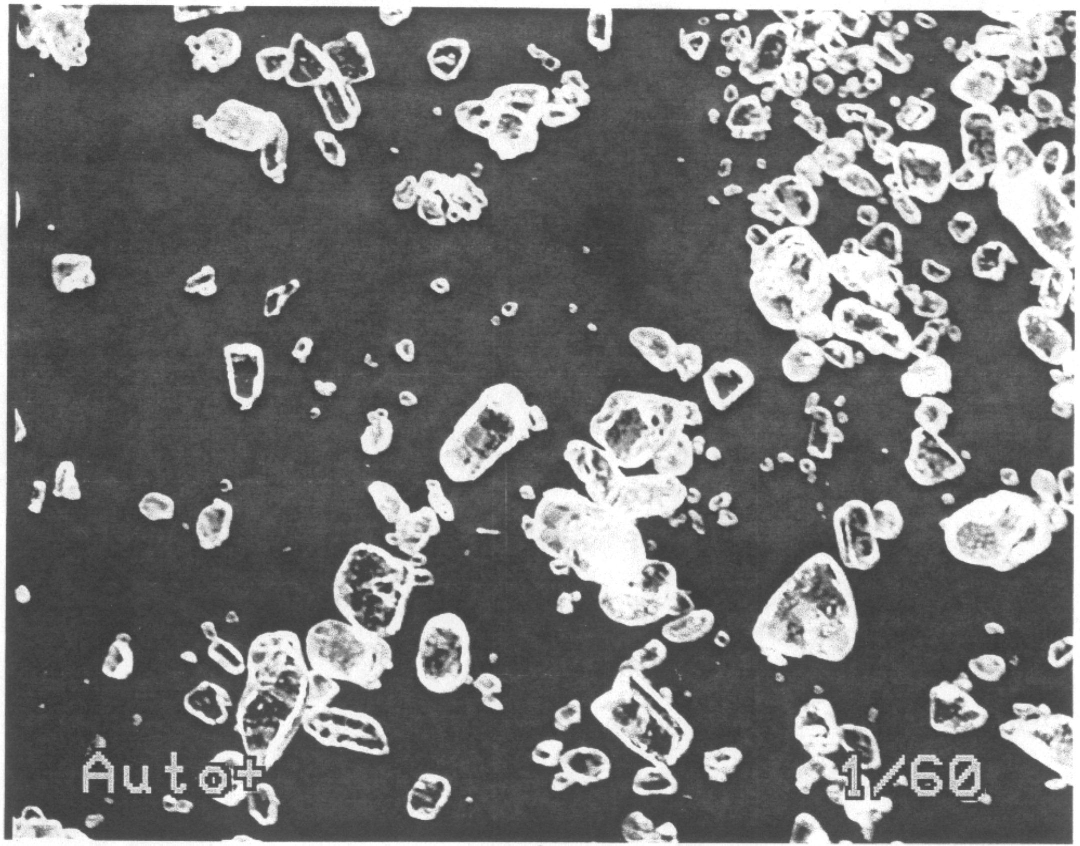


Grade 4 spherical 6 hour bed dryer NTBK # A2878-17

Grade 4 . lot # 2070F
6 hours .
NTBK #A2878 -
60X



Grade 4 lot # 2070F bed dryer 6 hours NTBK # A 2878-17



Spherical Greck 4 -200 mesh- 60X