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# The Influence of Electrolytes on Certain Characteristics of Pulp

Wayne Eugene Kendrick
*Western Michigan College*

# THE INFLUENCE OF ELECTROLYTES ON CERTAIN CHARACTERISTICS OF PULP

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Wayne Eugene Kendrick

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## Introduction

This thesis is an endeavor to bring out the reasons for strength variations due to the presence of electrolytes in the process water, occuring either naturally or in the form of additives. The subject is subdivided into effects caused by cations and effects caused by anions plus special cases.

Material was obtained from the science library of Western Michigan College of Education, the Kalamazoo Public Library and microfilmed articles from the New York Public Library.

W.E.K.

## Literature Survey

Certain electrolytes, it has been found, have either a detrimental or advantageous effect on many of the characteristics of pulp. Cations seem to cause the change in the values of tests in some cases, whereas anions seem responsible in others. Two main places where electrolytes may be traced as causes for concern are in the process water or from additives. As a rule the effect of the electrolyte varies with its concentration and with its valency. The higher the valence, the more detrimental the effects.

### Cations

As has been mentioned above the valency of the cation and its concentration are the two factors affecting variations in sheet properties. The effects change within limits and with certain properties being affected in different degrees. The retardation of beating in the main effect that leads to decreased strength characteristics.

Cohen, Farrant and Watson(1), with their work on cation effects on pulp, worked with cations in groups according to their valence. Results indicated that monovalent cations show an increase in strength properties, divalent cations have little effect and tri- and tetra- valent cations result in substantial reductions in strength. Freeness, however, is always increased by the presence of electrolytes, the effect increasing with the valency of the cation. Acid-

washed pulps, it is reported, produced an appreciable reduction in strength. Therefore, unless it is imperative that the ash content of the pulp be kept as low as possible, pulp should not be washed with acid washes. The ideal condition is a thorough water washing. Economic reasons, however, do not make this feasible.

The beatingeffect was found to be enhanced by the presence of monovalent cations and retarded by the presence of trivalent cations. However, when mono- and tri- valent ions were both present in the process water, their effects opposed one another so that their effects counteracted one another. Table I, taken from the article by the above mentioned authors, demonstrates this point.

Due to the fact that water-washed pulps and acid-washed pulps are both sensitive to the presence of electrolytes and because pulps that have different carboxyl contents are egually sensitive to electrolyte effects, Cohen, Farrant and Watson conclude that carboxyl groups do not play a major part in the effects caused by electrolytes. Instead the effect is explained as due to the electrokinetic potential or zeta-potential of the cellulose fibers. Since the cellulose fiber has been shown to be a negatively charged particle, it is to be expected that cations would have a greater influence and effect than would anions.

Therefore, due to the mineral content of mill water

Table I

Antagonistic Effects of mono- and Tri- Valent Cations on Pulp Properties
(washed eucalypt kraft pulp beaten for 4500 rev. in the Lampen mill)

| prossesing medium | freeness C.s.f. ml. | bulk | burst factor | tear factor | breaking length Km. |
|---|---|---|---|---|---|
| Distilled water | 337 | 1.56 | 46.6 | 110 | 8.13 |
| Distilled water plus NaCl,200p.p.m. | 401 | 1.54 | 55.1 | 109 | 9.15 |
| Distilled water plus $CeCl_3$,50p.p.m. | 507 | 1.56 | 43.0 | 99 | 7.70 |
| Distilled water plus NaCl,100p.p.m. $CeCl_3$,50p.p.m. | 482 | 1.55 | 46.1 | 102 | 8.06 |
| Distilled Water plus NaCl,200p.p.m. $CeCl_3$,50p.p.m. | 494 | 1.56 | 48.0 | 106 | 8.45 |
| Distilled water plus NaCl,400p.p.m. $CeCl_3$,50p.p.m. | 494 | 1.54 | 47.3 | 102 | 8.39 |

Each value is the mean of four replications.

varing from mill to mill, the same pulp sample may be evaluated differently at any two mills.

## Anions

Anion effects upon the strength properties of pulp have been found not to have as great an effect as cations, except in cases where the pH is appreciably influenced or in extraordinary cases. Cohen, Farrant and Watson(2) in their work with anions, used anions most commonly found in process

water or used as additives. The influence upon water-washed eucalypt kraft pulp, when the process water contained any one of them, was in this order:

1.) sodium hexametaphosphate

2.) sodium hydroxide
sodium citrate
sodium bicarbonate
di-sodium phosphate
sodium acetate

3.) potassium ferrocyanide

4.) sodium nitrate
sodium sulfate
sodium chloride

With the exception of sodium hexametaphosphate and sodium citrate, the order above is approximately the same as their effect on pH.

Group 2., pH is greater than 7.0 at all concentrations.

Group 3., pH is greater than 7.0 at high concentrations.
pH is less than 7.0 at low concentrations.

Group 4., pH is less than 7.0 at all concentrations.

Sodium Hexametaphosphate, pH is only 6.7 to 6.9 at all concentrations.

Sodium Citrate, pH is only 7.2 to 7.5 at all concentrations.

The effect of concentration, excluding sodium hydroxide and sodium hexametaphosphate (possibly sodium citrate), can be attributed to the univalent cation associated with the anion.

## Alum

Papermaker's alum, aluminum sulfate ($Al_2(SO4)_3 \cdot 18H_2O$), used in most mills as a means of size precipitation, has been discovered to have very definite harmful effects on strength characteristics. Keller, Simmonds and Baird(3) point out that possible obvious causes of the losses in strength were; the alum, the degree of acidity due to the hydrolysis of the alum, the combined effect of the alum and the dissolved components of the process water or any combination of the preceeding factors. As the composition of the process water changes and becomes more alkaline, due to an increase in the amount of bicarbonates and hydroxides, there is an increase in alum demand to keep the pH between the limits of 4.2 to 5.2. This increased amount of alum combines with the bicarbonates and hydroxides to form floc, which is retained by the fibers with subsequent strength losses. This seems to indicate that there would be less fibers per unit area due to the space occupied by the floc. In closed white-water systems, the relatively large amounts of alum present may be the cause of deleterious effects on sheet strength. Mills that use well water, or even river water, will find that the amounts of bicarbonates present, varies, as is the case with water used by the city of Kalamazoo(4),which varies from 323 to 344 parts per million depending upon the location of the well.

