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A Study of the Chemical and Physical Changes Affecting Strength During the Hypochlorite Bleaching of Neutral Sulfite Semichemical Aspen Pulp

Leo F. McDonnell

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A STUDY OF THE CHEMICAL AND PHYSICAL CHANGES AFFECTING
STRENGTH DURING THE HYPOCHLORITE BLEACHING OF NEUTRAL
SULFITE SEMICHEMICAL ASPEN PULP

A thesis submitted by

Leo F. McDonnell

B.Sc. in Ch.E. 1948, The University of Alberta
M.S. 1955, Lawrence College

in partial fulfillment of the requirements
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GLOSSARY

A.	Angstrom
A.R.C.	Alkali-resistant cellulose; the residue from the 16% hemicellulose extraction
Bleach 10	NSSC pulp, fiberized, chlorinated and extracted
Bleach 11	Bleach 10 treated with 0.5% chlorine as hypochlorite
Bleach 12	Bleach 10 treated with 1.5% chlorine as hypochlorite
Bleach 13	Bleach 10 treated with 3.0% chlorine as hypochlorite
Bleach 14	Bleach 10 treated with 6.0% chlorine as hypochlorite
Bleach 15	Bleach 10 treated with 9.0% chlorine as hypochlorite
c_p	Compressibility function = the equilibrium compressed consistency of a pulp pad, g./cc.
cuen	cupriethylenediamine
D.P.	Degree of polymerization
Fines	Fraction of pulp through 150-mesh screen
5% hemicellulose	The fraction extracted from pulp with 5% KOH under nitrogen and precipitated in alcohol
16% hemicellulose	The fraction extracted from the 5% hemicellulose residue with 16% KOH under nitrogen and precipitated into alcohol
IM	Institute method
k	Kozeny constant = 5.55 for pulp fibers
meq.	milliequivalent
mmu	millimicron
NSSC	Neutral sulfite semichemical
O.D.	Ovendry
R	Filtration resistance of pulp, cm./g.
RBA	Relative bonded area

S_o Hydrodynamic specific surface area, sq. cm./g.

S_t Total light scattering area of water-dried, un-bonded fibers

S_u Unbonded light scattering area of fibers in hand-sheet

S_b Bonded area of dried fibers in handsheet

s_t Specific scattering coefficient of water-dried, un-bonded fibers, sq. cm./g.

s_u Specific scattering coefficient of fibers in dried handsheet, sq. cm./g.

TAPPI RC   TAPPI routine control method

v   Effective specific volume, cc./g.

VVP   Viscosity-velocity product, kp. cm./sec.

WRV   Water-retention value, % of dry fiber

SUMMARY

The objectives of this thesis were to explain the mechanism by which tensile strength is increased when neutral sulfite semichemical aspen pulp is bleached with hypochlorite, and to contribute to an understanding of the factors which influence the tensile strength of paper.

Aspenwood was pulped by a neutral sulfite semichemical process, bleached with chlorine, and extracted with alkali. From the resulting material, six pulps were prepared by treating with various amounts of sodium hypochlorite solution containing up to 9.0% available chlorine (based on the pulp). The pulps were examined for chemical and physical character; and handsheets, prepared from unbeaten stock, were evaluated for physical properties.

The most significant chemical change effected by hypochlorite bleaching was delignification. The bleaching was also responsible for a reduction in the D.P. of the cellulose, but the hemicelluloses were not affected greatly either in amount or in D.P. There was also, apparently, a small increase in the degree of carboxylation of the cellulose.

As a result of delignification, ray parenchyma cells were freed from tracheids, increasing the quantity of fines in the pulp. This did not affect the optically measured, weighted average fiber length. Also, with heavier applications of bleaching agent, the removal of lignin from the outer layer of the fibers apparently weakened the

primary wall to the extent that the mild swelling action of the bleach solutions caused the outer wall to rupture and, in many instances, to separate from the parent fiber. It was usually retained, however, as an attached sheet. These two mechanisms account for the increase in hydrodynamic specific surface area from about 15,300 sq. cm./g. to 16,650 sq. cm./g. The data indicate that the specific volume of the pulp increased about 11%.

The interfiber bonding strength was considerably enhanced by bleaching due to increased surface area, possible better fiber flexibility, and increased efficiency of utilization of the available surface area. Increased efficiency was the result of exposing better bonding surfaces. The two factors responsible for this were removal of lignin, which probably is a bonding inhibitor, and opening of the fiber wall by splitting off the outer layer. The latter phenomenon was shown by the electron microscope.

Small amounts of bleaching agent did not affect the intrinsic strength of the fibers, but heavy applications had a marked influence in reducing this property. A relationship was found between fiber strength and the D.P. of the pulp, as would be expected from related work.

The tensile breaking length of handsheets made from unbeaten pulp was considerably improved by the bleaching. Interpretation of the data showed that handsheet strength was improved by better bonding but reduced by weakened fibers when other factors are held constant.

Reflection on the concomitant changes showed that the findings corroborate the concept that the strength of paper depends on both fiber strength and interfiber bonding. In a particular system, the level of strength is defined by the balance between bonding and fiber strength, but the maximum achievable strength is limited by whichever of the two factors is the weaker, relative to the other, from a functional standpoint.

INTRODUCTION

There have been many investigations and discussions of the factors which logically might be expected to influence paper strength, and from these, various hypotheses have been developed and are purportedly supported by experimental data.

Direct methods of investigating the factors which influence the strength of paper are difficult to implement because processes designed to vary one factor almost invariably affect others. As a result, many of the conclusions which have been drawn were based on forced correlations and the true mechanisms of many phenomena have not been unequivocally shown.

Recently Jappe (1) completed a study on the effects of sodium hypochlorite as a third stage in the bleaching of neutral sulfite semichemical (NSSC) aspen pulp. Although the pulp constitutes a complex system, Jappe found that the chemical changes attributable to the hypochlorite treatment were relatively slight. The outstanding physical change, apart from an increase in brightness, was a decided increase in the tensile and bursting strength of papers produced from the bleached pulp. This system, then, appeared to offer a relatively simple system for studying some of the factors which influence the strength of paper.

It was the purpose of the present thesis to study the influence of selected chemical and physical changes in a pulp on the strength properties of the pulp and thereby to contribute additional knowledge on the mechanism of strength development.

HISTORICAL BACKGROUND

The modern concept of the mechanisms of paper formation and rupture is based on the chemical and colloid-chemical properties of papermaking fibers.

The degree of polymerization (D.P.) of naturally occurring cellulose is probably of the order of 8,000 to 10,000 (2). Paper pulp fibers contain cellulose chains with viscosity average D.P.'s considerably lower than this. The physical arrangement of the anhydroglucose chains in cellulose is probably correctly pictured by the crystalline micelle concept (3) wherein the chains are arranged in a more or less parallel fashion and are held together by secondary valence forces to form crystalline micelles. The micelles are about 800 A. long and contain perhaps 65 cellulose chains. A particular cellulose chain may run through several micelles which need not necessarily be aligned. The regions between micelles are amorphous and are more readily attacked by chemical agents than are the crystalline zones. Crystallite chains are grouped into a fibril; fibrils, in spiral layers, constitute the pulp fiber. Wood fibers, then, are held in bundles in the raw wood by interfiber incrustants which include lignin and hemicelluloses (non-cellulosic carbohydrates). The lignin and hemicelluloses also penetrate the fiber structure but probably exist in greatest concentration near the fiber surface or primary wall. Bailey (4) worked with micro-dissections of fibers and found that the middle lamella of Douglas-fir contains about 70% lignin and also has a significant hemicellulose content. The outer primary wall is composed of randomly oriented

cellulose fibrils interpenetrated with lignin and hemicelluloses (5, 6). It appears to be relatively smooth and coherent, and acts as a sheath restricting the secondary wall.

Although the mechanical entanglement theory still finds proponents (7), this hypothesis is apparently inconsistent with several experimental observations. For example, it has been found that paper with only slight tensile strength is produced by wetting a dry sheet (8), by forming a handsheet in a nonpolar solvent (9), by freezing a wet handsheet and subliming off the ice (10), or by making paper with completely acetylated pulp (11). Also, Clark (12) showed that two sheets of cellophane, when wetted and dried while in contact with each other, form a very tenacious lamination. The popular current theory, then, considers the effects of entanglement negligible and that the primary source of strength is the secondary valence bonding forces between fibers. That hydrogen bonding is probably the most important type of secondary valence force is evident from the decrease in strength properties when the hydroxyl groups of cellulose are replaced with groups which are less hydrophilic.

Strachan (13) has visualized cellulose papermaking fibers coated with a hydrophilic colloid while Campbell (14) conceived of molecular cellulose chains attached at one end to the fiber while the other end was free and dissolved in the aqueous suspension medium. Campbell's concept is the more explicit and may serve to explain the phenomena observed not only with wood pulps, but also with pure cellulose fibers such as cotton. In all probability a picture involving both concepts

may well be the fact, and the extent to which each mechanism contributes probably varies with the source and treatment of a pulp.

The modern concept of paper formation provides that the hydrophilic fibers be suspended in a dilute water slurry. Most of the water is removed by filtration, leaving an agglomeration of the wet fibers. As the remaining liquid is removed by evaporation, tremendous surface-tension forces draw the fibers and fiber elements together to such short distances that secondary valence forces are effective. As the last portion of water leaves, hydrogen bridges are established between the alcoholic hydroxyl groups of neighboring fibers or fiber elements, thus uniting the fibers. It is to these bonds that the strength of paper is attributed.

Jayme and Hunger (15) have shown, with electron photomicrographs of paper, that fibrils and outer wall lamellae attached to parent fibers span the interstices between adjacent fibers with the "free" ends of the fibrils apparently bonded securely to the other fiber.

The limit of tensile strength in a paper is the strength of the fibers. The actual strength to anticipate in fibers is difficult to estimate. Mark (16) calculated the limit of tensile strength at 51,000 meters based on the assumption of completely crystalline cellulose. This value does not account for the reduced density and alignment of cellulose chains, nor for the fact that stress concentrations and imperfections will be responsible for lower values. From a practical point of view, tensile strengths in the range of 10,000

meters have been determined in strong papers. This value is dependent not only on the strength of the fibers but also on the tenacity of interfiber bonds.

Past studies have indicated that the tensile strength of paper is not greatly influenced by fiber length (17). Jayme (18) found this to be true so long as the average fiber length exceeds 0.3 mm. Steinschneider and Grund (19) have demonstrated an increase in strength with decreasing fiber length on beating. The strength change can be attributed to better bonding resulting from fines production and probably from increased conformability of the fibers. On the other hand, it has been shown (20) that when wet fibrous mats are cut with a guillotine cutter to reduce the fiber length, papers subsequently made from the furnish have lower strength than those made from the original fibers.

Relationships between fiber strength and D.P. of cellulose have been demonstrated for textiles (21), but the same general relationship has not been shown for paper pulp fibers (17). Cottrall (22) stated that the data available to him indicated that so long as pulp viscosity is above a certain minimum it has no relation to the papermaking strength (tensile) of the pulp. The inference, from published speculation, is that if the D.P. of cellulose in the fibers is greater than about 1200, variations have no significant effect on the strength of paper made from the fibers.

Many investigators have recognized that fiber-to-fiber bonding is

an important factor in the strength of paper. Klauditz (23) pulped
thin veneer sections of aspen by the kraft process and formed paper
from the delignified fibers which had been maintained in their origi-
nal alignment. He found that papers of greater strength were derived
from aligned fibers rather than from those randomly deposited. The
greater strength observed can be attributed to more extensive bonding
between the parallel fibers.

Both Casey (24) and Keeney (43) have claimed that fiber-to-fiber
bonding is the most important single factor affecting the strength of
paper. Lignin is of considerable significance in this respect for
two reasons. In the first place, it hinders bonding (1, 26, 27) pre-
sumably because it is a partner in fewer and weaker bonds. Lignin
also is probably responsible for stiffer fibers because the outer
wall of the fiber, which is interpenetrated with lignin, acts as a
sheath on the fiber retarding the imbibition of water and thus restrict-
ing swelling. Many past studies, such as those of Jahn and Holmberg
(25), Peterson, Bray and Ritter (28) and of Kimura, Teratani and Tachi
(29), have been designed to show the effect of lignin on paper
strength. It has been difficult to draw valid conclusions from most
of these because of concomitant changes as the lignin content varied.

Very often, pulps have been characterized chemically, and
attempts have been made to relate the chemical nature of the pulp to
the strength of paper made from it. Because of the complexity of pulp
systems, it is usually difficult to determine such relationships.
Generally, such analyses give a clue to the strength characteristics

which might be anticipated only by virtue of extended experience. For example, it is well known in the rag industry, that cotton pulps low in hemicellulose develop high strength after extensive mechanical treatment. On the other hand, a pulp rich in hemicellulose will develop high strength with considerably less mechanical work. The difference is attributed to the hemicelluloses, but the mechanism by which they act is vague.

The role of hemicelluloses in paper has been debated at length. Cottrall (22) and Greenane (30) have observed that the presence of hemicellulose is coincident with strong papers. Jayme and Rosenfeld (31) postulate that the more highly swelling hemicelluloses in sulfite pulps are concentrated in the outer layers of fibers.

Hemicelluloses may act by one or both of two mechanisms. The proponents of the "mucilage" theory assume that the hemicelluloses swell by imbibing water to form a colloidal mucilage which tends to glue the fibers together, presumably through hydrogen bridges between the fiber elements and the hemicellulose chains. On the other hand, hemicelluloses are conceded to imbibe water to a greater extent than cellulose, so that, by their presence within the structure, the fiber may take up water and swell. The entire fiber structure is thus swollen and loosened, making the fibers more flexible and conformable. At the same time, and perhaps with the added impetus of some mechanical action, some of the fibrils and cellulose chains, particularly those in the noncrystalline regions, are freed from close association with the fiber. Then, when water is removed from the paper structure, the

flexible fiber elements will more readily conform to the influence of surface tension forces so that hydrogen bridges may form between the alcoholic hydroxyl groups of the cellulose chains. Provided the swelling and loosening action can be brought about (although with greater effort) simply by mechanical working, then the latter hypothesis can explain the development of strength in papers made from fibers low in hemicelluloses, such as cotton. Probably both mechanisms obtain.

The flexibility and specific volume of the fibers must affect the conformability and therefore, the bonded area. Giertz (17) stated that thin-walled fibers produce a sheet with higher tensile strength than thick-walled fibers and suggested that this was because of greater flexibility and collapsibility resulting in larger contact surfaces. McKenzie and Higgins (32) caused pulp to swell in pyridine and noted a 50% increase in the strength of papers made from the swollen stock. Subsequent soaking in ethyl alcohol had the opposite effect.

In recent years, a great amount of work has been done on the viscoelastic nature of paper. The earliest reports were those of Kienzl (33), Gibbon (34) and Edge (35). They were followed by a comprehensive study and analysis by Steenberg and others (36-39) and by Mason (40), Rance (41) and Nissan (42). These writers recognize the dual nature of paper as an elastic and a plastic material.

Various mechanical arrangements of ideal elastic springs and viscous dashpots have been conceived to amply describe the behavior of paper under tensile stress and strain, but they shed no light on

the actual mechanism responsible for the behavior. As is well known to all who work with model theory, one must constantly guard against the error of considering two systems identical in all properties simply because they are analagous in some. Although the work on the visco-elastic nature of paper constitutes a good foundation for inductive reasoning, no attempt has yet been made to relate it to the fundamental aspects of the phenomena responsible for sheet strength.

