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The Effect of Silica Surface Area on Microparticle Retention Systems

Jason P. Hoffmann
Western Michigan University

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The Effect of Silica Surface Area on Microparticle Retention Systems

Written by

Jason P. Hoffmann

April 24, 1997

A thesis written
in partial fulfillment of a
Bachelors of Science degree

Advisor: Dr. John Cameron

Western Michigan University

Abstract

Retention of fines and fillers has always been a concern in the paper industry. There has been many different types of retention aids in the past, but they lack performance under the vigorous conditions in today's paper mills. High shear forces associated with high speed paper machines destroys flocs created with conventional retention aids leaving them useless. The influx of recycled materials into the mill brought along with it high fines content and a lot of anionic trash which readily reacts with cationic polymers. Consequently, the dosage must be increased which can lead to poor formation and increased chemical cost. A new retention aid was needed to combat these problems. Microparticle retention systems were developed by a group of papermakers, scientist, and process control experts in the late 1970's. A dramatic improvement in retention and drainage was achieved, which allowed higher filler loading, increased machine speeds, and better formation. To this date, continuing research is being done on the improvement of microparticle retention aids as well as developing new retention aids.

This paper deals with microparticle retention systems in a different way. Normally, the dosage of microparticle, anionic silica in this research, to the system is on a weight basis, i.e., pounds of microparticle per ton of paper. In this study, silica dosage will be done on a surface area basis. Silica particles have a very high specific surface area, which can range anywhere from around $500 \text{ m}^2/\text{g}$ to $1200 \text{ m}^2/\text{g}$. Using this information and the typical dosage rate on a weight basis, a surface area dosage can be calculated. For example, $600 \text{ m}^2/\text{g} \times 1.0 \text{ lb}/\text{ton} = 272,155 \text{ m}^2/\text{ton}$ and $1200 \text{ m}^2/\text{g} \times 0.5 \text{ lb}/\text{ton} \times 272,155 \text{ m}^2/\text{ton}$. Both give the same surface area dosage, but different only half of the weight basis dosage is needed for the high surface area silica. Therefore, the objective of this thesis is to test the hypothesis that equivalent retention will be obtained when equal surface area dosage is applied to the system.

A two level, three variable factorial design was used to test the effects of surface area of microparticle, surface area dosage, and polymer dosage. Two different furnishes were used, a fine paper grade and a wood containing grade. Both grades are similar to those found in industry. All retention studies were carried out using a Britt Dynamic Drainage Jar. Percent fines and ash retention was measured.

The results for the fine paper furnish showed no conclusive trends other than an effect of polymer dosage on fines retention. The variability in the system was extremely high. The wood containing furnish, however showed several promising results. Again, the polymer dosage was found to have a large effect on the system. There was an interaction between surface area dosage and polymer dosage. At low polymer dosages, the surface area dosage had an effect on retention, but at high polymer dosage, there was not an improved retention response as the surface area dosage increased. Finally, the wood containing furnish followed the hypothesis that equivalent retention will be obtained at equal surface area dosage.

Many chemical suppliers pride themselves on the high surface area of their microparticle and the improved performance it offers. The results of this thesis show that this may not be exactly true. The dosage needed to get the same retention with a high surface area microparticle may be less, but not necessarily improved performance. If retention could be measured as a function of surface area added to the system per ton of paper, a mill could determine what is the most economical microparticle to use. For example, a supplier could supply a low surface area microparticle at a very low price, while the another supplier is offering a high surface area microparticle at an extremely high price. The mill would have to use a lot more of the low surface area microparticle to get the retention they want, but it still may be more economical.

Jason P. Hoffmann

I April 25, 1996

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I would like to thank Julio Dimperio from Allied Colloids and Greg Bengston from Eka Chemicals. Without the help from these two fine gentlemen, I do not believe I would have had the resources to perform this experiment.

Julio deserves credit for the idea of this study. He also supplied me with a lot of chemicals that I needed. Due to the distance, Julio was not able to help physically help me in the lab, but he offered plenty of tips and advise. Thanks Julio.

Without Greg Bengston, the laboratory work would have been a huge disaster. He supplied many chemicals as well. Greg also supplied make-down procedures for a lot of the chemicals. He loaned me a Britt Jar since the schools was not in good working order at the time, as well as syringes, a timer, and other things that made the lab work a lot easier. Thank you Greg for your help and support.

Finally, I would like to thank Dr. John Cameron, my advisor. He offered his knowledge of statistics and helped me set up the factorial design. He also helped me in the analysis of the results. Thank you Dr. Cameron and I hope we can keep in touch after I graduate.

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Introduction

The paper industry is a water intensive industry. Paper cannot be made without the use of water. A large fully integrated paper mill with a wood yard, pulp mill and several paper machines uses approximately 35 million gallons of water per day (1). Since paper mills use so much water, they are a target of many water regulations. To help meet these regulations, paper mills want to retain as much of the fiber, filler, and additives used in the paper making process without losing quality. Another driving force behind improving retention is the conversion of acid papermaking to alkaline papermaking. There are economic, as well as quality issues behind converting to alkaline papermaking. Some of these benefits include reduced raw material cost through higher filler loading, increased permanence of the sheet, and a less corrosive operating system (2). To achieve these benefits, high retention of the filler must be recognized. Microparticle retention systems were developed to meet these requirements.

Retention on the paper machine is defined two ways, overall retention and first-pass retention. Overall retention is defined as the amount of fibers, fillers, and additives retained in the finished paper sheet divided by the amount added to make up the stock (3). First-pass retention is the amount of fibers, fillers, and additives retained in the wet sheet divided by the amount of stock from the headbox (3). Paper quality and paper machine operations are more affected by first-pass retention (4). The paper industry is heading towards full closure of the water system on paper machines, which means all the water used in the paper making process is recirculated back around and reused without any treatment. This is done to reduce the amount of water used by the mill and

thus reduce the amount of effluent. Before the water system on a paper machine can be closed, the retention must be very high, otherwise paper properties will be adversely affected as will the runnability. A low level of first-pass retention means a lot of furnish materials are being recirculated through the white water system. This leads to poor paper properties and runnability problems. Therefore, good first-pass retention is the basis for closure of the water system in the paper mill and thus reduced effluent.

When studies in retention and retention response are done, the basis used for measuring the amount of microparticle added to the system is done on a weight basis. For example, a typical addition rate found in industry is 0.5 – 1.0 pounds of microparticle per ton of paper. This can be converted to a surface area basis by multiplying the weight basis addition rate by the specific surface area of the silica. After unit conversions, the product is surface area, in square meters, per ton of paper. An example is given in table 1 below.

| Surface Area Example | | |
|-------------------------------|-----------------------------|----------------------------------|
| Surface Area of Silica | Dosage Rate | Surface Area Dosage |
| $600 \text{ m}^2/\text{g}$ | $1.0 \text{ lb}/\text{ton}$ | $272,155 \text{ m}^2/\text{ton}$ |
| $1200 \text{ m}^2/\text{g}$ | $0.5 \text{ lb}/\text{ton}$ | $272,155 \text{ m}^2/\text{ton}$ |

Table 1

The objective of this thesis is to test the hypothesis that equivalent retention will be recognized if equal surface area of silica is added to the system, but using silica with different specific surface areas. In other words, to show that it is surface area and not weight of silica that controls retention. If this hypothesis is found to be true, it would imply that silica size and shape does not have a significant effect on the retention system. The second objective is to verify that retention will increase as higher dosages of silica, on a surface area per ton of paper basis, is added to the system.

Background and Theoretical

The first generation of a retention aid is papermakers alum, $\text{Al}_2(\text{SO}_4)_3$. At a slightly acidic pH, alum can hydrolyze to form an ionic polymer which serves as a retention aid. This aluminum polymer has a significant flocculation effect, which improves retention. The mechanism by which this occurs is bridging. The polymer bridges from particle to particle and thereby forming large flocs. Alum is very sensitive to changes in pH though. With many paper machines converting from acid paper making to neutral or alkaline paper making, alum is not as effective as a retention aid. Another down fall of alum is its poor floc strength. When the fibers, fillers, etc. are flocculated, these flocs are not very resistant to shear forces. Today's high speed machines have very high shear forces associated with them. This generally renders alum ineffective as a retention aid. Alum is still good for neutralizing the system though and even serves as a promoter in microparticle retention systems. Therefore, alum will be used in the paper industry for a long time to come.

The next generation of retention aid is single polymer systems. This system was designed specifically for retention improvements, unlike alum which was found to improve many things in the wet end of the paper machine. The single polymer system uses a cationically charged polymer. There are two mechanism by which these retention aids work, depending on the molecular weight of the polymer and the charge density. The first mechanism is bridging. The bridging mechanism uses a high molecular weight polymer with a low charge density. In the paper making process, the furnish is predominately anionic in charge. Therefore, when a cationic polymer is added to the system, it adsorbs onto the fibers and other anionic particles. Since a long chain polymer with low charge density is used, it loosely adsorbs to the surface of the particles. This allows for parts of the polymer to extend from the surface of the particle and attract other anionically charged particles, thus causing flocculation.