Dohne and Libby(5) noticed from experiments in size precipitation that the method of size precipitation had a marked effect on certain sheet properties. When the beater pH was adjusted with alum alone, the strength characteristics were not as good as when the pH of the beater was adjusted with a combination of alum and sodium aluminate( $Na_2Al_2O_4$ ). Bursting strength showed a loss up to 10.7 per cent when alum was employed to adjust the beater pH from 4.0 to 6.0; with alum-aluminate-sized sheets, between a pH of 4.0 to 7.0, there was an increase of up to 15.0 per cent. Fold tests showed that with alum adjusted sheets the loss was as high as 35.7 per cent; with alum-aluminate adjustment there was an increase of 154.0 per cent. Tear showed a 12.2 per cent increase with alum precipitated papers, and a 14.4 per cent loss in strengthwith alum-aluminate-sized sheets.

The aluminum ion has been shown to have detrimental effects on sheet properties. Cohen, Farrant and Watson(1) state that trivalent ions are harmful to most strength properties due to the retardation of beating. In studies by the abuve mentioned men, aluminum chloride( $AlCl_3$ ) was used and indicated sharp losses in the burst factor, tear factor, breaking length, drainage time and air resistance. Cohen, Farrant and Watson(2) have also noted that the sulfate ion and the chloride ion had little

effect on sheet properties.

Jayme(6) points out that aluminum sulfate materially lowers the degree of swelling of pulp. This indicates that if the degree ofswelling is notkept up there will be subsequent losses in strength. To determine the degree of swelling a given quantity of pulp is centrifuged in a special device for ten minutes at standard conditions. The result is calculated by the following equation:

$$\text{Swelling factor} = \frac{\text{wet wt. - moisture free wt.}}{\text{moisture free wt.}} \times 100.$$

The following is a table taken from the article of Jayme showing the swelling degree change:

Table II

Change of Swelling Degree of an Unbleached Sulfite Pulp in Diluted Solutions of Aluminum Sulfate.

| concentration of solution | swelling degree % |
|---|---|
| 0 (pure water) | 150.7 |
| $\frac{M}{2,000,000}$ | 143.7 |
| $\frac{M}{100,000}$ | 143.1 |
| $\frac{M}{10,000}$ | 142.6 |
| $\frac{M}{1000}$ | 138.1 |

It is evident then that papermaker's alum does have injurious effects on paper strength properties. The fact that aluminum is a trivalent ion and that the concentration of the ion is important, tends to indicate that these are the main causes for strength losses. It may be noted that increase of strength characteristics when sizing with a combination of alum and aluminate, may be t he results of using a compound, sodium aluminate, where the aluminum ion serves as an anion and not as a cation.

## Sodium Hexametaphosphate

As has been stated before, the valence of the cation and the concentration of the cation determine the variations in sheet strength. Anions are usually not responsible except in cases where the anion has a definite effect on pH, or has extraordinary properties. Such is the case with the hexametaphosphate ion.

Cohen, Farrant and Watson(2) in their work with anions in relationship to strength characteristics, found that the hexametaphosphate ion had very extraordinary properties, especially at low concentrations (0.001-0.002 N.) where its maxima occur. Air resistance, burst, tensile and freeness are the properties affected most by the hexametaphosphate ion. Freeness, however, follows the same curve as the rest of the sodium salts.

Since the presence of sodium hexametaphosphate( $Na_6(PO_3)_6$ ) or Graham's salt produces effects greater than can be accounted for by the sodium ion alone, the effect cannot be considered as a normal cation effect. Also their maxima occur at much lower concentrations than any of the other of the sodium salts do.

Cohen, Farrant and Watson point out that there seems to be two properties of sodium hexametaphosphate on pulp that influence the properties of paper, independent of beating. These properties are dispersive action and separation or sequestration of multivalent cations.

The dispersive action of sodium hexametaphosphate at its optimum concentrations have been observed to have noticeably more homogeneous characteristics in formation of sheets than in those sheets made from pulp processed in the presence of higher concentrations. Even lower concentrations, as in the making of sheets( 0.00007 N. ), sodium hexametaphosphate exerted its maximum dispersive action.

A pulp's response to beating is considerably enhanced by pretreatment with sodium hexametaphosphate. Its ability to sequestrate calcium and magnesium promotes cation exchange on carboxyl groups with the substitution of sodium for the bivalent cations. Carboxyl groups which are relatively inactive in water-washed pulps are made active as

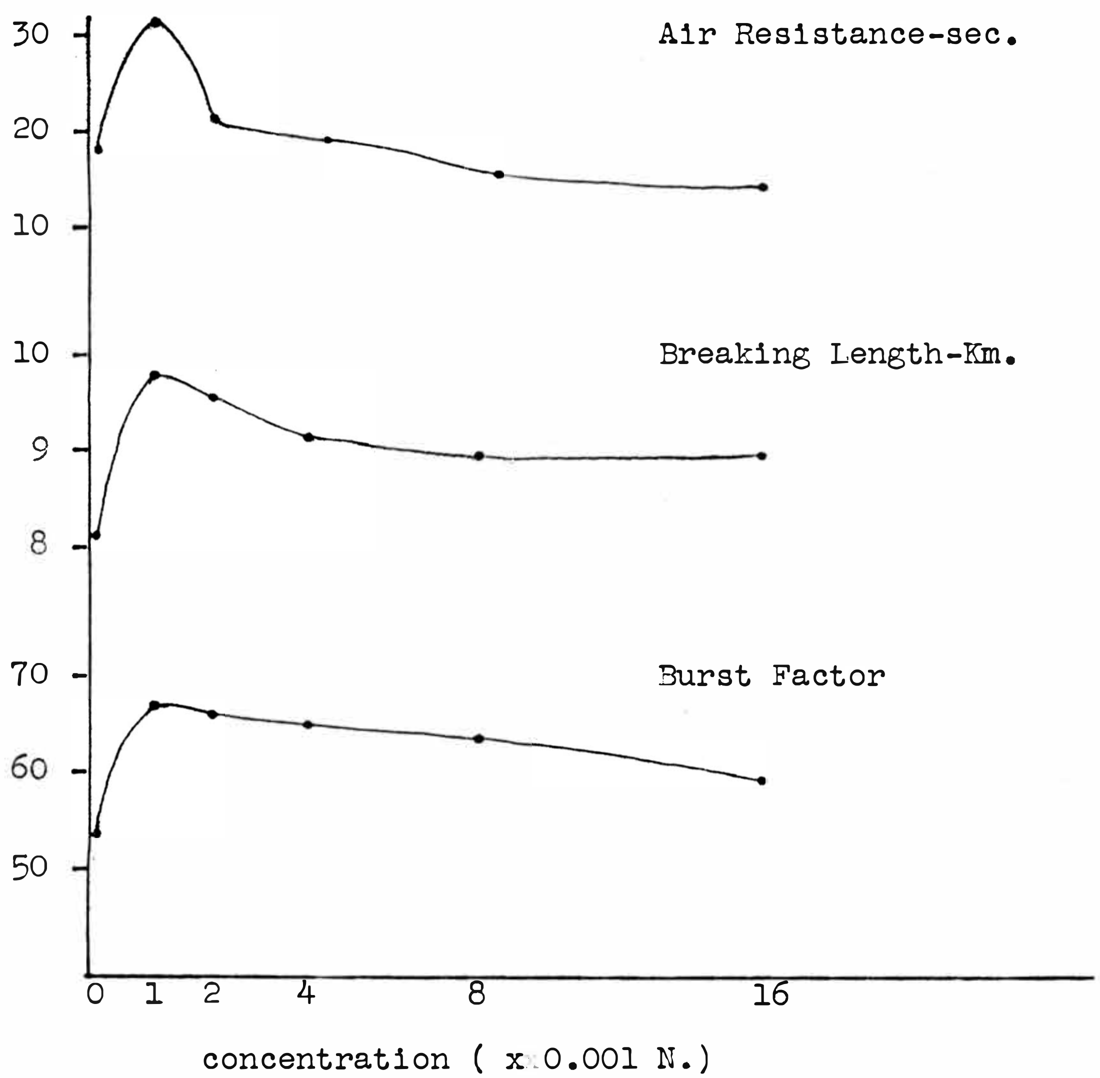
the pulp swells and absorbs water more readily and is therefore more responsive to beating.