The strength of paper is limited to the strength of the fibers but many have assumed that it is defined by the nature and the extent of interfiber bonding (43, 44). More recently, the simultaneous impor÷ tance of both factors has been recognized. In a recent study, Van den Akker, et al. (45) showed, with selected dyed fibers, that the proportion of broken fibers in a rupture zone could be increased by increasing the bonding between fibers. This thesis illustrates the simultaneous influence of fiber strength and interfiber bonding strength on the tensile breaking length of paper in a specific system.

PRESENTATION OF THE PROBLEM

STATEMENT OF THE PROBLEM

Many isolated studies have shed considerable light on the mechanism whereby paper strength is achieved. Quantitative information has been difficult to obtain because of interference from related variables which inadvertently are altered in most attempts to control the change in only one variable.

Jappe (1) showed that as neutral sulfite semichemical aspen pulp was bleached in the final stage with progressively more chemical, within a certain range, the strength of paper made from the pulp was increased considerably. Apparently, strength changes were accompanied by a minimum number of other alterations; hence, this pulp is a desirable system with which to work in studying paper strength.

The present work involved a study of selected chemical changes in a pulp in an effort to show how they influence the strength of paper made from the pulp. Two objectives were to be served. First, it was proposed to explain the tensile breaking length increase in chlorinated and extracted neutral sulfite semichemical aspen pulp, when the pulp is bleached with hypochlorite. The second objective was to use the controlled conditions of this system to help elucidate the qualitative contributions of fiber strength and capacity for fiber bonding to tensile strength.

ANALYSIS OF THE PROBLEM

For the purpose of this study the definition of strength was limited to the tensile breaking length of paper as defined by TAPPI standard T-404. The object of this limitation was the provision of an acceptable strength test which was relatively simple to define and analyze.

The principal factors which influence the tensile breaking length of paper may be listed as:

I. Intrinsic fiber strength

    A. Crystallinity of the cellulose

    B. Cellulose chain length (D.P.)

    C. Injury and weak spots

II. Frictional effects

    A. Shear effects resulting from proximity of fibers

    B. Other resistive effects

        1. Fiber stiffness

        2. Degree of distortion (curliness, fibrillation)

III. Interfiber bonding strength

    A. Bonded area

        1. Specific surface area of the pulp

        2. Shape of the fibers (including the effects of beating)

        3. Fiber-length distribution

        4. Fiber conformability (swelling tendency, plasticization)

        5. Surface tension of the pulp vehicle

    B. Bonding strength per unit of bonded area

        1. Number of bonds per unit of bonded area

        2. Strength of bonds

            a. Chemical constitution of the surface

                i. Identity spacing of units ($-OH$, etc.)

                ii. Activation energy of the bonding layer

                iii. Tendency to association of water

IV. Stress distribution

    A. Shape of fibers

    B. Sheet formation

This analysis appreciates the probable influence of four major factors on the strength of paper. It also recognizes the dependence of these factors on possible variations in the pulp and paper system, many of which are difficult to define and measure. The individual influences of several considerations affecting a particular factor can very often not be separated. For example, there are two considerations which influence bonding strength per unit of bonded area. These are the number of bonds and the strength of the individual bonds. Although this division can be recognized in the analysis, there is, as yet, no way to separate the individual influences. The above analysis serves to point up the considerations which must be made in evaluating changes in the system.

Jappe speculated that the effect of hypochlorite treatment on fiber strength could only be in the direction of a reduction as a result of the decrease in D.P. of the cellulose. He concluded that the increase

which was observed in the strength of papers could be attributed only to better bonding. His work was not extended to determine which aspects of bonding were actually responsible for the strength increases.

Jappe's speculation with respect to the effect of bleaching on fiber strength was examined in this study. For this purpose, zero-span tensile strength could be used to provide a relative measure of fiber strength. It is conceivable that fiber strength might have been increased. It is imaginable that this could result from a loosening of the fiber elements, because of the removal of incrustants, permitting a more advantageous distribution of stress over the fiber cross section. On the other hand, reduced fiber strength might be anticipated on the basis of lowered D.P. of the cellulose as in the case of cotton fibers.

The effect of frictional resistance to rupture is generally conceded to be negligible relative to that of interfiber bonding. The strength analysis suggests that the frictional effect may be considered in the light of two phenomena. One is the true frictional shearing resistance due to the proximity of adjacent surfaces. Since this proximity is directly related to interfiber bonding, the effect may be considered an aspect of bonding. This is true particularly here where, as will be shown, it is not presently feasible to attempt a complete separation of the factors involved in bonding.

The other aspect of friction is attributable to mechanical inter-twining of fibers, and this is negligible relative to other effects as demonstrated by Klauditz (23) and Van den Akker (10). This has also

been shown to be the case where interfiber bonding was inhibited by forming sheets in nonpolar liquids (9). Thus, for the present purpose, frictional effects will not be considered.

A measure of the specific surface area of pulp may be derived from constant-rate filtration studies using the method described by Whitney and Ingmanson (46). This technique measures the external surface area of water-swollen fibers. Therefore, it is a measure of potential wet-fiber surfaces which may be brought into contact during sheet formation.

Light-scattering measurements, described by Parsons (9) and used by Ratliff (47), Leech (48), Keeney (43) and Haselton (49) may be used to yield estimates of the per cent bonded area. The technique has recently been modified by Ingmanson and Thode, as explained in the appendix.

The shape of fibers should not be altered by bleaching except in so far as some fibers may be collapsed. This effect cannot be measured quantitatively, but it may be qualitatively described from microscopic observations.

A relative measure of the degree of swelling may be obtained from the specific volume of pulp as determined from filtration studies.

The hydrodynamic specific volume is defined as the volume denied to flow; that is, the swollen volume of the fibers plus the volume of water immobilized by the fibers. There is no good method for determining this characteristic of pulps, but the filtration technique probably is one of the best although the error may be as large as 10% (50).

Fiber conformability can perhaps best be described on the basis of compressibility measurements. It probably is dependent on the specific volume or fiber diameter, and therefore on the tendency of the fiber to swell.

The swollen specific volume of pulp fibers has been recognized by many as a factor in the determination of strength. For any particular pulp, this value is a relative measure of the volume or diameter of fibers. A higher volume suggests that the fiber elements are not held so rigidly in the structure, and therefore they may move more easily, relative to one another, under the influence of a stress. Thus, for a given load, a swollen fiber would be deformed to a greater extent with the result that it might contact more surface area of adjacent fibers, increasing the relative bonded area and contributing to an increase in fiber-to-fiber bonding strength.

The presence of plasticizing agents need give no concern as only water was employed in the system.

The chemical constitution of the fiber surface is also a factor which certainly will affect the bonded area per unit of pulp surface area. If it is assumed that lignin does not form hydrogen bonds to the same extent as carbohydrates, there should be increases in per cent bonded area as delignification proceeds. Also, differences might reasonably be expected in the extent to which various carbohydrates (cellulose, hemicelluloses) bond.

The viscosity-velocity product (VVP) (51) is an index of the total

effective bonding strength, and it may be used, together with per cent

bonded area, to indicate changes in bonding strength per unit of bonded

area or the intensity of bonding. Although the analysis of the factors

affecting tensile strength shows a breakdown of bonding strength per unit

of bonded area into two components, it is felt that the separation pro-

bably cannot be achieved. Corte and Schashek (52) investigated the

deuterium exchange reaction with cellulose and applied it to papers

having different degrees of interfiber bonding in an effort to determine

the number of hydrogen bonds and the strength of the bonds. The free or

unbonded hydroxyl groups would be expected to enter into reaction more

readily than those involved in hydrogen bonding. Unfortunately, a sound

thermodynamic basis for a sharp distinction is not evident and therefore,

the method is not defensible. The strength analysis serves simply to

recognize the factors which influence bonding strength, but it was felt

that an investigation of this group of variables, designed to effect a

separation of the number from the strength of the bonds, was beyond the

scope of this thesis.

Stress-raising effects and surface tension of the solvent system

need not be considered. The system did not include fillers nor other

foreign bodies, and the solvent was water at room temperature.

Fiber shape and fiber-length distribution are factors which in-

fluence bonding and have been considered in that light.

Sheet formation certainly will effect the tensile strength of

paper, but it was not proposed as a part of this study. Formation may

be controlled by variations in the sheetmaking procedure. The experimental data indicated that this was unnecessary.

The analysis of tensile strength indicates the several factors which may influence the strength of paper and suggests methods of measurement and control. The purpose of the work was to vary some of these factors while controlling others and to relate the strength changes to alterations in the physical and chemical nature of the pulp.

APPROACH TO THE PROBLEM

For the purpose of this study, the hypochlorite bleaching of neutral sulfite semichemical aspen pulp was selected as the means of effecting changes in the strength and other properties of the pulp. This choice was based on the previous discovery that relatively few changes are realized in the pulp system when treated in this manner. Therefore, it appeared that a pulp system was available which was amenable to relatively simple control.

The approach involved the production of a neutral sulfite pulp from aspenwood by cooking according to a schedule used by Jappe (1). This pulp was washed, screened, bleached with chlorine and finally extracted with caustic soda to produce the starting material for the thesis. Variations were then wrought in the pulp by treating with sodium hypochlorite solutions of varying concentration.

The changes induced by hypochlorite bleaching in the system under consideration may be classified into two groups:

A. Chemical changes

　　1. Lignin

　　2. Cellulose

　　3. Hemicelluloses

B. Physical changes

　　1. Specific surface area

　　2. Specific volume

　　3. Compressibility

　　4. Fiber length

　　5. Bonding potential

　　6. Strength of fiber.

Factors (1) through (4) listed under physical changes contribute
to a quality which describes the extent to which fibers may be brought
into proximity, but they tell nothing of the extent of bonding to anti-
cipate. For example, fibers may have a considerable surface area; they
may be swollen; they may be flexible; they may be collapsed, but they
need not necessarily be amenable to bonding. The bonded area, number
of bonds and strength of the bonds, that is, the bonding, depends on
the nature of the surface. So far as bonding is concerned, then, the
factors which should be considered include those which affect the
proximity of surfaces at the time the bonds are formed and also the
factors which influence the tendency of those surfaces to associate
tenaciously. The latter factor may be visualized as surface activity
or perhaps the ability to adsorb materials. It is thus evident that
the nature of the fiber surface should be considered.

EXPERIMENTAL PROCEDURE

WOOD PROCUREMENT

Pulpwood was cut in the Ottawa National Forest of upper Michigan the latter part of October, 1956. Two nine-inch diameter aspen (P. tremuloides) trees, which were 42 and 43 years old, were felled. The lower two feet of each tree was discarded in order to avoid reaction wood. The trees were cut into 4-foot logs which were barked by hand using an axe and a drawknife. Knots and limbs were removed as best as possible to reduce the quantity of shives in the pulp. About half of the wood was chipped in the Institute Carthage two-knife, 36-inch chipper set to cut a 3/4-inch chip. The chips were screened on a 1/4 by 1/4-inch screen and large chips and pieces of knots were removed by hand. The chips had an ovendry content of 57.0%.

PULPING

Cooking was done in an A. O. Smith rotary digester using 41 kg. of O.D. wood with a water-to-wood ratio of 5 cc. water per gram of O.D. wood. The cooking liquor contained 18.0% sodium sulfite and 5.0% sodium carbonate (based on the O.D. wood). The initial pH of the liquor was 11.0 and the final pH was 8.8. The cooking schedule (detailed in the appendix) included a rise to a maximum temperature of 172°C. over a three-hour period and cooking at that temperature for an additional 1-1/2 hours at a maximum pressure of 130 p.s.i. The charge was blown to a blowpit and immediately recovered for refining in the Institute

Bauer refiner with plates set at zero clearance, producing a fairly
well-refined pulp with a minimum of shives.

The pulp was washed at high consistency with tap water for three
hours and was then screened through 0.010-inch flat screens. The
screened pulp was dewatered by centrifuging, broken up in a laboratory
pulp shredder and stored in polyethylene bags at 5°C., with formalin
added as preservative. The pulp yield was 66.0%. The permanganate
number (TAPPI RC-242) was 74 indicating a bleach demand of about 18.5%
chlorine.

PRELIMINARY BLEACHING

A series of preliminary chlorinations was run on small batches
(100 g., O.D.) of pulp with a view to determining the optimum quantity
of chlorine to apply in the first bleaching stage. Chlorine was
applied to various batches in the amount of 12 to 20% of the pulp.
Consistency was 3.0%. Extraction was accomplished with two per cent
caustic soda.

The total lignin content was considered to be the sum of the
Klason lignin and apparent soluble lignin. The latter was determined
from the optical density of the Klason lignin filtrate measured at
230 mmu with the Beckman spectrophotometer as described by Brauns,
Buchanan and Leaf (47). On the basis of the total lignin contents of
the above pulps, a larger batch was chlorinated with 23% chlorine.
It was desired that the pulp for study have a total lignin content of

about 2.5% so that the possible effect of lignin on strength could be determined.

The larger chlorination was run on an exploratory basis to insure that the chosen conditions would produce the desired pulp. The pulp appeared brighter than expected, and a lignin determination indicated that practically all of the lignin had been removed. This finding bore out Jappe's contention that bleaching in small-scale equipment is difficult to scale up, probably because of differences in chlorine losses.

A large exploratory chlorination (750 grams of pulp) was finally made using data provided by Jappe (1). The resultant pulp appeared satisfactory. It had a Klason lignin content of 1.41% and total lignin content of 2.61%.

In order to study the effect of delignification on strength properties it was desired to minimize other changes in the system. The determination of hemicelluloses and D.P. of the hemicelluloses indicated that this was the case.

BLEACHING

Ten batches of the screened pulp were chlorinated in the large laboratory chlorinator at a consistency of 2.55%. The chlorinator was covered with rubber dental dam in an effort to retain the gas in the system. Chlorine was applied in the amount of 14.7% of the O.D. pulp, and the reaction was carried to exhaustion. The chlorinated pulp was washed with warm filtered tap water to a pH of at least 7.0.

Extraction was carried out for 2 hours at 40°C. in a Pfaudler mixer with two per cent caustic soda (based on the O.D. pulp furnished to the chlorinator). Extraction consistency was 10%. Each extraction batch was washed thoroughly with warm, filtered tap water and then blended with the rest of the extracted pulp in a large stainless steel wash tank, where the entire batch was washed with warm tap water for about four hours. The pulp was dewatered in a centrifuge, and fines were recovered on a muslin-covered washbox. The blended pulp was broken up in a laboratory pulp shredder.

The composite of all ten batches is referred to as Bleach 10. This was the starting material for the thesis.

The third bleaching stage was applied to the pulp rapidly after the initial treatment so as to obviate the necessity for solvent drying prior to hypochlorite treatment. Jappe (1) found that storing the chlorinated and extracted pulp in the wet state caused a change in bleach demand. This phenomenon apparently is due to diffusion of hypochlorite-consuming materials from the inner parts of the fiber structure to the surface, where they are immediately available to the hypochlorite. Solvent drying of the chlorinated and extracted pulp checked this tendency to change in bleach demand, but the solvent-exchange procedure was difficult to duplicate.