The second mechanism involved in single polymer systems is patching, which incorporates a low molecular weight polymer with high charge density. This type of

polymer adsorbs tightly to the surface of the anionic particle, essentially changing the local charge of the particle to a positive charge. These cationic “patches” attract anionic particles and form ionic bonds with them. It is important that the entire surface of the particles are not covered by the polymers or the retention aid will be rendered useless. This mechanism is not as effective as the bridging mechanism due to very weak flocs.

Single polymer systems are generally used on slower paper machines with lower shear forces. The flocs formed by these retention aids are not very strong. They are, however, stronger than the flocs formed by alum. The retention drops significantly when shear force is applied to the flocs. When the flocs undergo shear forces, the flocs breakup and do not reform very well. Generally, the flocs that do reform are formed by the patching mechanism. They are also not very sensitive to pH fluctuations either, which allows them to be used in acid, neutral, and alkaline paper making conditions.

The next generation of retention aids used is dual component or dual polymer. Dual component retention aids have been developed to give improved strength to the flocs, thus improving retention when higher shear forces are applied. These systems consist of a two step addition of polymers. First a cationic, low molecular weight polymer with high charge density is added. This bonds to the anionic particles in the furnish, effectively changing the local surface charge to positive. This is very much like the patching mechanism discussed earlier. An anionic, high molecular weight polymer with low charge density is then added to induce flocculation by forming bridges between cationic patches. This type of bonding between particles is stronger than the single polymer mechanism. Strong ionic bonds are formed at the site where the anionic polymer meets the cationic patch. These bonds are stronger than directly bonding a cationic polymer to the particle, as in the single polymer method.

As with single particle retention systems, the flocs formed are subjected to shear forces. While these flocs are initially quite strong and do exhibit a reformation of flocs after shear forces, they are considerable weaker than the original flocs. On high speed machines, the furnish is exposed to high shear forces as the web passes over each foil.

The bonds formed with single and dual polymer retention aids cannot withstand these forces and retention is lost.

The newest form of retention aid is the microparticle system. Microparticle retention aids work similar to dual polymer systems. First, a cationic polymer of high molecular weight and high charge density is added under low shear conditions. This allows the polymer to adsorb onto the surface of the fibers or particles (5). For optimum retention, the entire fiber and particle is covered (6). This changes the entire surface charge of the particles to cationic and effectively the entire system. After a short retention period, the paper furnish is put under high shear to break up any flocculation. Just prior to the headbox, the microparticle is added. The microparticle, most commonly bentonite or silica, is anionically charged and has a very high specific surface area. Allied Colloids makes a colloidal silica which has a surface area of $1200 \text{ m}^2/\text{g}$ (7). This high surface area gives the microparticle a very high charge density, which allows for more bonding sites with the cationic polymer added earlier. This produces very strong flocs, which have been found to reform very quickly after shear forces break them up (5). The flocs that reform are small and even stronger than the original flocs, which lead to excellent first-pass retention, formation, and drainage.

Figures 1 through 4 show the mechanisms of microparticle retention systems. Figure 1 shows the addition of the cationic polymer or cationic polyacrylamide (CPAM). In figure 2, large scale flocculation has occurred by the bridging mechanism. The flocs that form here are a good representation of what a single polymer system would look like. The large flocs can lead to poor formation though. Figure 3 shows the system after a shear field has been applied and the flocs are broken up. Finally, in figure 4, the anionic silica is added to the system and reflocculation occurs. The size of the flocs that form in this stage are much smaller and since silica particles are readily available in the system, the flocs will reform very quickly after shear is applied.



Fiber

Cationic polyacrylamide

Filler

Filler

Filler

Filler

Filler

Mechanism
#1 Addition of Cationic Polyacrylamide

EKA Chemicals



Figure 1



Fiber

Filler

Filler

Mechanism
#2 Bridging Flocculation

EKA Chemicals



Figure 2



Fiber

Filler

Filler

8

Mechanism
#3 Deflocculation and Redistribution
of Polymer

EKA Chemicals

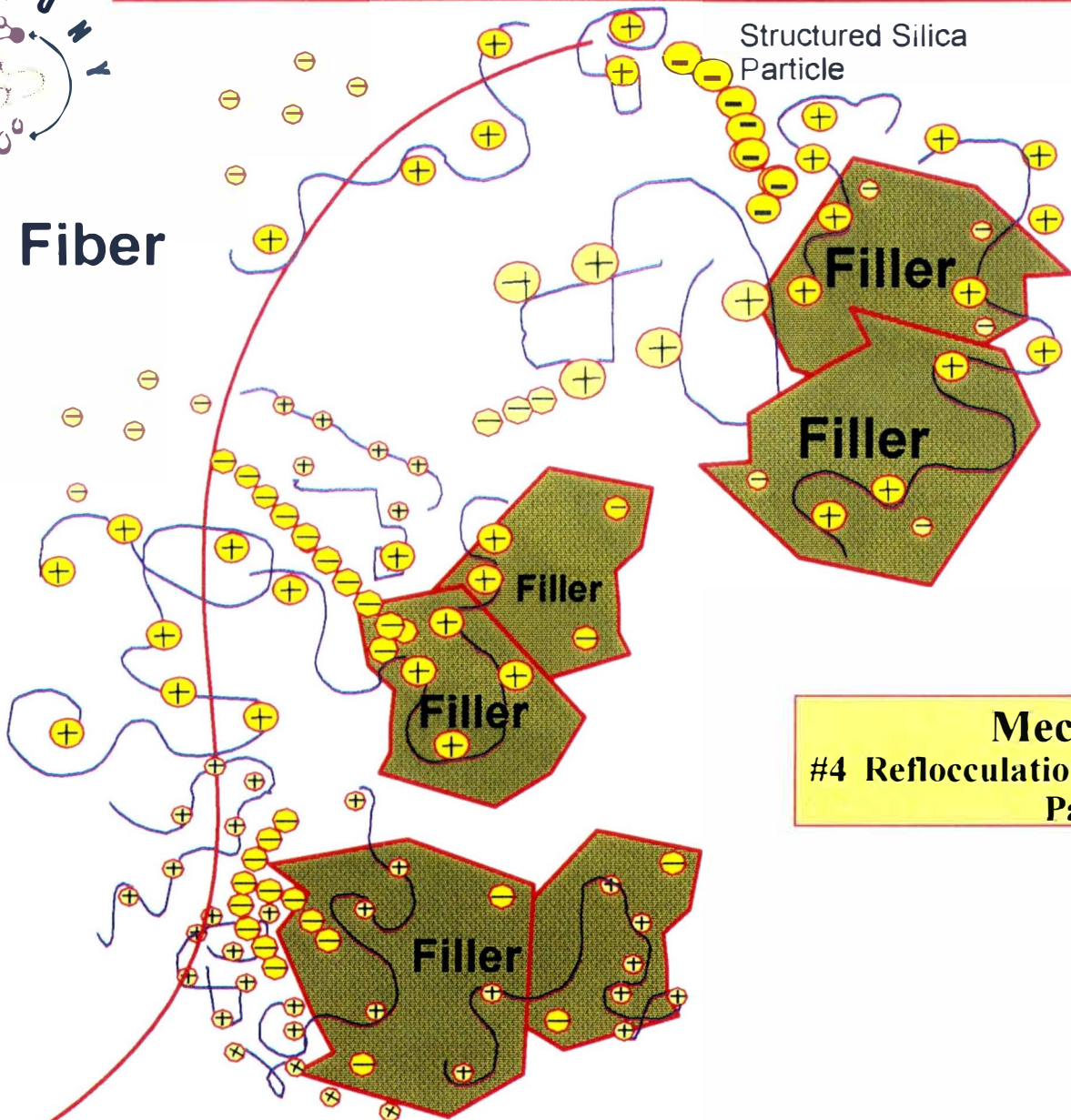


Figure 3



Fiber

Structured Silica Particle



Mechanism
#4 Reflocculation by Structured Silica Particle

EKA Chemicals



Figure 4

Experimental Procedures

Experimental Design

A two level, three variable factorial design was used in the design of the thesis.

The variables include surface area of silica, addition rate or dosage of silica on a surface area per ton of paper basis, and finally polymer dosage. Table 2 shows the variables and the dosage rates that apply to each. Table 2 also shows the runs necessary to cover every variable in the experiment.

| Trial Design to Measure the Effects of Silica Surface Area | | | |
|---|-------------------|-------------------|--|
| Variable | Low(-) | High(+) | |
| Type of Silica (T) | 500 m^2/g | 1200 m^2/g | |
| Target Surface Area (S) | 100,000 m^2/ton | 400,000 m^2/ton | |
| Dosage of Polyacrylamide (P) | 0.5 lb/ton | 1.0 lb/ton | |

| Run # | Variables | | |
|--------------|------------------|-----------------------|------------------|
| | (T)ype | (S)urface area | (P)olymer |
| 1 | - | - | - |
| 2 | + | - | - |
| 3 | - | + | - |
| 4 | + | + | - |
| 5 | - | - | + |
| 6 | + | - | + |
| 7 | - | + | + |
| 8 | + | + | + |

Table 2

The runs were run in triplicate to give repeatability. This allows a significant amount of statistical analysis to be done on the data. The interactions between the variables are easily interpreted. Figure 5 gives a graphical representation of the factorial design. The interactions can be visualized by drawing a plane between two sides. For example, the interaction between microparticle surface area dosage and microparticle type would be the plane 1-2-3-4.