Although there are significant changes in strength properties, the pulp is still sensitive to cations and also to sodium hexametaphosphate.

Following is a graph from the article by Cohen, Farrant and Watson(2).

Figurel.

The Influence of Sodium Hexametaphosphate on Pulp and Paper Properties



## Caustic Soda and Muriatic Acid

The pH of stock seems to have no definite correlation with the properties of treated pulp. However, in the case of caustic soda, sodium hydroxide( NaOH ), pH seems to have a secondary effect that is superimposed on that of the cation.

Cohen, Farrant and Watson(2) state that in the case of sodium hydroxide the slopes of the regressions of bursting strength and tensile strengthon concentration, are steeper, and those of freeness and air resistance flatter, than the slopes of the corresponding regressions for other electrolytes, thus indication of a secondary pH effect. It is possible that swelling, fibrillation and water retention are enhanced by a higher pH, so that stronger bonds are established in the sheet.

Muriatic acid, hydrochloric acid( HCl ), effects on pulp properties may be looked on as hydrogen ion effects. Cohen, Farrant and Watson(1) state that hydrochloric acid produced an effect intermediate between those of di- and tri- valent groups. A study of the pH influence on strength properties has shown that within a pH range of 3.1 to 6.4, the freeness and bulk of the pulp were increased, and the burst and tensile strengths decreased as the system was made more acid.

Following is a table taken in part from the article

by Cohen, Farrant and Watson(1) showing the effects of hydrochloric acid.

Table III

The Influence of Hydrochloric Acid on Sheet Properties (water-washed eucalypt kraft pulp beaten 4500 rev. in the Lampen mill)

| conc. molar | bulk | burst factor | tear factor | bk. ln. Km. | free- ness C.s.f. | drain- age sec. | air resis. sec. |
|---|---|---|---|---|---|---|---|
| ---- | 1.55 | 52.9 | 110 | 8.93 | 332 | 6.1 | 11.9 |
| 0.00025 | 1.54 | 51.8 | 111 | 8.74 | 455 | 5.8 | 1o.5 |
| 0.0005 | 1.54 | 49.3 | 109 | 8.04 | 497 | 5.6 | 8.1 |
| 0.001 | 1.54 | 47.4 | 111 | 7.45 | 528 | 5.5 | 6.3 |
| 0.002 | 1.56 | 40.2 | 112 | 6.86 | 547 | 5.3 | 4.9 |
| 0.004 | 1,54 | 40.3 | 106 | 7.06 | 548 | 5.2 | 5.4 |

Each value is the mean of either four or six replications.

Salt Solutions on Wood Cellulose

Wood that has been allowed to stand in salt water for considerable length of time is found to have lower strength properties after sulfite pulping, as has been found by Richter(7).

On the coasts where wood is transported to mills by floatingin salt water, is possibly the only place where this trouble may be found. The time that the wood is allowed to stand in the salt solution is critical, with the critical time being from two to three months. Any time

after three months seems invaribly to result in lower physical qualities.

The fiber, thus contaminated, after cooking gave inferior fiber qualities, lower strength, lower freeness and higher copper number. Bleached stock seemed to be affected most and brown stock not so much. Richter states that an increase in effect was caused by using a cation with higher molecular weight. Sulfates were determined to be at least as detrimental as chlorides.

December 19, 1951

Wayne E. Kendrick

Wayne E. Kendrick

"END"

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(2) Cohen, W.E., Farrant, G., Watson, A.J., Paper Trade J., 133, No.4: 16-22; ( July 27, 1951).

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(5) Dohne, W.P., and Libby, C.E., Tech. Assoc. Papers, 25: 663-69; (1942).

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Laboratory Work

on

# THE INFLUENCE OF ELECTROLYTES ON CERTAIN CHARACTERISTICS OF PULP

May 1952

Wayne E. Kendrick

## TABLES



## GRAPHS

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## ABSTRACT

In laboratory work, I endeavored to find out whether the pulp strength losses caused by the use of alum, as shown in the literature survey, were due to the acidity of the alum or due to the floc retained by the sheet. It was found that the strength loss was caused by the floc retained and not by the acidity of the stock. Acidified stock tended to show strength gains.

## LABORATORY CONDITIONS

In the laboratory Weyerhaeuser bleached sulfite pulp was beaten, in a laboratory scale beater, to a freeness of 400 ml. Canadian standard freeness. Sheets were then made on the Noble and Wood sheet machine. The sheets made were then conditioned in a relative humidity room for testing. Regular Kalamazoo city water was used in all work.

The first group of sheets were those made where the pH was adjusted at the headbox(proportioner) with (1) alum, (2) hydrochloric acid and (3) decanted alum to pHs of 6.5, 6.0 and 5.5. The decanted alum was made up ahead of time and allowed to stand for at least three hours to allow the floc to settle out.

The second group of sheets were those made where the pH was adjusted in the beater with (1) alum, (2) hydrochloric acid and (3) decanted alum to pHs of 6.5, 6.0 and 5.5.

All sheets were tested under like conditions in the relative humidity room( 70-74° C. and 50-54% R.H.). The following tests

were made: basis weight, mullen, tensile, tear, fold and ash.

Table 2 gives data on the various beater runs. Table 3 gives the various pH measurements made during the sheet making process.