Portions of pulp from Bleach 10 were treated with sodium hypochlorite solution ("Hi-lex"). Five different pulps were produced by applying 0.5, 1.5, 3.0, 6.0, and 9.0% available chlorine (as hypochlorite)

to different batches. The bleaching containers were five-gallon earthenware crocks. The conditions were: consistency of 10% O.D., temperature 40°C., pH maintained between 10.0 and 10.5 with caustic soda, and reaction time two hours or until the chlorine was exhausted.

When the chemical was not exhausted within two hours, the reaction was stopped by the addition of sodium sulfite solution. The pulps were washed with hot, filtered tap water for about twenty minutes and then soaked for four hours in the crocks and finally thoroughly washed on a muslin-covered washbox. They were dewatered in a Büchner funnel to a consistency of about 25% O.D., broken up in the laboratory pulp shredder and stored in polyethylene bags at 5°C., with formalin added as preservative.

The initial phase of the pulp examination indicated that the fines content of the Bleach 10 pulp was inordinately high. This pulp had not been treated with hypochlorite and washed as the others. Accordingly, it was given the same washing treatment to which the other pulps had been subjected.

Handsheets for physical testing were made from unbeaten stock.

EVALUATION METHODS

The test methods used in this thesis are listed below:

Permanganate number	TAPPI RC-242
Analysis of bleach liquor	IM 112

G. E. brightness   IM 412

Extractives   IM 428

Klason lignin   IM 428

Soluble lignin   Brauns, et al. (53)

Ash   Described by Jappe (1)

Hemicellulose   Quick (55)

Alkali-resistant cellulose   Quick (55)

Viscosity of hemicellulose   Jappe (1)

Viscosity of pulp and A.R.C.   Jappe (1)

Filtration resistance   Ingmanson (46)

Water-retention value   See appendix

Fiber length   Graff (58)

Fiber classification   IM 415

Handsheet preparation   IM 411

Handsheet formation   Davis, et al (80)

Relative bonded area   Ingmanson (77), see appendix

Bonding strength   Wink, et al. (51)

Apparent density   IM 411

Intrinsic fiber strength   TAPPI T-231 sm-53

Tensile breaking length   IM 511

Elongation   See appendix

Rupture work   See appendix

Tearing strength   IM 512

EXPERIMENTAL DATA

PULP NOMENCLATURE

Much of the discussion which follows makes reference to the experimental pulps by number. Bleach 10 was the first pulp of the series. It was a fiberized neutral sulfite semichemical aspen pulp which had been chlorinated and alkali extracted to remove most of the lignin. The other pulps, Bleaches 11 through 15, differed as a result of the subsequent treatment. Each was subjected to a further increasingly severe bleaching operation with sodium hypochlorite as indicated in Table I.

TABLE I

HYPOCHLORITE TREATMENT

Bleach No.	Chlorine Applied as Hypochlorite, %
10	0
11	0.5
12	1.5
13	3.0
14	6.0
15	9.0

ANALYTICAL DATA

Analytical determinations were made on well-mixed samples of the whole pulps, retained for the purpose. The experimental laboratory data are summarized in Table II. Electron photomicrographs of fibers from Bleach 11 and Bleach 15 are shown in Figures 1 through 4.

TABLE II

SUMMARY OF EXPERIMENTAL TEST RESULTS

	10	11	12	13	14	15
Bleach						
Chlorine applied (as hypochlorite), %	0	0.5	1.5	3.0	6.0	9.0
Pulp yield (ovendry wood basis), %	54.9	53.4	53.3	52.5	51.5	51.1
G. E. brightness, pt.	51.8	66.2	80.4	83.4	85.4	86.2

ANALYTICAL DATA

	10	11	12	13	14	15
Alcohol soluble (ovendry pulp basis), %	1.12	1.22	1.36	1.17	1.32	1.20
Lignin, %[a]						
Klason	1.94	1.55	1.49	1.29	0.58	0.72
Apparent soluble	1.21	1.08	0.97	1.13	1.01	0.64
Total	3.15	2.63	2.46	2.42	1.59	1.36
Carbohydrates (ovendry pulp basis), %						
5% hemicellulose (ash free)	13.8	14.1	14.0	14.5	14.6	14.4
16% hemicellulose (ash free)	5.8	6.1	6.3	6.6	5.4	5.5
Alkali-resistant cellulose (ARC)	78.1	77.7	77.0	76.1	76.6	76.3
Quality of carbohydrates:						
D.P. of 5% hemicellulose	130	150	150	140	135	125
D.P. of 16% hemicellulose	145	145	140	120	150	140
Weighted average D.P. of hemicellulose	135	145	140	135	145	135
Pulp viscosity, cp.	46.07	42.93	34.45	28.01	19.62	13.30
Approximate pulp D.P.[b]	1990	1940	1810	1680	1460	1220

FIBER PROPERTIES

	10	11	12	13	14	15
*Hydrodynamic specific surface, sq. cm./g.	15,390	15,330	—	15,780	16,340	16,650
*Specific volume, cc./g.	1.57	1.61	—	1.72	1.73	1.75
*Water retention value (WRV), %	320.1	315.1	321.5	322.7	324.8	325.9
Specific volume (calculated from WRV), c.cm./g.[c]	3.8	3.8	3.8	3.8	3.9	3.9
*Weighted average fiber length, mm.[d]	1.03	0.92	—	0.93	—	0.87
Tracheids, %	87	79	—	87	—	89
Vessels, %	8	18	—	10	—	8
Screen classification of handsheet stock:						
On 20-mesh, %	9.1	9.7	8.5	7.6	4.7	0.5
On 20, through 35-mesh, %	45.3	47.8	48.1	48.0	48.9	46.7
On 35, through 65-mesh, %	26.7	25.1	25.8	26.0	26.5	28.9
On 65, through 150-mesh, %	12.6	12.4	12.7	12.8	13.1	14.9
Through 150-mesh (by diff.), %	6.3	4.3	4.9	5.6	6.8	9.0

PHYSICAL PROPERTIES OF HANDSHEETS:[i]

	10	11	12	13	14	15
Thwing formation, units	46.3	47.8	50.0	48.0	50.8	59.2
Apparent density, g./cc.	0.677	0.676	0.704	0.734	0.745	0.782
*Relative bonded area (RBA), %	31.5	32.4	33.7	35.1	38.5	41.7
*Viscosity-velocity product (VVP), kp.cm./sec.	3.04	4.10	4.53	5.50	5.47	6.42
VVP/RBA, kp.cm./sec.	9.65	12.65	13.44	15.68	14.22	15.41
Intrinsic fiber strength (zero-span breaking length), m.	13,550	13,100	13,160	13,050	11,620	11,100
Tensile breaking length, m.	4,325	4,490	5,160	5,160	5,340	5,800
Elongation, %[e]	2.01	2.05	2.39	2.43	2.32	2.46
Rupture work in tension, in.-lb.[f]	0.385	0.385	0.523	0.600	0.573	0.625
Tear factor	0.779	0.770	0.724	0.716	0.649	0.590
Breaking length, % of fiber strength	31.9	34.3	39.2	39.6	46.0	52.2
Increase in tensile strength, %[g,h]	—	5.3	12.5	19.5	28.7	34.3
Increase in relative bonded area, %[g,h]	--	2.5	7.0	13.0	23.2	31.7
Increase in VVP, %[h]	—	23.3	49.2	71.0	95.7	106.5

[a] Based on ovendry, extracted pulp
[b] Determined from a slide rule designed by the Buckeye Cellulose Corporation
[c] Pycnometric specific volume of cellulose taken as 0.62 cc. /g.
[d] Optical projection method
[e] Specimen length, 2.93 in.
[f] Work required to rupture specimen 2.93 in. x 15 mm. wide
[g] Based on Bleach 10
[h] Data from smoothed curves
[i] Basis weight 65.2 g./sq.m.

* Determinations were carried out with assistance

The G.E. brightness of the pulps is not significant for the purpose of this thesis, but it verifies Jappe's finding that the maximum brightness attainable under these conditions was about 86 points G.E.

The alcohol-soluble fractions of the pulps were not significantly different. There was considerable variation in the results and no trend was indicated. This has been the experience of others working with hardwood pulps (54). The variation in extractives content appeared to be random and the numerical average of all determinations was taken. Averaged this way, the alcohol-soluble extractives amounted to 1.26%.

Difficulties were encountered in the lignin determination, similar to those met by Jappe. Several modifications of the method were attempted with little success. The values reported for Klason, soluble and total lignin are averages of six determinations. The values reported are considered to be representative, relative estimates of the actual lignin contents of the pulps, within the accuracy of the determination. The lignin determination is discussed more fully in the appendix.

When an attempt is made to obtain a summation of the analytical data on page 29, certain limitations become apparent. In Bleach 10 a summation of the extractives, total lignin and total carbohydrates on the O.D. pulp basis gives the value 102.0 per cent. Some of the summations which follow are also over 100 per cent; exceptions are found in the last two. There appears to be an overlap of data—part of which

may be due to the questionable so-called "soluble lignin". On the other hand, there is a certain trend, indicating a decrease on the total carbohydrates with increasing severity of the bleach. Cellulose decreases gradually whereas the hemicelluloses show an initial rise with subsequent drop. Whether the hemicellulose loss is real or simply due to the analytical limitations is a moot question. A modest loss from highly bleached pulps might be anticipated as a result of oxidative cleavage in alkaline solution as explained on page 62. The data indicate no significant variation in the proportions of carbohydrates in the pulps.

Wise (61) cites work which indicates that the D.P. of hemicelluloses may vary between 50 and 300 with an average of about 150. Also, it appears from the meager information available that this value is not significantly altered by bleaching or alkaline treatments. For example, even an extensive treatment with chlorine dioxide in pyridine caused a reduction only to about 120 in the D.P. of beechwood hemicelluloses.

The present data indicate that the hemicelluloses are resistant to attack, but that the cellulose is rather severely degraded and solubilized to a slight extent. Another hypothesis is that bleaching and subsequent alkaline extractions are responsible for progressively increased losses, through solution, of both alkali-resistant cellulose and hemicellulose. At the same time, some of the hemicelluloses lost may be replaced by degraded cellulose, functioning as hemicellulose, with the result that there apparently is no net change in the

hemicellulose content. It is difficult to believe that the degradation
of cellulose to hemicellulose would fortuitously balance the hemicellu-
lose loss in each case. The data are not sufficiently accurate to spe-
culate further.

Apparently, there was no measurable change in the average D.P. of
the hemicelluloses. On the other hand, it appears that the cellulose
was rather severely attacked, particularly when large quantities of
bleaching agent were. applied. The number average D.P. of the pulp was
reduced about 40%.

Microscopic examination of fibers dyed with bis- (p-dimethyl-
amino) -azobenzene added subjective evidence to the data of Jappe (1)
indicating an increase in carboxylation of the carbohydrates.

PHYSICAL PROPERTIES

The increase in specific surface area from 15,300 sq. cm./g. to
about 16,650 sq. cm./g. represents an increase of about 9.0%. This
can be accounted for on the basis of the deshiving action of the
bleaching process, and by the opening of the fiber wall, illustrated
by the electron photomicrographs of Figures 1 to 4. The delignifica-
tion and deshiving were responsible for the moderate change in the
content of fines in the pulps, effected by more severe bleaching and
evidenced by the screen classifications. Microscopic examination
showed that the material passing a 150-mesh screen (fines) consisted
primarily of ray parenchyma cells. These cells apparently were re-
leased from shives and fibers as delignification progressed.

The specific volume of a pulp is not so accurately determined by filtration methods as the specific surface area. The data indicate that the hypochlorite bleaching caused an increase from 1.57 to 1.75 cc./g. in the specific volume of the pulps. This increase is only slightly greater than the accuracy of the determination but, paralleling Jappe's findings, the trend is consistent and therefore the effect probably is real. The water-retention value data also suggest an increase in swelling as indicated by the upward trend in water retained during the test, even though the change is not great.

The electron photomicrographs of Figures 1 to 4 show that the fibrous character is altered in a manner which would have a similar end effect to an increase in specific volume. The photographs show that the more severely treated pulps (represented by Bleach 15) have had the outer fiber wall broken and in many places "peeled" from the parent fiber, thus exposing the inner part of the fiber. The effect of this phenomenon, apart from increasing the surface area available for bonding, would be to weaken the fibers and fiber elements so that they might be more easily deformed during the papermaking process, giving a more conformable fiber.

The data of Table II show that there was no difference in fiber length determined by the optical technique. Observations of stained fibers with the light microscope showed no great differences between the pulps. However, an experienced operator, studying the fibers, suggested that he gained an impression of greater flexibility in those pulp fibers that had been treated with greater quantities of bleaching

agent. This was deduced from the manner in which the dried fibers lay
in association with each other on the slides. It must be emphasized
that this is a subjective observation, but it was made by a man with
considerable experience in the field of fiber microscopy (57) and was
an unexpected observation volunteered as a point of interest.

MICROSCOPIC STUDIES

LIGHT MICROSCOPE

The weighted average fiber length, determined by the optical
projection technique of Graff (58), indicated that increased amounts
of bleaching agent had no significant effect on fiber length. Exami-
nation of the slides showed an increase in the quantity of debris with
bleaching. The Bauer-McNett classification confirmed this observation,
and an examination of the fines fraction (through 150-mesh) from the
classification showed that this fine debris was composed of about 80%
(by weight) of parenchyma cells, that is, ray cells separated from the
tracheids as a result of bleaching. Little if any physical difference
between fibers was obvious from the examination of dried fibers with
the light microscope. There was a definite reduction in the number
and size of shives resulting from a more severe bleaching treatment.

Fibers stained with "C" stain and with bis- (p-dimethylamino)
-azobenzene corroborated previous information that most of the
residual lignin resides in the shives. The azo dye also produced evi-
dence of oxidation in the cellulose. This dye is used for the detec-
tion of lignin, but it probably also stains carboxyl groups (56). Dyed

slides showed a progressive decrease in coloration of shives, indicating lower lignin contents as bleaching was enhanced. At the same time, there appeared to be a slight increase in the coloration of tracheids, suggesting an increase in carboxylation. This corroborates the increase in carboxyl content determined by Jappe (1). Although the present information is subjective, it is in harmony with some of the findings discussed later.

ELECTRON MICROSCOPE

Since the examination of fibers in the light microscope showed few differences between pulps, the electron microscope was used. Very significant differences then became evident between fibers from Bleach 11 and Bleach 15. Bleach 11 fibers could be characterized as intact, smooth-surfaced entities illustrated by Figures 1 and 2. On the other hand, fibers from Bleach 15 had many breaks in the surface with the primary wall wrinkled, checked, cracked, and severed, exposing the inner part of the fiber. The initial stages of this action were evidenced by a wrinkling of the surface. More progressive action resulted in the rupture of the outer wall as shown in Figure 3. This layer appeared to be unfolded from the fiber and the free edge was generally curled in the direction in which it originally lay around the fiber. Figure 4 illustrates part of an extensive area of the exposed inner side of the primary wall.