2³ Factorial Design

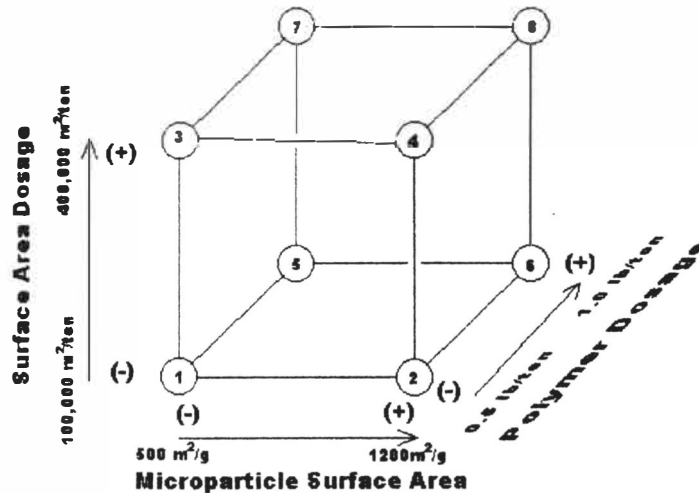


Figure 5

All drainage test were carried out in the Britt Dynamic Drainage Jar. Two different stocks were chosen for this experiment, the first is a fine paper grade stock and the second is a wood-containing grade.

Materials

Furnish 1. Below is a list of materials, which make up the fine paper grade stock.

| Fine Paper Grade Makedown | | |
|---------------------------|----------|----------------|
| Composition | Material | Freeness (csf) |
| 80% | Hardwood | 350 – 400 |
| 20% | Softwood | 350 – 400 |
| 15% | PCC | |
| 2 lb./ton | AKD | |

Table 3

The hardwood pulp used in this experiment is fully bleached kraft dry-lap pulp and the softwood is fully bleached kraft dry-lap pulp. The dry pulp will be disintegrated and beaten, separately, according to TAPPI standard T-200 to a Canadian Standard Freeness of 350 – 400 csf. The two pulps were then combined to give the 80/20 hardwood to softwood ratio. Filler, precipitated calcium carbonate (PCC) at 15%

solids, was then base loaded to the furnish to a filler concentration of 15% on total solids. The furnish was then diluted down to 0.5% consistency. AKD, supplied by Eka Chemicals under the name Keydime C222, was then added to the furnish at a dosage of 2 lb./ton. The furnish was kept under constant agitation using a Lightning mixer. This type of furnish was chosen to simulate the typical fine-paper furnish used in the United States (8).

Furnish 2. In table 4 below is a list of materials, which make up the wood containing grade stock (9).

| Wood Containing Grade Makedown | | |
|---------------------------------------|-----------------|-----------------------|
| Composition | Material | Freeness (csf) |
| 50% | Groundwood | 115 |
| 40% | Hardwood | 350 – 400 |
| 10% | Softwood | 350 – 400 |
| 10% | Calcined Clay | |
| 15 lb./ton | Wet End Starch | |
| ~20lb./ton | Alum | |

Table 4

The groundwood used in this experiment was recycled newsprint supplied by Western Michigan University. The newsprint was recycled in the pilot plants Black Clawson Hydrapulper. The stock was then run through the forward cleaners in the pilot plant. No further modifications were made to the stock. The freeness was 115 csf. The hardwood and softwood stock was taken from the batch prepared above in furnish 1. The appropriate amounts of each stock was taken to obtain the percent composition of the final furnish mentioned in the table above. The furnish was then diluted down to 0.5% consistency and agitated with a Lightning mixer. Dry calcined clay was then added to the furnish under high shear for several minutes and then

returned to normal agitation. Next, HICAT 543 potato/corn starch was added to the mixture. The procedure for cooking the starch can be found in appendix 1. Finally alum was added to bring the pH of the stock down to 5.0.

Cationic polymer. A medium charge density, medium molecular weight cationic polyacrylamide (CPAM), supplied by Allied Colloids under the name Percol 175, was used as the polymer in this study. The order of addition of the polymer, as well as the microparticle will be discussed below in the retention measurements section. This polymer was chosen to represent the average charge density and molecular weight polymer used in microparticle retention system in the United States (10). Some mills use a low, medium, or high charge density CPAM, depending on what they find works best for there particular mill (10).

Microparticle. Anionic silica was used as the microparticle in this thesis. Two different types of silica will be used. The first, supplied by Eka Chemicals called BMA-0, had a surface area of $500\text{m}^2/\text{g}$ and the second, supplied by Allied Colloids under the name Particol, will have a surface area of $1200\text{m}^2/\text{g}$.

It should be noted that the furnishes were made up immediately before the experimentation was done. The stock should sit for no longer than 2 hours (10).

Retention Measurements

Britt Jar. Retention measurements was carried out in a "Britt Dynamic Drainage Jar" (BDDJ) with the RPM set at 800. The steel screen to be used will have a mesh number of 200. Table 5 shows the variables of this experiment and what sequence they should be done in. The following table gives a time line of the procedure for running a sample.

| Addition Sequence | | | | |
|--------------------------|------------------------|----------------|----------------------|----------------------|
| Time[sec] | 0 | 20 | 30 | 40 |
| Operation | Add 500 mL Of stock | Add Polymer | Add Microparticle | Take 100mL Sample |

Table 5

A 100 mL sample will be collected in a volumetric flask. The remaining stock will be discarded and the BDDJ will be disassembled and thoroughly cleaned, especially the screen. This will be repeated for the remaining runs with the appropriate dosages of polymer and microparticle.

First-pass retention and first-pass ash retention. The 100mL samples will be filtered through a pre-weighed Watman 142 slow drain ashless filter pad. The pad will then be placed in the oven at 105°C for approximately 24 hours. After drying, the pad will be weighed and percent solids retained will be calculated. The dried pad will then be “ashed” according to TAPPI standard T-211 for PCC and T-413 for clay. The percent ash will then be calculated. From this data, the first-pass retention and first-pass ash retention can be calculated.

Results Presentation

The raw data for this experiment can be found in appendix 3 at the end of this report. In table 6 below, an average of the three runs for furnish 1 is given.

| Furnish 1 Results - Average of Three Runs | | | | | | |
|--|------------------------|-------------------|--------------------|----------------|---------------------|--------------------|
| Condition Number | Wt. Solids Retained(g) | % Fines Retention | Standard Deviation | S ² | Wt. Ash Retained(g) | Standard Deviation |
| 1 | 0.022 | 65.6 | 10.01 | 100.19724 | 0.0083 | 0.0069 |
| 2 | 0.028 | 57.4 | 9.01 | 81.26233 | 0.0131 | 0.0029 |
| 3 | 0.034 | 47.2 | 6.22 | 38.65878 | 0.0143 | 0.0027 |
| 4 | 0.020 | 69.7 | 11.34 | 128.59961 | 0.0111 | 0.0018 |
| 5 | 0.017 | 74.4 | 3.87 | 14.99014 | 0.0082 | 0.0003 |
| 6 | 0.018 | 72.8 | 6.22 | 38.65878 | 0.0065 | 0.0009 |
| 7 | 0.016 | 75.4 | 3.08 | 9.46746 | 0.0046 | 0.0020 |
| 8 | 0.013 | 80.0 | 1.54 | 2.36686 | 0.0046 | 0.0013 |
| Base Run | 0.083 | 27.2 | 0.09 | | 0.0609 | 0.0006 |

Table 6

The condition number corresponds to the conditions listed in table 2 and figure 5. In figure 6, the results are incorporated into the graphical representation of the factorial design for easier analysis.