## SUMMARY OF RESULTS

The results from this laboratory work seems to verify that found in the literature survey, in that the floc formed when alum is added to the stock is responsible for the subsequent strength losses. Using hydrochloric acid, acidity seemed to raise strength properties. This seems to indicate that the more alum added to the stock to lower the pH, the lower the strength properties will be due to the additional floc present. The more floc present the less fibers per unit area, thus strength losses.

It has therefore been shown that alum has a detrimental effect on certain characteristics of pulp due to the floc formed and not to the acidity it causes. The decanted alum solution used seemed to have intermediate effects between those of alum and hydrochloric acid. This seems to show again the the floc is the cause of the pulp strength losses.

May 31, 1952

Wayne E. Kendrick

Wayne E. Kendrick

Table 1. Data Plotted in Graphs I-VII.

| pH | Fold (md-cmd) | Tear Factor (md-cmd) | Burst Factor | Breaking Length | Ash (%) |
|---|---|---|---|---|---|
| Original sheet, no additives. | | | | | |
| 7.5 | 60.0-44.0 | 69.4-75.7 | 24.2 | 4125 | 0.46 |
| Sheets adjusted with alum at headbox. | | | | | |
| 6.5 | 6-4 | 74.0-74.0 | 12.1 | 2560 | 1.89 |
| 6.0 | 4-2 | 60.2-69.8 | 9.15 | 2150 | 2.89 |
| 5.5 | 3-2 | 70.6-67.6 | 8.16 | 1960 | 3.54 |
| Sheets adjusted with hydrochloric acid at headbox. | | | | | |
| 6.5 | 45-29 | 63.6-77.6 | 23.95 | 3980 | 0.45 |
| 6.0 | 319-310 | 68.4-76.1 | 35.0 | 5240 | 0.31 |
| 5.5 | 332-308 | 73.2-78.1 | 33.8 | 5240 | 0.31 |
| Sheets adjusted with decanted alum at headbox. | | | | | |
| 6.5 | 284-186 | 77.2-80.5 | 32.7 | 5320 | 0.41 |
| 6.0 | 195-213 | 70.4-81.6 | 32.2 | 5030 | 0.70 |
| 5.5 | 133-129 | 62.8-70.6 | 32.9 | 5260 | 0.79 |
| Sheets adjusted with alum in beater. | | | | | |
| 6.5 | 163-170 | 74.6-77.6 | 29.6 | 4310 | 0.66 |
| 6.0 | 112-125 | 70.3-80.8 | 29.75 | 4650 | 1.06 |
| 5.5 | 136-141 | 67.0-73.2 | 27.5 | 4380 | 0.66 |
| Sheets adjusted with hydrochloric acid in beater. | | | | | |
| 6.5 | 185-334 | 72.6-82.1 | 33.2 | 5250 | 0.28 |
| 6.0 | 244-282 | 74.8-79.3 | 33.7 | 4910 | 0.32 |
| 5.5 | 229-328 | 71.4-80.6 | 33.6 | 5000 | 0.31 |
| Sheets adjusted with decanted alum in beater. | | | | | |
| 6.5 | 151-175 | 66.3-75.8 | 31.4 | 4700 | 0.83 |
| 6.0 | 127-180 | 68.3-78.3 | 30.6 | 4760 | 0.56 |
| 5.5 | 277-197 | 69.1-76.8 | 30.9 | 4790 | 0.78 |

Note; the above are averages of several tests.

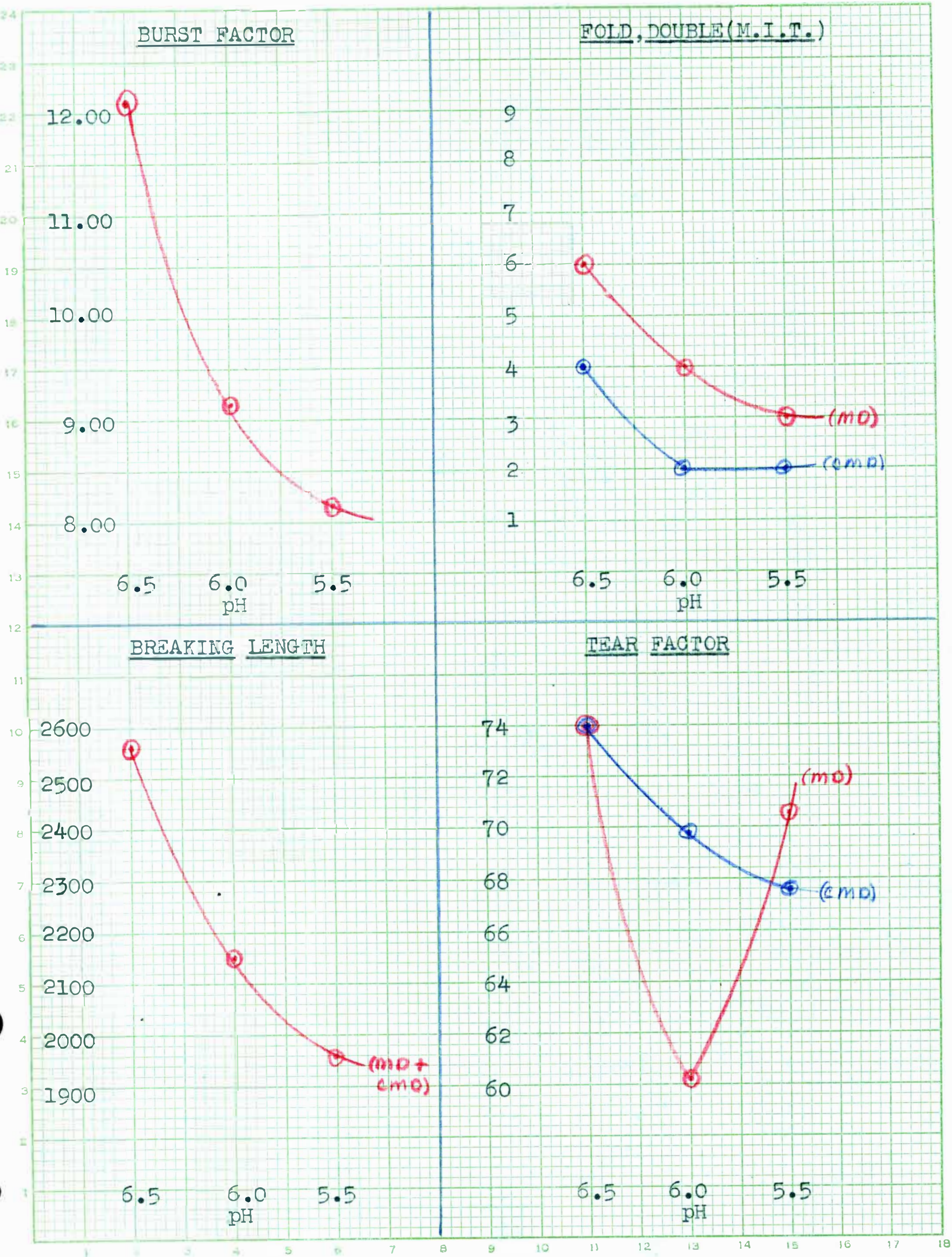
Table 2. Data on Beater Runs.