HANDSHEET PROPERTIES

The Thwing formation numbers of the handsheets were determined

Figure 1. Electron Micrograph of Typical Bleach 11 Fiber Showing
Smooth Surface. (Chromium shadowed at 30°; light part
is fiber)

Figure 2. Electron Micrograph of Bleach 11 Fiber Showing Intact Fiber
Wall. (Chromium shadowed at 30°; light portion is fiber)

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Figure 3. Electron Micrograph of Bleach 15 Fiber Showing Outer
Layer of Fiber Wall Split from Parent Fiber. (Chromium shadowed at 30°; light portion is fiber)

Figure 4. Electron Micrograph of Bleach 15 Fiber Showing Part of
a Detached Outer Layer Held to the Fiber by Several Fi-
brils. (Chromium shadowed at 30°; light portion is fiber)

and are reported in Table II. Favis, Robertson and Mason (76) found a slight dependence of strength properties on formation. There was no significant change in the formation of the present handsheets, within the limits of reliability of the test, and the effect was not considered further.

The determination of relative bonded area was based on the optical method of Parsons (9), modified so as to avoid the use of butanol and to provide a better measure of the scattering coefficient of unbonded handsheets. This method is described in the appendix.

The zero-span breaking length of handsheets was taken as a measure of intrinsic fiber strength. There is some debate about the legitimacy of this procedure. It assumes that fibers are only broken and not pulled from the sheet so that variations in interfiber bonding are of no consequence. Studies by Wink (62) have shown that the test is reproducible, when well-designed jaws are employed and care is exercised in operating the instrument. Van den Akker, Lathrop, et al. (63) have demonstrated a very good correlation between zero-span breaking length and individual fiber strength for both coniferous and deciduous fibers.

The tensile properties of handsheets were determined with a Baldwin-Southwark universal testing machine operating at constant rate of strain. Rupture work in tension was measured as the area under the recorded load-elongation curve and represents a relative measure of the energy absorbed by a specimen before rupture.

The significance of the data and relationships between the several aspects considered is the subject of the next section of this dissertation.

DISCUSSION OF RESULTS

Jappe's study of hypochlorite as the third bleaching stage for
NSSC aspen pulp showed that a tensile strength increase resulted from
the bleaching. This was attributed to delignification with a con-
comitant increase in specific surface area. It was theorized that an
increase in bonding was responsible for the strength increase.

The results of this study confirm Jappe's finding that hypo-
chlorite bleaching degrades lignin to soluble products, and that its
removal from pulp is almost complete.

Some difficulty was encountered in determining the lignin con-
tents of the pulps. A variation study of this determination, applied
to the pulps, suggested a technique for optimum results. This is
described in the appendix. Past work has pointed to shortcomings of
the Klason lignin determination (1, 81, 82). The method was originally
conceived as a means of measuring the lignin content of untreated con-
iferous woods. The value determined is defined by the method. The
accuracy of the method is limited when applied to deciduous woods,
to products with low lignin content (pulps), to degraded lignin, to
such modified lignin as lignosulfonates, and particularly, to bleached
pulps. However, in the opinion of the writer, the Klason lignin deter-
mination still is the best available measure of lignin-like material
in a pulp. Although there is some misgiving about discussing speci-
fic values derived from this measure, the trend (paralleling that
previously determined) has been shown and may be used as the basis
for argument.

Although the reaction of hypochlorite was primarily with lignin, the cellulose was degraded but not greatly changed in amount. The effect of this degradation on fiber strength will be discussed later. The uronic acid content of the cellulose was found by Jappe to be increased as a result of the oxidizing action, and this might account in some measure for increased bonding strength. Hypochlorite bleaching appeared to have no measurable effect on the hemicellulose content of the pulp studied.

Jappe's findings with respect to surface area and specific volume changes have been verified and his concept of the action of hypochlorite has been expanded in the light of additional information. His thinking was that lignin interpenetrated the fiber wall, shielding some of the cellulose and restricting the swelling tendency of the pulp. By examining lignin residues with the light microscope, he observed a decrease in the quantity of lignin in the fiber wall. He also found an increase in specific surface area which he attributed to increased swelling of the fibers as a result of delignification.

The changes in specific volume found in the present work do not fully account for the increases in specific surface area. The photographic evidence of Figures 1 to 4 indicates that delignification exposes more surface area through a form of fibrillation. It appears that the removal of lignin permits a relaxation of fibrils in the outer regions of the fiber. Increased surface area, therefore, apparently results both from more swollen fibers and from fibrillation.

Enhanced bonding strength is probably due to the increased surface area thus available and to an improvement in the bonding capability of the surfaces of bleached fibers.

INTERFIBER BONDING

The data show a continued reduction in lignin content with increasing application of hypochlorite. The direct result of lignin removal was a modest increase in the fines content of the pulp. This was not obvious from an optical determination of fiber length, but it was demonstrated by the screen classification data. Microscopic observation of the fine fractions (through 150 mesh) of the various pulps, showed that they consisted almost entirely of parenchyma cells. With the removal of the intercellular lignin, these fragments were free to exist as individual entities, whereas in the unbleached pulp they remained attached to the fiber tracheids. This supports Jappe's finding that bleaching caused a deshiving action.

Figures 1 to 4 are electron photomicrographs which show a destructive effect on the outer wall of fiber tracheids. The hypochlorite treatment caused a wrinkling, cracking and severing of the outer wall from the parent fibers. The outer wall probably consists of a more or less coherent fiber sheath composed of an interpenetrating system of carbohydrate and residual lignin. As a result of hypochlorite treatment, most of the lignin was dissolved, leaving a weaker structure so that a very mild swelling action caused it to wrinkle and rupture. Thus, as lignin was removed from the outer regions of the fiber,

fibrils were released to produce the fibrillated structure shown by the photographs. In cases where the outer layer was split off as an entity, the surface created was probably composed of cellulose and hemicellulose. It should be pointed out that this line of reasoning does not assume the chemical removal of a sheath as an entity, but rather the dissolution of part of the components in the layer. Three effects are postulated: the remaining structure is richer in carbohydrate; the wall is weaker and more readily ruptured, and the new surface resulting from rupture consists of less contaminated carbohydrates.

The fact that delignification reduces the resistance of the outer wall to a swelling action was borne out by Jappe's swelling study. It was shown that all pulps exhibited ballooning, but the pulp treated with six per cent hypochlorite dissolved in $0.25\underline{M}$ cupriethylenediamine solution in 1.5 minutes, while 12 minutes was required to dissolve pulp treated with only 1.5% chlorine as hypochlorite.

The change in hydrodynamic specific surface area from 15,300 sq. cm./g. to 16,650 sq. cm./g. may be accounted for by the increase in fines released from fibers as a result of delignification, and by the development of fiber or "fibril" surface area when outer wall material is severed from the parent fibers. The development of fiber surface area with bleaching is shown in Figure 5. The change appeared to be approximately linear over the initial range of the study, but after the lignin content was reduced below about 1.5% the trend seemed to level off. The increase in surface area as delignification proceeded is shown in Figure 6. Thus, it is evident that extensive delignification

results in an increase in surface area; this is due, in part, to release of fines, and, in part, to the generation of new surface resulting from splitting off of the outer layers of the fiber wall.

The effective specific volume of the pulp, as measured by the filtration technique, increased about 11% over the range of pulps studied, as shown by Figure 7. Although the change is only slightly greater than the accuracy of the determination, the upward trend is consistent, and therefore a real effect appears to be the fact. The trend and magnitude of the increase parallels that found by Jappe, but the percentage change is double. The water-retention value determinations also indicate a moderate increase in specific volume. This conclusion is based on the trend rather than on the magnitude of the change. The specific volumes, calculated from the water-retention values, are much greater than seems reasonable.

Jappe found that the surface area he measured corresponded to the respective specific volumes, basing his analysis on the assumptions that swelling alone was responsible for increased surface, that fibers are cylindrical, and that nocchange of length is produced by bleaching. Since surface area depends on the first power of the diameter and volume on the square of the diameter, the relationship

$$\underline{v} = k\underline{S}^2 \tag{1}$$

should hold. Proportions calculated from

$$\underline{v}_2 = \underline{v}_1 (\underline{S}_2/\underline{S}_1)^{1/2} \tag{2}$$

should also represent the experimental data. When the best estimates

Figure 5. Hydrodynamic Specific Surface Area of Pulps

Figure 6. Specific Surface Area vs. Total Lignin Content

Figure 7. Effective Specific Volume of Pulps

of the present data, taken from the smoothed curves of Figures 5 and 7 are substituted into (2), it is found that increases in specific volume account for only a portion of the increases in surface area. The remainder of the increased surface area can be accounted for on the basis of fibrillation shown in Figures 3 and 4 and by liberation of fines.

Specific volume has been considered because it presumably measures the extent of swelling in a pulp. In a swollen pulp fiber the outer wall might be ruptured, and also, intrafiber bonding between fiber elements would probably be decreased so that shearing resistance to deformation would be reduced. The wetting, softening, and loosening action of a swelling agent would thus make the fibers more conformable.

There is no satisfactory method available for measuring individual fiber conformability. It is possible that wet fiber pad compressibility is an indication of this property. The compressibility data for the present pulps, shown in Table VII of the appendix, were of such a nature that no distinction could be made between pulps. However, this does not preclude the possible existence of an effect that the technique did not measure.

The conformability of fibers is a factor of considerable significance in the development of paper strength. Fiber conformability connotes a minimum resistance to deformation. That is, a conformable fiber is one which is readily deformed by mechanical or hydraulic pressures so that existing surfaces may be brought into such close

proximity that hydrogen bonds may be formed at the critical stage of paper strength development.

In the case of pulps used for this study, it has been shown by photographs that hypochlorite treatment causes the fiber surface to be ruptured. The sheath which initially surrounded the fiber, restricting deformation, is no longer intact so that the fibers might more readily bend at the point of such a surface imperfection. The net effect of this would also be to increase the conformability of the pulp fibers.

The significance of fiber surface rupture, shown with the electron microscope, is threefold. The effect accounts for an increase in fiber specific surface area of the pulp and for enhanced fiber conformability. The third important factor is the nature of the fiber surface.

The outer walls of the fibers appear smooth and probably are composed of an interpenetrating system of carbohydrate and lignin. Much of the area may be shielded from bonding by lignin. In the case of those fibers with cracked, open fiber surfaces, the secondary wall of the fiber is exposed. This possibly is carbohydrate, relatively free from lignin. This would be expected to be more apt to bond so that the portion of area bonded (relative bonded area) should be increased and so might the strength of bonding per unit of bonded area. As discussed below, both of these hypotheses are supported by the data plotted in Figures 8 and 10.

The relative bonded area exhibits a continued increase over the range of pulps studied, as shown in Figure 8. This might be attributed to increased fiber conformability and to the removal of lignin from available surface area. The first factor permits surface tension forces in the sheet to deform fibers and bring a greater proportion of available surface area into contact, increasing the extent to which this surface is utilized. Then, as a consequence of the existence of surface more apt to bond (less shielding or restriction by lignin), a greater proportion does, in fact, bond together. The increased effectiveness of the original wet surface in achieving bonding in the final dried handsheet is indicated by the ratios of relative bonded area to specific surface tabulated in Table III.

The result of higher relative bonded area, and perhaps of greater bond density, is an increase in the over-all interfiber bonding strength shown in Figure 9.

TABLE III

RATIO OF RELATIVE BONDED AREA TO HYDRODYNAMIC
SPECIFIC SURFACE AREA
(Based on data from smoothed curves)

Bleach No.	RBA/S_0
10	2.06×10^{-3}
11	2.11×10^{-3}
12	2.15×10^{-3}
13	2.25×10^{-3}
14	2.37×10^{-3}
15	2.50×10^{-3}

Figure 8. Relative Bonded Area of Standard Handsheets

Figure 9. Interfiber Bonding Strength

A further factor contributing to increased interfiber bonding strength is an apparent increase in the bonding strength per unit of relative bonded area over the range of conditions studied in the series of pulps. This is demonstrated by Figure 10. This treatment of the data was first used by Keeney (43) and is intended to compare the increase in over-all bonding (VVP) with the increase in relative bonded area and to show that the over-all bonding increases more rapidly than the relative bonded area.

The continued increase in interfiber bonding strength per unit of bonded area, shown in Figure 10, must be due to either an increase in bond density (more bonds per unit of bonded area) or to an increase in the strength of the bonds, or both. It is impossible, with present techniques, to separate these two possibilities. In the present case, it is probable that both phenomena are responsible for the increase shown. It is reasonable, in the first place, to expect a greater bond density in the case of a pulp with lignin or other interfering constituents removed. If two purified fibers are brought into intimate contact, one would expect more bonds per unit of contacting surface than if the surface areas were contaminated with lignin. Secondly, greater bond strength might be a legitimate speculation. Microscopic examination of dyed fibers and Jappe's analytical work indicated an increase in carboxylation of the cellulose resulting from hypochlorite treatment. Jappe's data show an increase in carboxyl content of the A.R.C. from 3.1 meq./100 g. for the pulp corresponding to Bleach 10 to 4.1 meq./100 g. for the pulp corresponding to Bleach 14.

Figure 10. Efficiency of Bonded Area

Hydrogen bridges involving carboxyl groups may have a greater bond energy than those in which aliphatic hydroxyl groups are partners. Pauling (64) demonstrated this fact by comparing the hydrogen bond energy of formic and acetic acids with the energy of the hydrogen bond in ice. "The increased strength of the carboxyl hydrogen bond can be accounted for on the basis of resonance to structure B which gives a resultant

A   B

positive charge to the oxygen atom which donates the proton in hydrogen bond formation, and thus increases the ionic character of the O-H bond and the positive charge of the hydrogen atom. It also gives to the other oxygen atom, the proton acceptor, an increased negative charge. Both of these effects operate to increase the strength of the O-H...O bond".

Figure 11 shows the change, through the series of pulps, of the ratio of over-all bonding strength to hydrodynamic specific surface area. This indicates that pulps bleached under the conditions employed in the thesis work developed a given interfiber bonding strength with less specific surface area than the unbleached pulp; that is, bleached surface is more effective in developing strength.

Independent evidence of the effectiveness of the bleached pulp

surfaces in contributing to strength, and substantiating the
conclusions based on Figure 10, is discussed on pages 69 to 74.

SUMMARY

Hypochlorite bleaching of chlorinated and extracted NSSC aspen
pulp was responsible for delignification as shown by Jappe. This re-
sulted in increased hydrodynamic specific surface area by two mecha-
nisms: deshiving of the pulp and fibrillation caused by splitting of
the outer layer from the fibers. The relative bonded area increased
faster than did the specific surface area. This means that, as the
surface area was increased, there was also an increase in the effec-
tiveness of this surface in making optical contact. Besides changes in
surface area and relative bonded area, there was also a marked in-
crease in bonding strength—even greater than the increase in relative
bonded area. This implies an increase in the bonding per unit of
bonded area which could come about either by an increase in bond
density or in strength of the individual bonds. In effect, bleaching
provided a surface better capable of bonding.

FIBER STRENGTH

The maximum strength possible in a paper is limited by the strength
of the fibers. Some writers, such as Klauditz, Marschall and Ginzel
(65), have claimed that the tensile strength of paper depends on the
strength of the fibers and have implied that interfiber bonding
strength is sufficiently extensive that rupture of the paper results

Figure 11. Contribution of Surface Area to Over-all Bonding

from rupture of the fibers. Cowan (66), in a limited study of the effect of precrushing wood, noted a reduction in fiber strength and a concomitant decrease in sheet strength. Van den Akker, Lathrop, et al., (63) examined tensile failures of sheets containing a small percentage of selected dyed fibers and reported that up to 80% of these fibers were broken in a sheet rupture.