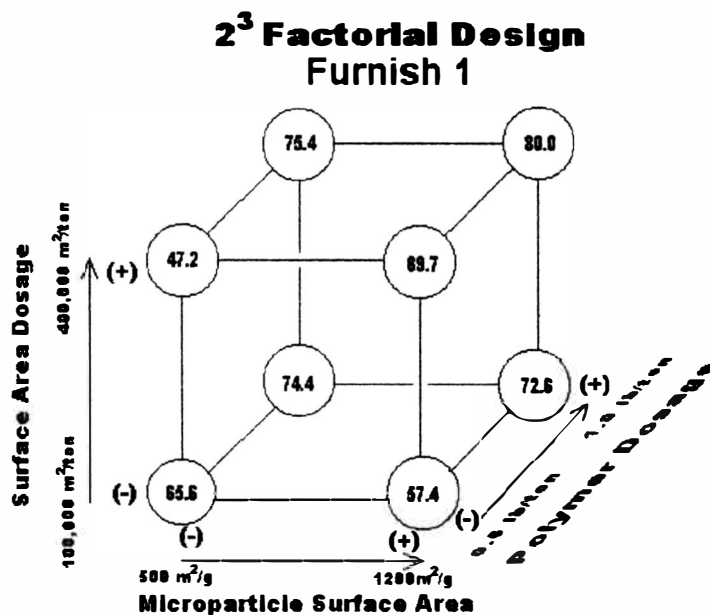


Figure 6

In table 7, the effects of each component are given. These results are calculated using standard equations given for analyzing factorial designed trials (10).

| Furnish 1 Main Effects - % Fines Retention | | | | | | | |
|---|-----------------|-----------------|-----------------|------------------|------------------|------------------|-------------------|
| <u>Mean</u> | <u>I</u> | <u>S</u> | <u>P</u> | <u>TS</u> | <u>TP</u> | <u>SP</u> | <u>TSP</u> |
| 67.8 | 4.36 | 0.513 | 15.6 | 9.23 | -2.82 | 3.59 | -6.15 |
| S ² =51.77514793 | | | | | | | |
| Standard error =12.9 | | | | | | | |

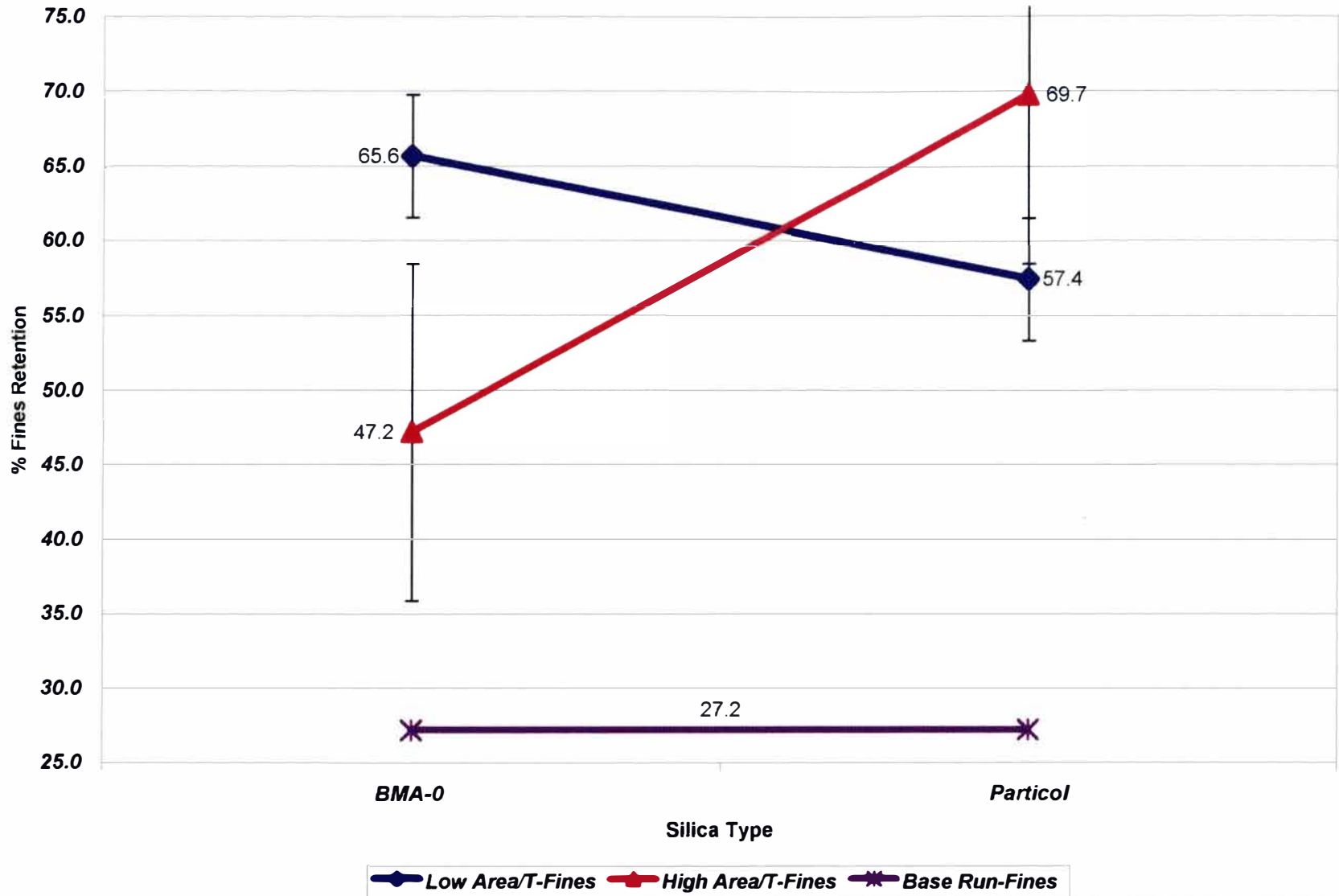
Table 7

Each of the letters represent the variables in the experiment given in table 2. For example, **TSP** would mean the interaction between the **Type** of silica, **Surface area** dosage, and **Polymer dosage**, respectively.

Figures 7 and 8 show the effects of microparticle surface area on percent fines retention at low and high polymer dosages, respectively.

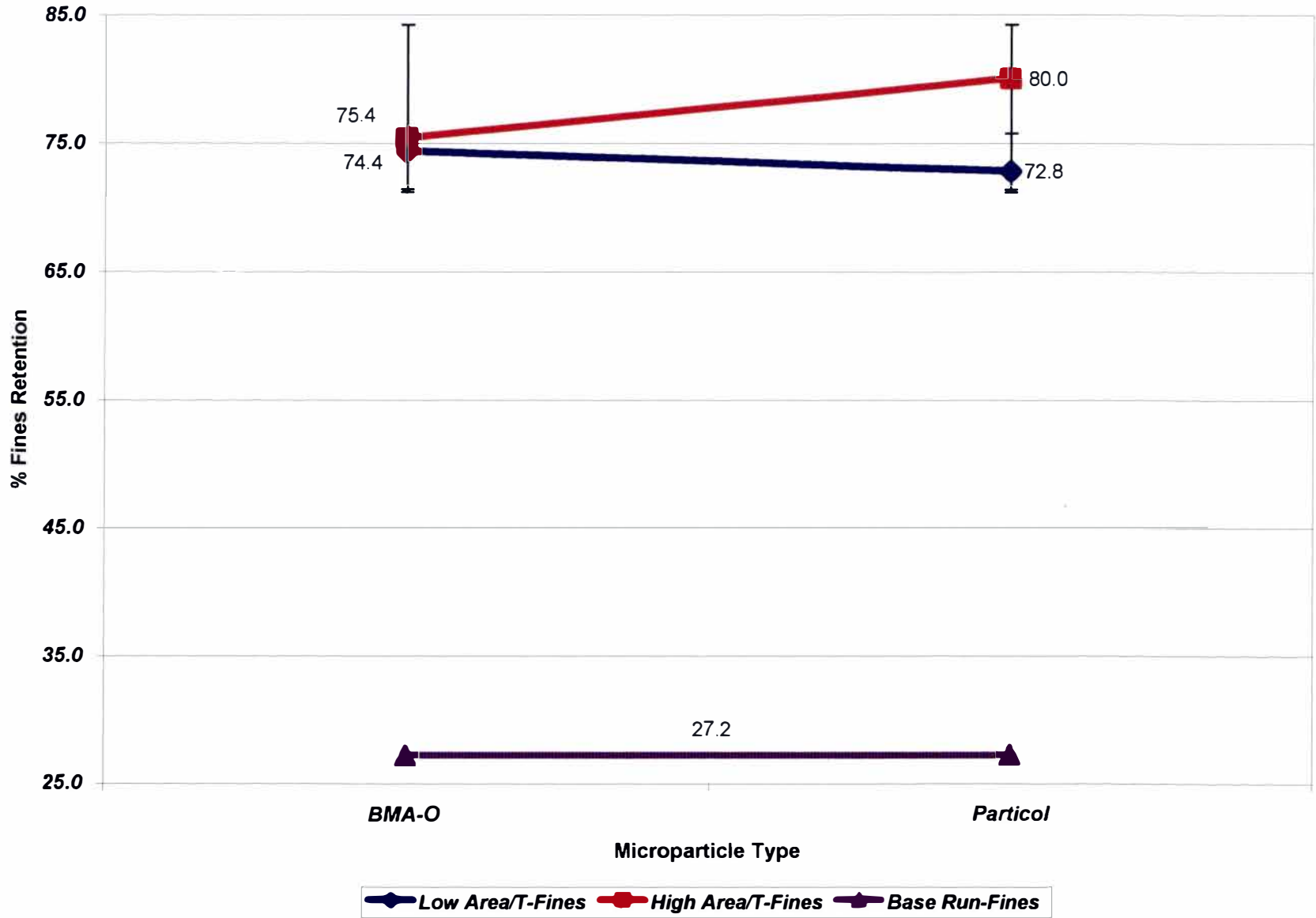
The Effect of Silica Type on % Fines Retention