| Beater Additives | Beater pH | Beater Consistency (%) | Beating Time (sec) | Freeness C.s.f. (ml) |
|---|---|---|---|---|
| none | 7.5 | 1.56 | 1660 | 397 |
| none | 8.5 | 1.72 | 1600 | 403 |
| alum | 6.5 | 1.51 | 1485 | 395 |
| alum | 6.0 | 1.59 | 1460 | 403 |
| alum | 5.5 | 1.49 | 1510 | 400 |
| HCl | 6.5 | 1.69 | 1500 | 401 |
| HCl | 6.0 | 1.60 | 1460 | 398 |
| HCl | 5.5 | 1.59 | 1730 | 395 |
| dec.alum | 6.5 | 1.49 | 1360 | 395 |
| dec.alum | 6.0 | 1.60 | 1535 | 400 |
| dec.alum | 5.5 | 1.58 | 1600 | 395 |

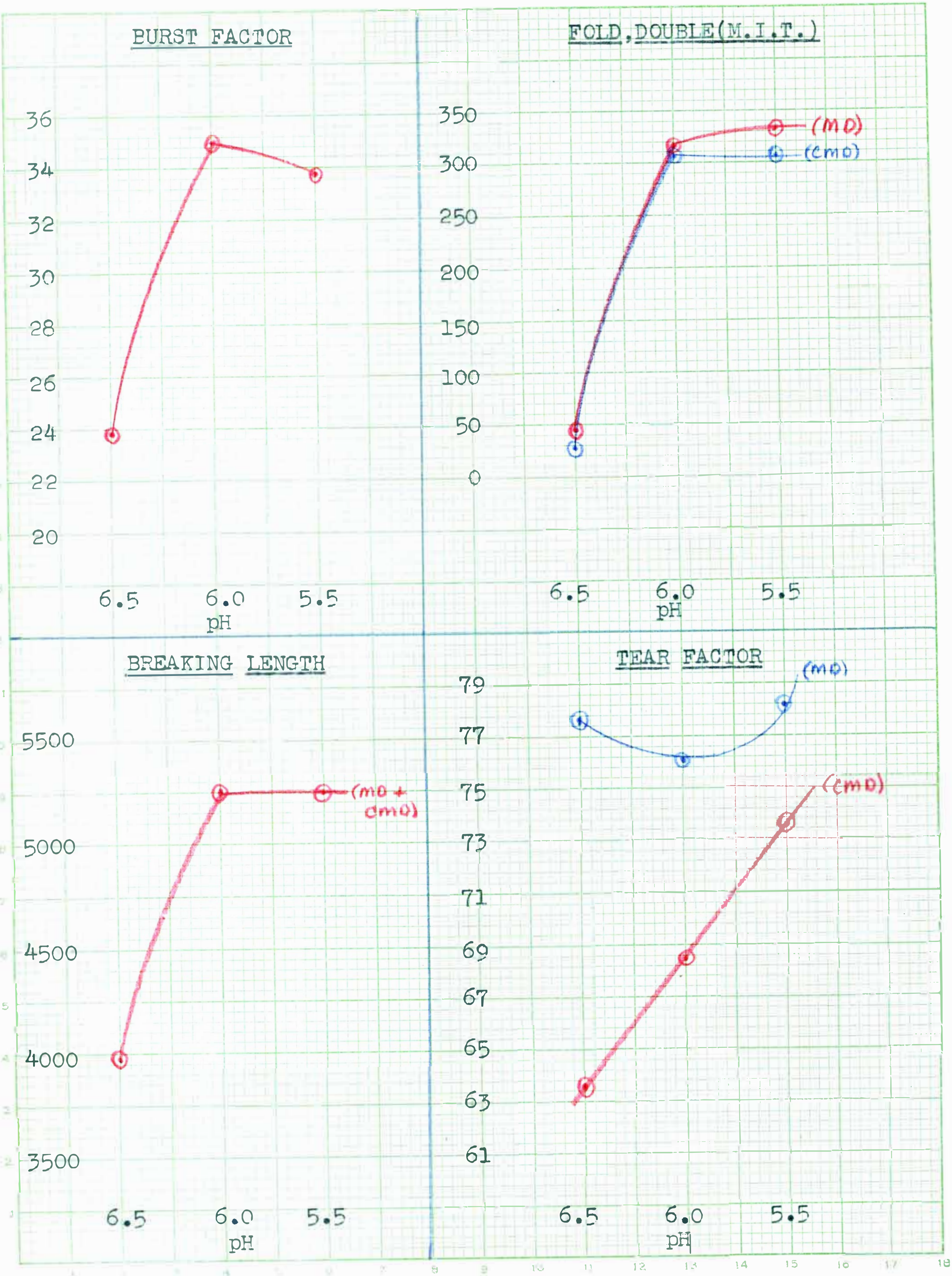
Table 3. Data on Sheet Making pHs.

| pH adjuster | stock pH | proportioner pH | sheet mold pH |
|---|---|---|---|
| none | 7.5 | 7.1 | 7.2 |
| alum | 7.5 | 6.5 | 7.15 |
| alum | 7.4 | 6.0 | 7.0 |
| alum | 7.4 | 5.5 | 7.1 |
| HCl | 7.4 | 6.5 | 7.1 |
| HCl | 8.4 | 6.0 | 7.1 |
| HCl | 8.4 | 5.5 | 6.9 |
| dec.alum | 7.4 | 6.5 | 7.1 |
| dec.alum | 7.4 | 6.0 | 7.05 |
| dec,alum | 7.4 | 5.5 | 7.1 |
| alum | 6.5 | 7.2 | 7.2 |
| alum | 6.0 | 7.2 | 7.15 |
| alum | 5.5 | 7.2 | 7.2 |
| HCl | 6.5 | 7.25 | 7.25 |
| HCl | 6.0 | 7.2 | 7.2 |
| HCl | 5.5 | 7.2 | 7.2 |
| dec.alum | 6.5 | 7.25 | 7.3 |
| dec.alum | 6.0 | 7.3 | 7.3 |
| dec.alum | 5.5 | 7.3 | 7.25 |