Hoffmann Jacobsen (67) proposed measuring the tensile strength of paper with the edges of the two sets of jaws of the tensile tester in contact with each other as a measure of the average ultimate strength of the fibers. Clark (68) designed a set of zero-span jaws specifically for the purpose. The zero-span tensile test measures the tensile breaking load of the randomly oriented fibers in a sheet of paper. Wink, et al., (62) have demonstrated that it can be reproducible if well-designed jaws are employed and the necessary precautions are observed. Van den Akker, Lathrop, et al., (63) determined the breaking load of individual fibers and showed a very good correlation between this value and the zero-span breaking load of handsheets made from similar fibers, indicating that the zero-span test may be used as a measure of fiber strength.

In the series of pulps studied in this work, probably the only chemical change which had a direct bearing on fiber strength was a change in the D.P. of the cellulose. The possible indirect effect of delignification will be discussed later. The variation of "cuen" viscosity of pulp solutions with bleaching is shown in Figure 12. An

Figure 12. Pulp Viscosity

attempt was made to determine the D.P. of the A.R.C. by measuring solution viscosity, but there was so much scatter in the data, with no trend, that the results were valueless. A possible explanation for this is the fact that there may have been extensive uncontrolled degradation of the cellulose, despite the precautions observed, during the alkaline preparation of the A.R.C.

Cellulose is attacked by numerous oxidizing agents, and many of these are selective in their action--either as to the position of attack in the anhydroglucose unit, or the nature of the product. Hypochlorite is not selective. It may attack the 2, 3, or 6 position resulting in conversion of hydroxyl groups to carbonyl and then to carboxyl under favorable conditions.

Figure 13

Cellulose Structure

Cellulose molecules containing strongly electronegative groups, such as carboxyl, are unstable in alkali, and cleavage may result in a shortening of the molecule with a consequent lowering of D.P.

The cellulose of the bleached pulps is probably oxidized to a

considerable degree. The subsequent exposure to strong alkali during the hemicellulose extraction procedure could have been responsible for chain scissions (59, 60) reducing the D.P. of the cellulose. It was found that the D.P. of the hemicellulose fraction was not altered significantly by bleaching, and therefore it appears that the change noted for the pulp must be attributed to the A.R.C.

The effect of hypochlorite bleaching on fiber strength is shown in Figure 14. The application of a moderate amount of hypochlorite apparently did not affect the strength of the fibers much even though the D.P. of the cellulose was altered. Overbleaching, on the other hand, caused a marked reduction in fiber strength.

A correlation between fiber strength and D.P. of the pulp is shown in Figure 15. Relationships of this type have been shown for textile fibers (69 - 74), but there appears to be no previous report of this nature for wood pulp cellulose. There is some question about a cause-and-effect relationship between fiber strength and cellulose molecular chain length. Past work (69 - 74) on cotton and modified cellulose suggests a linear relationship between D.P. and fiber or film tensile strength over a relatively narrow range of low D.P. for regenerated cellulose products. However, as Mark (75) pointed out, increased D.P., above a certain minimum of about 500, appears to have no effect on the strength of regenerated fibers and films. On the other hand, Hessler, Simpson and Berkley (74), Clibbens and Ridge (21), and Ridge and Bowden (73) present evidence in favor of such a

Figure 14. Fiber Strength

Figure 15.   Fiber Strength – D.P. Correlation

relationship for natural fibers having D.P.'s up to about 10,000, both in the natural state and degraded by various agents.

The maximum zero-span breaking length of handsheets was 13,300 meters, as shown by Figure 14. Conversion of this value, assuming a density of 1.57 g./cc. for cellulose, gives a zero-span fiber strength of 20.9 kg./sq. mm. This is in good agreement with the information of Lathrop (63) who determined a value of 22.1 kg./sq. mm. for unbeaten sweetgum kraft fibers. A statistical treatment of fiber distribution in handsheets (63) shows that the zero-span tensile strength should be 37.5% of actual fiber strength. The accuracy of this estimate was verified by a very good correlation between theoretical and actual zero-span tensile strength. On this basis then, the maximum fiber strength should be about 56 kg./sq. mm. Mark (75) calculated 119 kg./sq. mm. as the maximum strength of an idealized system of regularly overlapping cellulose chains assuming complete orientation and crystallinity.

In the case of the present study, the loss in fiber strength cannot be attributed solely to decrease in molecular chain length although a strong argument, based on the data, can be made for assigning a considerable portion of the loss to this cause. A reduction in D.P. would be expected to cause a loss in fiber strength, except for the fact that the effect of a decrease in cellulose chain length is compensated for by extensive hydrogen bonding between molecular chains. Therefore, for a significant strength loss to be noticeable,

a considerable reduction in D.P. would have to be effected. The data show that initially there is little change in fiber strength (Figure 15) until the viscosity is reduced by one-third. Subsequently, even slight changes in D.P. have considerable influence on fiber strength.

A second consideration to be made in evaluating test results on fiber strength is the brittleness of the fibers. It has been shown that bleaching results in increased bonding between fibers. There is probably also an increase in bonding within the fiber, between fiber elements, so that the entire structure becomes more rigid. When such a rigid structure is strained, components which otherwise would yield, permitting a distribution of load, are restricted from doing so with the result that localized stresses may be considerably increased over what would be the case if the fiber were not so completely bonded. The breaking load on a given fiber element would thus be exceeded at a lower value of total fiber load and before other elements bear any load. The consequent rupture of some of the fiber elements would result in increased stress on those remaining intact—all at a relatively lower value of total fiber load than if the structure were not so rigid. The net result would be increased stress on fiber elements at each level of total fiber load than in the case of a fiber less completely bonded and more able to distribute stress.

The third factor contributing to loss in fiber strength is explained on the basis of findings with the electron microscope and exemplified in Figures 1 to 4. Delignification of the pulps with consequent splitting-off of part of the fiber wall would tend to

create points of stress concentration in tensile-loaded fibers because part of the original load-bearing cross section is detached and no longer in position to carry a portion of the load. This results in increased stress on the remaining cross section and a consequent lower fiber strength.

SUMMARY

It has been shown that fiber strength is considerably reduced by overbleaching with hypochlorite while moderate amounts of this bleaching agent have little effect in this respect. The oxidizing action also leads to a regular decrease in D.P. of the pulp depending on the extent of bleaching. A relationship has been shown between pulp D.P. and fiber strength, analogous to similar correlations for other cellulose fibers. Although an argument can be made for such a relationship, it is felt that the loss in D.P. is only one of three causes contributing to decreased fiber strength. Other factors may be stress-raising effects due to removal of fiber-wall material from parent fibers, and possible fiber embrittlement.

SHEET STRENGTH

Two of the main factors which influence the level of handsheet strength are fiber strength and interfiber bonding. A tensile specimen under load is a structure embodying numerous entities held together by secondary valence forces. The load at which the specimen fails will depend on both the internal strength of the components and on the strength of the binding forces, but will be defined by the weakest link

in the structure. In the pulp system under consideration, the strength of a sheet, at a particular level of bleaching, will therefore depend largely on the balance between fiber strength and interfiber bonding.

The variation in handsheet breaking length with bleaching, for the pulps of this study, is shown in Figure 16. This is a plot of tensile breaking length determined with the Baldwin-Southwark testing machine. A similar relationship, shown in Figure 17, was found for the effect of bleaching on the rupture work in tension. The rupture work is measured as the area under the load-elongation curve of a specimen, and it represents the energy absorbed by the specimen before failure.

The trend in the strength development curves, in Figures 16 and 17, may be explained on the basis of findings with respect to inter-fiber bonding and fiber strength. Through the series of pulps studied, the interfiber bonding was progressively increased as a result of bleaching. This had the effect of increasing sheet breaking length. On the other hand, fiber strength was not changed much through the initial portion of the series, but it decreased as the pulp was more heavily bleached. Thus, in the first part of the range studied, fiber strength had little effect because it was the strong link in the chain. In the latter part of the range, however, fiber strength was reduced to the extent that sheet strength was impaired.

The effectiveness of bonded area for achieving sheet tensile strength is further illustrated by the data presented in Figures 18 and 19. Ingmanson and Thode (77) found that, for a given pulp, the total

Figure 16. Tensile Breaking Length

Figure 17. Rupture Work in Tension

surface area of water-dried fibers remains constant and is independent of the degree of refining. Although swelling, fibrillation and fines act to increase the surface area of wet pulp, the surface area of water-dried fibers remains the same because the fibrils and fines apparently bond to the surface of fibers and the effect of swelling is reversed by drying the pulp. Since the specific scattering coefficient of a pulp is a measure of scattering, or unbonded surface, the total bonded area in a sheet may be represented by the difference in scattering coefficients for water-dried, unbonded fibers and for the fibers in the sheet. A constant is involved in the relationship

$$k\underline{S}_b = k(\underline{S}_t - \underline{S}_u) = \underline{s}_t - \underline{s}_u \qquad (3)$$

between the total bonded area and the difference in scattering co-efficients. Since the magnitude of this constant is unknown, no attempt has been made to estimate the total or bonded area but the difference in scattering coefficients is taken as a number proportional to the total bonded area.

Figure 18 shows the tensile breaking length developed by a given total "bonded area" for each of the pulps. The curves were derived from data which were taken to determine relative bonded area as described in the appendix. Initially, breaking length increases very rapidly with bonded area, but, as the bonded area becomes greater, the rate of change of tensile strength is reduced. There is no reason to expect a decrease in bonding strength per unit of bonded area for any particular pulp and therefore the decreased slope of the curves is explained on the basis of increased influence of fiber strength. The
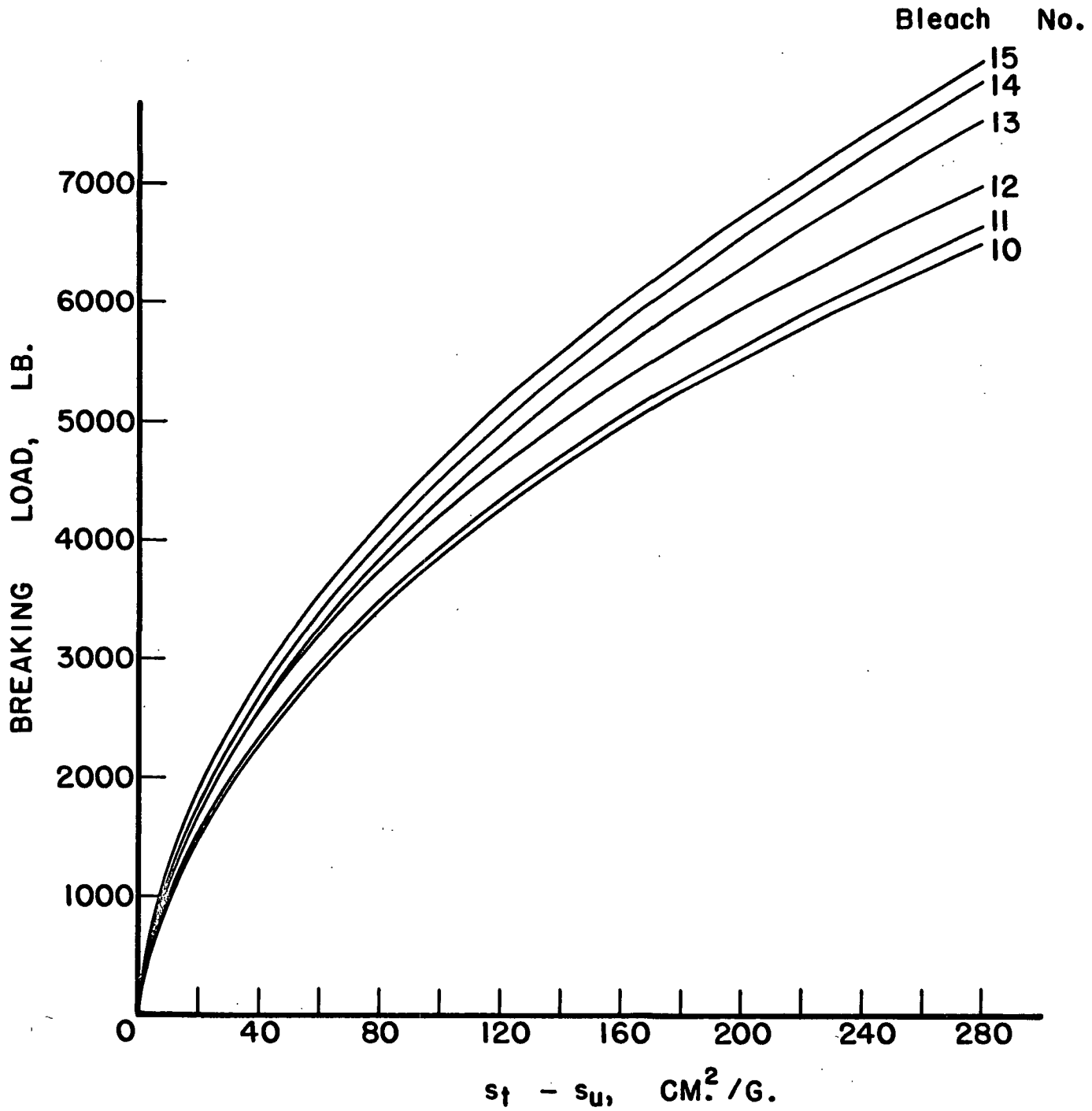
Figure 18. Effectiveness of "Bonded Area" for Achieving Sheet Strength

curves also illustrate the continually changing balance between inter-fiber bonding and fiber strength in defining the tensile strength of a sheet of paper.

Figure 18 also illustrates the increased bonding strength per unit of bonded area of the pulps as the bleaching treatment was intensified. At any value of total bonded area the tensile strength of successive pulps was increased. Since fiber strength was progressively reduced through the series of pulps, as shown by Figure 14, the increased tensile strength must be due to greater bonding strength per unit of bonded area. This is independent evidence for the phenomenon discussed on page 57. The variation of total bonded area required to produce various levels of breaking strength, as bleach application was increased, is shown in Figure 19.

The influence of fiber strength is also illustrated by Figure 20, which shows the ratio of tensile breaking length to WP. It is evident from this curve that the efficiency with which increased inter-fiber bonding strength is applied to increase sheet strength is seri-ously impaired when the fibers cannot carry a load equivalent to the bonding strength.

The concomitant variations in fiber strength, bonding and breaking length are illustrated in Figure 21. In the initial range of the series of pulps used in this study, the sheet strength was limited by interfiber bonding strength. On the other hand, over the final portion of the range, sheet strength was restricted by fiber strength. At a

Figure 19. Bonded Area Required to Develop Various Levels of Tensile Strength

given level of fiber strength, the number of fibers broken in a test specimen will vary in proportion to the level of interfiber bonding strength. Thus, it is evident that handsheet breaking length depends on both interfiber bonding strength and fiber strength, but it is defined by the balance between these two attributes. In other words, if other factors are equal, the strength of paper depends on both the extent of interfiber bonding and the intrinsic strength of the fibers; it is defined by the balance between the two, and limited by one or the other, depending on the level of each.