Furnish 1 - Low Polymer Dosage



The Effect of Silica Type on % Fines Retention

Furnish 1 - High Polymer Dosage



18

Figure 8

The same format for the presentation of results can be found in the following tables and figures for furnish 2.

| Furnish 2 - Average of Three Runs | | | | | | |
|-----------------------------------|---------------------|-------------------|--------------------|----------------|------------------|--------------------|
| Condition Number | Wt. Solids Retained | % Fines Retention | Standard Deviation | S ² | Wt. Ash Retained | Standard Deviation |
| 1 | 0.028 | 79.3 | 0.74 | 0.5487 | 0.0877 | 0.1187 |
| 2 | 0.027 | 79.8 | 1.86 | 3.4751 | 0.0234 | 0.0031 |
| 3 | 0.020 | 85.2 | 1.96 | 3.8409 | 0.0240 | 0.0038 |
| 4 | 0.018 | 86.4 | 2.60 | 6.7673 | 0.0211 | 0.0027 |
| 5 | 0.014 | 89.6 | 1.48 | 2.1948 | 0.0203 | 0.0050 |
| 6 | 0.015 | 88.9 | 2.67 | 7.1331 | 0.0178 | 0.0095 |
| 7 | 0.014 | 89.4 | 2.60 | 6.7673 | 0.0197 | 0.0054 |
| 8 | 0.015 | 88.6 | 1.54 | 2.3777 | 0.0203 | 0.0032 |
| Base | 0.055 | 59.0 | 0.01 | | 0.0413 | 0.0012 |

Table 8

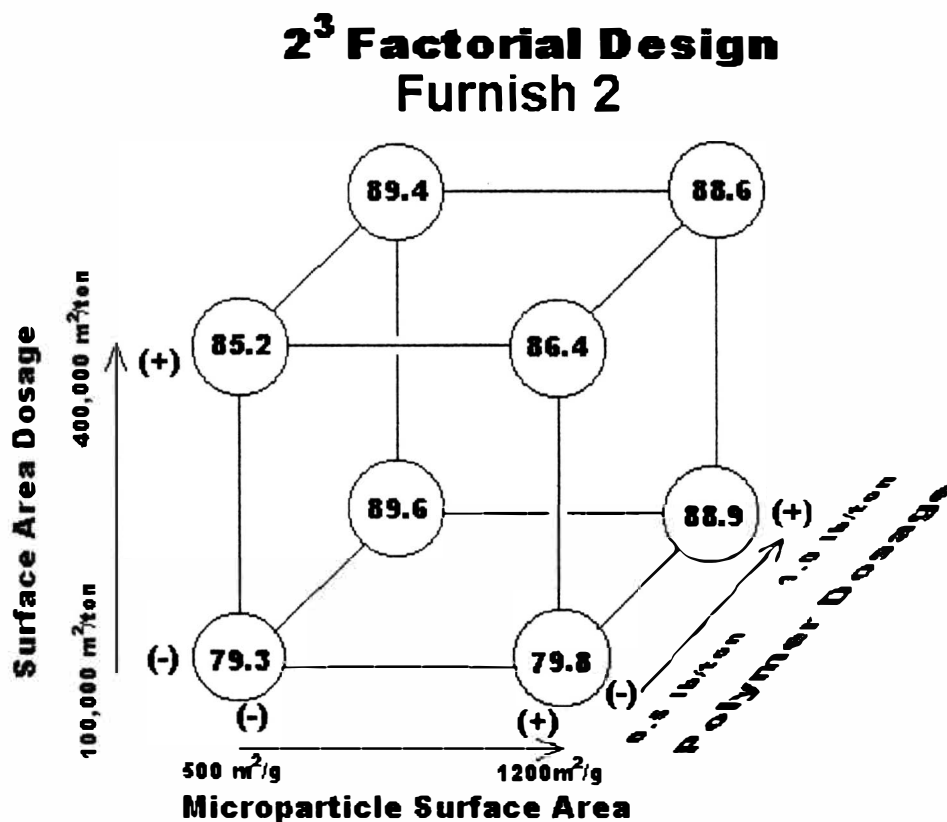


Figure 9

| Furnish 2 Main Effects - % Fines Retention | | | | | | | | |
|--|----------|----------|----------|-----------|-----------|-----------|------------|--|
| <u>Mean</u> | <u>I</u> | <u>S</u> | <u>P</u> | <u>TS</u> | <u>TP</u> | <u>SP</u> | <u>TSP</u> | |
| 85.9 | 0.0617 | 3.02 | 6.48 | 0.185 | -0.802 | -3.27 | -0.185 | |
| S ² =4.138088706 | | | | | | | | |
| Standard Error=1.03 | | | | | | | | |

Table 9

Figures 10 and 11 can be found on the following pages. In figure 12, the interaction between surface area dosage and polymer dosage is shown graphically.

Furnish 2 - % Fines Retention Microparticle dosage/Polymer dosage interaction

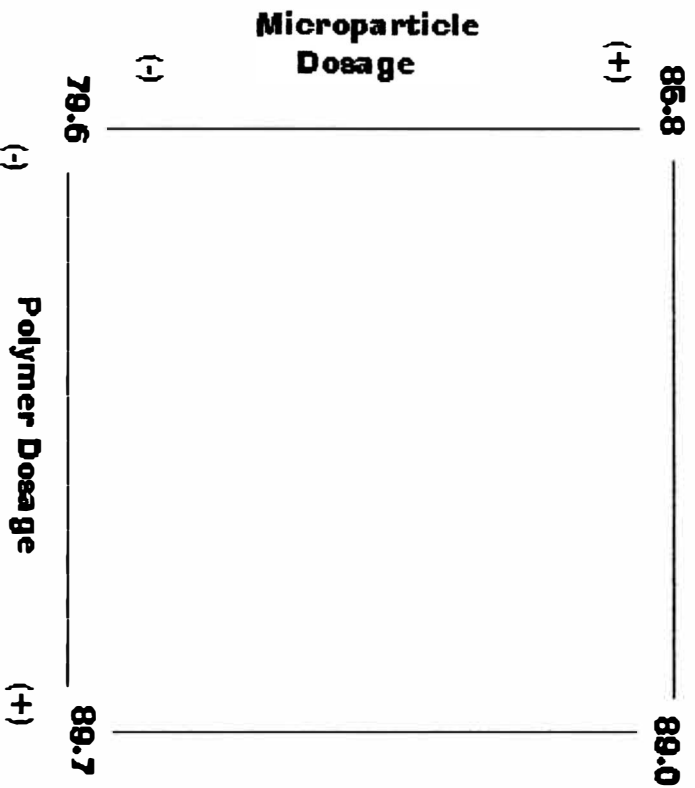
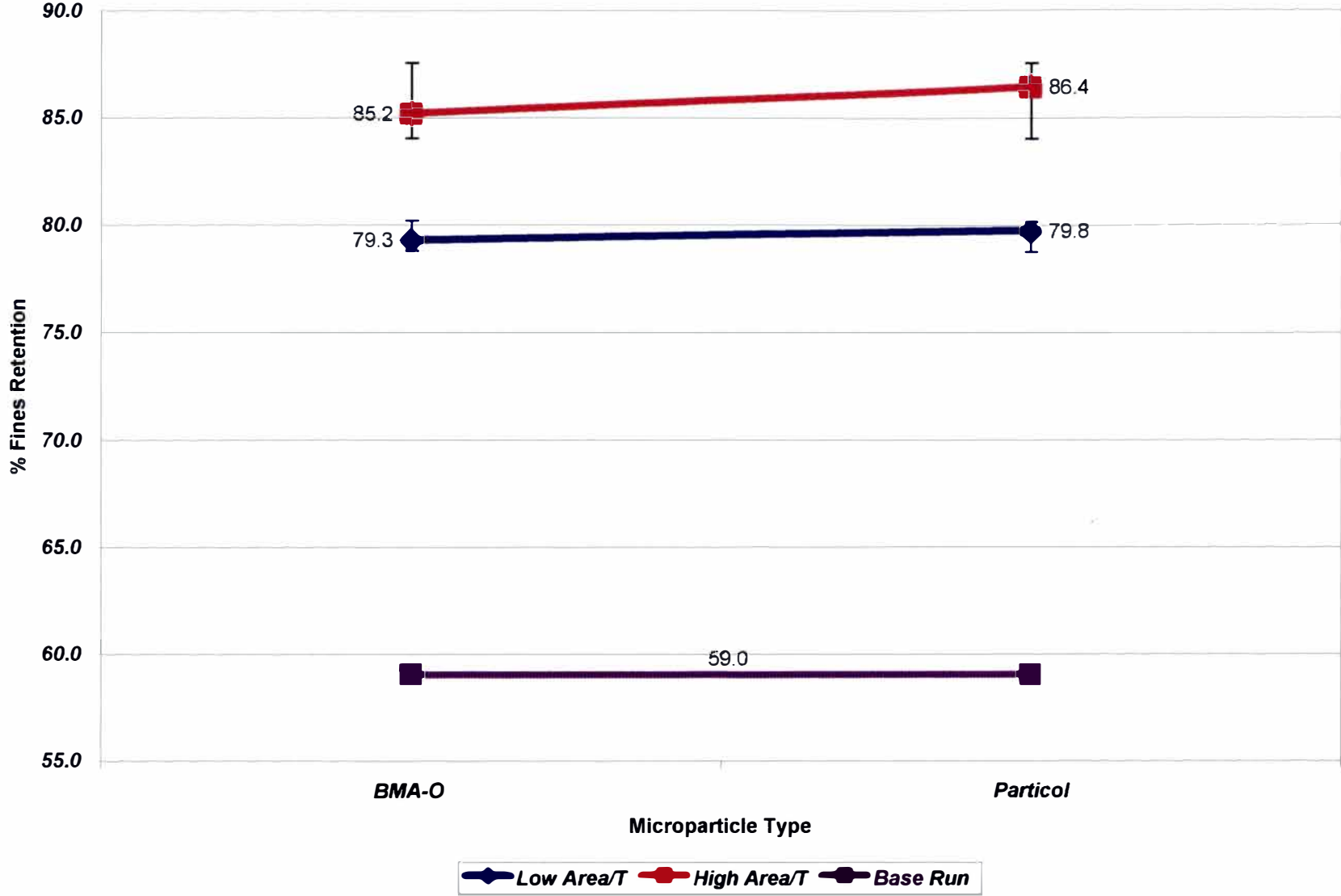