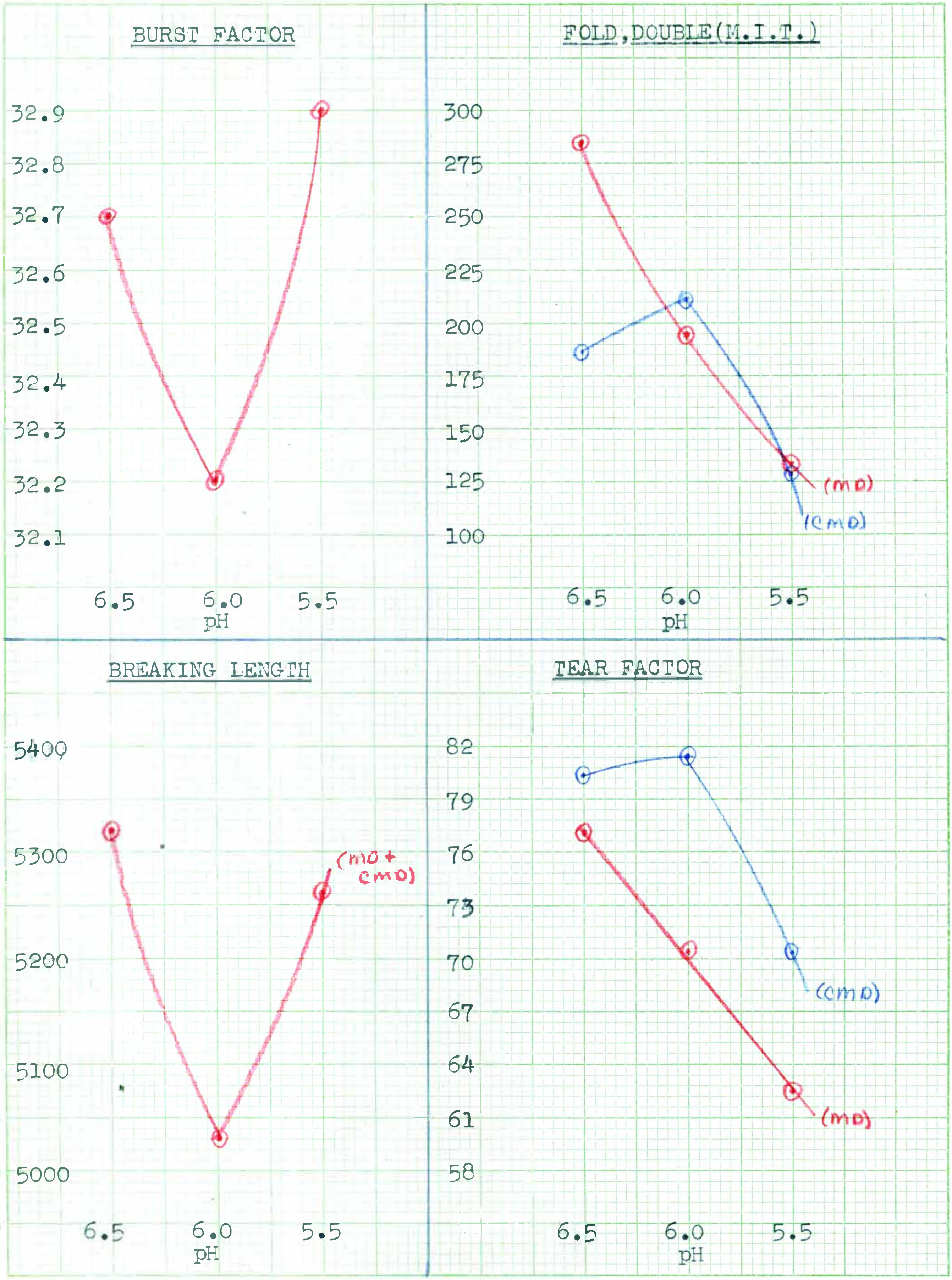
Graph I. pH adjusted with alum; added at the headbox.



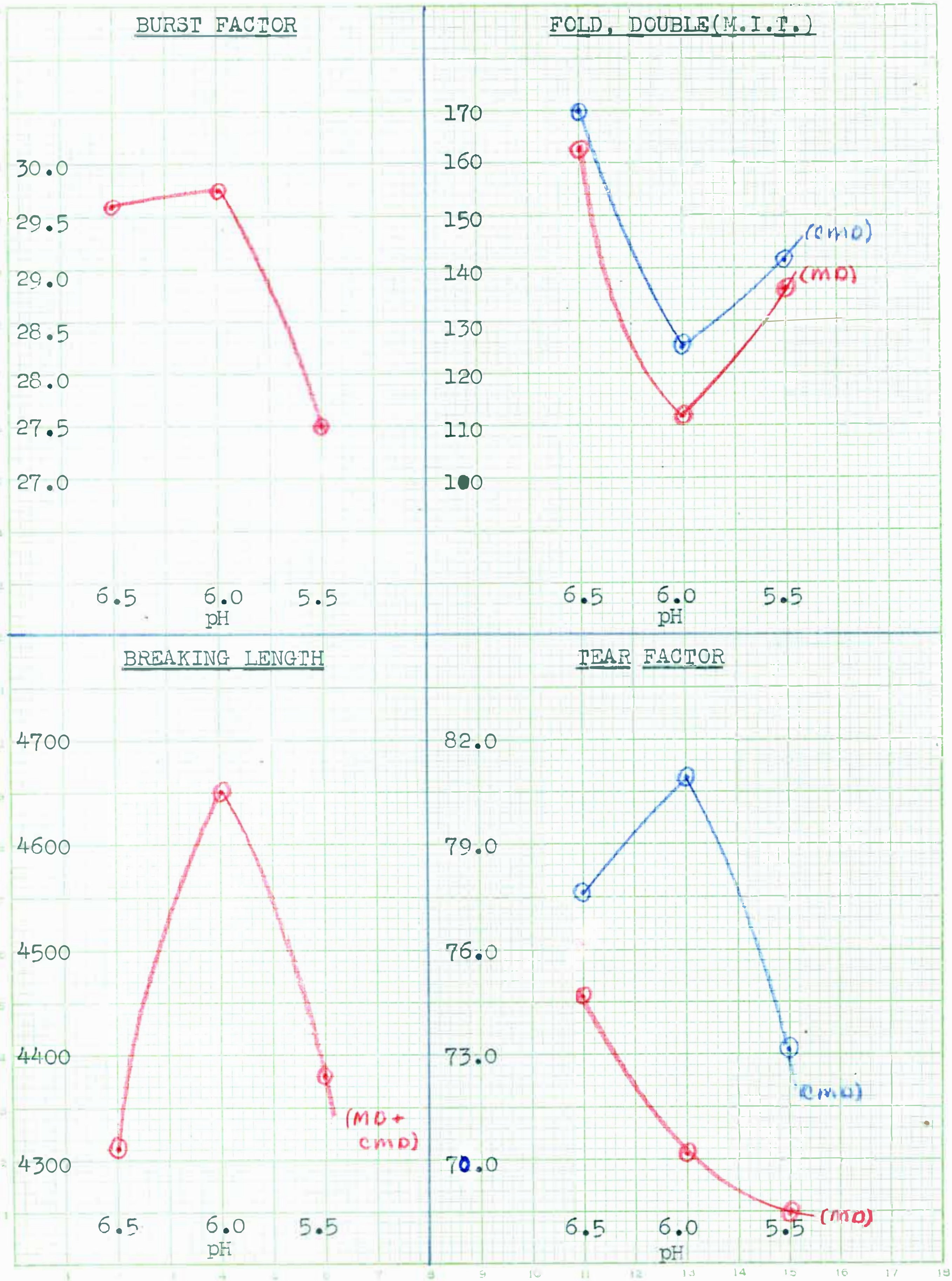
Graph II. pH adjusted with hydrochloric acid; added at the headbox.