In this respect, it is interesting to note that fiber strength had sufficient influence, in the latter portion of the range of the study, that sheet tensile strength was considerably impaired at a relatively low level of per cent bonded area. Also, the ratio of sheet tensile strength to zero-span strength was relatively low. Generally, fiber strength is not of such relatively great importance until interfiber bonding is developed to the extent that sheet tensile strength approaches 60-80% of the zero-span tensile strength (78). The apparent anomalous behavior of the present pulp system can be explained in part on the basis of the fact that fiber strength was significantly degraded. Also, the manner in which this degradation was effected—rupture of the outer wall—was of such a nature that points of potential extreme stress concentration were developed in the fibers.

The preceding explanation of the manner in which fiber strength and interfiber bonding influence paper strength is borne out by the variation of tearing strength with bleaching shown in Figure 22.
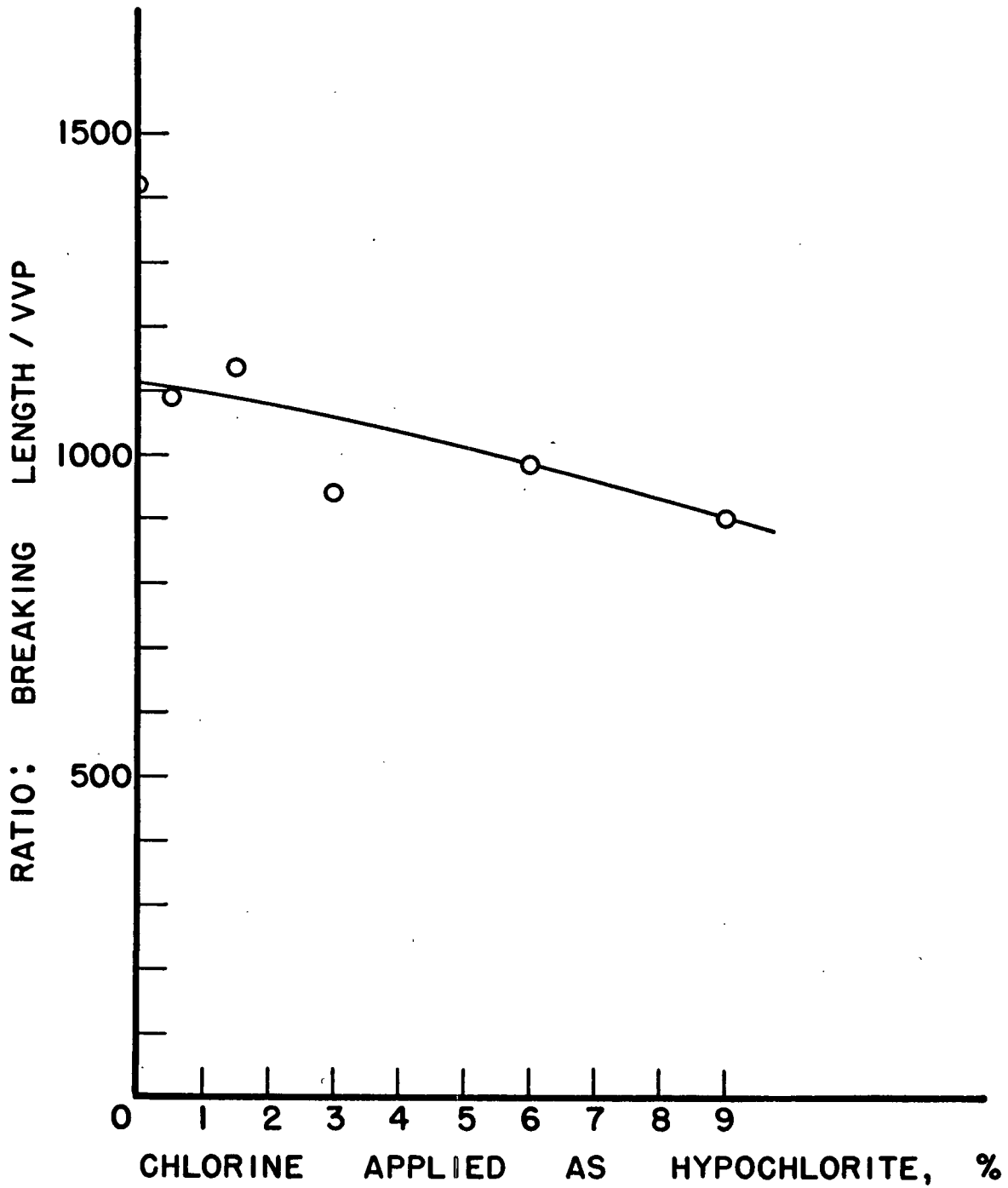
Figure 20. Influence of Fiber Strength on Tensile Strength
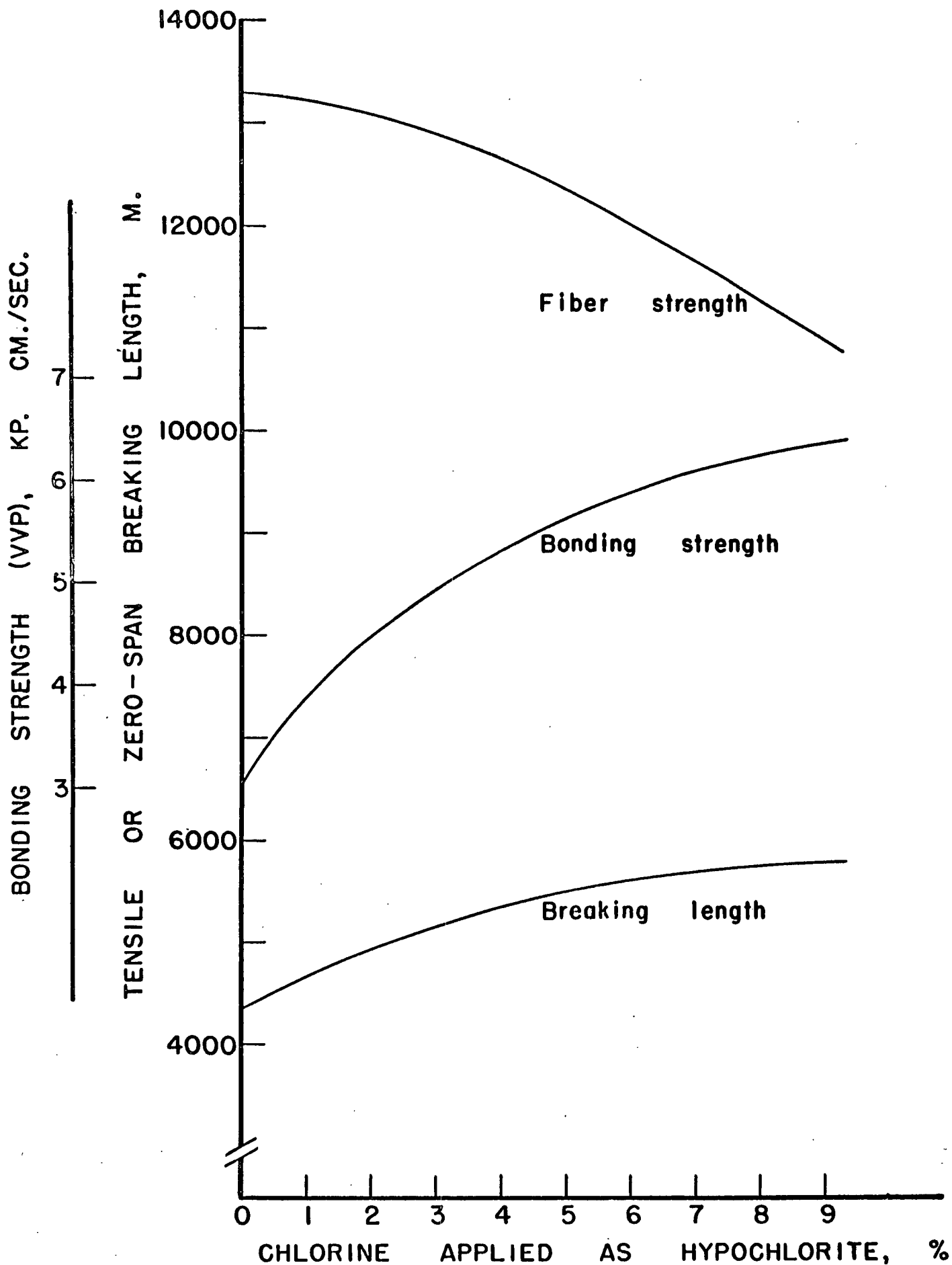
Figure 21. Concomitant Strength Changes

According to the modern concept of the mechanism of failure in the Elmendorf tear tester (79), the internal tearing strength of a paper depends on the balance between bonding and fiber strength. As the extent of bonding increases, relatively more fibers are broken and fewer are pulled from the sheet structure. Since shorter distances are involved in breaking fibers, less work is required to tear the sheet. A further factor contributing to the definition of the trend in tearing strength in the present study was the loss in fiber strength with bleaching. This would have the effect of causing more fibers to break, and with less load, at a given level of bonding, than in the case where stronger fiber were employed.

SUMMARY

Hypochlorite bleaching of NSSC aspen pulp was responsible for an increase in the breaking length of handsheets made from the pulp. Over the range of conditions studied in this work, the extent of interfiber bonding increased progressively, and this was responsible for the strength rise. At the same time, the intrinsic strength of the fibers was diminished, and the effect of this was to limit the extent to which sheet strength could be developed by enhancing the bonding quali- ties of the pulp. On the basis of the analysis of tensile strength, it appears that if other factors are equal, the breaking length of hand- sheets prepared from bleached pulps is dependent on fiber strength and interfiber bonding, and in this particular case it is defined by the balance between fiber strength and bonding but limited by one or the other.
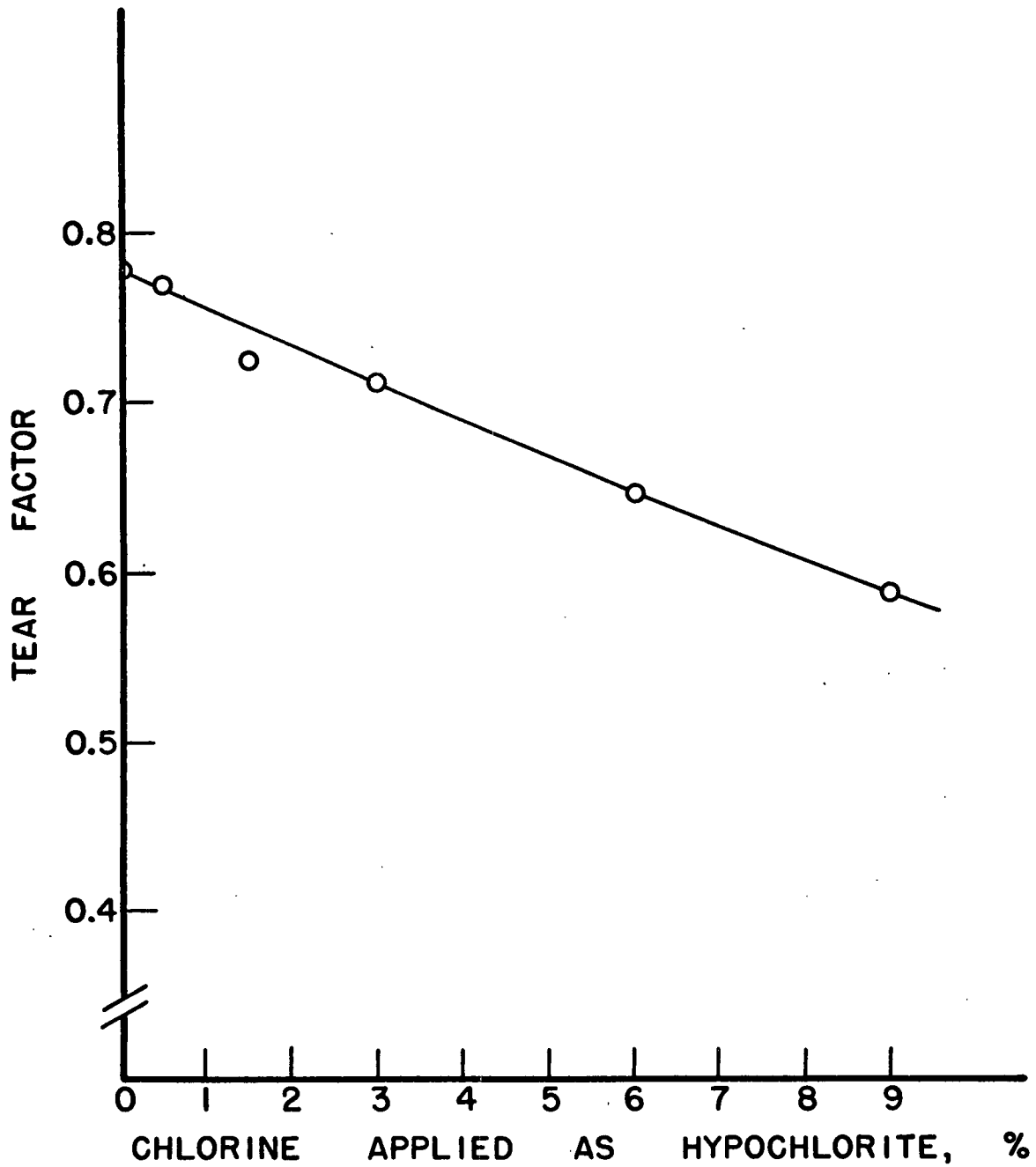
Figure 22. Tearing Strength

CONCLUSIONS

1. Several of the findings in the thesis of Jappe (1) who studied hypochlorite as the third stage in the bleaching of NSSC aspen pulp have been confirmed. These include the following six:

a. Delignification was the primary chemical effect of bleaching NSSC aspen pulp under the conditions employed.

b. Delignification was responsible for deshiving.

c. The amount of carbohydrates was only slightly affected.

d. Hydrodynamic specific surface area was increased.

e. Effective specific volume was increased.

f. Initial strength of handsheets was increased.

2. Increased surface area resulting from hypochlorite bleaching of NSSC aspen pulp appeared to be due to three phenomena:

a. Swelling.

b. Deshiving with release of fines.

c. Opening of fiber by splitting the outer wall.

The "fines" portion of the pulp appeared to consist primarily of parenchyma cells. These were probably ray cells released from fiber tracheids when delignification was effected.

Delignification by hypochlorite bleaching weakened the outer layer of fibers to the extent that mild swelling and minimum mechanical action resulted in splitting of the outer fiber layer. This acted to increase the specific surface area of the pulp, and it also exposed inner wall material.

3. Over-all bonding strength increased over the range studied. This

was due not only to the increase in specific surface area, but also to the apparent increase in the effectiveness of the wet surface area for achieving bonding in the final dried sheet. Part of the bonding strength increase was attributed to higher relative bonded area and part to greater strength per unit of bonded area.

By way of explaining the higher relative bonded area, it is proposed that the bleached fibers were more conformable; that is, more readily deformed, as a result of surface imperfections at points where the outer fiber wall was ruptured and because of increased fiber swelling. The speculation respecting conformability may not be valid as indicated by the fact that there was no significant difference in wet fiber compressibility as measured in the filtration resistance apparatus. Better conformability could follow from delignification or swelling which probably reduced the extent of intrafiber bonding, diminishing the rigidity of fiber structures.