Figure 12

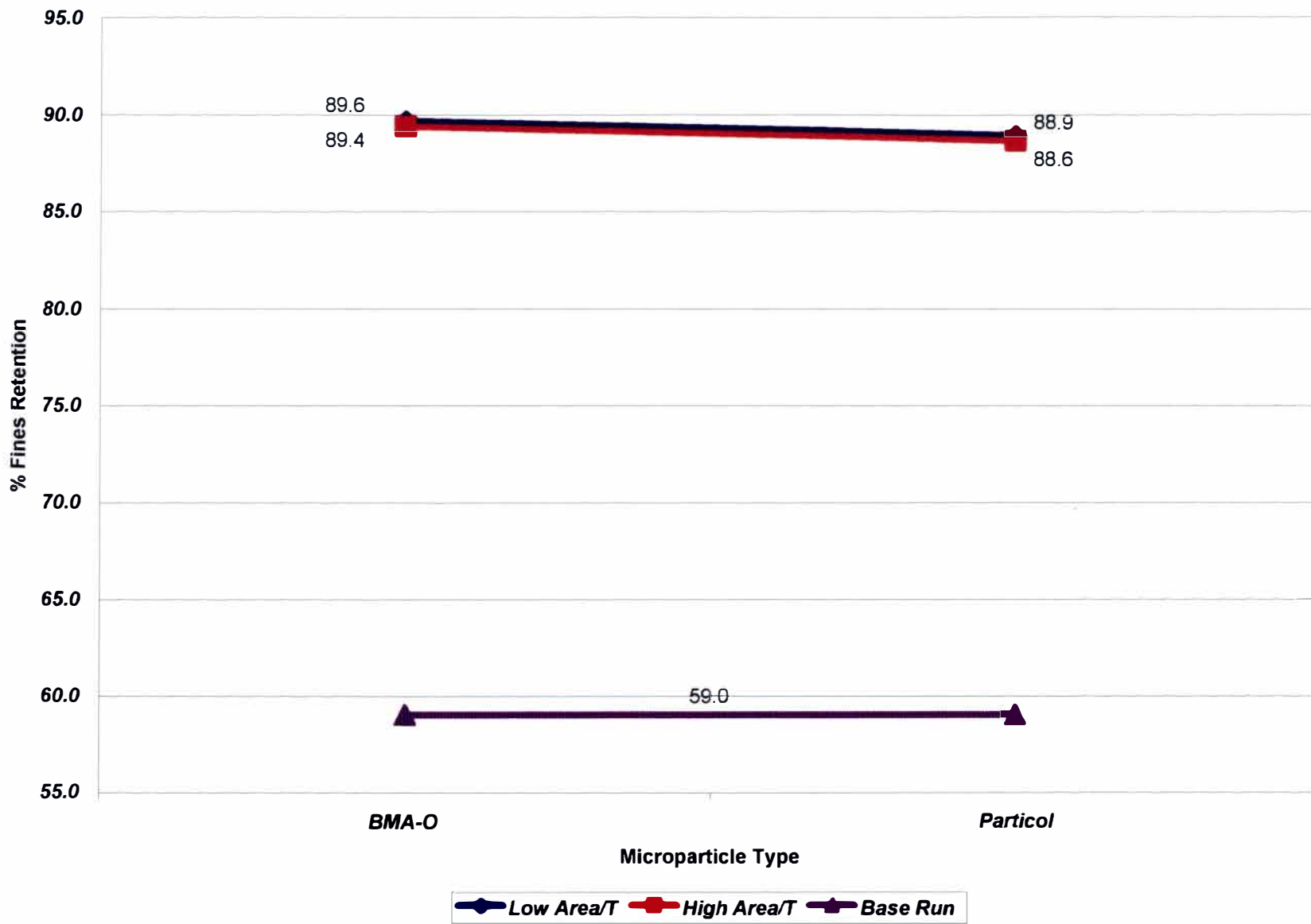
The Effect of Silica Type on % Fines Retention

Furnish 2 - Low Polymer Dosage



The Effect of Silica Type on % Fines Retention

Furnish 2 - High Polymer Dosage



Discussion of Results

Furnish 1

Furnish 1 showed high variation for both percent fines retention and ash retention. The variability in the system was very high. In table 7, the effects of each variable are given, as well as the standard error. If the standard error is larger than the quantity of the effect, the effect cannot be considered statistically significant. If the standard error is smaller than the quantity of the effect, the effect is considered to have an effect on the system and this can be proven statistically. For furnish 1, the standard error was extremely large, which means the variability in the system was large. The standard error for furnish 1 was 12.9. Since this is larger than all the effects except polymer dosage, the only conclusive effect for this system is the polymer dosage. The polymer dosage did have a large effect on the system. When it was added to the BDDJ, flocculation could be seen.

Figures 7 and 8 show the effects of varying the surface area of the microparticle on percent fines retention. The blue line represents a low surface area dosage, while the red line is high surface area dosage. Notice how the error bars overlap. This indicates high variability in the system. The results did not follow the expected trends. According to the hypothesis stated in the introduction, the lines should be parallel to the x-axis. The red line or high surface area dosage should be skewed up from the low surface area dosage. Instead, the low surface area dosage decreased upon addition of the high surface area microparticle while the other increased. This is a further indication of variability in the system. There should be some trend, whether it be up or down, both of the lines should follow the same trend.

Figure 8 showed somewhat better results. The change in retention did not increase or decrease more than 6.1%. This supports the hypothesis that the surface area dosage is the controlling factor and not the surface area of the microparticle. This cannot be supported statistically though and it must be considered to have some randomness to the results.

Possible sources of error for furnish 1 are most likely due to operator error. Due to lack of experience using the BDDJ, many possible errors could have occurred. For example, inconsistent timing on the addition of the polymer and microparticle would cause inaccurate results without any kind of trend in the results. The ash results had to be disregarded as well. Two of the three repeats were lost during ashing. The procedures were not followed precisely. Caps were not put on the crucibles after heating and placing in the desiccator. A vacuum had been created within the desiccator and when the lid was removed, the ash went flying all over.

Other sources of variability could be due to the furnish. It is difficult to say with this amount of data, but this type of variability could be inherent with fine paper furnish in a laboratory setting.

Furnish 2

Furnish 2 showed much better results than furnish 1. The variability in the system was dramatically reduced in this furnish. As with furnish 1, the ash retention has been omitted from the discussion. For some unknown reason, the weight of the ash was higher after being ashed in the furnace than the weight of the solids added. This can be seen in table 8 and in the raw data in appendix 3. The weight of the ash was consistently higher than the weight of the solids added, therefore an error in the

preparation of the crucibles is most likely the cause. TAPPI procedure T-413 was followed exactly though (even the crucible caps).

When looking at table 9, the standard error for furnish 2 is 1.03. Following the same procedure as in furnish 1, it can be said that the type of microparticle (surface area of microparticle) had no significant effect on the system. This is different than for furnish 1. In furnish 1, the standard error was so large that almost all of the effects were disregarded. In furnish 2 though, the error is low and when something is found not to have an effect on the system, it must be analyzed. The effect of the type of microparticle is 0.0617, but the effects of the surface area dosage and polymer dosage are 3.02 and 6.48, respectively. This means the surface area and polymer dosage are controlling the retention and not the type of microparticle used, which is what the hypothesis states.