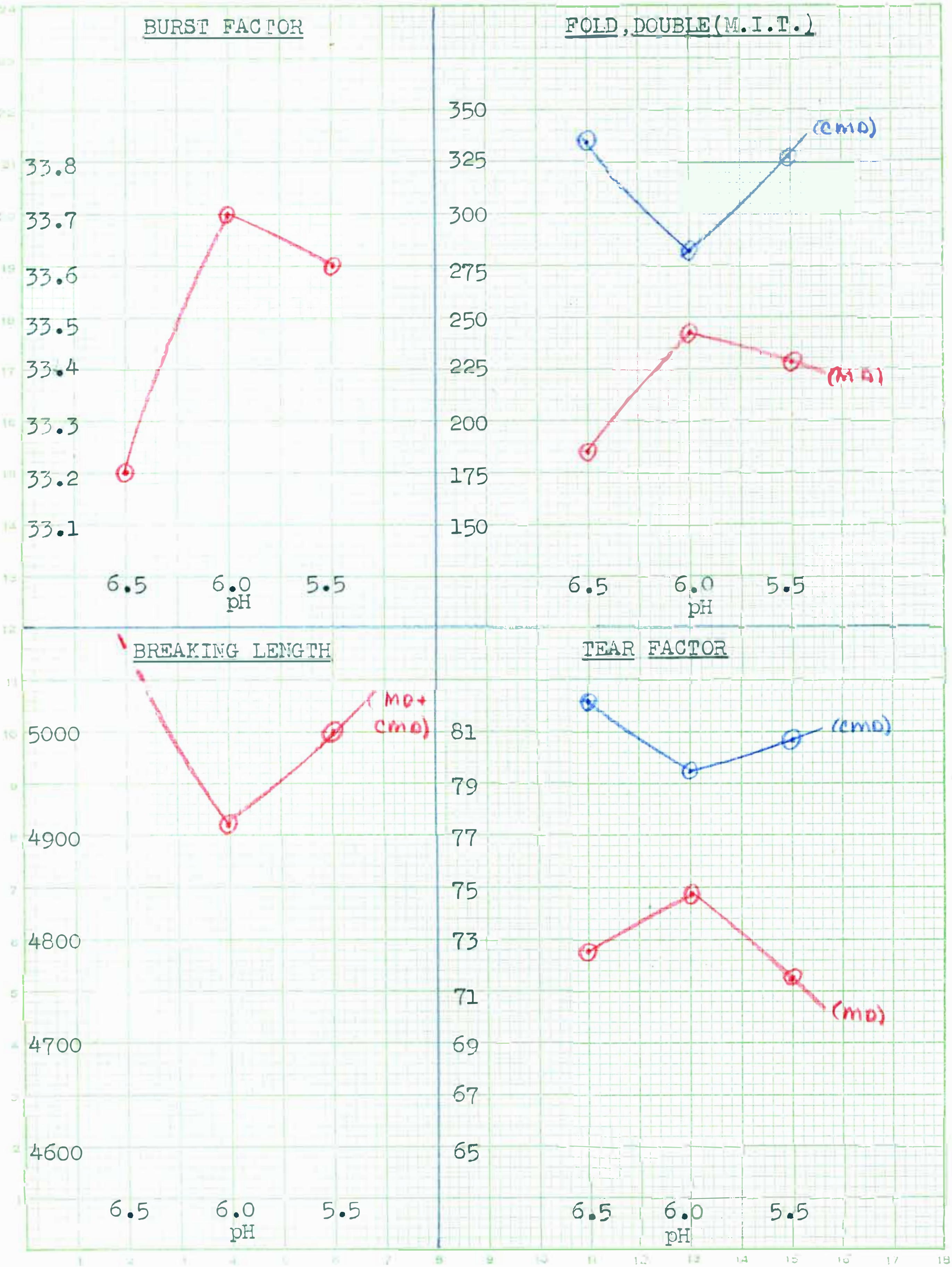
Graph III. pH adjusted with decanted alum; added to headbox.