Greater bonding strength per unit of bonded area must have been due to either intensified bond density or to stronger bonds, as a result of a change in the chemistry of the surface. Increased bond density might follow from delignification, which produced surfaces less shielded by lignin, on which the carbohydrate bond density was enhanced. Carboxylation of the carbohydrates, determined by Jappe (1) and qualitatively indicated in the present work, may have produced stronger bonds if the hydrogen bond energy of this system can be compared with behavior in simpler circumstances where hydrogen bonds involving carboxyl groups are stronger than those in which only hydroxyl groups are partners.

In effect, greater bond strength per unit of bonded area was due to

the production of surfaces more capable of bonding.

4. Bleaching was responsible for concomitant decreases in fiber strength and in the D.P. of the cellulose.

A correlation has been shown between fiber strength and pulp D.P. It is possible that this is a forced correlation because the loss in fiber strength might be attributed in part to the production of surface imperfections which would act as points of stress concentration in loaded fibers.

5. The strength of the chlorinated and extracted aspen fibers of this study was estimated to be about 56 kg./sq. mm.

6. Hypochlorite bleaching of NSSC aspen pulp was responsible for increased breaking length of handsheets prepared from the unbeaten pulp. This sheet strength increase was due to increased interfiber bonding. Sheet tensile strength was limited by overbleaching because of the adverse effect on fiber strength.

7. Among other factors, the breaking length of handsheets in this study was found to depend on both fiber strength and interfiber bonding. In this case, it was defined by the balance between fiber strength and bonding but limited by one or the other. These observations support and broaden the concept of balanced fiber strength and fiber bonding in establishing the strength of paper.

SUGGESTIONS FOR FURTHER WORK

Although this investigation has resulted in information which more fully explains the reasons for strength increases when NSSC aspen pulp is bleached with hypochlorite, there are a number of facets which have not been resolved.

It was shown that the wet surface area of the more severely bleached pulps was more effective in developing fiber-to-fiber bonds. The data do not show whether this was due to better fiber flexibility or to a change in the chemical nature of the surface.

The increase in bonding strength per unit of bonded area can be attributed only to greater bond density or to an increase in the strength of the bonds. Separation of these two factors has not been achieved.

The presence of hemicelluloses in a pulp is generally associated with facility in the development of strength. There are at least two mechanisms by which hemicelluloses may act. They may contribute to strength by virtue of a cementing effect, or they may expedite swelling and the effects of mechanical action. The specific role of hemicelluloses has not been demonstrated.

The chemical nature of the hemicelluloses may be an important consideration in their effectiveness. In the case of the present work, there appeared to be a slight loss in cellulose while the hemicellulose contents of the pulps remained constant. If both hemicellulose and

cellulose are degraded, with the hemicellulose replaced by degraded cellu-
lose functioning as hemicellulose, the hemicellulose hydrolyzates would
show a continuing decrease in xylose with a possible concomitant increase
in glucose.

Experience has indicated that the presence of lignin is concomitant
with low strength. Although the present work has done much to show the
improvement of strength with delignification the specific mechanism has
not been shown.

The significance of fiber swelling to sheet strength has not been
elucidated.

ACKNOWLEDGEMENT

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APPENDIX

A. EXPERIMENTAL CONDITIONS

1. PULPING SCHEDULE

The NSSC pulp was prepared in one cook consisting of 41,050 g. c... chips (O.D. wood basis). The liquor ratio was 5 cc. water/g. wood. Cooking chemical was 7380 g. anhydrous, reagent-grade sodium sulfite (18% of the O.D. wood) and 2055 g. anhydrous, reagent-grade sodium carbonate (5% of the O.D. wood). The initial pH was 11.0 and the final pH was 8.8.

The time-temperature-pressure schedule is shown in Table IV. The digester was purged after 30 minutes and blown from about 30 p.s.i. pressure after 285 minutes.

The chips were immediately recovered from the blow pit and refined hot in the Institute Bauer refiner with plates set at zero clearance.

TABLE IV

NSSC COOKING SCHEDULE

Time, min.	Temperature, °C.	Pressure, p.s.i.	
		Digester	Steam Jacket
0	30	0	0
15	75	10	20
30	100	20	15
45	120	20	45
60	130	42	67
75	—	—	—
90	135	50	40
105	138	50	—
120	135	52	—
135	148	70	—
150	150	80	150
165	165	110	150
180	166	—	—
195	170	—	—
210	170	—	—
225	170	—	—
240	170	—	—
255	172	130	130
270	172	130	128
285	165	100	0

2. CHLORINATION AND EXTRACTION

Ten batches of pulp were chlorinated under the following conditions:

Pulp: 850 g. O.D.

Water: 30,000 g.

Chlorine gas: 120 g. (14.7% of O.D. pulp).

The chlorine was applied in 20 minutes and was exhausted in one hour. Each batch was washed with warm, filtered tap water to at least pH 7.0.

Caustic extraction succeeded washing of the chlorinated pulp. Extraction was carried out in a Pfaudler mixer under the following conditions:

Charge: two chlorination batches (1700 g. O.D.)

Consistency: 8.5%

NaOH: 40 g. (2.35% of pulp)

Temperature: 40°C.

Time: 60 minutes

Each extraction batch was washed well with hot, filtered tap water and then blended in a stainless steel wash tank where the entire batch was further washed with hot tap water. Finally, it was dewatered by centrifuging. Fines were recovered on a muslin-covered washbox and recombined.

3. HYPOCHLORITE BLEACHING

Thousand gram (O.D. basis) portions of the chlorinated and extracted

pulp (Bleach 10) were placed in five-gallon earthenware crocks with most of the 9000 g. water required to give a consistency of 10%. The crocks were placed overnight in a large water bath, controlled by a thermostat, so that the whole might come to temperature equilibrium at 40°C.

A commercial solution of sodium hypochlorite ("Hi-lex") containing 56.4 g.p.l. available chlorine was used for the third-stage bleaching. The amount of chemical applied to each batch is indicated in Table V.

TABLE V

CHEMICAL APPLICATION FOR HYPOCHLORITE BLEACHING

Bleach No.	Chlorine as Hypo, %	"Hi-lex" Solution Used, ml.
11	0.5	89
12	1.5	266
13	3.0	531
14	6.0	1062
15	9.0	1593

Each batch was kept thoroughly mixed and buffered with caustic soda to pH 10.0 - 10.5.

The active chemical was exhausted in Bleach 11 after about 10 minutes. Each of the other batches had excess chemical so the reaction was stopped, in each case, after 120 minutes by adding a sufficient amount of sodium sulfite which served as an anti-chlor.

The pulps were thoroughly washed, dewatered, and stored in poly-ethylene bags at 5°C. with formalin added.

B. TEST METHODS

1. DETERMINATION OF LIGNIN

The determination of the lignin content of a pulp, as indicated in
the thesis discussion, is a difficult undertaking if for no other
reason than the fact that lignin is defined by the analytical method.
Brauns (83) and Browning (82) have indicated that others have encountered
difficulties.

For the purpose of this thesis, a variation study of the Klason
lignin determination was made in an attempt to find a reproducible
procedure with which to compare pulps. Some of the variations included
pre-extraction with 95% alcohol, grinding the pulp to a fine meal,
various methods of filtering the hydrolyzed residues, and solvent dry-
ing of the pulp.

The most reproducible procedure included pre-extraction of the pulp
with 95% alcohol, solvent exchange and oven drying from benzene. The
pulp was then ground through a 20-mesh screen in a laboratory Wiley mill.
The ground meal was hydrolyzed at 20°C., for 3.5 hours with 20 ml. of 72%
sulfuric acid per gram of pulp, as specified by Institute Method 428.
The mixture was then diluted to an acid concentration of three per cent
and digested for four hours. The residue was filtered on balanced
Whatman No. 40 filter papers (84), washed thoroughly, oven dried, and
weighed. Apparent soluble lignin was determined by measuring the
absorbance of the lignin filtrate at 230 mmu, as described by Brauns,
Buchanan and Leaf (53).

There are many uncertainties in the soluble lignin determination. One is the value of the absorptivity of lignin in weakly acidic solution. The data of Brauns, et al. (53) are for isolated aspen native lignin in dioxane. Whether or not the material in the pulps of the present study absorbs in the same range is not known. Carbohydrate dehydration products, such as furfural and hydroxymethylfurfural, formed in the boiling stage of the Klason lignin determination, may contribute to the absorbance of the filtrates. The effect of this contribution was minimized by measuring the absorbance at 230 mmu. (85). With these reservations admitted, the soluble lignin content is taken as a measure of a portion of the lignin-like material in the pulps.

Because the lignin determination lacked precision, triplicate determinations were made twice, and the lignin contents reported are averages of six determinations, as shown in Table VI.

TABLE VI

SUMMARY OF LIGNIN DETERMINATIONS

Bleach number		10	11	12	13	14	15
Klason lignin, %		2.03	1.69	1.20	1.79	0.45	0.68
		2.00	1.39	1.30	1.43	0.79	0.72
		2.14	1.47	1.04	1.52	0.83	0.62
		1.74	----	1.51	0.96	0.52	0.74
		1.72	1.61	1.77	1.02	0.47	0.70
		1.98	1.58	2.11	0.99	0.43	0.89
	Average	1.94	1.55	1.49	1.29	0.58	0.72
	Std. deviation	0.16	0.12	0.39	0.34	0.18	0.09
Apparent soluble lignin, %		1.88	1.67	1.56	1.48	1.37	1.18
		1.56	1.30	1.17	1.46	1.58	1.43
		1.44	1.29	1.17	1.19	0.93	0.87
		0.82	----	0.64	0.87	0.72	0.10
		0.78	0.61	0.62	0.90	0.73	0.11
		0.79	0.55	0.63	0.90	0.72	0.15
	Average	1.21	1.08	0.97	1.13	1.01	0.64
	Std. deviation	0.48	0.49	0.39	0.28	0.37	0.59
Total lignin, %		3.91	3.36	2.76	3.36	1.81	1.85
		3.57	2.69	2.47	2.89	2.37	2.15
		3.58	2.76	2.21	2.71	1.76	1.49
		2.56	----	2.15	1.83	1.24	0.84
		2.50	2.22	2.39	1.93	1.20	0.81
		2.76	2.13	2.74	1.89	1.15	1.04
	Average	3.15	2.63	2.45	2.43	1.59	1.37
	Std. deviation	0.60	0.49	0.26	0.63	0.48	0.55

Although it is believed that precision could be improved by repetition, it was felt that these results show the trend sufficiently well for the purpose of this thesis.

2. WATER-RETENTION VALUE

The water-retention value of a pulp was proposed as a measure of the degree of swelling. The method used was a modification of the technique proposed by Jayme and Rothamel (86).

A quantity of pulp, approximating 0.15 g. (O.D. basis), at a consistency of about 0.445% was placed in the centrifuge bottle shown in Figure 23. Excess water was allowed to drain from the sample which was then centrifuged for 10 minutes at 2200 r.p.m.; this was equivalent to an acceleration of 800 times gravity. The sample was then transferred to a tared weighing bottle, weighed, oven dried at 105°C., and reweighed. The water-retention value was calculated from:

$$\text{WRV } (\%) = \frac{\text{Moist pulp weight} - \text{Dry pulp weight}}{\text{Dry pulp weight}} \times 100 \qquad (4)$$

3. RELATIVE BONDED AREA

The most widely used method for estimating the amount of bonded area in papers is the optical technique originally proposed by Parsons (9) and further evaluated by Haselton (49). The optical method utilizes values of the specific scattering coefficient, which may be calculated from the original theory of Kubelka and Munk (87, 88). This theory quantitatively relates the scattering and absorption of light to the diffuse reflectance of a light scattering medium. The most convenient form of the theory, as adapted specifically to paper, has been presented in equations and charts by Steele (89) and Judd (90). The definition of specific scattering coefficient and specific absorption coefficient in terms of basis weight instead of thickness, as suggested by Van den Akker (91), is generally accepted by workers in the paper field. The specific scattering coefficient is assumed to be a measure of the unbonded (scattering) area of a sheet. If the specific scattering coefficients of a water-dried sheet and an unbonded sheet, prepared
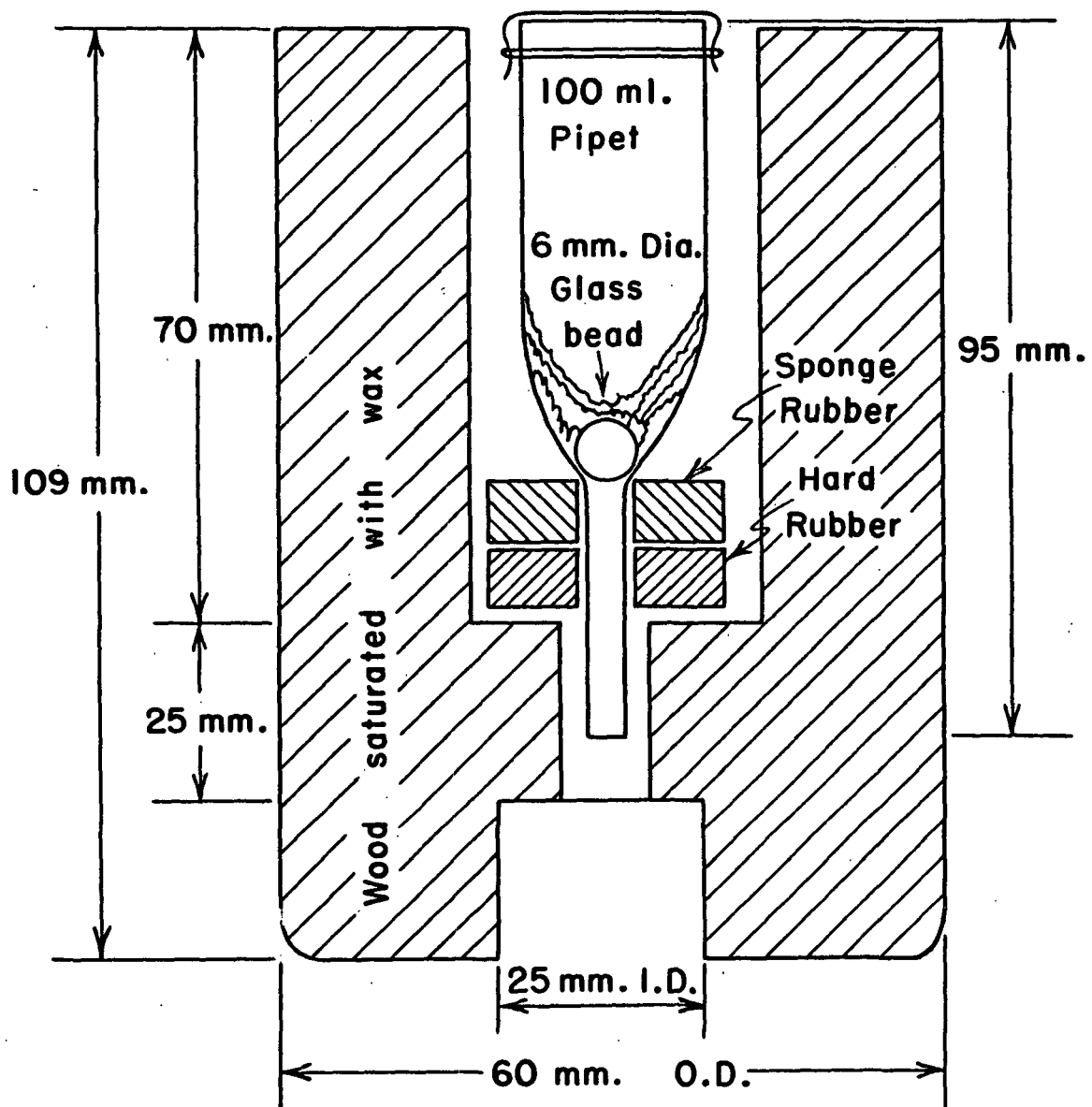
Figure 23. Equipment for Water-Retention Value Determination

from the same pulp, are determined, the bonded area of the waterleaf sheet corresponds to the difference in the two scattering coefficients. The relative bonded area is then given by comparing this difference with the scattering coefficient for the unbonded sheet.