Figure 10 shows this relationship graphically. The low surface area dosage is lower than the high surface area, but it is almost parallel to both the x-axis and the high surface area dosage. When going from BMA-0 (low surface area microparticle) to Particol (high surface area microparticle), the change in retention is less than the standard error of 1.03. Therefore, this change in retention is cannot be considered to be solely due to the change in microparticle, but also to variability in the system. Figure 11 supports this somewhat, but there is not effect of surface area dosage on retention.

Referring back to table 9, there is a significant interaction between the surface area and the polymer dosage (labeled SP). Figure 12 shows this relationship as related back to the factorial design. It can be seen that the microparticle dosage has an effect at low polymer dosage, but not at high polymer dosage. This could be due to the

polymer over powering the system and causing too much flocculation at high polymer levels. This system was not run under high shear conditions, which may have allowed the polymer to create flocs that were strong enough to withstand the shear forces being applied.

Summary of Results

Furnish 1

1. Polymer dosage was the largest and only effect that was statistically significant.
2. Variability in the system was extremely high, therefore many of the effects of the variables had to be dismissed as random.

Furnish 2

1. Polymer dosage was had the largest effect on the retention of fines.
2. Microparticle surface area had no significant effect on the retention of fines.
3. Surface area dosage showed a significant effect on the retention of fines.
4. At high polymer dosage, surface area dosage showed no significant effect on the retention of fines.

Conclusions

The following conclusions are based on furnish 2 due to the extremely high variability in furnish 1. In addition, these conclusions may not hold to be true under higher shear conditions found on high speed paper machines.

Polymer dosage was found to have the largest effect on the retention of fines. The retention increased as much as 12.7% when the polymer dosage was increased from 0.5 lb/ton to 1.0 lb/ton and the other variables were held constant.

Surface area dosage had an effect on the retention of fines at low polymer dosage. As the surface area dosage was increased, the retention increased by 7.8%. This supports one of the goals of this thesis, which was to verify that increasing surface area dosages would increase retention. The surface area dosage did not have a significant effect on the retention of fines at high polymer dosage though. This is believed to be due to the polymer over flocculating the system and creating flocs that are strong enough to resist the shear forces applied by the BDDJ at 800 RPM.

The final and most important conclusion is the effect of microparticle surface area on the retention of fines. The analysis of the factorial design shows that the surface area of the microparticle had no significant effect on the retention. This was the main hypothesis for this thesis. This means that a low surface area microparticle can give the same retention as a high surface area microparticle, but a higher dosage rate must be applied.

Many chemical suppliers pride themselves on the high surface area of there microparticle and the improved performance it offers. The results of this thesis show that this may not be exactly true. The dosage needed to get the same retention with a

high surface area microparticle may be less, but not necessarily improved performance. If retention could be measured as a function of surface area added to the system per ton of paper, a mill could determine what is the most economical microparticle to use. For example, a supplier could supply a low surface area microparticle at a very low price, while the another supplier is offering a high surface area microparticle at an extremely high price. The mill would have to use a lot more of the low surface area microparticle to get the retention they want, but it still may be more economical.

Recommendations

Below is a list of recommendations based on the results gained from this thesis.

1. Furnish 1 should be rerun to reduce the variability of the system. The results should then be compared to furnish 2 to see if similar results are found. Having to different furnishes with the same results would give added strength to the current results. It may also be necessary to develop other furnishes and run the experiment on them as well to reinforce the conclusions made in this thesis.
2. Study the interaction between surface area dosage and polymer dosage to find out why surface area dosage does not have an effect at high polymer dosage. An optimum dosage of each may be obtained in the analysis.

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Appendix I

LABORATORY COOKING OF BMB STARCHES

Equipment Requirements

Glass Beaker: 1 liter or smaller

Magnetic stirring / hot plate

Thermometer

Teflon Coated magnetic spinbar

Weigh out the required amount of starch for a 1% solution. If moisture content is unknown, use an oven dried sample.

Preweigh the 1L, or smaller, beaker then pour the required volume of water into the beaker. Distilled or deionized is recommended if possible.

Set the magnetic stirrer at a high speed then pour the starch into the side of the vortex created by the spinner. Increase the stirrer speed as necessary to compensate for any increase in viscosity. Turn on the heater to high.

Insert the thermometer into the beaker and cover with a watch glass or aluminum foil to prevent evaporation.

Reduce the temperature of the hot plate as necessary so as to stop the temperature of the solution at 95°C. Cook at 95°C for 20 min. DO NOT ALLOW TO BOIL.

After 20 min. remove starch from hot plate and allow to cool. The beaker can be submerged in water to cool down, but be careful not to temperature shock it or it will break.

Once cool, check the weight and adjust with distilled or deionized water if required. Pour the solution into a plastic beaker and mix (to ensure the water used for weight adjustment is mixed in).

This solution can be refrigerated and used up to 4 days if necessary.

PAM POLYMER MAKE DOWN PROCEDURES

In the past most people made down polymers by adding neat solution to water inside a Nalgene bottle and shaking. This is, by far, the simplest method there is and only a balance is required. Unfortunately, because the solid polymer is contained in a droplet of oil-based carrier solution, shaking does not release all of the polymer chains. The result is that each time you perform the procedure not only do you take the chance of “gel balls” forming, you may actually have a different content of active polymer for each make down. Patrik Simonson (in Sweden) has determined that for the best, most consistent results, **high shear forces for short periods of time are needed** to “break” the polymer emulsion and result in a smooth, well dissolved, high viscosity PAM.

In light of this, we have developed two options for polymer make down, both consistent with methods used overseas differing only in the way the person measures the PAM emulsion. The first uses gravimetric measuring where as the second uses volummetric. Gravimetric will take a little longer and be more precise, where as volummetric will save the most time and be the easiest to use in the field.

Apparatus required is a stirrer that uses a controller with RPM readout (analog or digital); Beakers, graduated cylinders and syringes (and possibly a balance) will also be required. Be careful, we found that some lab mixers don't get up to 1500 RPM. If you're using that type, turn the RPM setting to the highest level and let your solution mix for longer than 1 minute. The best setup is a DDJ stirrer, with controller, mounted on a ringstand. This will give you the ability to adjust the stirrer to the best height for maximum shear (which might not be achieved using the Britt jar stand). Using the DDJ jar in conjunction with the DDJ stirrer will not produce enough shear on polymer near the outer wall, however for large quantities (over 500 ml), with the screen removed and with a wide-bladed stirring apparatus use of the jar may be possible (make sure the finished product is uniform in smoothness and viscosity). If for some reason you don't have the required equipment, as last resort use the shaking method for make down.

In lab testing, we found that best results were achieved when making 250 ml of “strong” solution in a 600 ml beaker then making a 100 ml 0.1% solution in a 250 ml beaker.

Gravimetric Make Down

(Refer to Table 1)

- * Based on SOLIDS calculate for a 0.5% (Strong) solution of PAM.
- * Weigh the correct amount of water needed into a beaker.
- * Zero a balance with a syringe on it, with approximately the right amount of emulsion.

Appendix II - 2

- * Using a DDJ (or like) stirrer set at 1500 RPM, add the emulsion quickly into the vortex and stir for 1 min.
- * Reweigh the syringe to determine the amount of emulsion delivered.

From this 0.5% solution further dilution is required for the recommended 0.1% solution.

- * Once you have calculated the actual concentration of your strong solution,

When Calculating for X

$$100 / (\% \text{ solids}) * X = \text{Amount delivered or (RP-96) } 100 / (29) * (X) = 15.60$$
$$X = 4.52 \text{ g/L or } 0.45\% \text{ solution}$$

recalculate the amount of 0.5% solution needed to achieve a 0.1% solution.

| | | | | | |
|-------------------------|-----|----|------------|-----------|-----------------|
| <u>Ml's of solution</u> | X | or | <u>100</u> | X | = 0.45 (X) = 10 |
| % solutions | 0.1 | | 0.45 = .1 | X=22.2 g, | dilute to 100 g |

- * Weigh out the amount of water and PAM solution necessary into a beaker.
- * Stir for 20 min (10 min. for anionic PAMs) at 500 RPM

Volumetric Make Down

(Refer to table 1)

- * Based on SOLIDS calculate for a 0.5% (Strong) solution of PAM.
- * Using a Graduated Cylinder (beakers leave too much room for error), measure the correct amount of water needed.
- * Draw out the amount of emulsion needed using a syringe.
- * Using a DDJ (or like) stirrer set at 1500 RPM, add the emulsion quickly into the vortex and stir for 1 min.
- * Once complete using a dilution factor 1:4, weigh out (or use a cylinder and syringe) the amount of water and PAM solution necessary into a beaker.
- * Stir for 20 min (10 min. for anionic PAMs) at 500 RPM.