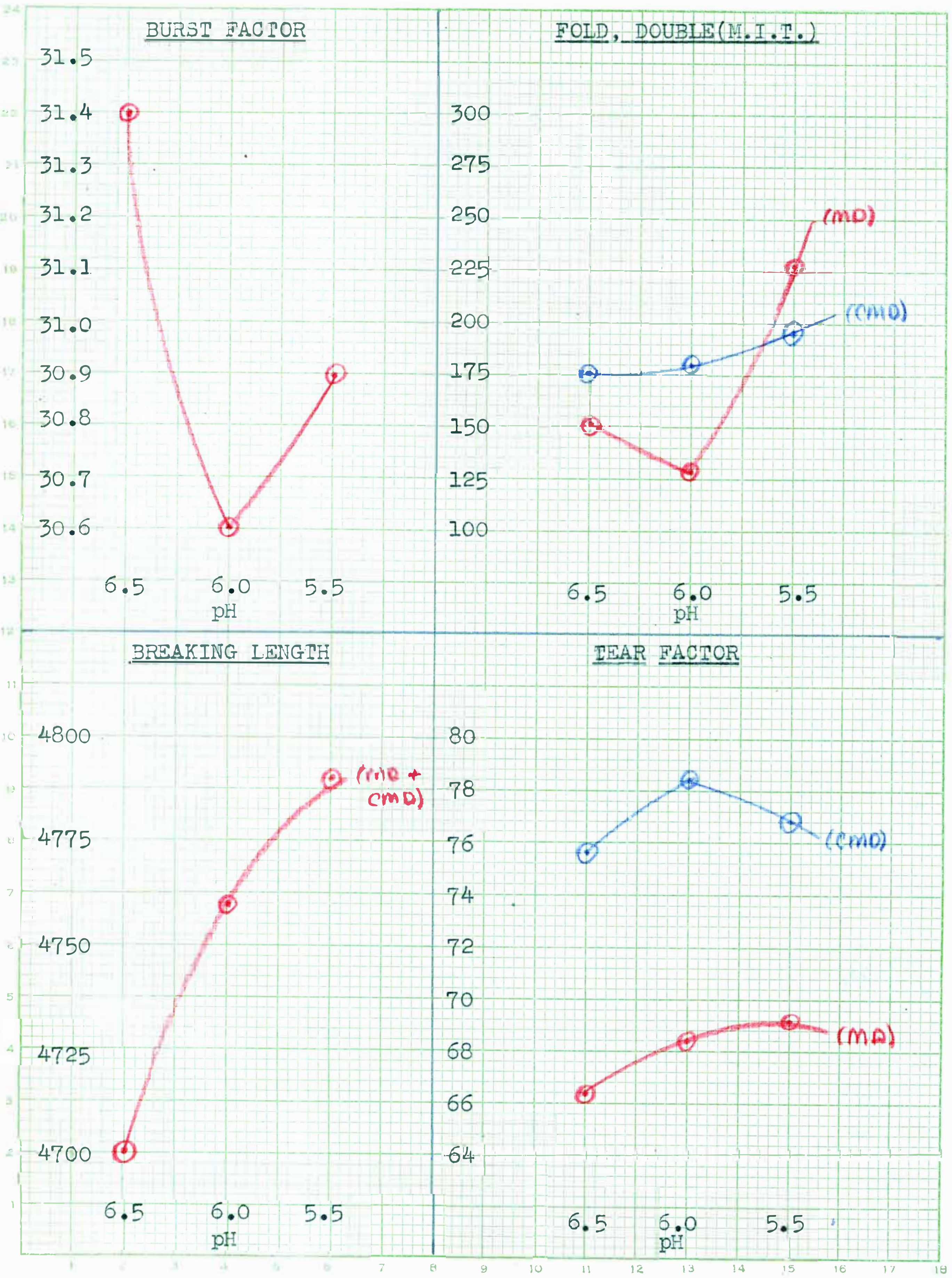
Graph IV. pH adjusted with alum; added to beater.



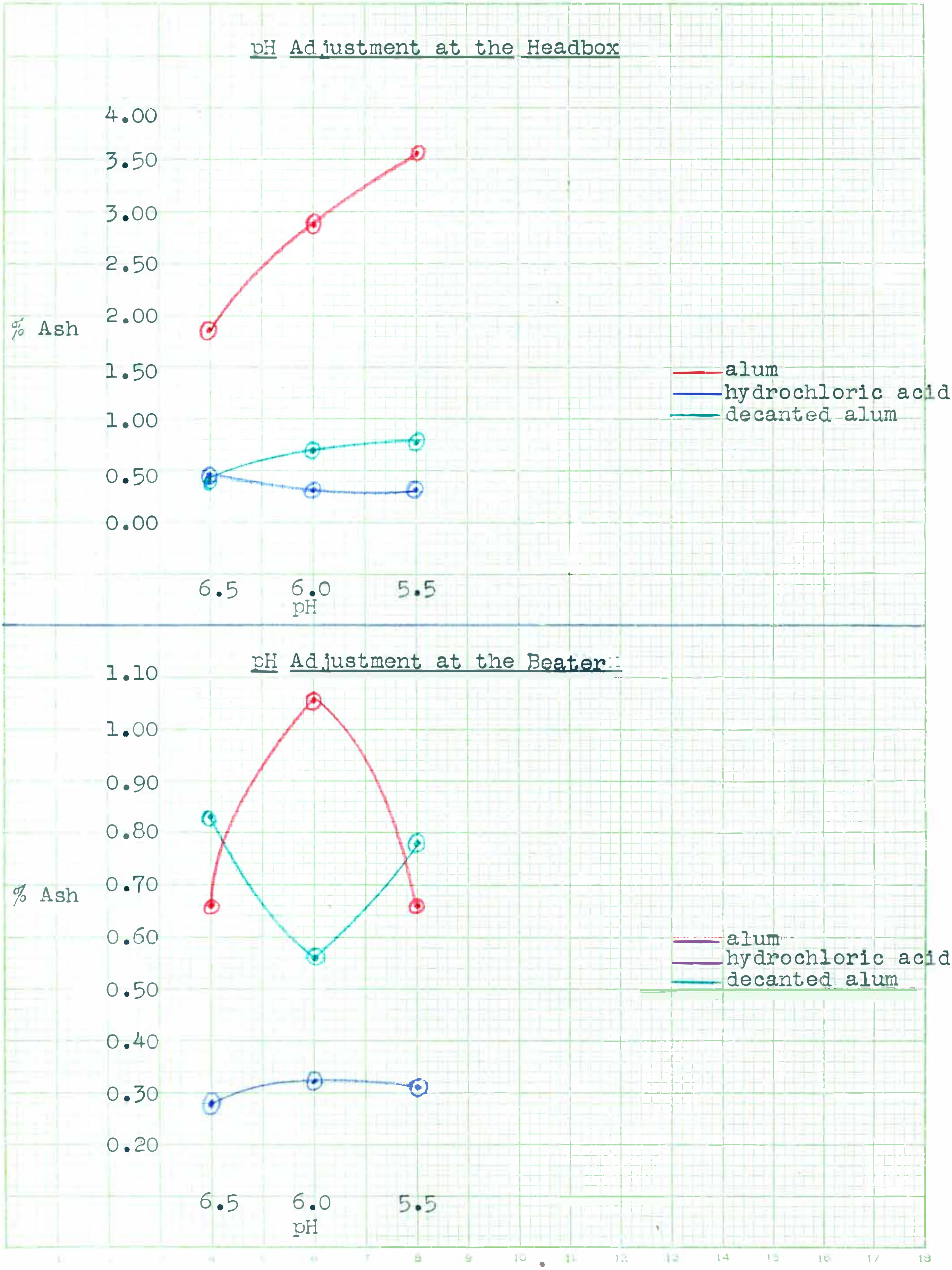
Graph V. pH adjusted with hydrochloric acid; added to beater.



Graph VI. pH adjusted with decanted alum; added to beater



Graph VII. Ash tests.



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