Previous workers have used solvent drying to prepare unbonded hand-sheets to estimate the area available for fiber bonding. Recently, Ingmanson and Thode (77) have shown that this technique gives spuriously high values of relative bonded area because of the effects of fiber shrinkage and solvent surface tension. To obviate the inherent error, a new technique was proposed for determining the total dry fiber area available for fiber bonding, based on the concept that in estimating the total area available for bonding, the area required is the total area of water-dried, unbonded fibers. Apparently, this area is lower than indicated for solvent-dried fibers because of fiber shrinkage, bonding of fibrils to parent fibers, and bonding of part of the lumen surface.

The method for determining the total dry fiber area available for bonding involved the preparation of a series of handsheets having different strengths and different bonded areas. This was effected by pressing at various wet pressures up to 150 p.s.i. The specific scattering coefficients were measured with the General Electric Record-ing Spectrophotometer using monochromatic illumination at 650 mmu. Scattering coefficient was plotted against tensile strength, and the curve was extrapolated to zero strength. The corresponding scattering

coefficient was taken as the specific scattering coefficient of water-dried, unbonded handsheets. The results are shown in Figure 24.

The extrapolated values of specific scattering coefficient for successive pulps of the study increases, indicating successively greater total fiber surface areas for the water-dried, unbonded handsheets. The reason for this is probably a change in the shape of light-scattering particles as progressive delignification produced a continuing deshiving of the pulp. The particles in dry, unbonded handsheets prepared from pulps of the initial part of the series probably consist of fiber agglomerates, or shives. Some of the fiber surface contained in the inner portion of such a shive would be exposed in a dry, unbonded sheet prepared from fibers not so aggregated.

The relative bonded area of standard handsheets was calculated from the relationship:

$$\text{Relative bonded area} = \frac{s_t - s_u}{s_t + 10} \qquad (5)$$

where s_t (the intercept) is the specific scattering coefficient of water-dried, unbonded fibers, s_u is the specific scattering coefficient of standard handsheets, and 10 is a factor which accounts for the scattering of the sheet surfaces.

4. ELECTRON MICROSCOPE STUDIES

Samples for examination with the electron microscope were solvent dried to preclude the tendency of fibrillae to bond back to parent fibers. The solvent-exchange procedure included soaking the wet fibers
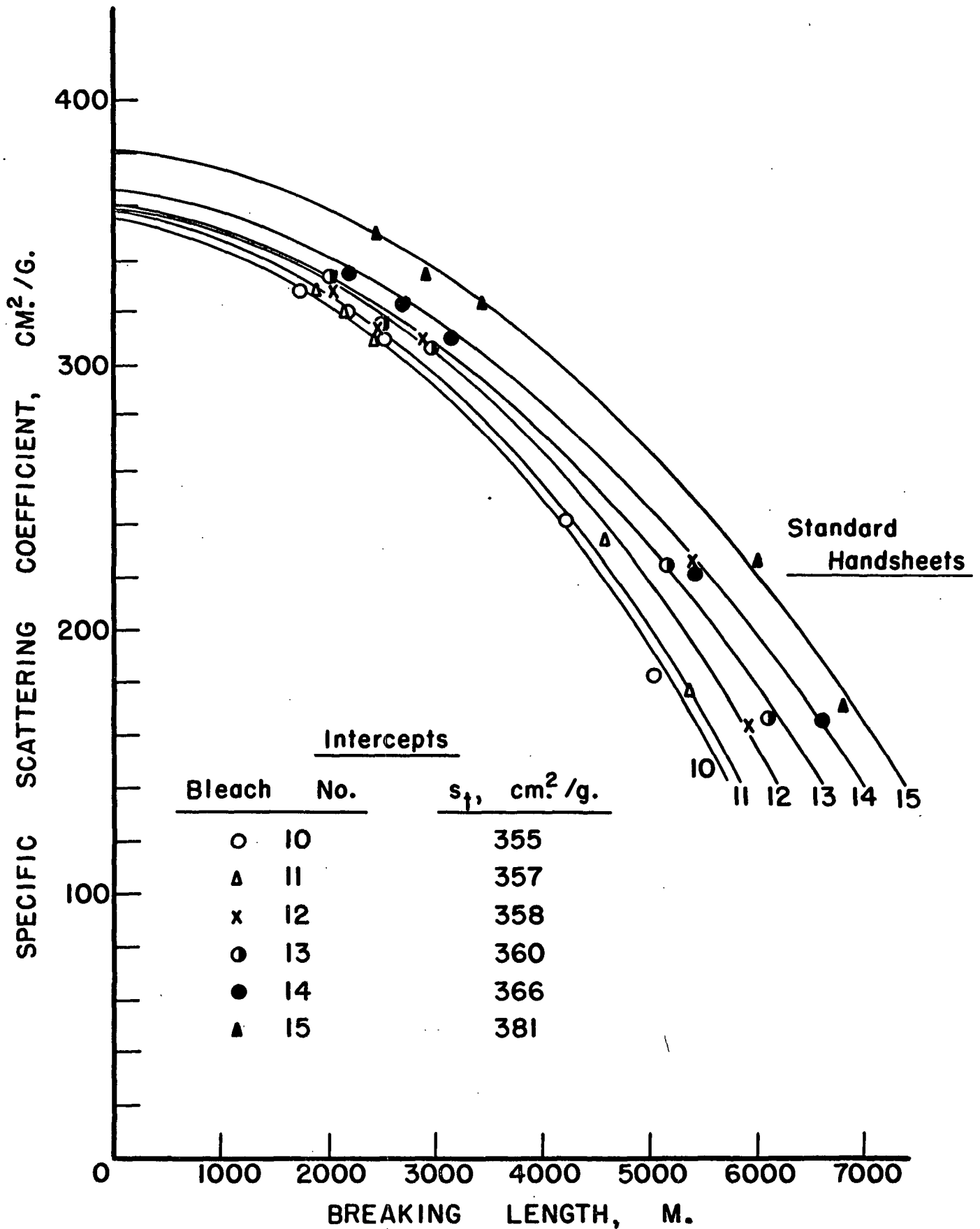
Figure 24. Scattering Coefficient — Tensile Strength
Relationships for Determining Relative
Bonded Area.

successively in acetone and n-butanol, removing the solvent by filtration and finally drying at 40°C. under reduced pressure. The fibers were then mounted on collodion covered grids, using n-butanol as carrier, and air dried. They were chromium shadowed at 30° and examined with the electron microscope at a magnification of 16,500 x.

Some difficulty was encountered in obtaining satisfactory photographs because the fibers were not firmly bound to the grids. As a result, there was a tendency for the free ends of fibers to move in the electron beam.

Positive plates were made from the microscope slides, and the photographs were enlarged to about 53,000 magnification.

The interpretation of findings was based on personal observation in the electron microscope, where a better concept of the existing phenomena could be obtained by varying the field of observation. The photographic evidence, presented in the thesis, is the best which could be recorded.

5. STRENGTH PROPERTIES

Breaking length, elongation, and work to rupture, of handsheets made from unbeaten stock, were measured with a Baldwin-Southwark universal testing machine equipped with a sensitive air cell weighing device. The load indicator and a microformer type of deflectometer were mounted to actuate a load-deflection recorder.

Specimens were 15 mm. wide and were held between Instron jaws spaced 2.93 inches apart. The load was applied by ram pacing at 0.125 in./min. to cause failure in about 20 seconds. Tensile load at failure was read from the machine indicator. Elongation at break was determined from the recorded load-deflection curve. Rupture work to failure was found by measuring the area under the load-deflection curve with a planimeter and converting to units of work.

C. COMPRESSIBILITY AND FILTRATION RESISTANCE DATA

The compressibility of the pulps was measured by the technique described by Ingmanson (46). This involves determining the equilibrium consistencies of a wet pulp pad under a series of static pressures. Results for the several pulps are tabulated in Table VII. No difference between pulps could be ascertained from these data so average values were used.

TABLE VII

COMPRESSIBILITY OF PULPS

$$c_{p}, \text{ g./cc.}$$

$\Delta p_f/\rho$ g. cm. water Bleach	12.33	17.8	27.1	41.7	66.4	98.8
10	0.0629	0.0786	0.0943	0.1123	0.1367	0.1572
11	0.0633	0.0658	0.0858	0.1085	0.1328	0.1539
12	0.0715	0.0829	0.0971	0.1151	0.1357	0.1573
13	0.0587	0.0729	0.0912	0.1094	0.1326	0.1535
14	0.0536	0.0731	0.0931	0.1119	0.1360	0.1551
15	0.0583	0.0721	0.0885	0.1067	0.1272	0.1492
Average	0.0614	0.0742	0.0917	0.1106	0.1335	0.1544

When the compressibility function

$$c_p = \Delta m (p_f / \rho g)^N \qquad (6)$$

was plotted on logarithmic coordinates, the slope, N, of the linear re-
lationship was found to be 0.387.

The constant rate filtration resistance of the pulps is shown as a
function of pressure drop in Table VIII and plotted in Figure 25.

The general upward trend in filtration resistance with bleaching is
evident from these data. Over the entire range of the study (up to
9.0% chlorine applied as hypochlorite) the filtration resistance in-
creased about 20%.

The data for Bleach 12 were not included because they were not
consistent and no reason for this could be found. The data could not
be reproduced and several repeat trials resulted in successively
increasing values of filtration resistance for some unexplained reason.

TABLE VIII

FILTRATION RESISTANCE OF PULPS

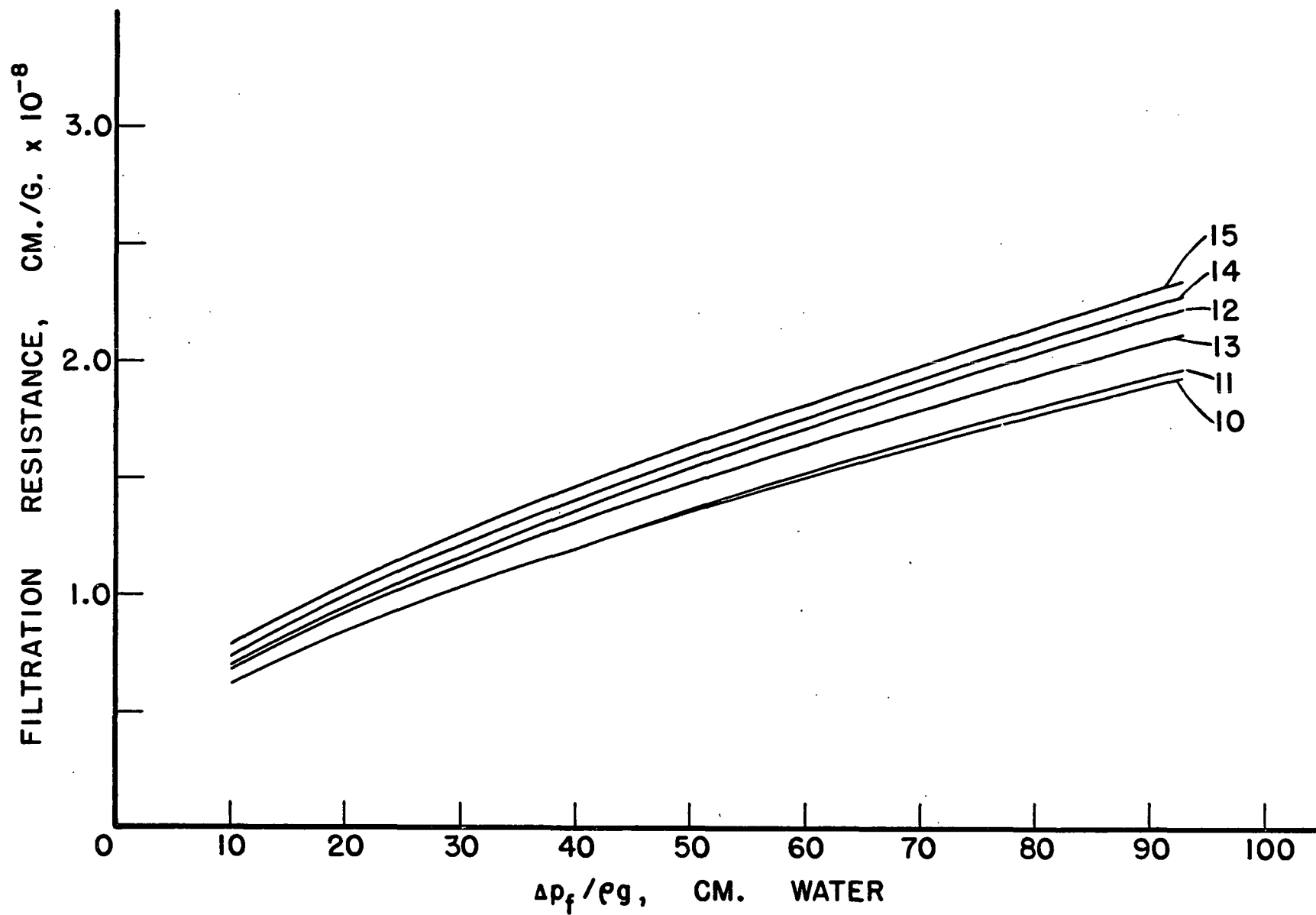| $\Delta p_f / \rho g$, cm. H_2O	Bleach No.					
	10	11	12	13	14	15
10	0.622	0.620	-----	0.684	0.736	0.783
20	0.845	0.849	-----	0.930	1.000	1.049
30	1.036	1.032	-----	1.132	1.217	1.269
40	1.201	1.206	-----	1.315	1.412	1.470
50	1.353	1.364	-----	1.480	1.586	1.644
60	1.498	1.516	-----	1.642	1.759	1.818
70	1.640	1.657	-----	1.794	1.920	1.983
80	1.773	1.801	-----	1.941	2.086	2.145
90	1.911	1.938	-----	2.085	2.240	2.306

Figure 25. Filtration Resistance of Bleached Pulps

A surprising finding is that the filtration resistance of Bleach 11 was the same as that of Bleach 10. Examination of the screen classification data in Table II shows that the fines content of Bleach 10 was inordinately high. This would have the effect of increasing filtration resistance.

Hydrodynamic specific surface area and effective specific volume were determined from rectified plots of Equation (7).

$$\left[\frac{(1-N)c_2}{R}\right]^{1/3} = \frac{1}{kS_o'^2}\left[1 - (1-N)vc_p\right]$$

(7)

This is an approximation of an integrated form of the Kozeny-Carman relationship (46) and assumes an average bed porosity over the range of pressures employed. It has been demonstrated (92) that the error introduced in using the approximation is negligible.