NOTE:

For dry PAMs heavy stirring is needed for 2 - 3 min. then use 500 RPM for 30 min. If you are doing comparison testing with dry and emulsion PAMs, USE THE GRAVIMETRIC METHOD, since weight is used for dry PAM calculation.

Appendix III - 1

Furnish 1 - Raw Data

| Run # | Wt. Pad+Solids | Wt. Pad | Wt. Solids | %Fines Retention | Wt. Crucible+Ash | Wt. Crucible | Wt. Ash |
|-------|----------------|---------|------------|------------------|------------------------|--------------|---------|
| 1-1 | 0.575 | 0.559 | 0.016 | 75.4 | 54.7003 | 54.6872 | 0.0131 |
| 1-2 | 0.607 | 0.575 | 0.032 | 50.8 | 53.3909 | 53.3796 | 0.0113 |
| 1-3 | 0.591 | 0.553 | 0.038 | 41.5 | 56.0541 | 56.0422 | 0.0119 |
| 1-4 | 0.561 | 0.547 | 0.014 | 78.5 | 53.6982 | 53.6874 | 0.0108 |
| 1-5 | 0.562 | 0.545 | 0.017 | 73.8 | 57.9489 | 57.9409 | 0.008 |
| 1-6 | 0.595 | 0.573 | 0.022 | 66.2 | 51.6083 | 51.6013 | 0.007 |
| 1-7 | 0.561 | 0.545 | 0.016 | 75.4 | 56.7789 | 56.7764 | 0.0025 |
| 1-8 | 0.564 | 0.551 | 0.013 | 80.0 | 55.3327 | 55.329 | 0.0037 |
| 2-1 | 0.581 | 0.559 | 0.022 | 66.2 | Lost ash due to vacuum | 51.9281 | |
| 2-2 | 0.601 | 0.580 | 0.021 | 67.7 | 53.905 | 53.8935 | 0.0115 |
| 2-3 | 0.594 | 0.564 | 0.03 | 53.8 | 53.4167 | 53.4029 | 0.0138 |
| 2-4 | 0.583 | 0.555 | 0.028 | 56.9 | 66.196 | 66.183 | 0.013 |
| 2-5 | 0.578 | 0.564 | 0.014 | 78.5 | Lost ash due to vacuum | 52.589 | |
| 2-6 | 0.589 | 0.575 | 0.014 | 78.5 | 54.5227 | 54.5172 | 0.0055 |
| 2-7 | 0.578 | 0.564 | 0.014 | 78.5 | 54.2247 | 54.22 | 0.0047 |
| 2-8 | 0.56 | 0.548 | 0.012 | 81.5 | 50.5084 | 50.5045 | 0.0039 |
| 7-1 | 0.594 | 0.565 | 0.029 | 55.4 | 56.3243 | 56.3209 | 0.0034 |
| 7-2 | 0.592 | 0.562 | 0.03 | 53.8 | 57.7681 | 57.7517 | 0.0164 |
| 7-3 | 0.592 | 0.557 | 0.035 | 46.2 | 58.2848 | 58.2675 | 0.0173 |
| 7-4 | 0.554 | 0.537 | 0.017 | 73.8 | 54.2761 | 54.2666 | 0.0095 |
| 7-5 | 0.574 | 0.555 | 0.019 | 70.8 | 52.6965 | 52.6881 | 0.0084 |
| 7-6 | 0.577 | 0.560 | 0.017 | 73.8 | 52.5779 | 52.5709 | 0.007 |
| 7-7 | 0.587 | 0.569 | 0.018 | 72.3 | 58.442 | 58.4355 | 0.0065 |
| 7-8 | 0.569 | 0.555 | 0.014 | 78.5 | 57.399 | 57.3929 | 0.0061 |

Base Runs

| Run # | Wt. Pad+Solids | Wt. Pad | Wt. Solids | % Fines Retention | Wt. Crucible+Ash | Wt. Crucible | Wt. Ash |
|-------|----------------|---------|--------------|-------------------|------------------------|--------------|---------------|
| 5-1 | 0.655 | 0.567 | 0.088 | 35% | Lost ash due to vacuum | 53.7597 | |
| 5-2 | 0.649 | 0.565 | 0.084 | 29% | 53.6554 | 53.5949 | 0.0605 |
| 5-3 | 0.661 | 0.585 | 0.076 | 17% | 50.1477 | 50.0863 | 0.0614 |

Fines Fraction

| Run # | Wt. Pad+Solids | Wt. Pad | Wt. Solids |
|-------------------|----------------|---------|--------------|
| FF-1-1 | 1.975 | 1.54 | 0.435 |
| %FF= 13.0% | | | |

Appendix III - 2

Furnish 2 - Raw Data

| Run # | Wt. Pad+Solids | Wt. Pad | Wt. Solids | %Fines Retention | Wt. Crucible+Ash | Wt. Crucible | Wt. Ash |
|-------|----------------|---------|--------------|------------------|------------------|--------------|---------------|
| 3-1 | 0.578 | 0.549 | 0.029 | 78.5 | 54.7049 | 54.4806 | 0.2243 |
| 3-2 | 0.578 | 0.553 | 0.025 | 81.5 | 53.3983 | 53.3720 | 0.0263 |
| 3-3 | 0.596 | 0.575 | 0.021 | 84.4 | 56.0579 | 56.0336 | 0.0243 |
| 3-4 | 0.581 | 0.563 | 0.018 | 86.7 | 53.7031 | 53.6824 | 0.0207 |
| 3-5 | 0.575 | 0.559 | 0.016 | 88.1 | 53.7748 | 53.7566 | 0.0182 |
| 3-6 | 0.572 | 0.560 | 0.012 | 91.1 | 51.6060 | 51.5968 | 0.0092 |
| 3-7 | 0.584 | 0.570 | 0.014 | 89.6 | 56.7899 | 56.7728 | 0.0171 |
| 3-8 | 0.575 | 0.558 | 0.017 | 87.4 | 55.3447 | 55.3262 | 0.0185 |
| 4-1 | 0.579 | 0.551 | 0.028 | 79.3 | 51.9451 | 51.9163 | 0.0288 |
| 4-2 | 0.598 | 0.568 | 0.030 | 77.8 | 50.7970 | 50.7734 | 0.0236 |
| 4-3 | 0.597 | 0.580 | 0.017 | 87.4 | 53.4188 | 53.3912 | 0.0276 |
| 4-4 | 0.590 | 0.575 | 0.015 | 88.9 | 66.1980 | 66.1740 | 0.0240 |
| 4-5 | 0.580 | 0.568 | 0.012 | 91.1 | 52.4275 | 52.4015 | 0.0260 |
| 4-6 | 0.579 | 0.560 | 0.019 | 85.9 | 54.5293 | 54.5013 | 0.0280 |
| 4-7 | 0.594 | 0.576 | 0.018 | 86.7 | 54.2302 | 54.2043 | 0.0259 |
| 4-8 | 0.565 | 0.549 | 0.016 | 88.1 | 50.5166 | 50.4926 | 0.0240 |
| 8-1 | 0.583 | 0.556 | 0.027 | 80.0 | 56.3267 | 56.3168 | 0.0099 |
| 8-2 | 0.564 | 0.537 | 0.027 | 80.0 | 57.7683 | 57.7481 | 0.0202 |
| 8-3 | 0.600 | 0.578 | 0.022 | 83.7 | 58.2814 | 58.2614 | 0.0200 |
| 8-4 | 0.565 | 0.543 | 0.022 | 83.7 | 54.2823 | 54.2637 | 0.0186 |
| 8-5 | 0.576 | 0.562 | 0.014 | 89.6 | 52.6966 | 52.6798 | 0.0168 |
| 8-6 | 0.585 | 0.571 | 0.014 | 89.6 | 52.5801 | 52.5639 | 0.0162 |
| 8-7 | 0.582 | 0.571 | 0.011 | 91.9 | 58.4437 | 58.4275 | 0.0162 |
| 8-8 | 0.567 | 0.554 | 0.013 | 90.4 | 57.4042 | 57.3858 | 0.0184 |

Base Runs

| Run # | Wt. Pad+Solids | Wt. Pad | Wt. Solids | %Fines Retention | Wt. Crucible+Ash | Wt. Crucible | Wt. Ash |
|-------|----------------|---------|--------------|------------------|------------------|--------------|---------------|
| 6-1 | 0.627 | 0.565 | 0.062 | 54.07% | 57.9833 | 57.9411 | 0.0422 |
| 6-2 | 0.625 | 0.575 | 0.05 | 62.96% | 53.6371 | 53.5953 | 0.0418 |
| 6-3 | 0.617 | 0.563 | 0.054 | 60.00% | 50.1273 | 50.0873 | 0.0400 |

Fines Fraction

| Wt. Pad+Solids | Wt. Pad | Wt. Solids |
|-------------------|---------|--------------|
| 1.915 | 1.57 | 0.345 |
| 1.921 | 1.54 | 0.381 |
| Avg. = | | 0.363 |
| %FF= 27.4% | | |